ALLEN HUNTER'S YOUNGSTOWN STATE UNIVERSITY

X-RAY STRUCTURE ANALYSIS LAB MANUAL:

A BEGINNER'S INTRODUCTION[1]

OPTIMIZED FOR USE WITH SHELXTL AND DOS

Dr. Allen D. Hunter
Professor of Chemistry
Director of the YSU Structure Center
Department of Chemistry
Youngstown State University
1 University Plaza, Youngstown Ohio 44555-3663
adhunter@cc.ysu.edu
http://www.as.ysu.edu/~adhunter/index.html

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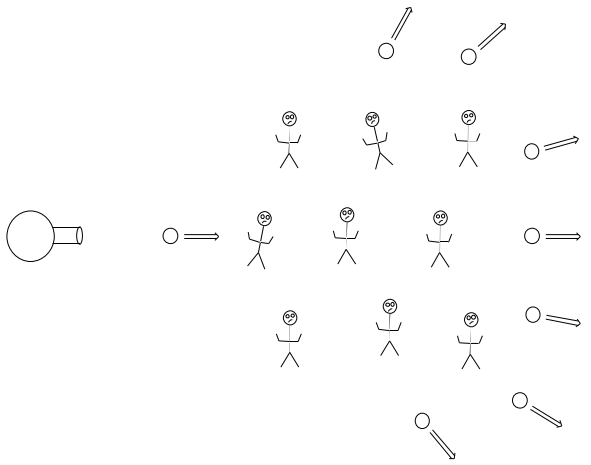
Detailed Comments On This Draft Manual Are Requested From All Users



[1] This lab manual is based on the authors experience teaching crystallography to undergraduates and MS students at Youngstown State University, his experience with the software, the SHELXTL manual (Version 5.1) from Bruker AXS (Siemens), George Sheldrick's SHELX manuals, as well as the other references listed in the appendix.

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[3] The limited term of this agreement is designed to encourage users to get the latest edition of this lab manual.

[4] The author does request that copies of any extensive annotations or supplementary materials be forwarded to him for possible inclusion in future editions.

[5] A single site is defined as one university campus or physical location.

To aid in the writing of future editions of this manual,[6] all users are strongly encouraged to send the author detailed comments[7] on this manual, including: spelling, grammatical, and typographical errors, errors in the description of how the software functions and is used, errors in the crystallography described, sections of the text that are unclear, confusing, or need further explanation or examples, omissions, formatting problems, additional literature/WEB references, etc. The author particularly wishes to encourage users to write or help write new sections of text to explain topics not covered, or are not covered in sufficient detail, in the current edition. He strongly encourages users to send him crystallographic data sets that would be useful in teaching. These will be posted on his WEB site. All data sets should include all required files and they should be in formats such that may be used directly in SHELXTL. Submission would also be much more valuable is they included information useful to students and instructors about the crystallography of each compound (in the form short text documents/commentaries describing interesting features and/or problems associated with the structure's solution).

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[6] It is expected that this manual will undergo major updates at least once a year for the next several years with minor updates occurring more frequently.

[7] Such "error messages" are most useful to me and will be more quickly incorporated into revised editions if they list the page, section, and line(s) of each error and suggestions for the correction of each.

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Please mail the signed forms to: Dr. Allen D. Hunter, Department of Chemistry, Youngstown State University, Youngstown, Ohio, USA, 44555-3663.

Suggestions for:

Improvements/Deletions/Additions/Changes (to Future Editions of this Manual)

I am writing this manual as a resource for the crystallographic educational community. I plan on improving future editions by incorporating feedback from manual users. This will be facilitated by the fact that it is being distributed as a .pdf file which will allow regular revision and rapid inexpensive distribution. For this to work, I need the user community to give me as much detailed feedback as possible. This could take the form of short notes to myself on any minor or major errors (and especially how to correct them!). I would also greatly appreciate longer sections of text that could be directly inserted into the main body or as separate appendices on topics not yet covered.

Known Problems With This Version of the Manual for Corrections in Future Editions:

1. The graphics is this .pdf file are at relatively low resolution because I have yet to find an acceptable way to get higher resolution graphics from XP (for DOS) into MS Word files, I welcome suggestions.
2. The list of teaching links is just starting, I need more suggestions.
3.

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[8] The diagram shown on the cover represents the thought experiment of bouncing quantum mechanical basket balls off of a team and using the resulting diffraction pattern to calculate the players' positions.

ACKNOWLEDGEMENTS

The author would like to gratefully acknowledge the contributions of the many people and organizations that have made the writing of this manual possible. I am a synthetic chemist who has learned sufficient crystallography to support my teaching and research but I do not have the expertise or experience to consider myself a professional crystallographer. However, I have been able to rely on substantial support, advice, and feedback from those more expert in crystallography than myself. I owe them a debt of gratitude for pointing out the errors in earlier editions of this manual and suggesting valuable additions and changes. I hope that they and others will continue to provide this invaluable service for this and future editions. I would particularly like thank the following individuals who have read over and made detailed comments and suggestions about this and earlier editions of this manuscript, especially: John Andrews, Rasika Dais, Jeanette Krause Bauer, Doug Powell, Zaki Sedge, Casey Raymond, and Tim Wagner. In addition, my Chemistry 832: Solid State Structural Methods students (especially Janet Gbur, Carrie Kolly, Mike Lufaso, Vince Lucarelli, and Jane Pollack) have provided me with invaluable feedback. I would also like to thank Bill Allen, John Jackson, Katy Landis, and Larry Curtin for providing crystals used to collect some of the diffraction data mentioned in this manual.

I would like to acknowledge the generous financial support of the National Science Foundation (NSF-RUI grant DUE-9403889), the Ohio Board of Reagents, (1994 OBoR Action Fund grant CAP-098, and a 1995 OBoR Investment Fund grant: "Ohio Crystallography Consortium at Toledo" CAP-075), and Youngstown State University for funds used to purchase and upgrade our diffractometers and data systems. I would also like to thank Youngstown State University for Research Professorships (for 1993/94,1994/95, and 1998/99), a Faculty Improvement Leave (1995/96), and Faculty Development Time (1994/1995, 1996/97, and 1998/99), parts of which were used to develop this laboratory manual. I would like to thank Bruker AXS (Siemens) for providing me with the SHELXTL for NT software used in the preparation of this manual.

Finally, I would like to thank my wife Susan and daughter April for their loving support, encouragement, and understanding while I wrote this manual.

PART I: GENERAL PROCEDURES FOR SOLVING STRUCTURES

CHAPTER I. INTRODUCTION TO THIS MANUAL AND X-RAY CRSYTALLOGRAPHY

A. PURPOSES OF THIS MANUAL

1. Crystallography and the Synthetic Chemist

As recently as the early 1980's, crystallography was still largely the domain of professional crystallographers. Since then, numerous advances in diffraction hardware, in computers, in the theoretical foundations of crystallography, and in crystallographic software have fundamentally changed how crystallography is carried out. These changes have rapidly increased the rate at which crystallographic data is collected, decreased the cost of collecting this data, while simultaneously making single crystal diffraction analysis more accessible to the novice. As a direct result, more and more non-specialists are participating in the solving of their crystal structures. Indeed, I strongly believe that by the early years of the next century, if this is not true today, crystallography will be second only to NMR as the characterization method of choice in chemistry. For this reason, I think all graduating chemists should have at least a basic working knowledge of X-ray diffraction.

In some cases, the participation of synthetic chemists in diffraction analysis might be limited to "watching over the shoulder" of a skilled crystallographer and preparing graphics and tables for publication while, increasingly, this participation involves doing most of the crystallographic data solution and analysis. Crystallography is a technique in which it is easy to get started in but it is also a technique which is very hard to master. Someone with "a little bit of knowledge" can easily produce results which look entirely convincing to them but that are also entirely incorrect. For this reason, crystal structure analysis should always be done under the guidance of an expert.

2. Reference Materials on X-ray Diffraction Analysis

There are many excellent reference materials for both beginners and experts on the theory and practice of X-ray crystallography. In chapter XII in the Appendix, I have included a listing of many of these materials that I regularly consult and/or are available in the YSU library. These reference materials include a selection of texts, review articles and book chapters, journals, literature papers, and WEB based materials. However, there is remarkably little material available to help the novice user through the intricacies of solving X-ray structures. For use by my undergraduate research students and in my crystallography class for undergraduates and MS students that I teach at Youngstown State University (i.e., Chemistry 832: Solid State Structural Methods), I felt this need very clearly. To help my students and myself learn more about crystallography, I therefore wrote this beginners guide.

3. My Crystallography Teaching Philosophy

In teaching crystallography, as in almost any area of Chemistry, I believe that students need simultaneous exposure to both "lectures" and labs (i.e., because most people like myself learn best "with their hands"). The theory and practice of a discipline such as crystallography can be well presented in lectures using one of the many excellent texts which are available. However, in my experience, little of this information "sinks in" without a strong laboratory experience. For crystallography, I believe this should include "hands on" exposure to each of the steps in data collection and analysis. For this purpose, we at Youngstown State University have available excellent crystallographic and computing facilities. We have each student carry out "skills" exercises on the individual steps of data collection, solve a variety of structures from previously collected data, and take one sample from crystals in a sample tube to final report. We use Bruker AXS (Siemens) P4 diffractometers for our data collection. These are easy for the students to learn to operate and the Tutorial Manual that comes with the **XSCANS** diffractometer makes an excellent lab manual for the data collection part of the course.

There are several excellent packages available for solving X-ray crystal structures. There are substantial variations in how each of these programs are used to analyze data (i.e., in terms of input files, commands, and other idiosyncratic features). These surface differences hide from a novice the high degree of similarity which resides in their interiors. Indeed, most use George Sheldrick's SHELX engine for structure solution and refinement. For instructional purposes, one needs a lab manual that describes in minute detail how to carry out each step of a diffraction analysis. I find that only after doing so do students really understand the theory of crystallography and the general principles its practice. I have not found it possible to write a program independent lab manual adequate to teaching the practical side of diffraction analysis to novice crystallographers and have not found such a manual in the literature. I therefore decided when I wrote the current manual to tailor it to one particular software suite.

4. Crystallographic Software, SHELXTL, and This Manual

Here at YSU, we use the commercial **SHELXTL** package from Bruker AXS (Siemens) and George Sheldrick to solve our crystal structures. Earlier versions of package came to us with the purchase of our diffractometers and these have recently been upgraded to version 5.1. This package is arguably the most powerful and versatile available for solving X-ray crystal structures. **SHELXTL** incorporates the most current version of George Sheldrick's **SHELX** package (i.e., **SHELXTL-97**) as its central core. It also includes a direct interface with the **XSCANS** data collection package from Bruker AXS (Siemens) diffractometers as well as numerous additional features that enhance its ease of use and graphical capabilities. Because of this, I have optimized this manual for the **SHELXTL**[9] package. The **SHELXTL** package runs similarly on SGI UNIX workstations and on Microsoft/Intel PCs running under **DOS** and **Windows NT**. The differences between these versions lie primarily in processor speed and file editing commands. The manuals

[9] The current version of **SHELXTL** is 5.1 for both **DOS** and **Windows NT**.

provided by Bruker AXS (Siemens) for **SHELXTL**[10] and that provided by Sheldrick for **SHELX**[11] are excellent resources for skilled crystallographers. The **present manual is optimized for the novice user** using a DOS based system since this is how we currently solve our structures here at YSU**.** When I become more familiar with its use, I will add supplementary material that describes any differences in the Windows NT version. However, my preliminary work suggests that these will be minor and only for the better.

5. Approach Taken by This Manual

The procedure for solving a crystal structure involves several iterative stages. This manual is designed for two main groups: beginning crystallographers just learning to do this and as a resource for more experienced crystallographers who want a quick reference guide. Because the commercial software package **SHELXTL** is what we use here at Youngstown State University and because it and its **SHELX** parent are so very widely used, I will illustrate the method for solving crystal structures using the **SHELXTL** programs. In Part I of the manual, I include step by step descriptions of the major stages of structure solution and refinement and the preparation of results for publication. I also include several annotated tables of the commands used most commonly by beginners. In Part II of the manual, I then walk the student through the solution of a representative data set. Finally, in Part III of the manual, I include several useful Appendices including a brief introduction to **DOS**, a list of crystallographic literature, and hints on growing single crystals.

6. When Should a Non-Crystallographer Attempt to Solve a Crystal Structure

Some crystallographic purists would argue that the answer to this question is never. Given the trends discussed above, my interest in exposing chemists to the full beauty and diversity of our field, and the pure joy that crystallography can bring, I lean towards teaching anyone with a desire to learn and a sufficient background in math, physics, and chemistry to understand. However, the skeptics are correct in pointing out the deep trouble that a crystallographic neophyte can get themselves into. Therefore, I will focus on helping the students solve the majority of *routine* crystal structures of "chemical interest" and amenable to the efforts of a novice. More complex and "crystallographically interesting" cases (e.g., twinned crystals, recalcitrant data sets, and ambiguous space groups) are observed from 10 to 30% of the time (i.e., depending on a person's luck). However, the successful solution of such cases by an unaided novice is extremely unlikely. Indeed, most experienced crystallographers, and I concur, would

[10] Copies of the **SHELXTL** manual from Bruker AXS (Siemens) are available in the X-ray crystallography lab and can be purchased from Bruker.

[11] Copies of George Sheldrick's SHELX manual come with the program as text files and are also available in the X-ray crystallography lab. It is also available in html format in a version prepared by Dr. Robert McDonald at the University of Alberta (Bob.McDonald@ualberta.ca, http://rocket.chem.ualberta.ca/). To obtain a copy, download and expand the file Shelxhtm.exe, available from our WEB page at http://www.as.ysu.edu/~adhunter/YSUSC/index.html, and use your favorite browser to read it.

say that for a beginner to even attempt them is dangerous (to their mental health if nothing else) and unwise.

For these reasons, and because of my own limited experience as a crystallographer, the solution of more complex crystallographic problems will not generally be addressed here. **[Note: Contributions about such topics, especially if they are written by or with the assistance of some of my readers, will be included as appendices to future editions.]** Indeed, when I come across such recalcitrant cases myself I tend to consult extensively with my crystallographic colleagues and/or to attempt to sidestep the crystallographic problem using tools more familiar to a synthetic chemist such as myself. My two favorite strategies are attempting to grow new crystals from a different solvent system (i.e., presumably of better quality and/or in a different space group) or synthesizing a derivative of the molecule of interest (e.g., preparing the methyl rather than the ethyl derivative).

7. Data Files to Practice Your Skills On

Mastery of any skill, be it basketball or crystallography, is only accomplished with "practice, practice, practice." While taking a typical crystallography lab course, a student will usually collect only one or a few data sets. This is certainly not enough for the mastery of data collection, however, modern diffractometer control software, especially **XSCANS**, is so user friendly that this is sufficient to give a student a good start for routine cases. In my experience, after this point a student can be trusted to use the instrument without constant supervision. However, solving only a few crystallographic data sets to give their structures produces a much lower level of mastery. This is because correctly solving crystal structures, and hence crystallographic software, is intrinsically much more complex than is data collection. Indeed, expertise in diffraction analysis comes only after both mastering the theory and solving hundreds of structures (in so doing, gaining "the touch"). Few can hope to obtain this level of mastery. However, a novice can aspire to reaching the point that they can solve routine structures under the guidance of someone more expert than themselves. In my experience, this takes working through a half dozen or more carefully chosen structures, with greater mastery coming with solving increasing numbers. Although diffractometer time limitations mean it is unlikely that most students will collect more than a few data sets, the low cost of personal computers and the speed with which they can process data means that students can be reasonably expected to solve a dozen or more structures as part of a semester long lab course.[12] To help meet this need for annotated data sets, I have collected a selection "well behaved" and more "challenging" data sets that a beginner can practice on. These are provided by my WEB site at http://www.as.ysu.edu/~adhunter/YSUSC/index.html. [Note: This site will be fully functional by late November 1998.]

Dear Reader: if you have any favorite data sets you would be willing to contribute (either "well behaved" data sets or data sets illustrating specific common and/or interesting problems)

[12] Indeed, with the provision of one or more "road trips" to a fully equipped diffraction facility, one should be able to do a great job of teaching diffraction analysis even if your school has only a computer lab and some software.

please send them to me in the form of files readable by **SHELXTL** along with any commentary on the solution you believe it would be worthwhile for the students to see.

8. Errors, Short Cuts, and Request for Readers' Help

To keep this manual accessible to crystallographic novices, I have only attempted to cover the basics of crystallographic data analysis. In so doing, I have left out many of the more powerful features of SHELX and SHELXTL which, in my opinion, were unlikely to be safely used by beginners. Also, to keep this manual from getting too intimidating, I have tried to keep the coverage focussed and taken some "short cuts" with my explanations.

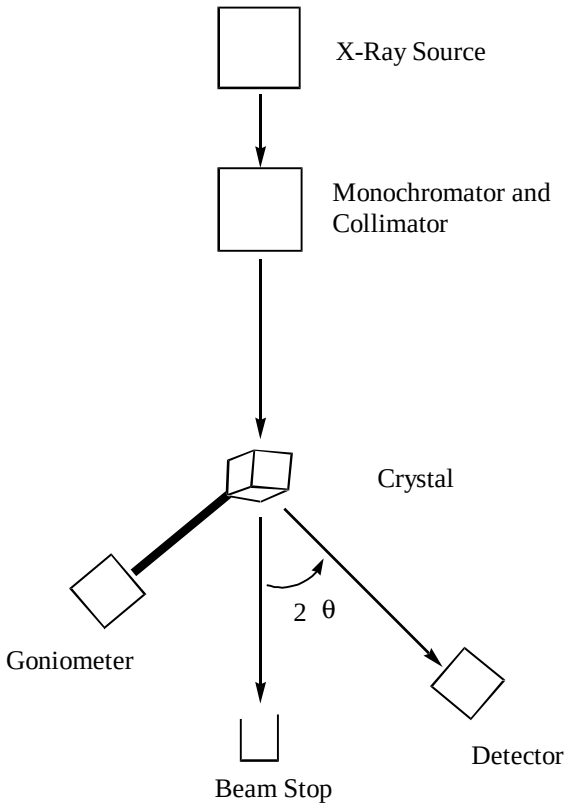
I hope that readers who find errors in spelling and grammar, consistency of format, clarity of presentation, accuracy of explanation, etc., while using this manual will let me know. Such advice is invaluable for the regular updates I plan to this manual.[13]

[13] Such "error messages" are most useful to me and will be more quickly incorporated into revised editions if they list the page, section, and line(s) of each error and suggestions for the correction of each.

B. BASIC COMPONENTS OF AN X-RAY DIFFRACTOMETER

1. Block Diagram of an X-ray Diffractometer

The details of construction of X-ray diffractometers varies from model to model, but they all contain the same basic components. These are illustrated in the block diagram below.



To gain familiarity with the parts of a diffractometer, read the relevant portions of our lecture text and the **XSCANS** manual and inspect our diffractometers in the crystallography lab. Be sure that you can identify their components for yourself. Over the years, increasing automation and the embedding of modern electronics and high technology into all diffractometer components have resulted in major changes to diffractometer design and operation. Our Bruker AXS (Siemens) P4 diffractometers, which were new in 1995/96, are representative of diffractometers in general.

2. X-ray Generators

a) Sealed tube X-ray generators

We have sealed tube X-ray generators on our two P4 systems. In the X-ray tubes of such systems, a high DC voltage is used to accelerate electrons towards a metal anode target. Upon striking this target, the electrons produce a broad background band as well as a series of sharp X-ray peaks. At the kV power levels used, this radiation centered in the X-ray band. The broad Bremsstrahlung radiation is produced as the electrons decelerate inside the metal target. The sharp bands are produced when electrons fall from the n = 2 to the n = 1 quantum shell of the metal atoms after an original 1s electron has been ejected from its orbital by an incident electron. Therefore, the position of these sharp bands will depend on the identity of the metal target. For most purposes, one chooses to use the K_α produced by the metal. One of our diffractometers has a Cu tube giving radiation with a characteristic wavelength of 1.54178 Å while our other diffractometer has a Mo tube giving radiation with a characteristic wavelength of 0.71073 Å. Because of its shorter wavelength, the Mo tube gives a much lower intensity X-ray beam than does the Cu tube at the same input power.

These X-ray generators are typically operated at about 80% of their rated power during data collection. This correspond to running the tubes at 40 kV and 40 mA to give 1,600 Watts of total power for Cu and 40 kV and 50 mA for 2,000 Watts of total power for Mo.[14] We typically turn the power level down to its minimum value (i.e., 15 kV and 5 mA) when the systems will be out of use for several days or more. The maximum power level of these tubes is limited mainly by how quickly the cooling water which circulates through the back of the tube can remove the heat the electron beam produces. In our lab, the water from both diffractometers is, in turn, cooled by a single water to water heat exchanger. The cooling power of this heat exchanger is sufficient to cool both diffractometers when the city water which cools it is not too warm. However, in Youngstown we can only use one of the diffractometers at a time in mid Summer when our local tap water becomes quite warm. We will soon add a refrigerated chiller to the heat exchanger to overcome this problem of summer overheating.

b) Increasing the S/N ratio in diffraction data by increasing the data collection time

The signal to noise ratio of observed diffraction data increases approximately linearly with incident X-ray intensity but only with slightly less than the square route of data collection time. Therefore, one needs to collect data at least four times longer to double the signal to noise ratio on a poorly diffracting crystal but one can get the same increase by doubling the beam intensity. A further complicating feature is that crystals decay in the X-ray beam at a rate which is

[14] Bob Sparks has pointed out that if one keeps the same total power setting but increases the voltage and decreases the current one will get a higher X-ray intensity. I will attempt to quantify the magnitude of this increase for a subsequent edition.

approximately linear with respect to time but that shows a much weaker dependence on beam intensity. Thus, one often sees much more radiation induced crystal damage when one chooses to increase the S/N ratio by increasing data collection time than when one increases beam intensity. It can also be hard to justify substantially increasing the data collection time in a busy and/or multi-user diffraction lab. However, it is still true that about the easiest way to increase S/N is to increase data collection time and if your crystal does not show too much decay and there is not too much of a line up to use the diffractometer this is often the route of choice (i.e., we may collect for up to several weeks as opposed to three to seven days for more typical samples).

c) Increasing the S/N ratio in diffraction data by increasing the beam intensity

A more powerful way to increase the signal to noise ratio of your data is to increase the X-ray beam intensity. In our lab, one of the first things we do to deal with weakly diffracting crystals is to turn the X-ray generator to its maximum power for that tube (i.e., 2,400 W for the Mo tube and 2,000 W for the Cu tube).[15] For samples that give insufficient data quality under longer collection time and maximum tube power, the traditional approach is to get even greater X-ray intensity. Since Cu radiation is intrinsically more luminous (with the same total power level), we often use the Cu instrument for samples where the intrinsically higher absorption coefficients of the longer wavelength Cu radiation is not a problem. You may also want to replace the X-ray tube if the old one has lost significant intensities since losses of 50% or even 75% after two or three years are common.

Another approach to dealing with this problem, is to try and prepare better formed and/or larger crystals which will generally give much better quality data sets for the same data collection conditions. This is because diffracted intensity is approximately proportional to crystal volume for most crystals and also increases substantially with crystal quality. Our Mo diffractometer is equipped with a low temperature system. This cools to crystal by blowing a stream of cold gas over the crystal on the goniometer head as data is collected. Using cryogens to cool the gas stream is expensive due to the high boil off rates (i.e., liquid nitrogen is used to refrigerate and generate the cooling gas) and limits the available angles at which data can be collected. However, this type of equipment is relatively inexpensive and the use of lower crystal temperatures can substantially increase diffracted intensities at higher angles (i.e., due to reduced atomic vibrations) where data collection is always slowest. To lower these cryogen costs, one can now purchase somewhat more expensive closed cycle refrigerators for cooling the gas stream. Because the amplitude of vibrations increases dramatically as one nears a crystal's melting point, this improvement is typically greatest for molecular solids which melt at or near ambient temperatures and is least for minerals, metal oxides, etc., which melt at over 1000 °C.

It is worth noting that collecting the thousand reflection having the greatest 2θ angles always takes much longer than collecting the first thousand reflections. Therefore, where the desired resolution of the structure makes this feasible, one of the best ways to increase S/N is to

[15] The X-ray generators are not operated at maximum power to conserve tube life which decreases dramatically with increased total power (and also if the tubes are turned on and off too frequently).

collect a data set out to only moderate angles. Where one needs or desires the maximum resolution in the final structure, one must collect data out to the highest possible angles and simply accept that this will mean a more difficult data collection.

In the most demanding applications where these simpler methods fail, one can use more luminous rotating anode or synchrotron radiation sources. The former can be found in many labs and give up to 15 kW of total power while the latter can be several orders of magnitude brighter. Suitable synchrotron sources are available only at the national labs, however, we have direct access to an instrument equipped with a Cu rotating anode. This instrument is located in the Ohio Crystallography Consortium facility at the University of Toledo and through our founding membership in the OCC we have guaranteed access to it. An alternative method of obtaining increased X-ray luminosity is to add focusing/mirror optics between the X-ray generator and the goniometer. The rotating anode system at Toledo is so equipped.

d) Summary of methods for increasing S/N ratios in collected data

To summarize, several of the most common methods of *increasing the signal to noise ratio, S/N, in a data set* include:

- Increase the power output of the sealed tube generator (S/N increases linearly with power).
- Increase the data collection time (S/N increases with the square route of time).
- Use a diffractometer/tube with a longer wavelength radiation (S/N increases linearly with incident intensity which increases approximately with the square of the wavelength).
- Replace the X-ray tube if the old one has lost significant intensities since losses of 50% or more after two years are not unexpected (S/N increases of from two to four times are easily observed).
- Grow or pick larger crystals (S/N increases linearly with the crystal volume).
- Grow better quality crystals (S/N increases with increasing crystal quality for typical crystals grown in the lab).
- Collect your data at low temperatures (S/N increases substantially, particularly at higher angles).
- Decrease the maximum 2θ angle (for a given data collection time this will substantially increase S/N but will simultaneously reduce the resolution of the data).
- Use a rotating anode generator (S/N may increase five or six times this way).
- Use a synchrotron source (S/N will increase several orders of magnitude).
- Use focusing/mirror optics after the X-ray generator (S/N may increase up to an order of magnitude)
- Use an area detector to obtain the multiplex advantage (S/N increases of over an order of magnitude easily obtained, especially for large unit cells).

3. Monochromator and Collimator

On our two diffractometers, as on most single crystal machines, we use a graphite crystal monochromator to select the desired K_α radiation from the other sharp bands and the broad wavelength distribution produced in the X-ray tubes. We use a tubular collimator to reduce the angular spread on the X-ray beam (i.e., making it more nearly collinear). This collimator contains a pair of disks whose pin hole size limits the size of the incident X-ray beam. We usually use disks having pin hole diameters of 0.5 mm and thus limit the diameter of the homogeneous X-ray beam on our systems to about 0.5 mm. The sets the maximum dimension of the crystals we study.

4. Goniometer and Crystal Orientation

a) Goniometer heads

We typically mount our crystals on the end of a glass fiber attached to an adjustable goniometer head. We use goniometer heads that can be adjusted on three axes so that one can center the crystals in the incident X-ray beam. These heads are numbered and a record *must* be kept at all times on the lab white board of which are in use, by whom, and with which samples. This is because these heads are rather expensive and so their supply is limited in any lab. These goniometer heads are attached to the goniometer on the diffractometers for data collection. They can be removed and remounted without losing the crystal positioning and orientation. One can therefore remove a sample and its goniometer head from the diffractometer (i.e., so that someone else can use the system) and replace it on the goniometer later to do additional data collection. Experience indicates, however, that for novices 10 to 30% or more of the time that one does this one accidentally knocks the crystal off of the goniometer head, ouch! We therefore try to minimize the number of times a sample and its goniometer head are removed from and replaced on the diffractometer. In particular, we generally leave crystals on the goniometer until data processing reveals that the data collection is complete.

b) Goniometer

The goniometer is the most expensive component of our diffractometers. This is because it is an extremely finely machined device. It accurately orients the crystal to almost any arbitrary angle with respect to the incident beam, the crystal coordinates, and the diffracted beam.[16] This is done under direction of the host computer which also is able to read the angles of the axes. Diffractometers require movement about four independent axes (φ, ω, X, and 2θ) on systems such as ours equipped with point detectors and two or three axes on area detector systems.

[16] Mechanical constraints limit the observable diffraction angles on our machines to -xxx° to +xxx° when using the point detectors and much smaller angles when using the area detector. In additions, these same mechanical limitations make some crystal orientations inaccessible, especially when the diffractometer is equipped for low temperature operations.

5. Detectors

a) Point detectors

On both of our diffractometers, we have point detectors which are used to measure the intensity of the diffracted X-ray beams. These detectors typically are composed of a phosphor coated screen that converts incident X-rays into visible photons, a photomultiplier tube to amplify the signal, and an analogue to digital converter to produce the digital intensity signal. These detectors are mounted on the sliding rails of the 2θ arms, the same arms that the Polaroid cameras can be mounted on. Our systems are typically used with the detector slid forward to the position on the arm nearest the crystal (i.e., with a crystal to detector distance of xxx Å). However, for crystals having exceptionally large unit cells, and hence having very small angular differences between their reflections, the detector is moved back on the arm further from the crystal.

Modern point detectors have excellent counting efficiencies and dynamic ranges but can only collect diffraction data for one reflection at a time. They do this by scanning through a peak, collecting both background intensity data and peak profiles (from which integrated intensities are calculated) during each scan. The data collection software is programmed such that most reflections are scanned twice. The first scan is done very quickly, typically taking a few seconds, and gives adequate counting statistics only for the strongest peaks. For weaker peaks, the software has the diffractometer scan the peak a second time at a much lower velocity, as long as 60 seconds on our systems, designed to give better counting statistics. The various data files produced in a data collection using such serial detectors typically total from a few to ten or twenty megabytes. After data processing these are reduced to a few megabytes or less.

b) Multi-wire area detectors

Area detectors allow one to collect many reflections simultaneously. The resulting multiplex advantage means that area detectors give inherently quicker data collection for a given crystal, especially if that crystal has large unit cell parameters. The first area detector was simply a stack of X-ray films which after exposure to the X-ray were developed and then the intensities of the peaks were measured using a manual or automated methods. Subsequently, a variety of electronic area detectors were developed. One of the most successful of these was the multiwire area detector. We have such a multiwire area detector available for our Cu machine. It has a 512 by 512 wire array and Xenon detector gas. This detector has an excellent counting efficiency, but like all multi-wire systems it has a relatively poor dynamic range. It also has poor sensitivity for shorter wavelength radiation like that produced by Mo and therefore the more readily absorbed Cu radiation must be used. As a consequence of these limitations, this detector is of limited utility for strongly absorbing single crystals (e.g., those containing the heavier transition metals) and for crystals having a wide range of peak intensities (i.e., small molecule samples). However, it is excellent for the collection of powder X-ray data and for collecting X-ray data on macromolecular

samples such as proteins. We use it extensively for the former purpose and much of the protein diffraction data in the literature has been collected on this type of detector. The various raw data files produced in a data collection using area detectors typically total up to a few gigabytes. However, these large file reduce to the same size as those produced from point detectors after initial data processing.

c) CCD and imaging plate detectors

In recent years, multiwire detectors have been largely supplanted for the study of single crystals by more capable area detectors. Currently, macromolecular crystallographers seem to prefer imaging plate systems while small molecule crystallographers prefer CCD, charge coupled device, systems. This preference is partially due to history but mainly due to the fact that traditionally imaging plate systems were more sensitive to Cu radiation which the protein people prefer and the CCD systems were developed to be more sensitive to shorter wavelength Mo radiation which most small molecule crystallographers prefer. The OCC facility at Toledo has both types of more capable area detectors. The Cu rotating anode/focussing optics system is equipped with a modern imaging plate detector while the Mo system is equipped with a modern CCD detector. The imaging plate system is especially useful for macromolecular samples and for small crystals that are not too strongly absorbing. The CCD system is ideal for all weakly diffracting crystals. Both of these systems are available to us through our founding membership in the OCC.

6. Data Systems

a) Room temperature and computer crashes

As anyone who has worked with computers knows, they function best at temperatures below about 70 °F. Unfortunately, in spite of building air conditioning the crystallography lab can get rather warm in mid Summer and this tends to make the computer systems on the diffractometers more crash prone. We are currently in the process of adding supplemental air conditioning to the lab to overcome this problem.

b) Embedded computers

All modern diffractometers contain embedded processors that control the X-ray generator, goniometer, variable temperature system, etc. Fortunately, these processors make the users job easier but are invisible to all but the maintenance personnel.

c) Diffractometer control computer

Modern diffractometers are controlled by an external computer. Our diffractometer uses a Siemens DOS computer. This computer controls all aspects of data collection and if it is not being otherwise used it can also run the SHELXTL structure solution software. Diffractometers may also be controlled by more powerful workstations. The latter are especially popular on area detector systems with their much larger data processing demands while basic DOS machines are entirely adequate to control conventional diffractometers.

d) Computers for structure solution

All modern personal computers are excellent for solving the structures of typical small molecules. For macromolecular structures, high end workstations such as Wintel Windows NT, SGI Unix, IBM RS-6000 Unix, and DEC VMS workstations are still preferred. Because of their cost, their familiarity to most students, their ease of use, and their utility for other chemistry software, we prefer to use the Wintel personal computers in our offices and research, departmental computing, NMR, and X-ray labs for structure solution. Although some quality programs will run on obsolete 386 systems, modern software requires computers that should, at a minimum, have Pentium chips running at 166 MHz, 2 gigabyte hard drives, 32 megabytes of RAM , and ZIP drives or Ethernet connections to the diffractometer. We use such computers running both DOS/Windows 95 and Windows NT in our department. In our department we are currently running **SHELXTL** version 5.1 under DOS and are in the process of installing it on our Windows NT machines.

7. Diffractometer Maintenance

a) Diffractometer maintenance

Modern single crystal diffractometers equipped with conventional Wintel computers, sealed tube X-ray generators, optics, goniometers, and point detectors require remarkably little maintenance. The major operating expenses are cooling water, electricity, and an average of perhaps one day a year of skilled servicing (almost all of which is within the competence of a typical electronics maintenance person) with various minor maintenance chores taking a few additional days of the crystallographers time. The largest expense comes from replacing the X-ray tubes. We find that by normally running them at 80% or less of their peak power and only turning them on and off when they will be out of use for several weeks or more a tube may last upwards of three years before its intensity drops off too far. In busier labs, such tubes typically last from one to three years. Such tubes cost almost three thousand dollars each and their replacement is one of the two trickiest maintenance chore which a diffractometer routinely requires. The other is realigning the diffractometer after a serious "bump", tube changes, etc., causes the X-ray beam path falls out of alignment. Both of these tasks can be carried out by a non-expert with some training and practice.

b) Lab maintenance

As with any other multi-user chemistry lab, without constant care an X-ray lab can quickly become a complete mess. We have found that the areas around the crystal mounting microscope, the sample storage area, the goniometer storage area, and the computers and printers are particularly prone to this "house keeping" problem. Regularly "cleaning" the hard drive on the control computer and archiving the massive amounts of data collected in a lab is also an essential job. We have found it particularly valuable to number each goniometer head and use a "white board" to keep track of who is using it and what samples are mounted on it at all times. The larger task of keeping the mess in the lab under controls remains a small but most annoying part of running a multi-user facility.

8. Comparison to Neutron Diffraction

In principle, the components of a neutron diffractometer are similar to those of an X-ray system and the processing of the resulting data is done similarly. The primary difference in the data processing lies in the fact the nuclei scatter neutrons with a much narrower range of scattering powers (i.e., the normalized scattering factors range from –1.00 to + 2.66 for ^{1}H to ^{56}Fe, respectively) and with both positive and negative signs. In contrast, the electron clouds around the nucleus scatter X-rays with a very wide range of scattering powers (i.e., the scattering factors at 0° range from 1.0 for ^{1}H to 92.0 for ^{238}U) and always with the same sign. The practical significance of this is that neutron diffraction patterns give much more information about light atoms such as hydrogen and lithium than do X-ray patterns and that neutron data can be used to distinguish isotopes of an element from one another. The fundamental difference in the hardware lies in the fact that the thermal neutrons, which have the appropriate wavelengths of about an Å for diffraction studies, used in diffraction studies are much harder to produce. For this reason, neutron beams of sufficient intensity are not available in "lab size." Instead, they are produced at the beam dumps of accelerators or in specially constructed nuclear reactors. In addition, even the best of these sources produce neutron beams of much lower intensity than the X-ray beam produced by a typical sealed tube generator. For this reason, neutron diffraction typically requires crystals a fraction of a centimeter on a side and data collection times measured in weeks or months.

Dear Readers: If you have any neutron data sets you could provide along with details in how to modify the **name.ins** files to process them with **SHELXTL** I would greatly appreciate it.

C. COLLECTING CRYSTALLOGRAPHIC DATA

1. General Procedures

General procedures for growing single crystals are presented in chapter XIV. Detailed procedures for collecting crystallographic data are outlined with exceptional clarity by the Bruker AXS (Siemens) manual **XSCANS** Software Tutorial/Users Guide and more detailed information is available in their **XSCANS** Technical Reference Manual. We will use the Tutorial Guide as the lab text for the first part of the lab course on data collection.

2. Evaluating Crystal Quality

a) Optical methods

There are several complementary methods for evaluating crystal quality. Perhaps the simplest is inspection of the crystal under both normal and polarizing light using a hand lens or low power microscope. Generally, crystals that have well defined faces and give uniform looking colors under polarizing light are the best candidates for diffraction analysis. However, sometimes "crystals" that have perfect gem like facets show no observable diffraction patterns and hence are really glasses while other samples that resemble nothing so much as a dried lump of dirt diffract exceptionally well.

b) Rotation photos

Taking Polaroid rotation photographs is the next step in evaluating crystal quality. For the diffractometer to be able to collect a reasonable data set under normal conditions, a rotation photograph taken for ten minutes should have spots over its whole area with at least of few weak ones being visible even near the top and bottom edges. These reflections should be well separated from one another and should be single with no streaking.

c) Peak profiles

Once you start centering reflections (i.e., to determining the unit cell) in **XSCANS**, the peak profiles shown on the display should be strong, narrow, and single. By the latter, I mean that they should not have two maxima or any visible shoulders.

3. Collecting the Crystallographic Data

One can use the excellent **XSCANS** manuals that were supplied with the diffractometers for all of the information required to set up the data collection. [Note: I have annotated this manual to include our standard data collection conditions where these differ from those suggested by Bruker AXS (Siemens).]

4. Powder Patterns

One question that is not widely answered in routine crystallographic analyses is whether the crystal one has collected data on is truly representative of the bulk sample. You may have chosen a good crystal that is literally "one in a thousand crystals"! It may have a different space group than the bulk sample, be one of two enantiomers present, or may even be a different compound (i.e., a minor byproduct that just crystallizes out well). Non-crystallographic information can give you some information on this but one shouldn't just rely on ones intuition that "it must be right because its what I wanted/expected." One of the best checks is to take some of the bulk sample, grind it into a powder, and collect its powder diffraction pattern. This can be compared with a powder diffraction pattern calculated for your crystal by the **SHELXTL XPOW/XFOG** subroutines. If the two powder patterns are identical, one can be much more confident that your crystal is truly representative of the bulk sample.

D. BRIEF DESCRIPTIONS OF THE MAJOR PROGRAMS INCLUDED IN SHELXTL

SHELXTL is a commercial software package from Bruker AXS (Siemens) for the solution and refinement of X-ray crystal structures and the preparation of these results for publication. It is based on George Sheldrick's **SHELX** core (currently the **SHELXTL–97** versions) and is composed of many individual components. Each of these programs serves a different function in the overall structure determination problem. Below, the key programs are briefly identified and the data files used by, and produced by, each is given.

1. General Capabilities

The **SHELXTL** package is capable of dealing with up to five thousand atoms for structure refinement and twice that for other calculations. On any decent personal computer, each cycle of calculations on small molecules typically take only a few seconds or minutes to complete. On the other hand, analyzing the results of each cycle takes many times (sometimes many orders of magnitude) longer. Even with routine structures, the speed of data analysis is almost entirely dependent on one's level of expertise and not on the speed of calculations.

2. XPREP for Data Preparation

This program is used to prepare the data one gets from the diffractometer (i.e., from **XSCANS** for our P4 diffractometers) for solution. It is used to determine the space group, modify unit cell contents, do absorption corrections, and scale and merge data sets, etc. It then writes the files needed by later programs.

Input: **name.raw**, **name.p4p**, and **name.psi** from **XSCANS**

Output: **name.ins** and **name.hkl** to **XS/XL**

name.prp as a log file

name.pcf for use in **XCIF**

3. XS for Trial Solutions

This program provides preliminary trial solutions for the positions of the first and/or heaviest atoms by either Direct methods or Patterson methods.

Input: **name.ins** and **name.hkl** from **XPREP**

Output: **name.res** as the results used for **XP**

name.lst as a log file

4. XL for Structure Refinement

This program carries out the iterative structure solution based on the experimental structure factors and crystal data and the atomic identities, positions, and displacements present in the model to be refined.

Input: **name.ins** and **name.hkl** from **XS** or previous **XL** cycles via **XP**

Output: **name.res** as the results used for **XP**

name.lst as a log file

name.cif and **name.fcf** after 'ACTA' command is used in the **name.ins** file

5. XP for Data Analysis and Graphics

This interactive program is used for examining the output from **XS** and **XL** calculations. It is used to assign atom identities, to visualize molecular and crystal structures, and to check these for "chemical reasonableness." It also provides a suite of interactive graphics and is used to produce publication quality plots of the final structure.

Input: **name.res** from **XS** or **XL**

Output: **name.ins** for **XL**

name.ort for orthogonal(Cartesian) coordinates

name.plt where PLT = a, b, c, etc. as plot files

6. XCIF for Table Preparation

This program is used for producing publication quality tables of data describing the final crystallographic results.

Input: **name.cif**, **name.pcf**, and **name.fcf** from **XPREP** and **XL**

Output: **name.ang, name.def** and **name.sft** for publication

7. Chi90 for Psi Scans

This non-Bruker AXS program (it was written by Doug Powell (powell@chem.wisc.edu) at the University of Wisconsin) is used to calculate which reflections should be used for ψ scans.[17]

Input: **name.raw** and **name.p4p**

Output: **name.chi** which you edit to give **name.psr**

8. XPS for Fragment Searches

This program is used to help carry out structure solutions using fragment searches (i.e., by positioning a phenyl ring or octahedral metal center at various orientations and positions in the unit cell). Its use is described in chapter 7 of the Bruker AXS (Siemens) manual.

Input: **name.inp** and **name.pat**

Output: **name.rep** and **name.lst**

9. XPOW and XFOG for Simulated Powder Patterns

This pair of programs can be used to calculate what the powder diffraction pattern. **XPOW** does this from the **name.hkl** file which you have generated in **XPREP** or simulated in **XFOG**. **XFOG** uses the unit cell parameters, the symmetry of the space group, and the atomic parameters to calculate a simulated **name.hkl** file for this compound.

Input: **name.hkl** and/or information from **name.ins**

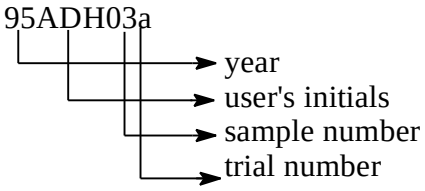
Output: **name.plt** and **name.pow** (the latter is the simulated **name.hkl** file from **XFOG**)

[17] These ψ scans are needed for samples containing highly absorbing elements, most organometallics and inorganics, and for "oddly" shaped crystals where the crystal dimensions are very different (e.g., needles or "chunks"). For more ideally shaped crystals (and many crystallographers contend in general) the face indexing method of correcting for absorption is preferred.

E. BRIEF DESCRIPTIONS OF THE MAIN FILE TYPES USED BY SHELXTL

1. A Short Note on the Naming of Compounds in Our Labs

To make the "book keeping" of structures in a multi-user environment easier, we have imposed a standardized and informative name for each structure. The "name" part of each file description is an 8-character code. The first 7 characters identify the sample with a 2-character year code, a 3-character user code (your initials), and a 2-character sample code. This is followed by a one character code that identifies the individual crystal and structure solution attempt. A typical example is as follows:



2. The Main File Types Generated by SHELX and its Component Programs

name._lg This file contains a log of everything you've done and all of the data you've collected.

name.ang This file contains the tables of structure solution parameters, coordinates, bond lengths and angles, etc., for publication. It is produced as the default option by **XCIF** or when the 'ang' option is selected. It produces tables in **SHELXTL** XTEXT format in units of Å. [Note: In previous editions of this manual this file was referred to as **name.tbl**.]

name.chi This file is produced by Chi90 and is a listing of this program's choices for the best reflections to use for ψ-scans.

name.cif This is a CIF format file produced by **XL** that contains crystal data, atoms, and refinement results. It is used by **XCIF**.

name.def This file is produced by **XCIF** while producing tables when you choose the 'def' option. It saves the selected tables in ASCII format for easy input in MS WORD, etc.

name.fcf This is a CIF format file produced by **XL** that contains the observed and calculated structure factors. It is used by **XCIF**.

name.hkl This file contains the reduced reflection data (i.e., after corrections or Lorenz and polarization effects (i.e., Lp effects), decay, merging, absorption, etc.). Initial processing of data gives a list of reflections, each entry containing h, k, and l indexes and corresponding

"intensity" data in the form of I and σ(I). These numbers are the integrated intensity of each reflection and the estimated standard deviation in this intensity. This file is produced by **XPREP** from **name.raw**, **name.psi**, etc. This data will be treated differently in **XS** and **XL** refinements depending on the **HKLF** code used: an **HKLF 3** code causes the data to be treated as F and σ(F) while an **HKLF 4** code causes the data to be treated as F^2 and $\sigma(F^2)$ (where F is the structure factor for each reflection and σ(F) is its standard deviation). [Note: For reasons discussed below, anthrogenic crystals typically have intensities almost proportional to F^2 while minerals typically have intensities more proportional to F.]

name.ins This file contains the input instructions to be used for **XS** and **XL** including the molecular formula, Z number, space group, equivalent positions, any assigned atoms, extinction and weighting parameters, etc. It is produced by **XPREP** from the data in the **name.p4p** file and based on your choice of space group, etc.

name.int This is the backup copy that you make of the initial **name.ins** file from **XPREP**. [NOTE: It is often useful to make a second backup file of **name.ins** called **name.inz**.]

name.lst This is essentially a log file of what **XS** or **XL** has done during the most recent refinement cycle.

name.ort This is an orthogonal(Cartesian) coordinates file that is generated by **XP**.

name.p4p This file contains a summary of all the data you've put in about the sample (e.g., color, size, temp.) as well as all the data collection parameters (e.g., unit cell dimensions, 2θ range, identities of standard reflections, the list of up to 100 centered reflections).

name.p4t This file contains the raw X-ray data including all of the angle data and each of the peak profiles for data collected in the theta/2theta mode (which we always use). The data reduction procedure in **XSCANS** converts this to **name.raw**.

name.pcf This is a data file in CIF format (i.e., for use in generating tables, Acta Cryst., etc.) used by **XCIF**. It is generated by **XPREP**.

name.plt (e.g., **name.a**, **name.b**, **name.c**) These are plot files that contain pictures of your molecule and are most commonly generated from 'telp' in **XP** and plotted by 'rast' or 'rast/c' in **XP**. Other types of **name.plt** files include plot files from other **XP** routines and simulated powder patterns from **XPOW**.

name.pow This is the simulated .hkl file generated by **XFOG** and used in **XPOW** to calculate powder patterns.

name.prp This is the log file from **XPREP**.

name.psi This file contains the reduced ψ-scan X-ray data. The reduction procedure in **XSCANS** converts **name.pst** to **name.psi**.

name.psr This file contains a list of the hkl indices for each of the reflections used to collect ψ-scan data. It can be calculated automatically by **XSCANS** or separately using **Chi90**. (Note: The **Chi90** program must be used for low temperature data collections.)

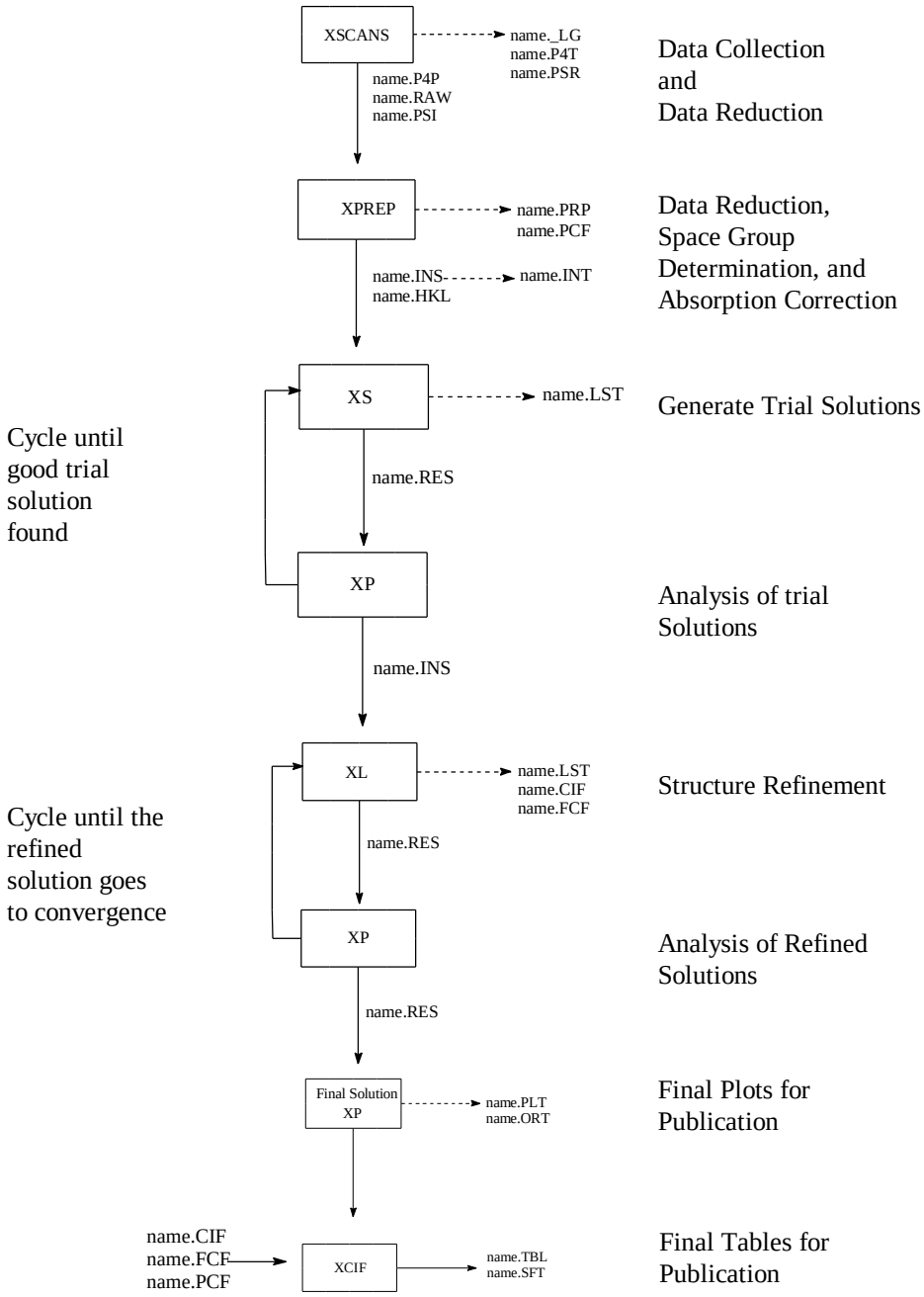
name.pst This file contains the raw ψ-scan X-ray data including each of the peak profiles. The reduce command in **XSCANS** converts this to **name.psi**

name.raw This file contains the reduced data set for each reflection measured. It contains at least hkl, I, σ(I) for each reflection rather that the peak profile and angle information found in **name.p4t**. If you want to be able to correct it for absorption, it must also contain the direction cosines. The reduce command of **XSCANS** converts **name.p4t** to **name.raw**. **XPREP** converts **name.raw** to **name.hkl** after suitable corrections have been applied.

name.res This is the output file from **XS** and **XL** that contains the old assigned crystal data and atomic positions used in the last run and new calculated positions for the Q-peaks. **XP** converts this file (after assignments of atoms, etc.) to **name.ins**.

name.sft This file contains the table of structure factors for publication. It is produced by **XCIF**.

F. FLOW CHART FOR A TYPICAL X-RAY STRUCTURE SOLUTION

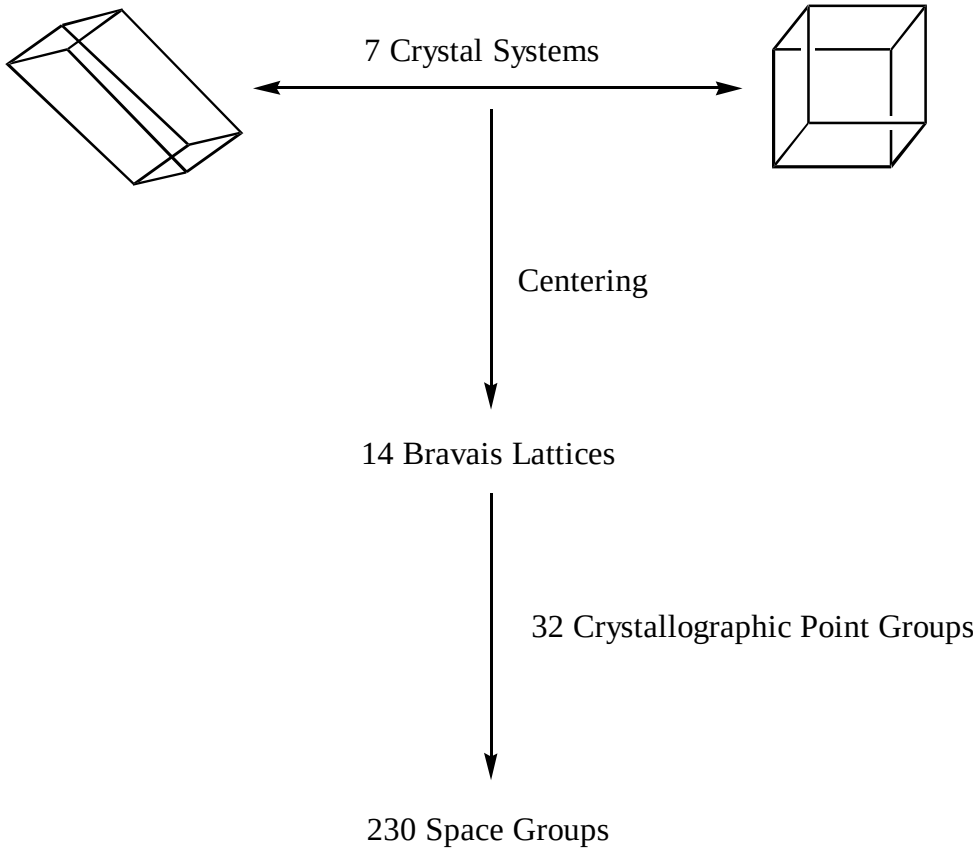


CHAPTER II. DATA PREPARATION USING XPREP

A. XPREP

Data preparation is done using this interactive menu-driven program. It duplicates some of the functions of the later stages of the diffractometer program, **XSCANS**, especially its Space Group Determination and Generation of SHELXTL Files chapters (numbers 22 and 23, respectively, in version 2.2 of the tutorial manual). **XPREP** uses the files **name.p4p, name.raw,** and **name.psi** (if you are doing empirical absorption corrections). It produces a log file, **name.prp**, a file for **XCIF**, **name.pcf**, and **name.hkl** and **name.ins** for **XS**.

From Unit Cells Through Symmetry to Space Groups



B. BEFORE STARTING YOUR WORK WITH SHELXTL BACK UP YOUR FILES (!!!!)

Copy at least the data files **name.p4p, name.raw,** and **name.psi** from the diffractometer PC onto a **new** labeled diskette(s) (the other **name.*** should be copied as well). ***WRITE PROTECT*** this diskette, it is your emergency backup!!!!! Load these files into a new directory (just for this compound) on the hard drive of the PC where you will do the solution. To copy your files from the data collection computer to your backup floppy, place your disk in the floppy drive and then type:

copy name.* a:*.* [ent]

To copy your files from your backup floppy to the processing computer, place your disk in the floppy drive and then type:

c: [ent]

This tells the computer to go to the C drive, the main hard disk on our systems.

cd \ [ent]

This command takes you to the main directory on drive c.

md c:\C832\YOURNAME\COMPOUND [ent]

This makes a new file, where YOURNAME is up to 8 characters of your name, and **COMPOUND** is up to 7 characters identifying the sample (i.e., **95ADH01**, Note: There is no trial number).

cd c:\C832\YOURNAME\COMPOUND [ent]

This puts you into the directory for your compound.

copy a:*.* [ent]

This copies the data on your backup floppy disk to this directory. Repeat for each of your backup disks.

dir [ent]

This gives you a directory of the contents of this file. Ensure that all of your files were copied.

C. USING XPREP TO PREPARE YOUR DATA

This package will provide you with information to help you choose the correct space group, absorption correction, etc. Usually, here and later, you can accept its default choice (i.e., the program's best guess). You do this by hitting enter.

To start **XPREP**, type:

XPREP name [ent] (where name is the 8 character code for your data set)

To accept the program's choice press the enter key, i.e.,

[ent]

1. Using XPREP to Determine the Correct Space Group

If you want to try a different crystal lattice type, type in the code for that lattice (i.e., to change the lattice type to "C" type the c key followed by the enter key), i.e.

c [ent]

Note: The first choice above accepts the computer's choice while the second overrides it to choose lattice type C. The package then shows the current data on the crystal/sample at the top of the screen and a list of options in the middle of the screen. It prompts you as to which option is typically run next.

For us, we typically *Search for Higher Metric Symmetry* next, i.e.,

H [ent]

The program gives you information on the current unit cell and then gives you some choices for other potential cells. Usually go with what it suggests, e.g.,

A [ent]

The program then updates the information on the current crystal/sample and gives you the list of options again.

For us, we typically *Determine or Input Space Group* next, i.e.,

S [ent]

You then have a chance to tell it if the sample is chiral (i.e., it had been previously resolved) or not, to input a known space group, or to Determine the Space Group, normally we choose the latter, i.e.,

S [ent]

It gives you the choice of crystal system (e.g., Triclinic, etc.), typically we accept its choice, e.g.,

A [ent]

You then have a choice to *change the lattice exceptions* (i.e., P, A, C, etc.), typically take its choice, e.g.,

P [ent]

It then goes through information about possible systematic absences, statistics on whether it is likely centrosymmetric, etc., and gives you choices for space group. You normally choose the one it does and in particular you usually want the highest symmetry space group that is reasonable with a low CFOM (i.e., combined figure of merit) and one that is quite common in the CSD (i.e., the Cambridge Structural Database),[18] e.g.,

A [ent]

You now have assigned the space group.

2. Using XPREP to Define the Unit Cell Contents

You now need to define the unit cell contents,

C [ent]

It tells you the current formula and Z value, the calculated density (rho) and non-H atomic volume (should be about 17-20 $Å^3$/non-hydrogen atom), and the unit cell contents. You can modify the formula (if it was wrong in **XSCANS** or you have had new data), or Z value, or the radiation (in rare cases). To accept current values when you are done.

E [ent]

This gives you an updated data table. **Write Down** the calculated absorption coefficient μ (i.e., the last entry, Mu[mm^{-1}]:x), you'll need it for the absorption correction in the next section.

[18] The CSD and CCDB are two terms for the same electronic database housed at Cambridge.

3. Using XPREP to do Absorption Corrections

At this point the default is to write **SHELXTL** files. However, you will usually want to do *absorption corrections*. One should be careful in applying absorption corrections if you don't have a good unit cell formula as this can actually hurt the quality of the solution.[19] To carry out the absorption corrections, enter

A [ent]

Depending on how you collected your data, you collected the information needed to do face indexed or ψ-scan absorption corrections. In this lab class we always collect the ψ-scan data and only face index the crystal where time permits and the crystal is appropriate. To process the ψ-scan corrections use:

P [ent]

It then asks you several questions where you normally accept its choices (but check that the choices it makes are physically reasonable! When in doubt, ask the instructor.).

[ent] [ent] [ent] [ent] [ent]

It then chooses a subset of your reflections to try out the different absorption correction models. You then have a choice of the Lamina or Ellipsoid Models (the former is best for many flat plates, the later is best in most other cases). For the ellipsoidal model:

E [ent]

You then try different values of μ x r (i.e., μ times r) where μ (i.e., mu) is the absorption coefficient and r is the average crystal diameter. You try and vary μ x r to minimize R(int) (the agreement between the intensities of equivalent reflections) and to maximize the (maximum transmission)/(minimum transmission) ratio. Sometimes it seems that you can't get both of these to vary the way you want them to. In that case, stick with minimizing R(int). Typically, the "true" μ x r should be used where the μ is the absorption coefficient calculated by the program (and which you wrote down earlier) and r is your average measured crystal diameter. Also, try to get a spread of max and minimum transmission factors similar to those you observed in your experimental ψ-scan plots. Example

0.2 [ent] N [ent] R [ent], etc. to calculate several values with the one finally chosen having say **0.3 [ent] Y [ent] P [ent]** to process the data.

---

[19] Where the formula for the unit cell is uncertain, or when you later find out that the one you initially chose was incorrect, you should not do the absorption correction at this point (or at least you should not trust it to be totally accurate). Instead, you should: (1) skip the absorption correction (or apply it with caution), (2) solve the structure using the uncorrected structure factors to get a better idea of the unit cell contents, (3) use the resulting unit cell contents to do a quality absorption correction, and (4) repeat the structure of the structure with the improved structure factors.

You next input the name of the raw data you want to have corrected i.e.,

name.raw [ent]

and the program corrects all that data.

You can do this to several data sets (i.e., different shells or from different crystals of the same compound) and then merge the corrected data. Then exit this step:

E [ent]

4. Using XPREP to View Reciprocal Space Plots

It is always advisable to check the absences in your experimental data by comparing "reciprocal plots" (available in **XSCANS** or **XPREP**) against the systematic absences expected for the chosen space group (available in the International Tables). Any significant differences should lead you to strongly question your space group assignment. One of the choices in the main XPREP menu is view reciprocal space plots (i.e., **[R] RECIPROCAL space displays**). If you choose this selection it will display reciprocal space intensity plots for any of the planes perpendicular to the crystal axis for your inspection.

5. Using XPREP to Set Up the SHELXTL Input Files

Next, you want to set up the input files for **SHELXTL**, i.e.,

F [ent]

You have to give an output file name. It is best if the 8th character in this is different from the raw data (i.e., if raw data was **95ADH03a**, you should use **95ADH03b** for the corrected data name) i.e.,

name [ent]

The program then shows you the projected contents of the **name.ins** file and asks you if you want to overwrite **name.hkl**.

Y [ent] (Note: This is **not** the default setting)

At this point you can easily go back to other possible space groups suggested earlier and make each with its own name (i.e., **95ADH03c**).

Q [ent] to quit

6. Duplicate and Backup Your SHELXTL Input files

You now have generated the **name.ins** and **name.hkl** files needed by **XS**. It is a good idea to make two backup copies of the INS file, (i.e., the **.int** and the **.inz** files):

COPY name.ins name.int [ent]

COPY name.ins name.inz [ent]

This will help you run both Patterson and Direct methods, if required, or retry one without having to rerun **XPREP**.

Make sure you back up these **SHELXTL** input files on your floppy disks.

CHAPTER III. FINDING TRIAL SOLUTIONS TO THE "PHASE PROBLEM" USING XS

A. THE PROGRAM XS

1. Basic Features of XS

The program **XS** is used to generate trial solutions to the phase problem. In essence, it uses of number of different methods to try and guess the identity and location of at least one of the atoms in your crystal. If it does this successfully, then analysis of this result by **XP** and subsequent refinement cycles by **XL** will eventually allow you to find all of the other atoms. The two most common approaches used by **XS** to do this are *Direct methods* and *Patterson methods.*

2. Direct Methods and XS

Direct methods is an approach based on statistical analyses of the intensities of the **name.hkl** reflections to find the most probable phase relationships. The automated *Direct methods* solutions from **XS** usually generates 10+ atoms as Qs. [Note: These Qs are peaks of presumed electron density found in the calculated electron density map.] *Direct methods* is most useful for organics or metal containing compounds where one atom isn't "too heavy" relative to the rest. It is less workable for 2nd and especially 3rd row transition element compounds and organics with heavy atom substituents. It also requires a relatively large number of observed reflections out to moderately high angles. This is not typically a problem for crystals of acceptable size and quality and where sufficient data collection time is available. It typically assigns several of the stronger peaks to the heavier atoms and gives a list of Q peaks in descending order of intensity. These assigned atom types are often incorrect and their exact identities should be treated with caution. However, the relative geometry's of the peaks (i.e., the presence of an octahedral coordinated metal center or a naphthalene ring) are generally much more reliable. On the first round, you should be very conservative in your assignments. Just pick out the few heaviest atoms or the substructures you are most sure about. For most molecules, *Direct methods* is the route of choice for finding a trial solution and for this reason it is the default **XS** program choice.

3. Patterson Methods and XS

The automated *Patterson method* used by **XS** is particularly suitable for structures dominated by one or a few heavy atoms (e.g., for transition metal coordination and organometallic compounds and organic compounds with a few "heavy" atoms such as P, S, Cl, Br, and I). Its output usually assigns tentative positions and identities for 1 to 8 of the heavier atoms. For organometallics/inorganics, one can often assign the metal and attached "heavy"

atoms by their shape and distances while for organics the "heavy" atoms typically show clearly. As with *Direct methods*, in many cases it will get the exact choices of these atoms wrong (e.g., it will confuse a Cr with a S or a O with a N). However, these mistakes are easily corrected within **XP** when analyzing the **XS** output (typically by running the 'pick' routine).

4. Setting Up and Running XS

The generation of the initial trial solutions for data refinement is done by **XS**. It uses the files **name.ins** and **name.hkl** files produced by **XPREP**.

Before starting. Ensure that you have made a backup copy of **name.ins** as **name.int**, i.e.,

copy name.ins name.int [ent]

Make a copy of all your files with a new 8 character name (e.g., if your raw data was **95ADH03a** and the ψ-scan corrected data from **XPREP** was saved as **95ADH03b**, make a copy **95ADH03c** on which to try solutions.

copy name.* name ¢* [ent]

(Where **name ¢**s the new file name you've chosen for the data analysis run.)

To run **XS** type:

XS name [ent] (Where **name** is your new 8 character name for this run.)

This produces a **name.res** file for use in **XP** (it has trial assigned atoms and Q peaks (these are peaks in the calculated electron density map that have not yet been assigned)) and **name.lst**, a log file of what **XS** did.

B. SETTING XS TO CARRY OUT A DIRECT METHODS OR PATTERSON SEARCH, THE NAME.INS FILE.

The default **name.ins** file from **XPREP** has a line of text (referred to for historical reasons as a "card") that says 'TREF'. This line sets **XS** up to do a Direct methods search for a solution just as the command 'PATT' on the same line sets XS up to do a Patterson solution. You can change this command line by editing this input file, i.e.

edit name.ins [ent]

You then use **XP** and later **XL** to see which give the best guess for the trial solution **XS** produces. [Note: the only difference in the two input files for a Direct methods and a Patterson methods run is the TREF vs. the PATT line.] *See the following sections and our text book for more information on the nature of Direct Methods and Patterson Methods.* Below are examples of two typical input files set up for the compound 95adh06e, (η^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$Cr(CO)_3$), by XPREP.

The input file, **95adh06e.ins** (i.e., **calctest.ins** see chapter IX), for a *Direct methods* solution on **95adh06e** by the program **XS**

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR   2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50
TREF
HKLF 4
END
```

The input file, **95adh06e.ins** (i.e., **calctest.ins** see chapter IX), for a *Patterson* solution on **95adh06e** by the program **XS**

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR   2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50
PATT
HKLF 4
END
```

C. LISTING OF THE MOST COMMON XS COMMANDS.

The **XPREP** program sets up the **name.ins** file for each structure automatically for you. In particular, it uses the information in its input files to put the following information in the **name.ins** file for use by **XS**. The program **XL** uses many of the same commands. These are modified by editing the instruction file for your data set (i.e., the **name.ins** file).

Note: the **<ctrl l>** key stroke combination (i.e., the control and "ell" keys being depressed simultaneously) causes **XS** and **XL** to stop at the next safe moment and results in all of the data that has been calculated being stored in the required files. The **<ctrl c>** key stroke combination (i.e., the control and "c" keys being depressed simultaneously) causes **XS** and **XL** to stop immediately and results in all of the data that has been calculated being lost.

Line Number in .ins file	Command and Page in the SHELXTL Manual[20]	Variables and Explanation
1st line	**TITL** 5-4	This line contains the name and space group of the sample, written in plain text.
2nd line	**CELL** 5-4	**l *a b c* a b g** The wavelength of the radiation used and the unit cell axial lengths and angles.
3rd line	**ZERR** 5-4	**Z esd(*a*) esd(*b*) esd(*c*) esd(a) esd(b) esd(g** The number of formula units in the unit cell and the estimated standard deviations in the unit cell axial lengths and angles.
4th line	**LATT** 5-4	**N** The lattice type (i.e., 1 for primitive (P), 2 for body centered (I), 3 for rhombohedral obverse, 4 for face centered (F), 5 for A centered (A), 6 for B centered (B), or 7 for C centered (C). For non-centrosymmetric space groups **N** is a negative number while it is a positive for a centrosymmetric space group.

[20] These page numbers are taken from the Bruker AXS (Siemens) reference manual for **SHELXTL**, version 5.1.

5th line	**SYMM** 5-4	The following values are the symmetry operations for that space group. They are the "general positions' of the space group taken from the "International Tables" and they can be used to convert any random position in the unit cell (i.e., X, Y, Z) into all its equivalent positions. For some high symmetry space groups this may correspond to many lines of **SYMM** codes. For the low symmetry triclinic space groups this line is absent. [Note: the identity operation, operations related by a center of symmetry, and cell centering operations should be omitted if this line is filled in my hand. They are not placed here by **XPREP**.]
6th line	**SFAC** 5-5	**element symbols** This line gives the symbols for the elements present in the crystal. The first two elements are always C followed by H (if they are present). The program will use the element identities to look up the scattering power of each atom type when it is doing calculations.
7th line	**UNIT** 5-5	**number of atoms of each type in the unit cell** These numbers have to be in the same order as the **SFAC** lists.
		NOTE: THE ORDER OF THE ABOVE SEVEN LINES MUST NOT BE CHANGED AND YOU CAN'T INSERT ANY OTHER COMMAND LINES IN HERE OR XS WILL CRASH.
8th line	**TREF** 5-10 or **PATT** 6-1	The command for a *Direct methods* structure search (see the previous sections). The command for a *Patterson methods* structure search (see the previous sections).
9th line	**FMAP** 5-8	This line is inserted by **XPREP** and helps **XS** to carry out the Fourier peak calculation. You don't need to worry about this one.

10th line or	**HKLF #** 5-9	This line tells **XS** and **XL** to read the reflections from the **name.hkl** file and how to treat the I and σ(I) data in the **name.hkl** file. When # = 3 (i.e., **HKLF 3**), **XS** and **XL** treat the intensity data as F and σ(F). When # = 4 (i.e., HKLF 4), **XS** and **XL** treat the intensity data as F^2 and σ(F^2). [Note: Intensity is proportional to F^2 in ideally imperfect crystals (i.e., as described in the kinematic diffraction model) but because of extinction's affects it is only proportional to F in perfect crystals (i.e., as described in the dynamic diffraction model). Real crystals behave somewhere between these extremes but those typically grown by synthetic chemists more closely resemble kinematic diffraction. Interestingly, mineral crystals, which grow many orders of magnitude more slowly than do anthropomorphic crystals, behave more like perfect crystal and extinction effects are much bigger for them. Thus, anthrogenic crystals are typically refined with **HKLF 4** mode while mineral crystals are refined with **HKLF 3**.]
11th line	**END** 5-10	This line tells **XS** that all required commands have now been read.
		The following lines *might* be put in before the HLKF 4 command if needed.
	MORE 5-6	**0** or **1** or **2** or **3** This command can be used to vary the verbosity (i.e., level of detail) of the output files (e.g., **name.lst**) with **3** being the most verbose.
	OMIT 5-6	This command can be used to omit reflections based on the angle they were collected at, their signal to noise ratios, and their index values.
	PLAN 5-8	This gives the number of Fourier peaks (Q peaks) that will be written to the **name.lst** and **name.res** files for later use by you and **XP**.
	REM 5-5	**text on the same line** This text isn't used by **XS** but is output onto the **name.res** file. It is a useful way to make comments to yourself.
	SIZE	The three dimensions of the crystal. This data is placed in the CIF file.
	TEMP	The temperature of the data collection. This data is placed in the CIF file.
	TIME 5-6, 12-4	**TIME t** This command sets the maximum time (**t** in seconds) for the **XS** or **XL** run. After this time has been exceeded, this command causes these programs to gracefully stop at the end of the current cycle.

Examples of the uses of these commands are given in the proceeding and following sections.

D. RUNNING XS TRIAL SOLUTION SEARCHES

The contents of each line in the input file, **95adh03e.ins**, for a *Direct methods* solution on **95adh03e** by the program **XS** are shown below as an example.

```
TITL 95ADH03E in C2/c
CELL 0.71073  24.115   6.155  15.924  90.00  99.92  90.00
ZERR    8.00   0.001   0.000   0.001   0.00   0.00   0.00
LATT  7
SYMM -X, Y, .5-Z
SFAC C H N O CR
UNIT 88 96 16 24 8
TREF
FMAP
HKLF 4
END
```

To use this to run **XS** on your data set, go to the **DOS** directory containing your input files for that compound (i.e., **95adh03e.ins** and **95adh03e.hkl**) in the above case.

XS name [ent]

This would then set up and run **XS** for your files. This typically takes a few seconds to a few minutes. Note: just use the eight letter name for your compound (i.e., without the **.ins** extension). For this particular example one would type:

XS 95adh03e [ent]

For a detailed discussion of the application of *Direct methods* by **XS**, see pages 5-10 to 5-20 in the Bruker AXS manual.

A detailed example of the use of **XS** and **XL** to solve the structure of **calctest , (h^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$Cr(CO)_3$**, is given in chapter IX.

E. EVALUATING THE QUALITY OF THE RESULTS FROM XS

1. Using R Factors to Evaluate the Success of XS.

The **XS** output printed to the **name.lst** file and the computer screen includes several parameters that are useful in telling you if **XS** gave a productive result (i.e., one that is likely to lead to the finding of all of the non-Hydrogen atoms). One of the most important classes of these is the calculated R factors. An R factor is the "residual index" and it is found near the end of the **name.lst** file and the data displayed on the screen. The theoretical value for the R factor is 0.83 for centrosymmetric structures and 0.59 for non-centrosymmetric structures for random atomic placement in the unit cell. *In practice, if the R factor after **XS** is not somewhat less than about 0.5 you will seldom get a solution that will refine to give you the molecular structure.* Indeed, unless you are desperate this **XS** result is not worth pursuing. Instead, run **XS** again with different input parameters (i.e., PATT vs. TREF). For this purpose, I pay the most attention to the first R factor printed out by **XL** which is the one for the subset of reflections having Fo > 4 σ(Fo). In my experience this is typically about 0.46 or smaller if even one heavy atom is assigned correctly.

2. Using XP to Evaluate the Success of XS

The routine **XP** is also used to evaluate if the trial solution produced by **XS** is likely to be useful. Load the results of **XS** into **XP**, e.g.

XP name [ent]

fmol [ent]

info [ent] or **mpln [ent]**

proj [ent]

Use the view in 'proj' to see if any chemically reasonable parts of the molecule "leap" out at you. [Note: Sometimes in more complicated structures this is easier to see if you first delete most of the weakest Q peaks, especially those below the intensity "drop off."] The utility 'bang' can also be useful for this. If even one of the peaks put out by **XS** is real, and you assign it correctly using 'pick' and then save the results using 'file' then the following **XL** cycle almost always will show that you are on your way to the correct structure.

F. WHAT TO DO IF XS FAILS TO GIVE A REASONABLE SOLUTION

When XS fails, as it can for even what are expected to be the simplest structures, then one typically has a hard road ahead. The first thing to try is to make sure you have given both *Direct methods* and the *Patterson method* a shot. Major problems can arise if you have chosen the wrong space group or if your crystal is twinned. If this is what has happened, working this out can be a very tough challenges for even an experienced crystallographer. What even a novice can do is check that the volume of the unit cell per non-Hydrogen atom is reasonable. This value is typically about 18 $Å^3$/non-hydrogen atom but ranges up to 20 or 30 for molecules with many heavier elements and down to about 13 for highly condensed structures such as polycyclic aromatic hydrocarbons. The value of R(int) is the average difference in intensities for sets of crystallographically equivalent reflections. Ideally, R(int) should be near zero with the deviation from zero being due to random statistical fluctuations in the peak intensities. However, in the real world it should be less than about 0.1 for quality data that has been correctly processed. A higher value may indicate the wrong space group was chosen and/or that a poor absorption correction was done (i.e., on a very non-spherical crystal). Similarly, the value of $|E^2 - 1|$ should be close to 0.968 and 0.736 for centric or acentric space groups, respectively.

1. Things to Check When Direct Methods Fails

This question is discussed at some length in the SIEMENS manual on pages 5-19 to 5-21. A special problem for *Direct methods* is the data quality. A successful Direct methods solutions requires adequate signal to noise ratios out to sufficiently high angles. If less than about half of the possible peaks are observed in the range of 1.1 to 1.2Å resolution (i.e., $\lambda/2\sin\theta$ which corresponds to θ angles of about 18 and 42 degrees for Mo and Cu, respectively) then *Direct methods* seldom works. Similarly, data should be collected out to sufficiently high angles of 2θ that the maximum index values of the collected reflections have values that are about equal to or greater than the unit cell axial lengths in Å. [Thus, if the unit cell had axial lengths of 6.6, 7.3, and 13.2 Å then one should have collected X-ray data out to reflections with indexes of at least about 7, 8, and 14 in h, k, and l, respectively.] It can also have problems if a heavy atom is near, but not on, a symmetry element in the unit cell.

2. Several Ways to Finesse Direct Methods

a) Use more brute force in your Direct methods calculation

Sometimes it pays to use brute force with *Direct methods*. To do so, change the **TREF** card in the **XS** input file (i.e., **name.ins**) from its default value to one that is more powerful but also much slower, e.g.

TREF 2000

or even

TREF 10000 50

[Note: What you are doing is increasing the number of **TREF** cycles (i.e., to 2,000 or 10,000, respectively) and changing the nE option in the **TREF** card (i.e., Jeanette Krause Bauer reports that values from 30 to 100 work for her and suggests 50, see above). Then, rerun **XS** with this more powerful version of the *Direct methods* routine.

b) Pick some of the other suggested Direct methods solutions

The *Direct methods* calculations in **XS** does not just find the single solutions present in the **name.res** file. Instead, it finds a large number of different solution that are listed near the middle of the **name.lst** output file for **XS** which is indicated by a * after its CFOM value (see chapter IX section A3 for an example of such a **XS** output file). **XS** chooses the "best" solution number (in the case of the example # 1155913 with a CFOM = 0.0806) for its subsequent analyses (i.e., it chooses the one with the best CFOM and semi-invariants). [Note: this is typically the last solution shown.] However, typically several other solutions have CFOM values which are almost as good (e.g., solutions 602457, 1522673, and 235117 in the example). One can often use one of these other solutions to get a better initial model. This is done by visually picking another good solution and then rerunning **XS**[21] with the **TREF** line edited to read:

TREF -solution # (e.g., **TREF -602457** in the example). [Note: There should be a negative sign before the solution number.]

3. Simple Things to do if Even These Steps Fail to give a Reasonable Solution

If these things fail, then look to the *Patterson method*, collect better data at higher angles, recheck your space group, and/or look to a higher being for help! If all else fails, blame the crystals and try to grow more "cooperative" crystals using different crystallization conditions, solvents, etc. This latter approach often works quite well, requires less crystallographic knowledge, and certainly takes less of your time, especially if you can get *someone else* to grow the crystals!

4. Advanced Crystallographic Techniques to Try When These Steps Fail to Give a Reasonable Solution

If one is a more skilled crystallographer with more experience and a deeper understanding of what one is doing, there are a wide range of more sophisticated methods for getting a starting solution. Most novice crystallographers will have little experience using these methods, but if the

[21] This second solution should be done on the same computer as the original **XS** run.

structure is important to you they may be worth pursuing. Below are listed some suggestions that have been made crystallographers more skilled than myself.

a) Modify the Symmetry of the Input Files

For problem structures, one can often artificially lower the symmetry of the space group and retry **XS** (removing centers of symmetry can be especially helpful). The structure is then refined in this "modified" space group until all atoms are found and converged isotropically. Then if necessary, one locates any additional symmetry operations between related molecular groups, moves all of the atoms to the appropriate positions for the higher symmetry space group, deletes the symmetry-related atoms, and changes the '**LATT**' and/or '**SYMM**' lines from the **name.ins** file to give those for the correct space group. [Note: this method was suggested by Doug Powell at the University of Wisconsin.]

b) Use XPS to find a solution

Dear Readers: I would greatly appreciate suggestions for this section as I have yet to use **XPS**!

Dear Readers: I would greatly appreciate any other hints and ideas on other relatively simple things that could be tried here.

G. THE USE OF XS TO FIND TRIAL SOLUTIONS FOR NEUTRON DIFFRACTION DATA

The program **XS** runs identically for analyzing neutron data with the exception(s) that……

Again Dear Readers: I would greatly appreciate suggestions for this section as I have yet to use **XS** for neutron data myself!

CHAPTER IV. THE ASSIGNMENT OF ATOMS USING XP

A. AN OVERVIEW OF THE PROGRAM XP

The **XP** program is a graphical interface between the data calculated by **XS** or **XL** and you. It basically converts the **name.res** file (which is an ASCII file containing the contents of the **name.ins** file from the start of the cycle (i.e., giving some space group, symmetry, etc., data, and the atomic positions and displacement parameters in the earlier model) and any Q peaks (i.e., peaks in the calculated electron density map that are not yet accounted for) calculated by the **XS** or **XL** run into an easier to use form. For example, there are various graphical molecule viewing subroutines (e.g., 'proj'), one for deleting and naming atoms using a graphical tool (i.e., 'pick'), and routines to view peak positions and intensities in a tabular format (i.e., 'info') and calculate bond lengths and angles (i.e., 'bang').

Every time you start it, **XP** takes the last **name.res** file and uses it to generate all this data. If you save the results of your efforts (i.e., using 'file'), they are saved to **name.ins**. This does not change **name.res** so if you rerun **XP** before running **XL** (which converts **name.ins** to a new **name.res** file) you will "lose" the work done under the last **XP** run. However, if you start **XP** by typing **XP name.ins [ent]** then it will load the atomic positions from the **name.ins** file.

The use of **XP** in structure solution will be discussed in the next several chapters. In chapter VIII, its use in generating pictures for publication is discussed. Detailed descriptions of the most useful **XP** commands are found at the end of chapter VII.

B. THE TYPICAL STEPS WHEN USING XP TO ASSIGN ATOMS

1. Starting XP to Analyze Data

In a typical cycle of assigning atoms, the various subroutines from **XP** (indicated by single quotes, i.e., 'proj') would be used in the following order. First though, you start **XP** by typing:

XP name [ent]

where name is the 8 digit code that includes the compound and trial number (e.g., **95ADH03c**). This reads the **name.res** file for that trial number into **XP**. [Note: if you type in **XP name.ins [ent]** the program loads the atomic positions from the .ins file.] The **DOS** screen then converts to the **XP** screen which has a "**Windows**" feel.

The first routine you must always run is 'fmol'. It converts the bare atomic and Q coordinates into the correct format for graphics and makes a connectivity list, i.e.,

fmol [ent]

It then displays the connectivity list.

Then run 'info', i.e.,

info [ent] or

info/L [ent] print [ent]

This routine displays information on the current list of atoms and Q peaks. The set of commands on the second line above sends the 'info' list to the printer. Most useful is the last column which lists the intensities of the Q peaks. The strongest of these are most likely to be real atoms. The weakest are often ghosts and often several are very close (<0.7 Å) to "heavy" atoms that haven't been made anisotropic yet. They can be killed with confidence as this distance is too close to be real. A careful inspection of the intensities will often show a "drop off" in intensities between strong peaks (i.e., more likely real) and weak peaks (i.e., likely garbage).

2. Evaluating and Assigning Atoms and Q Peaks

Remember: When in doubt, don't make an assignment. If the peak is real it will come back in the next XL cycle and if it's incorrect it might drive you away from the correct solution.

a) Evaluating atoms and Q peaks

First inspect in output from 'info'. Look for atoms that have suspiciously large displacement parameters compared to their neighbors and for Q's of such low intensity that they are unlikely to be real atoms. Then, run 'proj', i.e.,

proj [ent]

This routine is an interactive way to display and rotate the molecule. You look for insight into probable structural fragments (e.g., octahedral transition metals, aromatic rings). When you find an orientation you like, click on exit. This saves the view last used in 'proj' for input into other graphical routines, e.g., 'pick', 'pers', 'telp.'

b) Assigning Q peaks and changing the assignment of atoms

Then run 'pick', i.e.,

pick [ent]

This routine is an interactive way to delete Q peaks, assign Q peaks as particular atom types, and name or rename peaks interactively. To kill the blinking peak, push the [ent] key. To assign, name, or rename a peak type in the four letter ID (i.e., atom symbol followed by alphanumerics) then [ent]. To go backwards in the peak list, push the [←] key at the top right of the keyboard. To skip a peak without changing its type, push the space bar. Pushing the [/] key exits 'pick' and saves the result. Pushing the [esc] key exits 'pick' without saving your work. The 'pick' routine starts with the last Q peak on the 'info' list and works backwards to the strongest (i.e., "heaviest") atom. [Note: Some crystallographers prefer to use a combination of the 'diag' and 'name' commands to assign atoms rather than 'pick' but I find the use of 'pick' more intuitive for beginners.]

In this first round, you may not be able to tell similar peaks due to atoms having similar total numbers of electrons apart based on height or position. Thus, a C, N, O, or F or a Si, P, S, or Cl will often look similar. If however, you are sure the peak is really an atom and is one of these, it is safe in early refinement cycles to assign it a generic label (i.e., C or S, respectively) at first and change it to the correct atom type in a later cycle when your information will be better. Since the number of electrons is similar, this won't hurt you too badly in an early cycle.

c) Killing sets of atoms

An alternative to 'pick' that is very useful when many atoms need cutting is kill, e.g.,

kill Q7 to Q13 [ent] or

kill C11 H24 Q7 Q8 Q14 [ent]

kill $Q [ent]

This routine kills the specified ranges of atoms, lists of atoms, or types of atoms, respectively, very quickly.

d) Naming of atoms

You should start giving the atoms "complete" names (e.g., C12, H7) as soon as the structure is clear. Choose names that are reasonably intuitive and also consistent with common usage in the field (i.e., IUPAC) to save yourself work later on.

e) Sorting atom lists

You should also start to 'sort' your atom list early on and continue to do so after each cycle which adds new atoms. This will greatly increase the ease with which you can interpret the data tables later in the refinement process.

3. Checking Your Assignments for "Chemical Reasonableness"

You should check your assignments from 'pick' for chemical reasonableness. Use 'proj' to view them for reasonable bond lengths and angles visually and 'bang' to do this numerically (the set of commands on the second line below sends the 'bang' list to the printer), i.e.,

bang [ent] or

bang/L [ent] print [ent]

This 'bang' routine prints out, for atoms in "close contact" (within the sum of Van der Waals radii where they may be assumed to be bonded), a summary of bond lengths and angles that can be scanned to look for "chemical reasonableness" (≈1.5 Å for C-C bonds, 1.0 Å for C-H bonds, etc.).

4. Saving the Results of Your XP Analyses

Once you have assigned or killed all the Qs, you want to save and exit, i.e.,

file name [ent]

where name is the eight digit code for this run. It will then ask you which file to take the raw positions from, you can accept the default, i.e.,

[ent]

To exit back to **DOS**, type

exit [ent]

5. Returning to XP from the Parameters Saved in Name.ins

If you type:

XP name.ins [ent]

then **XP** will start by reading in the data from the **name.ins** file. This is particularly useful if you have already analyzed the data from the **name.res** file, saved the results, and then exited from **XP** and decide you want to do another plot, generate a new set of planes, look at a close contact or displacement parameter, etc.

CHAPTER V. REFINING ATOMIC POSITIONS USING XL

A. INTRODUCTION TO XL

The least squares program **XL** is the industry standard for refining crystallographic data. It is described in detail in chapters 8 and 9 of the Bruker AXS (Siemens) SHELXTL manual and is based on George Sheldrick's latest SHELX engine. The central principle of such a least squares refinement is an iterative approach to solving the "phase problem" and improving the quality of the structural model.

1. Refining Data

a) Intensities and structure factors

The data collection software measures the intensities of each reflection, I, as well as the standard deviation of these intensities, $\sigma(I)$. These values are later corrected in **XPREP** to produce a final set of I and $\sigma(I)$ that are used in structure analysis. For ideally imperfect crystals, a model which most crystals grown by chemists closely resemble, these measured intensities are proportional to the square of the structure factors, F_o^2. For perfect crystals, which some mineral crystals more closely resemble, the dynamic diffraction model is more appropriate and suggests that the measured intensities are proportional to the observed structure factors, F_o.

b) Refining versus F^2 or F

The **SHELXTL** program always refines the model versus F^2. Older software, written when computer resources were much more scarce, often refined the model versus F. For most crystals one is likely to see in a chemistry crystallography lab, refining against F^2 is superior. However, refining against F^2 will tend to increase the magnitude of the R values by about a factor of two. The **XSCANS** software on our P4 produces a **name.hkl** file with the intensities expressed as F_o^2 and $\sigma(F_o^2)$. However, one can change the **HKLF** instruction in the **XS** and **XL** **name.ins** input file from its default value of 4 (which treats the experimental data as F_o^2 and $\sigma(F_o^2)$) to a value of 3 (which treats the experimental data as F_o and $\sigma(F_o)$) if one is using an old diffractometer data processing program which still outputs the data in the latter form.

c) Refining on all of the data

In the past, people often refined the model against only part of the experimental data. Typically, all reflections having intensity over standard deviation values (i.e., $I/\sigma(I)$) less than or

equal to some arbitrary cut off (often $I > x\ \sigma(I)$ where x equaled 2, 3, or 4) were not included in the calculation. Since computers used to be slow and the computational difficulty of the calculation increases linearly with the number of reflections and with the square of the number of refined parameters, this was once widely practiced. It is now strongly discouraged since such an arbitrary cut off throws out useful information and systematically biases the results. However, including the statistically weak reflections does increase the R values as compared to refining against only the strongest reflections. Nevertheless, **SHELXTL** routinely refines against all of the data since this produces the most reliable crystallographic results. [Note: It does calculate for you what the R values would be if only the strongest data was used.] Sometimes it is scientifically justified to remove one or more individual reflections using the **OMIT** command. However, this should never be done by the novice and always done with great care and sound reasons for each reflection excluded. [Note: One of the most common acceptable excuses is when peak profiles show that one or more low angle reflections have been partially cut of by the beam stop or for some other such mechanical reason.]

2. A Qualitative (If Somewhat Misleading) Picture of How Crystal Structures Can Be Refined

What happens in the process of the refinement of your model against the experimental data can be qualitatively understood as occurring through the following steps. They are akin to some Fourier refinement methods still in use by some protein crystallography labs. This is not how **XL** actually carries out the refinement, but I often find it useful to think about it this way since the mathematics of a more correct picture can, for many people, lead to more "fog" than "clarity."

a) The 1st Step: Read the Data and Instructions

The software reads the instructions from the input file (i.e., **name.ins**) and the diffraction data from the (i.e., **name.hkl**) files.

b) The 2nd Step: Calculate Partial Phases

The software uses any assigned atoms (i.e., positions, sizes, and shapes) determined in previous refinement cycles to calculate a set of partially correct phases for the structure.

c) The 3rd Step: Calculate an "Observed" Electron Density Map

The software combines these calculated phases with the experimental intensities to calculate an "observed" electron density map.

d) The 4th Step: Calculate a "Difference" Electron Density Map

The software subtracts the electron density due to any atoms previously assigned from the "observed" electron density map to give a difference electron density map.

e) The 5th Step: Calculate Improved Structural Parameters

The software uses the positions and intensities (both positive and negative) of the residual electron density on this map to calculate better atomic coordinates, displacement parameters, and any other refined parameters.

f) The 6th Step: Repeat This Cycle

This process is typically cycled through several times to give the final output (i.e., **name.lst** and **name.res**) that is used by the crystallographer in the next step to evaluate the refinement results.

3. A Qualitative Description of How XL Actually *Carries Out a Least Squares Refinement*

[Note: this section needs substantial work yet and particularly input from my external reviewers! It needs to be accurate, it needs more detail, but it also needs to be accessible to the mathematically unsophisticated and give a better visual picture of what is going on! A real challenging combination!!!]

The least squares process actually used by **XL** can be visualized in terms of the following eight steps.

a) Read the Data and Instructions

The software reads the **XL** instructions from the **name.ins** and the diffraction data from the **name.hkl** files.

b) Calculate Structure Factors and Partial Derivatives and R Factors

The software uses this information to calculate structure factors and their partial derivatives and R factors.

c) Build Normal Equations and Invert the Matrix

The software determines the normal equations and inverts the matrix.

d) Calculate Shifted Positions and Shifted Displacement Parameters

The software uses this information to evaluates how the positions and displacement parameters should be shifted.

e) Repeat Items b Through d Until Completion

This process is typically cycled through several times to give the final output.

f) Calculate an Analysis of Variance

The software then carries out an analysis of variance.

g) Calculate Geometry

The software then uses this information to calculate the atomic positions and displacement parameters.

h) Calculate a Difference Electron Density Map

The software subtracts the electron density due to any atoms previously assigned from the "observed" electron density map to give a difference electron density map.

4. The R factors and GOOF

The R, wR, and GOOF parameters are very useful in monitoring the progress of a refinement from step to step where one wants to see the R and wR factors decreasing and GOOF approaching one. However, they are of less use in comparing the structure refinements of different molecules, especially if the data analysis assumptions are different. They are discussed in more detail in chapter VI section E.

B. TYPICAL STAGES OF AN XL REFINEMENT

There are an almost infinite number of ways that one could approach solving the structure of even a single sample. The stages that I follow for routine structures are outlined below. Examples of one such approach for one molecule (**95ADH06e** referred to as "calctest", (η^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$Cr(CO)_3$) are illustrated in chapter IX, below.

1. The 1st Stage: Find a Trial Solution Using XS and XP.

In general, one would first use *Direct methods* and then the *Patterson method* (only where required) to try to find a good trial solution using **XS**. This would be evaluated using **XP** as described above. At the end of this stage you have identified at least one atom to start your least squares refinement with in the next stage. See chapter IV for more details.

Hints for this stage of the process:

- You need to find only the approximate identity (i.e., it is a Cr or an Fe), size, and position of one atom for most structures.
- Assigning more atoms at this stage can speed later refinements but only if they are correct.
- Incorrect assignments can lead you to failure in later stages.
- It is therefore best to assign only the atom(s) about which you can be most confident.

2. The 2nd Stage: Using XL and XP to Refine All Non-Hydrogen Atoms with Isotropic displacement Parameters.

This stage involves the first of several isotropic refinement cycles by **XL**. In this stage, which may have to be repeated several times, one uses **XP** to try to assign the atoms and subsequently **XL** calculates improved atom positions and isotropic displacement parameters. The use of **XP** commands is discussed in detail in other chapters. At the end of this process one hopes to have reasonable positions and isotropic displacement parameters for all of the non-Hydrogen atoms. These spherical electron density models are typically adequate for locating and identifying all non-Hydrogen atoms.

Hints for this stage of the process:

- The first **XL** cycle should give R values of significantly below 50% if the initial atom(s) assigned from **XS** were correct.
- Assigning the maximum number of atoms in each cycle is tempting but may easily lead you away from the global minimum to some "dead end" local minimum.
- Therefore, only assign those atoms in each step about which you can be most confident. Assigning only one new atom in each cycle will eventually bring you to a

complete solution. There is also some reason to believe that slower assignment strategies are more likely to bring you to the globally best solution.

- You should never try and assign hydrogen atoms when the other atoms are still isotropic as many of these assignments will be incorrect.
- There is often a cutoff in the list of Q peaks between ones which are almost all real and ones which are ghosts. This cutoff will be found where the peak intensities list suddenly changes from a rather smooth decrease to a rapid drop off of in intensities to about half in one step followed by another rather smooth decrease.
- Use the displacement parameters (i.e., from the 'info' command) to tell you if your assignments are correct. They should be similar for atoms of the same type, especially if they are in the same part of the molecule. Atoms that become unusually large may be due to an assignment of the Q peak to an atom type with too many electrons and you should change the atom type appropriately (e.g., change an O to a C). Or the assigned Q peak might have been a ghost and this assigned atom should then be deleted. Atoms that become unusually small may be due to an assignment of the Q peak to an atom type with too few electrons and you should change the atom type appropriately (e.g., change a C to an O).
- Use the 'proj' and 'bang' commands to check that the refined atoms maintain reasonable three dimensional structures, bond lengths, and bond angles.

3. The 3rd Stage: Using XL and XP to Refine All Non-Hydrogen Atoms with Anisotropic displacement Parameters.

This stage typically involves one anisotropic refinement cycle by **XL**. It converts the non-Hydrogen atoms to displacement ellipsoids (i.e., football or pancake shaped objects) to better account for their real electron density distributions.

Hints for this stage of the process:

- This should be done only after all or almost all of the non-hydrogen atoms have been found and refined isotropically.
- You add the **ANIS** instruction to the **name.ins** file to convert all non-hydrogen atoms following this command on the list to anisotropic refinements.
- This will produce a dramatic drop in the R values after the next **XL** cycle.
- If more non-hydrogens are added later then the **ANIS** instruction must be repeated.
- If your data to parameter ratio drops to low (i.e., below about 7 or 8), you may elect to refine only some of the more strongly diffracting elements with anisotropic displacement parameters. If this does not reduce the number of parameters sufficiently, you may elect to refine some groups (e.g. phenyl groups) as rigid bodies or use other tricks.

4. The 4th Stage: Using XL and XP to Assign and Refine all Hydrogen Atoms.

This stage typically involves several refinement cycles by **XL**. In these, one uses **XP** to successively identify and refine most or all of the Hydrogen atoms from the Q peaks calculated by **XL** and, if necessary, by calculating their positions.

Hints for this stage of the process:

- Some authors advocate first placing the hydrogen atoms in calculated positions and perhaps even refining them as simply riding on their attached atoms.
- I require my students to first find the hydrogens in the Q peak list and then to fully refine them. With good data quality this is generally successful although it may take several refinement cycles.
- Only if this effort does not result in all hydrogens being located from the Q peak list do I place them in calculated position. I then still refine them isotropically.
- I only refine hydrogens with a riding model of some type if my data to parameter ratio is too low or the data quality is sufficiently low that these atoms "blow up" or "wander off" in subsequent refinement cycles.

5. The 5th Stage: Using XL to Refine Additional Crystallographic Parameters Such as Extinction

This stage typically involves several refinement cycles by **XL** in which additional parameters to be refined are edited into the **name.ins** file.

Hints for this stage of the process:

- If it is suggested in the **XL** output, refine the extinction parameter by adding the **EXTI** command to the **name.ins** file.
- At this stage it make sense to ask the program to make the files needed by **XCIF** to calculate tables by adding the **ACTA** command to the **name.ins** file and modifying the **BOND** command to say **BOND $H** in this same file.
- Near convergence one can modify the **WGHT** command by adding in the weighting values suggested by the **name.res** file into the **name.ins** file. [For example, in the worked example given in chapter IX you can see that I've shaded the weighting suggestion in the calctest.res file from the 7th cycle and used these numbers in the calctest.ins file of the 8th cycle.] This sometimes takes several refinement cycles to converge on a steady value and can't be completed until after the absolute structure is determined.

6. The 6th Stage: Using XL to Determine Absolute Structure

If the quality of your crystallographic data is good enough then you should be able to easily determine the absolute structure of your molecule or crystal. Quality crystallographic data for this purpose is characterized by: a good signal to noise ratio and a large number of reflections

per refined parameter (i.e., at least 9 or 10)), the collection of sufficient Friedel pairs (i.e., those reflections in reciprocal space most sensitive to the absolute structure), and the presence of elements with sufficiently strong anomalous dispersion. Generally, any good quality data set on a sample collected with Cu radiation with different atom types (not counting hydrogens) can be assigned the proper absolute structure. Data sets on samples collected with Mo radiation usually require atoms on different rows of the periodic table to make proper assignments of the absolute structure.

Only non-centrosymmetric space groups (i.e., those lacking an inversion center) can give optically active crystals but there are a number of non-centrosymmetric space groups that are not suitable for chiral compounds. These space groups contain no center of symmetry, but they do contain symmetry operations of the second kind which change the handedness of any molecular groups. Note that the absolute structure of these non-centrosymmetric but nonchiral space groups must also be determined. The chirality of the crystal may be due to the presence of molecules that were optically resolved before they were crystallized, to the presence of molecules that resolved themselves into right any left handed crystals (cf., Louis Pasteur), or to molecules that were not chiral in solution but crystallized into optically active crystals.

In many cases, the **XL** output on the screen warns you if you have solved for the wrong optical isomer. It does this by analysis of the value of the Flack parameter. The meaning of this parameter is described in detail in our text and on pages 8.4, 8.5, and 11.2 in the SHELXTL manual. In brief, this parameter tells you if you have picked the correct absolute structure. In theory, it should equal 0 if you have the correct structure and +1 if you have the opposite one. In practice, **XL** calculates this parameter and its estimated standard deviation. If the calculated Flack parameter is within 3 esd's of 0 one can conclude with confidence that one has the correct absolute structure.

In general, if you get this warning of possibly having the wrong absolute structure, then, for most space groups, you can usually use the 'invt' command in **XP** to convert it to the right one. If you are not sure you have the right isomer, then use 'invt' in **XP** to convert your structure to the other one and then rerun **XL** and see if the R factors get better or worse. The exceptional space groups also require a change of space group operator(s). The simple 'invt' command inverts around the center of the unit cell. The seven exceptional space groups (i.e. Fdd2, I4(1), I4(1)22, I4(1)md, I4(1)cd, I4bar2d, and F4(1)32), which are listed in the Bruker AXS (Siemens) **SHELXTL** manual (page 11-3), must be inverted around some other point in the cell. For these special space groups it is highly advisable to consult an experienced crystallographer.

7. The 7th Stage: Convergence

Your structure solution is done when the solution has gone to convergence and you have added all of the parameters you want to refine. By convergence, I mean that additional least squares cycles in **X**L no longer move any atomic positions, displacement factors, occupancies, etc., appreciably. The current standard for the definitive journal, *Acta. Cryst.*, is that the maximum absolute value of the shift/standard uncertainty should be less than 0.1. However, with

modern computers and methods this standard is widely considered to be too high and it is expected to be lowered soon. In my lab, the maximum value I typically aim for is substantially under 0.01 with less that a 0.001 change in any positional or displacement parameter.

8. Advanced Tasks and Problems for Refinement That Merit More Detailed Treatment in Future Editions

While solving more demanding structures, one needs a variety of more specialized and advanced skills that involve **XP** and **XL**. I will not include a detailed discussion of these in this edition of the manual. However, I hope to include such discussion as one or more appendices useful to the more advanced students. These sections will be written as my time permits, as my expertise in their use increases, and as users volunteer to supply and/or assist me in writing them.

Topics that merit more detailed treatment include:

- The general topic of constraints, restraints, and the difference between the two.
- The fixing of displacement parameters of related atoms (e.g., those of hydrogen atoms to values 1.2 times that of the atoms they ride or of all carbon atoms in a benzene solvate to the same value).
- The fixing of X-H distances.
- The use of riding models for hydrogens and other atoms.
- The use of **XPS** and Shake and Bake type refinements.
- Refining linked parameters (e.g., occupancies and U values).
- The refining of occupancies in general.
  - The refining of solvent occupancies.
  - The refining of structures with several atoms occupying the same or very close sites.
  - The refining of occupancies with the total occupancies for sites fixed.
- The use of rigid body models in refinement.
- The refining of twinned data sets.
- Dealing with Renninger reflections.
- Dealing with disorder in groups such as methyl groups.
-

C. ALPHABETICAL LISTING OF THE COMMAND LINES FOR XL AND XS

Many of the command lines for **XS** and **XL** are the same. Below are repeated the most important ones in alphabetical order.

Note: the order of the first seven lines of the name.ins file should remain the same for XL as it was for XS (i.e., TITL, CELL, ZERR, LATT, SYMM (where required), SFAC, and UNIT.

The commands of most use for beginners (e.g., in courses such as Chemistry 832: Solid State Structural Methods) are given shading below.

Command Code	Page in the SHELXTL Manual[22]	**Variables** and Explanation of the Use of These Commands
<ctrl l>		This key stroke combination (i.e., the control and "ell" keys being depressed simultaneously) causes **XS** and **XL** to stop at the next safe moment and results in all of the data that has been calculated being stored in the required files.
<ctrl c>		This key stroke combination (i.e., the control and "c" keys being depressed simultaneously) causes **XS** and **XL** to stop immediately and results in all of the data that has been calculated being lost.
ACTA	13-37	This command tells the program to save all the required data in "Crystallographic Information File", CIF, format for use in preparing tables with **XCIF** and for use in electronically submitting papers.

[22] These page numbers are taken from the Bruker AXS (Siemens) reference manual for **SHELXTL**, version 5.1.

AFIX	12-12	This powerful command applies constraints and/or generates atoms at idealized coordinates (often with respect to the heavier atoms to which they are bonded). I do not routinely use the **AFIX** or **HFIX** commands. My data sets have generally been of sufficiently high quality that not fixing these parameters has not been a problem. This is largely because our two dedicated diffractometers means we have sufficient data collection time that we usually get excellent signal to noise ratios on the peaks and data collected out to relatively large angles. This means that all of my hydrogen parameters are fully refined and not fixed to any idealized values. While this can give bonding parameters that are not "perfect" looking they are true experimental values. I only discard this approach and fix these parameters when refinement fails to give chemically reasonable answers. This is typically because of having very small or weakly diffracting crystals, disorder, and/or the presence of a very heavy atom that dominates the scattering of the crystal.
ANIS	12-12	**ANIS** Makes all of the following non-Hydrogen atoms anisotropic in the next **XL** refinement. **ANIS n** Makes the next **n** atoms anisotropic in the next **XL** refinement. **ANIS atoms** Makes the next **named** atoms anisotropic in the next **XL** refinement, e.g. **ANIS $P** **ANIS Cr O11 C14** would make all phosphorous atoms and the Cr, O11, and C14 atoms anisotropic in the next **XL** cycle, respectively.
BOND	12-35	This command tells the program to store bond lengths and angles. **BOND $H** includes Hydrogen atoms in the stored values.
CELL	5-4, 12-1	**l *a b c* a b g** The wavelength of the radiation used and the unit cell axial lengths and angles.
DELU		This command restrains all the named atoms to having the same displacement parameters.
DFIX	12-25	This command is used to fix the distance between two named atoms.

EADP	12-22	This command is used to give two or more atoms the same isotropic or anisotropic displacement parameters.
END	5-10, 12-4	This line tells **XL** that all required commands have now been read.
EQIV	12-18	This command along with **RTAB** gives information on symmetry and bonding of inter- and intra-molecular interactions.
EXTI	12-7	This command is placed in the **name.ins** file after the non-Hydrogen atoms have gone anisotropic to allow the program to refine for extinction in the crystal (i.e., to deal with effects discussed on pages 210 and 327 in Glusker's text).
EXYZ	12-17	This command is used to put two or more different atoms at the same position in a crystal (e.g., for different metals in a tetrahedral or octahedral site of a mineral). See **SUMP** for multiple atoms on the same site with restrained total occupancy.
FLAT	12-25	This command restrains to named atoms to be coplanar.
HFIX	12-16	This powerful command applies constraints and/or generates Hydrogen atoms at idealized coordinates. See page 8-24 for a detailed discussion of dealing with Hydrogen atoms. For the same reasons described above for **AFIX**, I do not routinely use the powerful **AFIX** or **HFIX** commands.
HKLF #	5-9, 12-4	This line tells **XS** and **XL** to read the reflections from the **name.hkl** file and how to treat the I and σ(I) data in the **name.hkl** file. When # = 3 (i.e., **HKLF 3**), **XS** and **XL** treat the intensity data as F and σ(F). When # = 4 (i.e., HKLF 4), **XS** and **XL** treat the intensity data as F^2 and $\sigma(F^2)$. [Note: Intensity is proportional to F^2 in ideally imperfect crystals (i.e., as described in the kinematic diffraction model) but because of extinction's affects it is only proportional to F in perfect crystals (i.e., as described in the dynamic diffraction model). Real crystals behave somewhere between these extremes but those typically grown by synthetic chemists more closely resemble kinematic diffraction. Interestingly, mineral crystals, which grow many orders of magnitude more slowly than do anthropomorphic crystals, behave more like perfect crystal and extinction effects are much bigger for them. Thus, anthrogenic crystals are typically refined with **HKLF 4** mode while mineral crystals are refined with **HKLF 3**.]

L.S.	12-29	This command sets the total number of least squares cycles to be performed by **XL**. I most commonly use 4 during refinement and then 10 at the last **XL** cycle to drive the solution to convergence, e.g. **L.S. 4**
LATT	5-4, 12-1	**LATT N** The lattice type (i.e., 1 for primitive, P 2 for body centered, I, 3 for rhombohedral obverse, 4 for face centered, F, 5 for A centered, 6 for B centered, or 7 for C centered. For non-centrosymmetric space groups **N** is a negative number.
LIST	5-7, 12-36	This command tells the program to save the h, k, l, Fo, etc., values to the specified tables.
MORE	5-6, 12-4	**0** or **1** or **2** or **3** This command can be used to vary the verbosity (i.e., level of detail) of the output files (e.g., **name.lst**) with **3** being the most verbose.
OMIT	5-6, 12-6, 12-18	This command can be used to omit reflections based on the angle they were collected at, their signal to noise ratios, and their index values.
PLAN	5-9, 12-39	This gives the number of Fourier peaks (Q peaks) that will be written to the **name.lst** and **name.res** files for later use by you and **XP**.
REM	5-5, 12-3	**text on the same line** This text isn't used by **XL** but is output onto the **name.res** file. It is a useful way to make comments to yourself.
RTAB	12-35	This command along with **EQIV** gives information on symmetry and bonding of inter- and intra-molecular interactions.
SFAC	5-5, 12-2	**element symbols** The symbols for the elements present in the crystal. The first two elements are always C followed by H (if they are present). The program will use the element identities to look up the scattering power of each atom type when it is doing calculations.
SHEL	12-6	This command is useful in the restriction of the resolution of the data.

SIMU	12-25	This command restrains all the named atoms within a certain distance to having the same displacement parameters.
SUMP	12-28	This command restrains total site occupancy for multiple atoms to a defined total value. See **EXYZ** for multiple atoms at the same site but no restraint on the total occupancy.
SWAT	12-8	This command allows one to model diffuse solvent molecules such as water in proteins. It is very seldom used for small molecules.
SYMM	5-4, 12-2	The following values are the symmetry operations for that space group. They are the "general positions" of the space group taken from the "International Tables" and they can be used to convert any random position in the unit cell (i.e., X, Y, Z) into all its equivalent positions. For some high symmetry space groups this may correspond to many lines of **SYMM** codes. For lower symmetry space groups this line is absent.
TEMP	12-38	This value is the temperature in degrees Celsius of data collection and is used to set default displacement parameters.
TIME	5-6, 12-4	**TIME t** This command sets the maximum time (**t** in seconds) for the **XS** or **XL** run. After this time has been exceeded, this command causes these programs to gracefully stop at the end of the current cycle.
TITL	5-4, 12-1	Name and Space group of the sample in text
TWIN	12-7	This command is used by X-ray crystallography "gods" to solve structures for twinned crystals.
UNIT	5-5, 12-3	This command gives the number of atoms of each type in the unit cell. These numbers have to be in the same order as the order of atoms in the **SFAC** lists.
WPDB	12-38	This command causes the program to save the results to a file that is in the Brookhaven Protein Data Base, PDB, PDB, format used by many other programs.

WGHT	12-33	This command sets the weighting function used. It is read off of the last **name.res** file and entered into the **name.ins** file at the very last refinement cycles.
ZERR	5-4, 12-1	**Z esd(*a*) esd** esd – the estimated standard deviations of the unit cell parameters **(*b*) esd(*c*) esd(a) esd(b) esd(g** The number of formula units in the unit cell and the estimated standard deviations in the cell axial lengths and angles.

D. A TYPICAL INPUT FILE FOR XL AT THE LATTER STAGES OF REFINEMENT.

Below is a typical XL input file at a late stage of refinement after all the atoms have been found and the non-Hydrogen atoms have been converted to anisotropic refinement, namely for: **95adh06e.ins** for (η^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$Cr(CO)_3$) from chapter IX.

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR   2.00   0.0003   0.0005   0.0005   0.004   0.003   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2

L.S. 4
BOND $H
FMAP 2
PLAN 5

ACTA

WGHT    0.008800    0.757500
EXTI    0.008535
FVAR       0.63137
CR    4   0.15437   0.72255   0.32865  11.00000   0.02708   0.02044 =
     0.01711   0.00356   0.00693   0.00579
O7    3   0.02391   0.95638   0.14839  11.00000   0.03839   0.02917 =
     0.02156   0.01085   0.00478   0.00407
O8    3  -0.24436   0.72970   0.07763  11.00000   0.03852   0.03729 =
     0.01976   0.00492  -0.00172   0.00598
O9    3  -0.31168   0.58266   0.26097  11.00000   0.03166   0.03245 =
     0.02869   0.00727   0.00489  -0.00214
O10   3   0.36356   1.00596   0.65321  11.00000   0.04816   0.04201 =
     0.02502   0.00272   0.00260  -0.00632
O11   3   0.18504   0.83025   0.69993  11.00000   0.04491   0.04754 =
     0.01861   0.01016   0.00669   0.00322
O12   3   0.32528   0.73856   0.11181  11.00000   0.07403   0.06557 =
     0.04144   0.01896   0.03824   0.02470
O13   3   0.11278   0.41768   0.28542  11.00000   0.07251   0.02427 =
     0.05871   0.00710   0.03214   0.01143
O14   3   0.54767   0.74489   0.52008  11.00000   0.03299   0.04417 =
     0.04133   0.00570   0.00033   0.01060
C1    1   0.00985   0.89155   0.24807  11.00000   0.03313   0.02488 =
```

```
     0.01988   0.00727   0.00762   0.00946
C2   1 -0.13074   0.76566   0.20811  11.00000   0.02809   0.02710 =
     0.01838   0.00371   0.00333   0.00700
C3   1 -0.16510   0.69418   0.30651  11.00000   0.02701   0.02521 =
     0.02511   0.00484   0.00748   0.00606
C4   1 -0.04674   0.73858   0.44128  11.00000   0.02936   0.02636 =
     0.02195   0.00708   0.00988   0.00745
C5   1  0.09870   0.85866   0.47788  11.00000   0.02946   0.02369 =
     0.01704   0.00225   0.00727   0.00754
C6   1  0.12695   0.93746   0.38236  11.00000   0.03204   0.02116 =
     0.01992   0.00402   0.00766   0.00635
C7   1  0.17784   1.07565   0.18084  11.00000   0.04567   0.03934 =
     0.02921   0.01467   0.00764  -0.00128
C8   1 -0.24277   0.60033   0.00593  11.00000   0.06628   0.05213 =
     0.02545  -0.00602   0.00149   0.01009
C9   1 -0.32999   0.49001   0.34961  11.00000   0.03775   0.03155 =
     0.03704   0.01047   0.01104   0.00120
C10  1  0.23272   0.90834   0.61905  11.00000   0.03253   0.02959 =
     0.01924   0.00387   0.00770   0.00925
C11  1  0.30598   0.86718   0.83922  11.00000   0.05012   0.07241 =
     0.01960   0.01275   0.00540   0.01423
C12  1  0.26048   0.73141   0.19507  11.00000   0.04211   0.03186 =
     0.02665   0.00819   0.01382   0.01239
C13  1  0.12626   0.53549   0.30093  11.00000   0.03536   0.02739 =
     0.02884   0.00625   0.01377   0.00766
C14  1  0.39564   0.73692   0.44579  11.00000   0.03359   0.02388 =
     0.02649   0.00327   0.00969   0.00722
H4   2 -0.06225   0.68644   0.50623  11.00000   0.02830
H6   2  0.21979   1.01241   0.40553  11.00000   0.02961
H7A  2  0.16707   1.10182   0.09730  11.00000   0.03647
H7B  2  0.30275   1.05073   0.22211  11.00000   0.04841
H7C  2  0.15582   1.14804   0.24042  11.00000   0.04394
H8A  2 -0.11521   0.61526  -0.00865  11.00000   0.12360
H8B  2 -0.25094   0.52828   0.04863  11.00000   0.10381
H8C  2 -0.31515   0.59076  -0.07707  11.00000   0.08579
H9A  2 -0.21767   0.45501   0.37756  11.00000   0.03525
H9B  2 -0.43432   0.41842   0.30449  11.00000   0.05373
H9C  2 -0.35499   0.53437   0.42955  11.00000   0.04830
H11A 2  0.32875   0.95414   0.87009  11.00000   0.08280
H11B 2  0.42265   0.84317   0.85339  11.00000   0.07204
H11C 2  0.23116   0.82075   0.88383  11.00000   0.07771

HKLF 4
END
```

E. THE USE OF XL TO FIND TRIAL SOLUTIONS FOR NEUTRON DIFFRACTION DATA

The program **XL** runs identically for analyzing neutron data with the exception(s) that……

Again Dear Readers: I would greatly appreciate suggestions for this section as I have yet to use XL for neutron data myself!

CHAPTER VI. CHECKING YOUR STRUCTURE FOR CHEMICAL REASONABLENESS (YOUR STRUCTURE MAY BE PRECISE BUT IS IT THE CORRECT ONE?)

One of the most difficult challenges in X-ray crystallography is determining if your final answer is the correct one. Very often one gets a very precise answer that is actually wrong, most commonly because the structure was solved in the wrong space group. Estimates vary, but it is widely estimated that significant errors occur in up to 10% of published structures! Fortunately, even a non-crystallographer can catch many of these errors by checking the results for "chemical reasonableness".

A. BY LOOKING AT YOUR PLOTS

Do a careful visual inspection of your molecules as they rotate in the 'proj' view of **XP** and in your plots. Look for unusual bond distances and angles, close contacts, etc. Pay attention to close intermolecular contacts as well. The eye can sometimes catch what is hard to see in tables, particularly symmetry effects.

B. BY LOOKING AT YOUR ATOMIC PARAMETERS

Careful inspection of your tables of atomic parameters (e.g., from 'info') and of the apparent sizes and shapes of ellipsoids in plots will often reveal atoms that "don't fit." In such cases, one has several good options. If a Q peak has reappeared in the expected position for each such "bad" atom (i.e., each atom that has "wandered out of place"), one can delete such "bad" atom(s), assign the Q peak(s) as the correct atom type(s), and continue with the refinement. Alternately, just delete the bad atom(s) but don't reassign it(them) during this refinement cycle. In this case, one hopes that in the next cycle they will behave more reasonably. If neither of these approaches work, I find that it is best to go back to the start of the refinement and assign the atoms more slowly (i.e., only one or a few per cycle) as this may lead you away from a bad local minimum towards the global minimum. Just be careful to check that the new atom(s) is(are) well behaved in the next few refinement cycles. Some combination of these strategies usually works for me. If this sequence of steps doesn't work, this probably indicates deeper problems with your model such as disorder or the wrong choice of space group.

C. BY LOOKING AT YOUR BOND PARAMETERS

Carefully look over the tables of bond lengths and angles from 'bang' in **XP** and from the **XCIF** tables. Look for unusual bond distances (particularly bond distances that are substantially under 1 Å or are surprisingly long), unusual bond angles (particularly those that are too large or small for the expected hybridization of the atom), close contacts between "non-bonded" atoms, etc. Compare the bond lengths and angles to typical values listed in the Handbook. If your values

deviate significantly, an error in the structure is more probable than you having found the first example ever in the whole universe……. of such unusual values.

D. BY LOOKING AT YOUR DISPLACEMENT PARAMETERS

The displacement parameters of all similar atoms in similar molecular positions are usually close in magnitude. Unusually large or small values should make you suspicious and can indicate that you have assigned the wrong atom type, that the site is only partially occupied, that there is major disorder, etc. A very small value for the displacement parameter indicates that you may need an atom of higher electron density than the one currently assigned (i.e., replace a C by a O). Likewise, as very large value for the displacement parameter indicates that you may need an atom of lower electron density than the one currently assigned or that there is really no atom in that position. Commonly, the smallest values of the displacement parameters are near the center of the molecule and these values increase substantially as you move to the molecular periphery, especially for "floppy" groups like alkyls. The various atoms on relatively rigid groups such as carbonyls and arenes should show similarly oriented anisotropic ellipsoids.

E. STATISTICAL MEASURES OF QUALITY

1. Definitions of R, wR, and GOOF

The most useful statistical measures of the progress of a refinement are R, wR,[23] and GOOF. The residual indexes R and wR are calculated by **SHELXTL** based on F_o^2. These values should decrease toward zero as the refinement progresses and will typically approach final values of 0.02 to around 0.1 when refinement is complete. These numbers are typically at least twice as large as old fashion refinements based on F_o. Because many scientists are more familiar with these obsolete refinement practices, **SHELXTL** also reports residual indexes that one would observe if the data had been refined this way. These "artificial" residual indexes are always substantially smaller. The goodness of fit, GOOF, parameter should approach one as a structure solution nears completion. These numbers are displayed on the screen after **XL** runs and appear in the **name.lst** files near the end. These parameters are shaded in the **calctest.lst** file presented in chapter IX, section H3.

The nature of these various parameters is summarized below:

- R - The actual residual parameter (based on F_o^2 and all data).
- wR - The actual weighted residual parameter (based on F_o^2 and all data).
- R1 - The simulated residual parameter (based on hypothetical refinement based on F_o)
  - R1 for $F_o > 4\sigma(F_o)$ - (calculated based on only the strongest data on F_o)
  - R1 for all data - (calculated for all data on F_o)

[23] Note, our textbook refers to the weighted R values as Rw while SHELXTL refers to it as wR. For the purposes of this manual, we will use wR to retain consistency with the SHELXTL output.

- wR2 – The simulated weighted residual parameter (based on F_o)

Note: The exact interpretation of the parameters and their significance is the subject of no little controversy amongst even skilled crystallographers. Personally, I use them with extreme caution (i.e., mostly looking for trends in their values between subsequent refinement cycles).

2. Limitations of R, wR, and GOOF

Be very careful about trusting numbers such as the R, wR, and GOOF parameters. They are correlated with structure quality and should approach the low single digits for R and wR (i.e., near 3 to 5 % for R, wR is generally somewhat larger than twice the R value) and approach one for GOOF when the structure solution is complete. They are most useful when comparing the various stages of one particular crystal structure solution to other stages of that solution and when checking if the last thing one tried resulted in an improvement in the model. However, these parameters are easily biased (intentionally or not) and are less reliable indicators of the quality of a refinement than things such as the esd values of bond lengths and angles.

3. The Residual Electron Density

After **XL** has completed a cycle, it uses the F_o and F_c data to calculate a residual electron density map. From this calculation is prints to the **name.lst** file the maximum and minimum peaks of electron density. For well behaved structures these should be substantially less than one electron per cubic Å. These parameters are shaded in the **calctest.lst** file presented in chapter IX, section H3.

F. THE CRITERIA OF CHEMICAL REASONABLENESS

When all else fails, look to your intuition. If the numbers seem "too interesting to be true," they probably are.

CHAPTER VII. GENERATING MOLECULAR AND CRYSTAL STRUCTURE PLOTS USING XP

A. HELP FOR XP COMMANDS.

The Chapter references are to the Bruker AXS (Siemens) manual, version 5.1, especially chapters 18 and 19.

Type the "HELP command", e.g.

help ARAD [ent]

to find out about the 'ARAD' command. A similar method can be used to find out about any of the other **XP** commands, i.e.

ARAD, ATYP, BACK, BANG, CELL, CENT, DEMO, DIAG, DRAW, ECHO, EDEN, EGSD, END, ENVI, EXAM, EXIT, EYES, FILE, FMOL, FUSE, GAPS, GROW, HADD, HELP, HIMP, HLPD, INFO, INVT, ISOT, JOIN, KILL, LABL, LIBR, LINE, LINK, LITE, LOSE, MATR, MGEN, MODL, MOVE, MPLN, NAME, NEWM, NEXT, NOPL, OFIT, ORTH, PACK, PAGE, PART, PAWS, PBOX, PERS, PGEN, PICK, POLP, POLY, POST, PREV, PRIN, PROJ, PRUN, PUSH, QUIT, RASD, RAST, READ, REAP, RESI, RIDE, RING, ROTA, SAVE, SFIL, SGEN, SLPF, SLPR, SLXP, SORT, SPIX, SPLT, SPOT, SRCH, SYMM, SYSD, TELP, TITL, TORS, UNDO, UNIQ, USER, VIEW, WAIT, WIPE, ZOOM

or the following facilities in **XP** (the first four letters of these suffice):

ATOMS, BUGS, COLORS, COMPATIBILITY, ESCAPE, INITIALIZATION, INTERFACE, KEYWORDS, LABELS, NEWS, ORIENTATION, PLOTFILES, SYMCODES

B. TYPICAL TYPES OF XP PLOTS

There are an almost limitless number of ways one can use **XP** to illustrate a particular least squares planes calculated by XP. Some of the most common are described in the following sections. Examples of such plots for one molecule (95ADH06e referred to as "plottest", (η^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$Cr(CO)_3$) are given in chapter IX.

Before you plot your molecule using **XP**, you have to ensure that you have the correct atoms loaded into XP and that you have established their connectivities using the fmol instruction. *In the discussion below, all of the file names have the form* ***plottest.?*** *(where the ? mark is replaced by a letter to give the plot number). When you do your plots, use the name of your sample instead of 'plottest'.*

1. Choosing Which Atoms Will be Labeled and How

The default plots in **XP** label only the non-hydrogen atoms and place brackets (parentheses) around the atom numbers (i.e. causing C(10) to appear as C10). If one wants the hydrogen atoms labeled or does not want the brackets one must use the 'labl' command. Use the commands shown below to get the desired labeling on your plots from 'diag', 'sfil', 'telp', 'eden', and 'ofit'.

labl 0 [ent]

would give no labels on your plots.

labl 1 [ent]

would give no labels on hydrogen and no brackets on the numbers.

labl 2 [ent]

would give no labels on hydrogen and brackets on the numbers (i.e. this is the default case).

labl 3 [ent]

would give labels on hydrogen and no brackets on the numbers.

labl 4 [ent]

would give labels on the hydrogens and brackets on the numbers. This command can also be used to adjust the size of the labels.

2. Ball and Stick Plots

pers [ent]

This command converts the current view of the molecule into a very realistic ball and stick view on screen. Unfortunately, it can not be plotted.

To make a Ball and Stick plot of your molecule, you would carry out the following steps after you had loaded the desired atoms into the **XP** program.

proj [ent]

This step loads the interactive 'proj' routine which you use to get the desired orientation of your molecule.

telp [ent] plottest.a [ent]

This step loads the interactive 'telp' routine which lets you label your atoms. When you are done, press the 'B' key to save your plot and exit from 'telp'. If you want to exit from 'telp' without saving the file press [esc].

rast plottest.a [ent] or

rast/c plottest.a [ent]

These two commands would send this plot for black and white or color printing, respectively.

3. Plots with Special Orientations

To make a plot of your molecule with a special orientation (e.g., parallel to one of the unit cell axes or perpendicular to a particular plane in the crystal), you would carry out **one** of the following steps after you had loaded the desired atoms into the **XP** program.

matr 1 [ent] or

matr 2 [ent] or

matr 3 [ent] or

matr 2 4 -7 [ent]

These commands orient the molecule so that it is parallel to the x, y, and z axes of the unit cell or perpendicular to the crystal plane having Miller indices of 2 4 -7, respectively.

proj [ent]

Reminder, this step then loads the interactive 'proj' routine which you use to see the resulting orientation of your molecule.

After you have done this, you can use 'telp' as described above and below to get plots of these views taken at these special viewing angles.

4. Displacement Ellipsoid Plots

To make a displacement ellipsoid plot of your molecule (which shows the three dimensional size and shape of your atoms and looks a lot like an ORTEP plot), you would carry out the following steps after you had loaded the desired atoms into the **XP** program.

proj [ent]

This step loads the interactive 'proj' routine which you use to get the desired orientation of you molecule.

You would then give a command such as the following to get various types of displacement ellipsoid views of your molecule. [Note: *It is the negative sign on the second parameter after 'telp' that tells **XP** to use displacement ellipsoids rather than ball and stick drawings.* It is the first and last of these parameters that specifies which type of stereo plot will be produced.]

telp 0 -50 0.04 0 [ent] **plottest.b [ent]** (i.e., for a view at 50% ellipsoids)

telp 0 -100 0.04 0 [ent] **plottest.c [ent]** (i.e., for a view at 100% ellipsoids)

telp 0 -75 0.04 0 [ent] **plottest.d [ent]** (i.e., for a view at 75% ellipsoids)

telp 0 -75 0.04 0 less $H [ent] **plottest.f [ent]** (i.e., for a view at 75% ellipsoids without Hydrogens)

telp 3 50 0.08 50 [ent] **plottest.g [ent]** (i.e., for a *stereo* view of ball and stick at 50% and with "fatter" bonds)

telp 3 -50 0.08 50 [ent] **plottest.i [ent]** (i.e., for a *stereo* view at 50% ellipsoids with "fatter" bonds)

[Note: most authors prefer to prepare graphics for publication as 30 to 50% ellipsoids. I prefer to use 75 to 100% ellipsoids only when I am looking for bad inter- or intra-molecular contact or trying to see if any of the atoms have unusually shaped ellipsoids.] These steps load the interactive 'telp' routine which lets you label your atoms. When you are done, press the 'B' key the save your plot and exit from 'telp'.

rast plottest.? [ent] or

rast/c plottest.? [ent]

These two commands would send each plot with the correct letter in place of the question mark for black and white or color printing, respectively.

5. Space Filling Plots

There are two ways of seeing space filling views of molecules, 'sfil' and 'spix'.

spix [ent]

This command converts the current view of the molecule into a very realistic space filling view on screen. If you type the 'P' key while in this view, it sends this picture to the plotter in black and white but does not save it.

sfil [ent] **plottest.r** or

sfil 3 50 [ent] plottest.s

These interactive commands allow you to label a space filling view of the molecule (the latter case being a *stereo* plot) for later plotting with 'rast' or 'rast/c', e.g.

rast plottest.r [ent] or

rast/c plottest.s [ent]

These two commands would send each plot for black and white or color printing for **plottest.r** and **plottest.s**, respectively.

6. Editing Bonds and Adding Dummy Atoms

Sometimes you want to edit bonds into or out of molecules or add dummy bonds to molecules (e.g., at the center of an aromatic ring). I prefer to first remove all bonds to an atom of interest to me using the 'prun' command, e.g.

prun Cr [ent]

This command would remove all bonds to the Cr atom (i.e., I have plotted the result as **plottest.j** in Chapter X).

I then add back all of the new bonds I want, e.g.

join Cr C12 [ent]

join Cr C13 [ent]

join Cr C14 [ent]

These three commands would add back bonds from the Cr atom to carbons C12, C13, and C14, respectively (i.e., I plotted the result as **plottest.k** in Chapter X).

cent/x C1 to C6 [ent]

join Cr X1A [ent] or **link Cr X1A [ent]**

This command would add a dummy atom in the center of a ring defined by carbons C1 to C6 (which in this case the program told me it named X1A) and then bond it to the Cr atom (i.e., I plotted the result as **plottest.l** in Chapter X).

I have used **telp 0 -75 0.04 0 [ent]** to create plots of this example and labeled them as **plottest.j**, **plottest.k**, **plottest.l** as indicated above.

7. Packing Diagrams for the Unique Molecule(s)/Fragment(s) in the Unit Cell

To make a displacement ellipsoid plot of your molecule (which shows the three dimensional sizes and shapes of your atoms), you would carry out the following steps after you had loaded the desired atoms into the **XP** program.

proj cell [ent]

This step loads the interactive 'proj' routine which you use to get the desired orientation of your molecule and an outline of the unit cell.

You would then give a command such as the following to get various types of displacement ellipsoid views of your molecule. [Note: you could just use **telp [ent]** if you wanted only a ball and stick plot with the unit cell shown.]

telp 0 -75 0.04 0 CELL [ent] **plottest.e [ent]** (i.e., for a mono view)

telp 3 50 0.08 50 CELL [ent] **plottest.h [ent]** (i.e., for a view with "fat" bonds)

These steps load the interactive 'telp' routine which lets you label your unit cell axes and your atoms. When you are done, press the 'B' key the save your plot and exit from 'telp'.

rast plottest.? [ent] or

rast/c plottest.? [ent]

These two commands would send each plot with the correct letter in place of the question mark for black and white or color printing, respectively.

8. Packing Diagrams for Multiple Molecules Packed Around the Unit Cell

pbox width depth [ent]

This command defines the size of the box that will be filled up with molecules. If you set the width and depth values (e.g., 5 to 10), which are in Å, as small numbers you will just get a few molecules. If you set them to large values (e.g., 20 and 40 or 30 and 30) you will get many molecules packed together but the calculation slows way down as you now are talking about thousands of atoms.

pack [ent]

This interactive utility is used to set up the packing plots with the size given by the 'pbox' command. If you like the looks of this command, you push the sgen/fmol button with the mouse to save the new molecules generated by these two steps. You can then use:

proj CELL [ent]

command to get the orientation of the molecule you want. You could also use one of the 'matr' commands to get a specific view down a unit cell axis or perpendicular to a lattice plane, e.g.

matr 1 [ent] or

matr 2 [ent] or

matr 3 [ent] or

matr 2 4 -7 [ent]

You would then give a command such as the following to get a Ball and Stick view of your molecule. [Note: you could just use **telp 0 50 0.04 0 CELL [ent]** if you wanted a displacement ellipsoid plot with the unit cell shown but this would calculated even slower.]

telp CELL [ent] **plottest.o [ent]** (i.e., for a mono view down the x axis)

telp CELL [ent] **plottest.p [ent]** (i.e., for a mono view down the y axis)

telp CELL [ent] **plottest.q [ent]** (i.e., for a mono view down the z axis)

These steps load the interactive 'telp' routine which lets you label your unit cell axes and your atoms. When you are done, press the 'B' key the save your plot and exit from 'telp'.

rast plottest.? [ent] or

rast/c plottest.? [ent]

These two commands would send each plot with the correct letter in place of the question mark for black and white or color printing, respectively.

9. Inverting Molecules (i.e., to their Enantiomers)

If you want to invert your molecule to its enantiomer, you may use the 'invt' command.

invt [ent]

proj [ent]

[Note: See the information in Chapter V, section B6 about a few special space groups where this command is not sufficient to change the chirality of the system.] This step loads the interactive 'proj' routine which you use to check the new structure of your molecule.

telp 0 -75 0.04 0 [ent] **plottest.m [ent]** (i.e., for a view at 50% ellipsoids)

These steps load the interactive 'telp' routine which lets you label your atoms. When you are done, press the 'B' key the save your plot and exit from 'telp'.

rast plottest.? [ent] or

rast/c plottest.? [ent]

These two commands would send each plot with the correct letter in place of the question mark for black and white or color printing, respectively.

10. Interatomic Lines, Least Squares Planes, and Torsion Angles

One often needs to know the equations of lines defined by various atoms in a molecule and the equations of planes defined by sets of atoms in the molecule (e.g., to answer questions about bonding, co-planarity, etc.). The commands 'line' and 'mpln' are used to calculate these lines and least squares planes. They also give the angles between them.

line Cr C12 [ent] and

line Cr C13 [ent]

These commands would calculate the lines for the Cr to C12 and Cr to C13 vectors, respectively, and if they intersect would also print the angle between them to the screen.

mpln C1 C2 C3 C4 C5 C6 [ent]

This command would calculate the least squares plane for the aromatic ring containing the carbons C1 to C6. It would also give you the deviations of all six of these carbons from the least squares plane, the distance of all other atoms in the molecule from this least squares plane, the equation of the normal to this plane, and the angle between the normal to this plane and the normal to any other planes previously defined and to any other lines defined previously (e.g., the Cr to C12 and Cr to C13 vectors calculated above).

For molecules you can define as many planes as you like and this command will then calculate the inter-plane angles as well.

mpln C12 C13 C14 [ent]

mpln O12 O13 O14 [ent]

Defining these additional planes would allow the program to calculate planes defined by the carbonyl carbons and oxygens, respectively, and the angles between the arene, carbonyl carbon, and carbonyl oxygen planes.

To determine the torsion angles about a bond use the 'tors' command, i.e.
tors C1 C2 C4 C5 [ent]

These commands would print the C1 C2 C3 C4 torsion angle to the screen.

To print any of the above values to the printer as well as the screen, make the following changes in the command lines.

line/L Cr C12 [ent] **print [ent]** prints the information on the line connecting the Cr and C12

line/L Cr C13 [ent] print [ent] prints the information on the line connecting the Cr and C13 and the angle between this line and that between Cr and C12

mpln/L C1 to C6 [ent] print [ent] prints the equation for the plane defined by the atoms on the atom list between C1 and C6, the equation of the normal to this plane, and the angles between this plane and any previously defined lines and/or planes. [Note: if 27 atoms lie between C1 and C6 because you haven't carefully sorted the atom list then all of them will be included in the plane.]

mpln/L C1 C2 C3 C4 C5 C6 [ent] print [ent] prints the equation for the plane defined by the atoms C1, C2, C3, C4, C5, and C6 and the angles between this plane and any previously defined lines and/or planes

mpln/L C12 C13 C14 [ent] print [ent] prints the equation for the plane defined by the atoms C1, C2, C3, C4, C5, and C6 and the angles between this plane and any previously defined lines and/or planes

mpln/L O12 O13 O14 [ent] print [ent] prints the equation for the plane defined by the atoms O13, O14, and O15 and the angles between this plane and any previously defined lines and/or planes

tors/L C1 C2 C4 C5 [ent] print [ent] prints the torsion angle about the C2-C4 bond

tors/L print [ent] prints all of the torsion angles

[Note: the 'nopl' command deletes the stored table of lines and planes.] Examples of these tables are given at the end of Chapter XII for the sample compound "calctest."

C. ALPHABETICAL LISTING OF XP COMMANDS, COMMON VARIANTS, AND EXAMPLES OF THEIR USE.

The following is a list of the **XP** commands that I find the most useful. They are generally composed of a four letter identity code followed by various parameters that can be varied to modify their effects. I have given a short discussion for each including examples of how they are most commonly used. There is also a page number from the Bruker AXS (Siemens)/**SHELXTL** Version 5.1 manual for each which generally gives a more detailed/general explanation of each.

The commands and common variants of commands of most use for beginners (e.g., in courses such as Chemistry 832: Solid State Structural Methods) are shaded in below.

Code	Page[24]	Discussion
'arad'	19-1	This utility sets atomic radii for space filling plots.
'atyp'	19-1	This utility sets how an atom in a molecule will be represented in subsequent 'telp' plots. It is used in the following format [Note: Type in help for a full description of using 'atyp']: **atyp type color KEYWORDS [ent]** where the various codes are given on page 19-1 and 19-2 of the manual and at the end of this table (e.g., the codes I use the most for **type** are: -3 is a "normal" boundary ellipse, -1 is a full displacement ellipse, 0 is "nothing" (i.e., for dummy atoms), 1 is a shaded circle with highlights, 2 is an open circle, etc., the **color** codes I use most for color are: 0 black, 1 green, 2 red, 3 blue, 4 orange, 5 magenta, 7 cyan, 8 green,

[24] These page numbers are taken from the Bruker AXS (Siemens) manual for SHELXTL, version 5.1. All of these page numbers will vary with the version of the manual you use.

		10 purple, etc., and the **KEYWORDS** are given at the end of this table For example: **atyp -1 less $H [ent]** **atyp 2 $H [ent]** would plot all non Hydrogen atoms as full displacement ellipsoids and all Hydrogen as open circles. **atyp -1 3 $Pd [ent]** **atyp 2 2 all less Pd [ent]** would plot all Palladium atoms as full displacement ellipsoids in blue and all other atoms as open circles in red. **atyp 1 10 C1 to C14 [ent]** **atyp 2 7 C15 to C37 [ent]** would plot all carbon atoms from C1 to C14 as purple shaded circles and all carbon atoms from C15 to C37 as cyan open circles. A full description of the 'atyp' command is available by typing **help atyp [ent]**
'bang/L'	19-2	**bang/L KEYWORDS [ent] print [ent]** This utility prints a list to the screen *and the printer* of all bond lengths and angles from the 'fmol' list, e.g. **bang/L [ent] print [ent]** **bang/L Cr2 [ent] print [ent]** would print a list of all the lengths and angles for the molecule and around the atom Cr2, respectively.
'bang'	19-2	**bang KEYWORDS [ent]**

		This utility prints a list to the screen of all bond lengths and angles from the 'fmol' list, e.g. **bang [ent]** **bang Cr2 [ent]** would print a list of all the lengths and angles for the molecule and around the atom Cr2, respectively.
'cell/L'	19-2	**cell/L [ent] print [ent]** This utility prints the current unit cell dimensions and angles *to the printer*.
'cell'	19-2	**cell [ent]** This utility displays the current unit cell dimensions and angles.
'cent/L'	19-3	**cent/L KEYWORDS [ent] print [ent]** This utility calculates x, y, and z coordinates of the centroid of the specified atoms (ATYP = 0) and sends it to the printer, e.g., **cent C1 TO C6 [ent] print [ent]** would calculate centroid of these six atoms (e.g., in a benzene ring) and send it to the printer.
'cent'	19-3	**cent KEYWORDS [ent]** This utility calculates x, y, and z coordinates of the centroid of the specified atoms (ATYP = 0), e.g., **cent C1 TO C6 [ent]** would calculate centroid of these six atoms (e.g., in a benzene ring).
'demo'	19-3	**demo [ent]** This utility runs the demonstration "video" of different types of XP graphical output. [esc] exits the 'demo' loop.
'diag'	19-4	**diag [ent]**

		This utility draws a labeled diagram that is saved as diag.plt and is displayed in the top right hand corner of the screen. The [F10] key toggles this on and off.
'draw'	19-4	**draw name.x [ent]** This utility converts the plot file (name.x) to a HPGL (Hewlett Packard Graphics Language or postscript format interactively. In newer version of the software it will also print the resulting plots to a postscript printer.
'eden'	19-5	This interactive utility calculates electron density contours for planes.[25]
'envi'	19-7	**envi delta KEYWORDS [ent]** This utility prints a list of all atoms and Qs within a distance defined as the sum of their covalent radii plus delta (e.g., for two carbons 0.77Å + 0.77Å + 0.5Å (default) = 2.04Å) around the atoms defined by **KEYWORDS**. This is very useful for finding Hydrogen bonds, close contacts, neighboring molecules, etc. For example: **envi 0.7 C11 [ent]** would list all atoms within $r_1 + r_2 + 0.7$Å of atom C11.
'exit'	19-7	**exit [ent]** This utility exits from **XP** but doesn't, in itself, save your work to the **name.ins** file (the 'file' command does that).
'file'	19-7	**file name [ent]** This utility saves the work you've done in **XP** as a **name.ins** file (where name is the 8 character name of your structure).
'fmol'	19-7	**fmol [ent]** This is normally the first instruction after you have started **XP**. It sets up a connectivity table of the atoms and Q peaks taken from the **name.res** file for which **XP** was started. The atoms are considered to be bonded if they are within the sum of their covalent radii plus delta. The default value of δ is 0.5 Å, thus, two carbons would be considered to be bonded if they were within 2.04Å (i.e., 2 x 0.77Å (the covalent radius of C) + 0.5Å). The command: **fmol 0.8 [ent]**

[25] Details of how to do this will be included in future editions.

		would change this delta value to 0.8Å. The default is generally appropriate.
'fuse'	19-9	**fuse delta [ent]** This command is used to fuse all the atoms within a defined distance of one another together (default distance is 0.5Å), e.g., **fuse 0.7 [ent]** would fuse all atoms within 0.7Å of one another together. After using the 'fuse' command, one almost always uses the 'uniq' command as well.
'grow'	19-9	**grow delta KEYWORDS [ent]** This utility uses all of the atoms in the 'fmol' list and the symmetry of the crystal (i.e., symmetry equivalent) to assemble complete molecules. The default value of delta is 0.5Å. This is commonly used to generate the symmetry equivalent atoms when a molecule is on a special position, e.g. **grow [ent]** **grow $P [ent]** would find the symmetry equivalent atoms of all atoms already assigned and of only the symmetry equivalent phosphorous atoms, respectively. [Note: this command can be reversed using the 'fuse' and 'uniq' commands.]
'hadd'	19-10	This utility generates H atoms in idealized positions on the named, C, N, and O atoms. The default distances are 0.96Å for C-H, 0.90Å FOR N-H, AND 0.89Å for OH. The default U values assigned to atoms by the 'hadd' instruction are –1.2 for most groups and –1.5 for methyl and hydroxyl groups. If you don't specify "type" it will make an " intelligent" guess but errors are possible, especially for poorly determined atoms. The various types are: type = 1 tertiary C-H type = 2 secondary CH_2 type = 3 methyl CH_3 type = 4 aromatic C-H or amide N-H type = 8 OH

		type = 9 terminal CH_2 or NH_2 This utility is good for visualizing where these atoms will occur but using **HFIX** in the **name.ins** file is better. The value of U is at 0.08 by default and is the isotropic U. As an example of this command: **hadd 3 0.95 C1 [ent]** or **hadd 8 1.1 O3 [ent]** or **hadd $C All [ent]** would convert atom C1 to a methyl group with a C-H distance of 0.95, would convert atom O3 to a hydroxyl group with a O-H distance of 1.1, and would convert all carbons to **XP**'s best guess of their atom types with the default C-H distances, respectively.
'help'	19-11	**help [ent]** This is the help utility. If you type the above entry, **XP** will give you a list of commands about which **HELP** can tell you. If you type: **help info [ent]** would give you the help message for the info command.
'info/L'	19-12	**info/L [ent] print [ent]** This version of info sends the list *to the printer*!
'info'	19-12	**info [ent]** This utility summarizes the positional, etc., parameters for each atom and Q peak and prints them on the screen.
'invt'	19-12	**invt Xi Yi Zi KEYWORDS [ent]** This utility inverts atoms through the origin (or other points if Xi, Yi, and Zi are specified). The KEYWORDS identifies which atoms are inverted. It is very useful for converting one enantiomer to another, i.e., **invt ALL [ent]** or **invt [ent]**

		would both invert all atoms. It can also be used to invert subsets of atoms, e.g., **invt Cr1 P21 C11 [ent]** would invert atoms Cr1, P21, and C11, only. [Note: See the information in Chapter V, section B6 about a few special space groups where this command is not sufficient to change the chirality of the system.] This command is closely related to the 'push' command. For example: **push 0 0 0 -1 [ent]** would invert each atom's coordinates about the origin (i.e., as does 'invt). If coordinates are added, the 'push' command inverts the unit cell contents about this new point. This is particularly useful for a few unusual space groups. It is thus more suitable for these special space groups.
'join'	19-12	**join BONDTYPE KEYWORDS [ent]** This utility draws in bond(s) between atoms. If precisely two atoms are specified then only the bond connecting them is drawn. If the bond was already present then its type is changed. The default BONDTYPE is type 1 (solid) for join (this is the only difference from the 'list' command which has type 6 as default). A list of BONDTYPE values is at the end of this section. For example: **join 2 C6 P2 [ent]** would draw an open bond between atom C6 and atom P2. **join 3 Cr [ent]** would draw all bonds to the chromium atom as dashed solids. **join C6 P2 [ent]** would draw an solid bond between atom C6 and atom P2. A full description of the 'join' command is available by typing **help join [ent]**
'kill'	19-13	**kill KEYWORDS [ent]** This utility kills the atoms specified by **KEYWORDS**, e.g.,

		kill $H [ent] would delete all Hydrogens from the list while **kill O4 C11 to C14 [ent]** would delete atoms O4 and C11 through C14.
'labl'	19-13	**labl code size [ent]** This 'labl' command defines how the commands 'diag', 'sfil', 'telp', 'eden', and 'ofit' label a plot. The **size** value is the height of the labels (in plot units, 600 is the default value). The **code** tells the programs which atoms to label and whether to use brackets around the atom numbers (the default code is 2), i.e., 0 = no labeling 1 = no labels on H and no brackets on atom numbers 2 = no labels on H and brackets on atom numbers 3 = labels on H and no brackets on atom numbers 4 = labels on H and brackets on atom numbers [Note: With codes 2 and 4, the plots omit the () parentheses around the atom labels (e.g., causing C(10) to appear as C10 and all of the other labels to be similarly transformed).] Thus, the following commands **labl 1 [ent]** or **labl 3 400 [ent]** would put standard size labels with no brackets on the non-hydrogen atoms only and would put labels with no brackets that were two thirds of standard size on all atoms, respectively.
'libr'	19-14	This command carries out a librational analysis of rigid body motion for the compound.
'line/L'	19-14	**line/L two atoms [ent]** This utility calculates the equation of the line joining the two atoms specified and outputs its angle with previously calculated lines and planes. 'nopl' deletes stored lines and planes, e.g. **line/L Cr C12 [ent]** **line/L Cr C13 [ent]**

		line/L Cr C14 [ent] print [ent] This set of commands would calculate the three vectors from the Cr to C12, C13, and C14, the angles between them, and print this data to the screen and to *the printer*.
'line'	19-14	**line two atoms [ent]** This utility calculates the equation of the line joining the two atoms specified and outputs its angle with previously calculated lines and planes. 'nopl' deletes stored lines and planes, e.g. **line Cr C12 [ent]** **line Cr C13 [ent]** **line Cr C14 [ent]** This set of commands would calculate the three vectors from the Cr to C12, C13, and C14, and angles between them, and print this data to the screen.
'link'	19-14	**link BONDTYPE KEYWORDS [ent]** This utility is essentially identical to 'join'. The only difference from 'join' is that the default **BONDTYPE** is 6 (dashes). This utility draws in bond(s) between atoms. If only two atoms are specified then only the bond connecting them is drawn. If one or more than two atoms are specified then all bonds to those atoms are changed. For example: **link 2 C6 P2 [ent]** would draw an open bond between atom C6 and atom P2 while **link 3 Cr [ent]** would draw all bonds to the chromium atom as dashed solids. A full description of the 'link' command is available by typing **help link [ent]**
'matr'	19-15	**matr variables [ent]** This utility is used to specify an orientation matrix for view. For example:

		matr [ent] would print the current orientation matrix to the screen (this can be useful if you write it down so that latter you can come back to the exact same orientation) while **matr p11 p12 p13 p21 p22 p23 p31 p32 p33 [ent]** would convert to the new specified matrix and **matr 1 [ent]** **matr 2 [ent]** **matr 3 [ent]** would orient for projection down the real crystal axes x, y, and z, respectively. The command: **matr 1 2 -4 [ent]** where 1 2 -4 are a particular h, k, l set of Miller indices gives an orientation with this crystal plane perpendicular to the view direction.
'mgen'	19-16	**mgen KEYWORDS delx dely delz XcYcZc [ent]** This utility generates all symmetry equivalent molecules in the specified volume. **KEYWORDS** defines which atoms are used. The volume is defined by Xc±delx, Yc±dely, Zc±delz. You run 'mgen' (i.e., molecules on special positions should be treated with 'grow' first). Since 'mgen' hunts down bonded atoms to the specified ones, it usually works best just to specify the/a central atom in your molecule (if you used all, etc., it is very slow).
'mpln/L'	19-17	**mpln/L KEYWORDS [ent] print [ent]** This utility calculates the best least squares plane through the specified atoms. It calculates the angles between this plane's normal and the normals to all previous planes from 'mpln' and to previous lines from 'line'. For example: **mpln/L C1 to C6 [ent] print [ent]** **mpln/L C7 C8 C9 [ent] print [ent]** would calculate the equation of least squares plane defined by the atoms in the atoms list between C1 to C6 and the plane define by atoms C7, C8, and C9, the angle between the normal to these planes and any lines previously defined by

		'line' and then prints this data *to the printer*. [Note: if 27 atoms lie between C1 and C6 because you haven't carefully sorted the atom list then all of them will be included in the plane.] [Note: 'nopl' deletes the stored table of planes and lines.
'mpln'	19-17	**mpln KEYWORDS [ent]** This utility calculates the best least squares plane through the specified atoms. It calculates the angles between this plane's normal and the normals to all previous planes from 'mpln' and to previous lines from 'line'. For example: **mpln C1 to C6 [ent]** **mpln C7 C8 C9 [ent]** would calculate the equation of least squares plane defined by the atoms in the atoms list between C1 to C6 and the plane define by atoms C7, C8, and C9 and the angle between the normal to these planes and any lines previously defined by 'line'. [Note: if 27 atoms lie between C1 and C6 because you haven't carefully sorted the atom list then all of them will be included in the plane.] [Note: 'nopl' deletes the stored table of planes and lines.
'name'	19-18	**name oldname newname SFAC code [ent]** This utility renames atoms and ranges of atoms and will redefine their atom types (using the SFAC code (this is SHELXTL's code for each element type)) if required. For example: **name Q7 C3 2 [ent**] would rename peak Q7 as atom C3 and give it an SFAC code of 2. **name Q?? C?? [ent]** would change Q peaks Q11 to Q99 to carbons C11 to C99, respectively. Note: It can generally guess the SFAC code from the atom names.
'next'	19-18	**next filename [ent]** This utility recalls the saved structural parameters from 'save'.
'nopl'	19-19	**nopl [ent]** This command deletes stored planes (from 'mpln') and lines (from 'line').

'ofit'	19-19	**ofit KEYWORDS [ent]** This interactive utility is used to fit atoms to models (i.e., rigid rings, another steroid, etc.). This could be used to compare related molecules.
'orth'	19-20	**orth filename [ent]** This utility converts the crystallographic coordinates of the atoms to orthogonal(Cartesian) coordinates based on the current view of the molecule. If the period (i.e., ".") in the filename is left out it saves them to the .ort file, e.g., **orth 95ADH03C [ent]** would save orthogonal(Cartesian) coordinates in **95ADH03C.ort**. This is useful for transferring coordinates to other programs such as Chem3D.
'pack'	19-20	**pack del2 del1 KEYWORDS [ent]** This interactive utility is used to set up packing plots for the symmetry related molecules within the box generated by 'pbox', which defines its size. When you get a 'pack' view that looks good to you, click on the sgen/fmol key which will add these new atoms to the atom list (so that you can now see them in 'proj', 'telp', etc). [Note: these extra symmetry generated atoms can be removed with the 'fuse' and 'uniq' commands.]
'page'	19-21	**page [ent]** This command adds a blank page between the last file to be printed and the next one.
'pbox'	19-22	**pbox width depth Xc Yc Zc [ent]** This utility defines the size of the box used by 'pack' where the width and depth are in Å (default width is 20Å and depth is 8Å). The height is defined as 0.75 the width. It includes all molecules with at least one atom in the box. Xc Yc Zc is the center of the box in crystal coordinates (0.5 0.5 0.5 default). For example: **pbox 10 5 0 0 0 [ent**] would generate all molecules touching a box 10Å x 5Å x 7.5Å centered at the origin. Each time you use 'pbox' it starts over from the unique portion of the cell even after you have used 'sgen'.

'pers'	19-22	This utility draws the molecule on the screen as a perspective ball and stick drawing, e.g., **pers bondrad KEYWORD [ent]** where bondrad is the radii of bonds (default is 0.05 Å) and **KEYWORD** is most commonly **CELL** (to show the unit cell outline).
'pgen'	19-23	This command is used to generate coordination polyhedra. If you need to use these, see Dr. Wagner for help.
'pick/H'	19-24	**pick/H [ent]** This utility labels all atoms on the screen including Hydrogens.
'pick'	19-24	**pick KEYWORDS [ent]** This interactive utility is used to assigns Q peaks, renames atoms, and changes their types, etc. Only non-Hydrogen atoms have their labels appear on screen. The space bar accepts the current name, [ent] deletes that peak if nothing was typed in or renames/assigns it to what you type in, and [/] saves what you've done in 'pick'.
'polp'	19-25	This command is used for drawing coordination polyhedra. If you need to use these, see Dr. Wagner for help.
'poly'	19-27	This command is used for drawing coordination polyhedra. If you need to use these, see Dr. Wagner for help.
'post'	19-27	**post plot file [ent]** This interactive utility combines text and graphics (e.g., for posters). It allows you to adjust the size and to annotate existing plot files.
'prev'	19-29	**prev [ent**] This command returns the molecule to the previous orientation.
'print'	19-29	**prin [ent]** or **print [ent]** This command sends the output that have been saved to the printer. Either 'print' or 'prin' may be used.

'proj'	19-30	**proj KEYWORDS [ent]** This interactive utility is used to orient views. **proj CELL [ent]** would include a unit cell outline as well.
'prun'	19-30	**prun nb KEYWORDS [ent]** or **prun d1 d2 KEYWORDS ent** Here the term 'nb' refers to the maximum number of bonds allowed to an atom and the terms 'd1' and 'd2' refer to the minimum and maximum allowed bond distances. This command prunes the connectivity table (i.e., it removes bonds), e.g. **prun Cr [ent]** **prun C1 to C6 [ent]** **prun $O [ent]** remove all bonds to Cr, to carbons C1 through C6, and to all oxygen atoms, respectively. **prun 4 C14 [ent]** would remove all but the four shortest bonds from C14. **prun 1.35 1.55 C14 [ent]** would remove all bonds shorter than 1.35 Å and longer than 1.55 Å from C14.
'push'	19-30	**push dx dy dz sign [ent]** This utility shifts all the atoms on the atom list. It first multiplies by sign (which must be +1 or -1) and then shifts coordinates by dx dy dz. For example: **push 0 0 0 -1 [ent]** would invert each atom's coordinates about the origin (i.e., as does 'invt). If coordinates are added, the 'push' command inverts the unit cell contents about this new point. This is particularly useful for a few unusual space groups.
'quit'	19-31	**quit [ent]**

		This command quits **XP** and kills any printer output.
'rast/c'	19-31	**rast/c filename [ent]** This command prints the specified filename in color.
'rast'	19-31	**rast filename [ent]** This command prints the specified filename in black and white.
'read'	19-31	**read filename [ent]** This command loads atoms, etc., from the specified filename. **read 95ADH03A [ent]** or **read 95ADH03A.res [ent]** reads them from the **.res** file **read 95ADH03A.ins [ent]** reads them from the .ins file.
'reap'	19-32	**reap filename [ent]** This command mimics 'read' except that it reads past one END instruction in the .res file to read the Q peaks.
'save'	19-33	**save filename [ent]** This utility saves the current structural parameters to the named file, 'next' returns them. Used to "backup" your work before trying "risky" operations on your data. This is used as a "temporary" save within **XP**.
'sfil'	19-34	**sfil s d KEYWORDS [ent]** This utility generates a *space filling molecular model* and writes it to a plot file. It asks you to name the plot file, use your compound's name.a, or .b or. c, etc. The character S is the stereo view angle and is used for stereo views. Its default is 0 for mono. For left-right stereo use 3 and use -3 for red-green stereo. The character d is the distance from eye to paper or screen and is normally left at the default of 50. You can use 'arad' and 'atyp' to change atomic radii and colors, respectively. It then asks you to interactively label atoms as in 'telp'.

'sgen'	19-34	**sgen SYMCODES KEYWORDS [ent]** This utility generates new atoms with the specified SYMCODES. These are often found from 'envi'. For example: **sgen 6554 [ent]** would generate the symmetry related molecule with SYMCODES 6554.
'sort/H'	19-33	**sort/H atom 1 atom 2 ... atom n [ent]** This utility is just like sort but it doesn't put Hs after their attached atoms.
'sort/N'	19-33	**sort/N atom 1 atom 2 ... atom n [ent]** This routine sorts the specified atoms by their numbers.
'sort'	19-36	**sort atom 1 atom 2 ... atom n [ent]** This utility sorts the atoms in the specified order. For example: **sort Cr1 [ent]** would make Cr1 the first atom in the list. **sort O2 N3 C11 C12 [ent]** would place C12 after C11 after N3 after O2 in the list. These commands place Hydrogens right after the atoms they are attached to. **Sort $Pt $S $P $N $C $H [ent]** Would put the atom types in the specified order (i.e., all of the Pt atoms in order, followed by all of the S atoms in order, followed by all of the P atoms in order, etc.).
'spix'	19-36	**spix KEYWORDS [ent]** This utility displays space filling molecules without generating a plot file. If you press the 'p' key while in the 'spix' view, a black and white copy of the view will be sent to the printer.
'telp'	19-39	**telp s p b d KEYWORDS [ent]** This interactive routine labels a plot and then saves it for later plotting by 'rast'

		or rast/C. The parameters are: s which is the stereo angle given as 0 for a mono plot, 3 for a left-right stereo plot, and -3 for a red-green stereo plot. [add 10C to suppress the frame around stereo plots]. p is the % probability of the displacement ellipsoid, a *positive number* gives ball and stick plots, a *negative number* gives displacement ellipsoid plots. The default value for p is 50%, most people use 30% to 50% for p to see clearly what is going on, and using values for p to 75% to 100% often gives plots that are too crowded to see clearly. b is the bond radius. The default value for b is 0.09 but a value of 0.04 or 0.05 gives thinner bonds and is generally preferred. d is the stereo view distance (default is 50 (cm)). The program will ask for the filename, you use filename.a, .b, etc. (e.g., **95ADH03A.b**). The **KEYWORD CELL** adds a unit cell outline ('pack' may be used, previously, to generate other equivalent molecules in the cell). For example: **telp [ent]** would generate a standard ball and stick plot. **telp 3 50 0.08 50 CELL [ent]** would generate a stereo view on paper with 50% probability ball and stick figure, bond 0.08 Å wide at a view distance of 50 cm with a unit cell outline. **telp 0 -50 0.04 0 LESS $H [ent**] would plot an 'displacement ellipsoid' diagram with full ellipsoids at 50% probability and 0.04Å bonds with no H atoms shown. See the discussion of 'labl' command above to: turn on/off the hydrogen atom labels, turn on/off the brackets around the atoms numbers, and to change the size of the atom labels.
'title'	19-40	This command reads in a title of up to 76 characters to identify a structure.

'tors/L'	19-40	**tors/L KEYWORDS [ent] print [ent]** This utility calculates torsion angles for the specified atoms, e.g.: **tors/L Cl C7 C8 Br2 [ent] print [ent]** would calculate the torsion angle about the C7-C8 bond of the C7-Cl and C8-Br2 bonds and then send them *to the printer*. **tors/L C1 C2 C3 C4 N Cl2 S4 [ent] print [ent]** would calculate all of the torsion angles involving this set of seven atoms and send them *to the printer*. **tors/L [ent] print [ent]** or **tors/L All [ent] print [ent]** (i.e., the 'All' is not needed) would calculate all of the torsion angles in the molecule and send them *to the printer*. **tors/L All less $H [ent] print [ent]** would calculate all of the torsion angles in the molecule not involving H atoms and then send them *to the printer*.
'tors'	19-40	**tors KEYWORDS [ent]** This utility calculates torsion angles for the specified atoms, e.g.: **tors Cl C7 C8 Br2 [ent]** would calculate the torsion angle about the C7-C8 bond of the C7-Cl and C8-Br2 bonds and send them to the screen. For details on more variations on using 'tors' see the entry on 'tors/L', above.
'undo'	19-41	This command is used to remove bonds between atoms, e.g.: **undo $H $H [ent]** or **undo Cr $C [ent]** or **undo C11 C12 [ent]**

		would remove all hydrogen-hydrogen, all chromium-carbon, and the C11 to C12 bonds, respectively.
'uniq'	19-41	**uniq KEYWORDS [ent]** This utility prunes the **FMOL** list to leave only the unique (i.e., not symmetry related) atoms that form unique molecules. It's great for removing all symmetry equivalent molecules and fragments and inequivalent molecules or ions. [Note: this command is approximately the opposite of the 'grow' command. After using the 'fuse' command, one almost always uses the 'uniq' command as well.]
'view'	19-39	**view plotfile [ent]** Can be used to view any specified plot file.
BONDTYPE	19-12	These parameters are used with 'link' and 'join'. 1 is solid 2 is open 3 is dashed solid 4 is dashed open 5 is full line 6 is dashes 7 is dots The default is 6 for 'link' and 1 for 'join'.
COLOR		These **COLOR** parameters are used to modify many XP instructions, they are: **code monitor inkjet suggested use** 0 brown black bonds 1 green green F, Al, Ni 2 dark red red Fe, Br, Pt

		3	dark blue	blue	Co
		4	yellow	orange	S, Na, Fourier peaks
		5	purple	magenta	P, K, Mn
		6	white	light green	H
		7	gray	gray	C
		8	blue	cyan	D, N, Ru, Ag
		9	dark green	green	Cl, others
		10	lilac	purple	Li, Cr, I
		11	orange	orange	B, Sn, Au
		12	turquoise	light blue	Cu, Si, Os
		13	brown	brown	Se, Sb, Mo
		14	dark gray	gray	As, Hg
		15	red	red	O
DELTA		This modifier is used to specify distances that atoms can be separated by but are thought of in contact (i.e., $r_1 + r_2 +$ **DELTA**).			
KEYWORDS		These parameters are used to modify many **XP** instructions, they are: **ALL** means all atoms in the list **TO** defines a string of atoms **LESS** is used to omit subsequent atoms **TYPEn** means all atoms of SFAC type n **PARTn** all atoms with part number n **$E** all atoms of element E (E is the element symbol) **/L** sends the output to the printer after you enter **print [ent]**			

		CELL used in 'pers', 'proj', etc. to add a cell outline
SFAC		This is the code number assigned by **SHELXTL** to each element in the structure.
TYPE	19-1	These **TYPE** parameters are used to modify many **XP** instructions, they are: -4: Dotted ellipse (displacement ellipsoid boundary ellipse) -3: Displacement ellipsoid boundary ellipse (normal lines) -2: Displacement ellipsoid boundary ellipse and principal ellipses -1: Full displacement ellipsoid with shaded segments 0: Nothing (useful for dummy atoms, e.g., in the middle of a C5H5 ring) 1: Shaded circle with highlight 2: Open circle 3: Circle with regular dot pattern 4: Circle shaded bottom left to top right 5: Cross-hatched circle 6: Circle shaded bottom right to top left 7: Circle with light random dot pattern and highlight 8: Circle with medium random dot pattern and highlight 9: Circle with heavy random dot pattern and highlight 10: Dotted circle (useful for minor component of a disordered atom)

CHAPTER VIII. GENERATING TABLES FOR PUBLICATION USING XCIF

A. USING XCIF TO GENERATE TABLES

1. What is XCIF

The program **XCIF** is used to generate the Tables used in reports and publications. It is highly interactive with the user answering several questions about what they are looking for. **XCIF** does all of the rest and then depending on your instructions either saves the desired files to disc or prints them out directly.

2. Using XCIF

a) Starting XCIF and using the default settings

Typically for Chemistry 832, we take all of the default values except *we **don't** print out the structure factor table*.

To use **XCIF**, we type the following at the **DOS** prompt:

XCIF filename [ent]

For example use **XCIF Calctest [ent]** with our test data set. If you have forgotten to put in the filename, then XCIF will put you through "40 questions" to get all of the required information. For the novice it is just easier to type **[ent]** and then **Q** to quit the program and then restart with the filename in the command.

We then accept all of its choices by pushing the enter key for all question except when it asks us if we want to print out structure factor tables for which you say no. Typical **XCIF** output tables for the example **calctest** are found in chapter XI.

b) [S] Change Structure Code

One uses this menu item to change the name of the compound/structure that will appear in the final tables. You just type in the name of the compound you want to use (if it is different then the name of the file you loaded into **XCIF**).

c) [R] Use another CIF files to resolve '?' items

Unless you have done some very complicated stuff to you data, you can just accept the default values presented to you by XCIF (i.e., press **[ent]** four times).

d) [C] Set compound code number for tables (currently 1)

If the compound number that you want printed on the tables is not one, simply type in the correct number and press **[ent]**. For example, one would do this if the crystal structure was done on compound number 7 in a paper.

e) [N] Set next table number (currently 1)

If the table numbers that you want printed on the tables aren't to be started with one, simply type in the correct number and press **[ent]**. For example, one would do this if the crystal structure tables were to be numbered 4 and above in a paper because other data made up tables 1 to 3.

f) [T] Crystal/atom tables from .cif

At the start of this menu item you are asked several questions about where the data to make the tables is coming from. Unless you are doing something funny, you can accept the **XCIF** default suggestions for the name of the .cif file and that the data be selected from data_calctest in this file (i.e., press **[ent]** twice).

You are asked how you want the data written in the files

- SHELXTL XTEXT format and Å — type **ang [ent]** or just **[ent]** since this is the default choice
- SHELXTL XTEXT format and metric — type **met [ent]**
- SHELXTL XTEXT format, German and metric — type **ger [ent]**
- ASCII format — type **def [ent]**

You are then asked for the filename of the tables.

- The default setting prints the files directly to the printer without storing them.
  - type **[ent]**
- Type in the filename to save the files to disk. I recommend:

- name.ang for 'ang' type files (if SHELXTL XTEXT format and Å units were chosen above)
- name.def for 'def' type files (if ASCII format was chosen above)

You are then asked to select which tables you want. The seven possibilities are shown in section 3 below. I typically take all of them except the selected bond lengths and angles.

[Note: the default for XCIF is to set the tables up for the longer European style paper. With longer tables, this can lead to the tables being split between several pages. To overcome this, save the file, exit XCIF and edit the name.ang file to change the first line to read "&L120" rather than "&L128".] Then reenter XCIF and use the [X] menu entry to print the name.ang table.

g) [F] Structure factor tables from .fcf

This menu item is used to print out the final table of observed and calculated structures factors. These are needed for publication but are very long and so are only printed out when absolutely required.

You are first asked to pick the name of the CIF structure factor table. Unless you have done something very funny, accept the **XCIF** default of **name.fcf**.

You are then asked for the filename of the structure factor tables.

- The default setting prints the files directly to the printer without storing them.
  - type **[ent]**
- Type in the filename to save the files to disk. I recommend that this file be named as the .sft table, i.e.,
  - type **name.sft [ent]**
- You are then asked whether you want to print to US or European size paper. In the US and Canada choose the former.

h) [X] Print from SHELXTL XTEXT format file

This menu item is used to print any **SHELXTL** XTEXT format file from within **XCIF**.

i) [Q] Quit

This menu item is self explanatory, it exits you from **XCIF**.

3. The Seven Standard Tables Which One Can Print From XCIF

Table 1Crystal Data and Structure Refinement
Table 2Atomic Coordinates and Equivalent Isotropic Displacement Parameters
Table 3Bond Lengths and Angles
Table 4Anisotropic Displacement Parameters
Table 5Hydrogen Coordinates and Isotropic Displacement Parameters
Table 6Selected Bond Lengths and Angles (may be wanted)
Table 7Structure Factors (wanted only just before publication)

Once one is in the **XCIF** program, one has a choice of printing files directly to the printer or saving them as a file. I routinely do both, however, I generally prefer to save the tables to a file in **SHELXTL** XTEXT format called **name.ang** if I plan on later printing those files with **XCIF** or in ASCII format called **name.asc** if I want the "word process" them later. The advantage of this is that one can then use a text editor to modify the contents of the files, especially the titles on the tables. In addition, for longer tables it is advisable to edit the first line of this file which always is "&L128" to change it to "&L120" since this results in tables that print out more smoothly on US standard paper sizes. One then restarts XCIF and prints out the revised tables.

B. USING XCIF TO PREPARE DATA FOR PUBLICATION IN ACTA CRYSTALLOGRAPHICA

1. What Are CIF Format Files

Almost all crystallographic journals and most inorganic journals now require the submission of all or part of the data in a special format called Crystallographic Information Format, CIF, that has been developed by the International Union of Crystallography, IUCr. This format substantially speeds the process of preparing this data for publication, archiving the data in databases such as the Cambridge Crystallographic Data Base, CCDB, and checking the data for internal consistency. This group is now developing an extension of CIF to better suit the needs of macromolecular crystallographers. When one adds the **ACTA** command to the **name.ins** file and edits the **BOND** line to read **BOND $H** before one runs a **XL** calculation, a basic CIF formatted file, **name.cif**, is generated.

2. Some Useful Things That Any Chemist Can Do With a CIF File

These CIF files aren't just useful to journals and data bases. Once in the CIF format, many good inexpensive and even free programs are available to read the crystallographic data. I am particularly fond of using the WebLab Viewer (and its free WebLab Viewer Lite version) from Molecular Simulations (i.e., at http://www.msi.com) to open **name.cif** files and make high quality views and drawings of my molecules that can be rotated and viewed with different styles (e.g., space filling, ball and stick, ribbons) on any platform. Such programs can also input data from **name.ort** files having the data saved as orthogonal(Cartesian) coordinates (i.e., using the 'orth' command in XP).

3. Modifying CIF Files for Electronic Submission to Acta Crystallographica

The IUCr has put out detailed instructions on how to write CIF files appropriate for electronic submission to journals and even provides and automated check program to see that they are correctly formatted. However, writing these files from scratch is quite tedious. One can more easily modify the **name.cif** file produced by **XL** for this purpose. Qualitatively, this is done by adding the title, authors, abstract, and text for the paper to the beginning of the existing **name.cif** file. The general procedures for doing this are covered in section 17.3 (page 17-4) of the SHELXTL Version 5.1 manual.

Note to Readers: I have yet to do such an electronic submission myself, but expect to add a chapter to the Appendix on this topic in early 1999, especially if I get volunteers with experience to help.

PART II: AN ANNOTATED EXAMPLE OF A STRUCTURE SOLUTION FOR (h^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$CR(CO)_3$), (I.E. "CALCTEST" AND "PLOTTEST") USING XS, XL, AND XP

CHAPTER IX A WORKED EXAMPLE OF STRUCTURE SOLUTION FOR A TYPICAL DATA SET, "CALCTEST", (η^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$CR(CO)_3$), USING **XS**, **XL**, AND **XP**

CHAPTER X EXAMPLES OF MOLECULAR PLOTS GENERATED USING **XP** FOR THE DATA ", (η^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$CR(CO)_3$)

CHAPTER XI EXAMPLES OF TABLES GENERATED USING **XCIF** FOR THE TEST DATA SET "CALCTEST", (η^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$CR(CO)_3$)

CHAPTER IX. A WORKED EXAMPLE OF STRUCTURE SOLUTION FOR A TYPICAL DATA SET, "CALCTEST", (h^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$CR(CO)_3$), USING XS, XL, AND XP

There are an almost infinite number of ways that one could approach solving the structure of even a single crystalline sample. Examples of one such approach for one molecule (**95ADH06e** referred to as "calctest", (η^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$Cr(CO)_3$) are illustrated by the inclusions of the appropriate input (i.e., **calctest.ins**) and output (i.e., **calctest.res** and **calctest.lst**) files from each cycle in its refinement. [Note: This is the same sample illustrated in the **plottest.*** plots, in chapter X, below. Tables of data on the eventual solution are presented in chapter XI, below.] This molecule has the formula $C_{14}H_{14}CrO_8$ and crystallized in the P-1 (read P one bar) space group with 2 molecules per unit cell (all related by symmetry in this case). There were 5627 unique data used in the refinement with a R(int) value of 0.0226.

A. THE 1ST CYCLE: FINDING A TRIAL SOLUTION WITH XS AND DIRECT METHODS

In general, one would use *Direct methods* first to try to find a trial solution using **XS**. It requires the following **calctest.ins** input file and produces the following **calctest.res** and **calctest.lst** output files.

1. CALCTEST.INS Input File for 1st Cycle: XS with Direct Methods

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR    2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50
TREF
HKLF 4
END
```

[Note: the 'TREF' card is what tells the XS program to run *Direct Methods*.] On a Gateway2000® Pentium computer running at 166 MHz and with 32 MB of RAM, this **XS** calculation look a total of 27 seconds.

2. CALCTEST.RES Output File for 1st Cycle: XS with Direct Methods

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR    2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50

L.S. 4
BOND
FMAP 2
PLAN 20

MOLE   1
CR1   4  0.1500  0.2203  0.8268 11.000000  0.05
Q1    1  0.0212  0.4553  0.6493 11.000000  0.05  185.99
Q2    1 -0.3111  0.0821  0.7628 11.000000  0.05  174.94
Q3    1  0.0992  0.3597  0.9790 11.000000  0.05  168.46
Q4    1 -0.2432  0.2300  0.5786 11.000000  0.05  159.79
Q5    1  0.1269  0.4391  0.8824 11.000000  0.05  158.31
```

```
Q6    1 -0.0482  0.2375  0.9417 11.000000  0.05  158.12
Q7    1  0.1841  0.3296  1.1967 11.000000  0.05  151.04
Q8    1 -0.1356  0.2643  0.7067 11.000000  0.05  146.33
Q9    1  0.3947  0.2368  0.9464 11.000000  0.05  141.50
Q10   1  0.5452  0.2464  1.0189 11.000000  0.05  140.20
Q11   1  0.0032  0.3880  0.7443 11.000000  0.05  138.38
Q12   1 -0.1657  0.1934  0.8050 11.000000  0.05  134.25
Q13   1  0.3643  0.5079  1.1548 11.000000  0.05  130.19
Q14   1  0.1270  0.0348  0.8014 11.000000  0.05  128.32
Q15   1  0.2315  0.4082  1.1185 11.000000  0.05  127.24
Q16   1  0.1108 -0.0828  0.7820 11.000000  0.05  122.66
Q17   1  0.2680  0.2359  0.6987 11.000000  0.05  116.18
Q18   1  0.1756  0.5758  0.6821 11.000000  0.05  113.26
Q19   1  0.3308  0.2400  0.6145 11.000000  0.05  109.72
Q20   1 -0.3245 -0.0057  0.8538 11.000000  0.05  106.75
Q22   1 -0.2419  0.1011  0.5046 11.000000  0.05   76.66
Q23   1  0.3085  0.3707  1.3403 11.000000  0.05   76.31
Q24   1 -0.2292  0.1984  0.6479 11.000000  0.05   51.92
Q25   1 -0.1816  0.3027  0.6389 11.000000  0.05   42.61
Q26   1 -0.0684  0.3292  0.7625 11.000000  0.05   42.50
Q27   1 -0.3408  0.0986  0.6881 11.000000  0.05   40.27
Q28   1 -0.2972  0.0064  0.9820 11.000000  0.05   38.22
Q29   1  0.1359  0.3036  1.3205 11.000000  0.05   36.09
Q30   1 -0.0746  0.2058  0.7158 11.000000  0.05   35.98
Q31   1  0.0489  0.2764  0.9206 11.000000  0.05   35.42
MOLE   2
Q21   1  0.4708  0.6713  0.4870 11.000000  0.05   81.69
HKLF 4
END
```

3. CALCTEST.LST Output File for 1st Cycle: XS with Direct Methods

```
++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
+ XS -  CRYSTAL STRUCTURE SOLUTION  - SIEMENS SHELXTL - Ver. 5.03  +
+ Copyright(c) 1994 Siemens Analytical X-ray - All Rights Reserved  +
+ calctest                started at 18:59:31 on 23 Mar 1997  +
++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR    2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2

V =     747.07     At vol =    16.2     F(000) =     372.0     mu =   0.81 mm-1

Max single Patterson vector = 179.2    cell wt =    724.50    rho =  1.610

TEMP -50
TREF
HKLF 4

  8074  Reflections read, of which     0  rejected
  Maximum h, k, l and 2-Theta =   11.   15.   16.   66.00
  5627  Unique reflections, of which   4360  observed
```

```
  R(int) = 0.0226     R(sigma) = 0.0488      Friedel opposites merged

NUMBER OF UNIQUE DATA AS A FUNCTION OF RESOLUTION IN ANGSTROMS

Resolution Inf   5.00   3.50   2.50   2.00   1.70   1.50   1.40   1.30   1.20   1.10   1.00   0.90   0.80
N(observed)    11.    24.    59.    94.   121.   130.   103.   129.   181.   236.   345.   509.   729.
N(measured)    11.    24.    61.    98.   127.   138.   114.   137.   192.   270.   390.   584.   924.
N(theory)      11.    24.    61.    98.   127.   138.   114.   137.   192.   270.   390.   586.   924.
Two-theta  0.0    8.2   11.7   16.3   20.5   24.1   27.4   29.4   31.7   34.5   37.7   41.6   46.5   52.7

Highest memory for sort/merge = 11708 / 28135

Observed E .GT. 1.000 1.100 1.200 1.300 1.400 1.500 1.600 1.700 1.800 1.900
Number         2586  2199  1889  1590  1330  1093   886   710   549   435

              Centric Acentric   0kl     h0l     hk0     Rest

Mean Abs(E*E-1)   0.968   0.736   0.807   0.872   0.831   0.835

     6.0 seconds elapsed time

   SUMMARY OF PARAMETERS FOR  95adh06e in P-1

ESEL  Emin  1.000    Emax  5.000    DelU 0.005    renorm 0.700    axis 0
OMIT  s  4.00    2theta(lim)  180.0
INIT  nn  13    nf   8    s+  0.800    s-  0.200    wr  0.200
PHAN  steps   10   cool 0.900   Boltz 0.400   ns  202   mtpr   40   mnqr  10
TREF  np     128.    nE   345    kapscal -0.900    ntan   2    wn -0.950
FMAP  code  8
PLAN  npeaks   -31    del1 0.500    del2 1.500
MORE verbosity  1
TIME  t    9999999.

    202 Reflections and   1607. unique TPR for phase annealing
    345 Phases refined using    6594. unique TPR
    534 Reflections and   13200. unique TPR for R(alpha)

      1.2 seconds elapsed time

   5635 Unique negative quartets found,  5635 used for phase refinement

      1.5 seconds elapsed time

Highest memory used to derive phase relations =   11778 /   83467

ONE-PHASE SEMINVARIANTS

 h   k   l     E      P+    Phi
-4   4   2   3.568   1.00
 6   0   2   3.111   0.43
 2   4   4   2.665   0.48
 0  -4   4   2.367   0.42
 4  -8   2   2.507   0.39

 2   0   2   1.984   0.40
-2   0   4   1.944   0.56
-4   0   2   1.765   0.48
-2  -4   4   1.998   0.56
-2  -6   4   1.954   0.39

 0   4   0   1.823   0.55
 0   6   0   2.147   0.41
 0  -4   6   1.739   0.41
 0  -2   8   2.014   0.73
-4   0   8   1.753   0.75

-6  -4   4   2.055   0.41
-6  -2   6   1.870   0.47
 0   4   8   1.989   0.47
-2   4   4   1.814   0.71
```

```
 0  0  2  1.492  0.52

-6 -4  6  1.916  0.41
 2  4  2  1.870  0.57
 2 -2  8  1.859  0.63
 2 -4  2  1.681  0.45
-4  6  6  2.066  0.51

 0  2  8  1.720  0.42
 0  0  6  1.587  0.49
-2 -8  4  1.830  0.44
 2  0  0  1.528  0.61
 0  2  0  1.226  0.44

-2 -2  4  1.213  0.44
-4 -2  2  1.353  0.44
 0  6  4  1.618  0.42
-6  0  6  1.573  0.51
-2 -8  2  1.437  0.43

 6  0  0  1.414  0.47
 4 -4  2  1.437  0.49
-6  0  4  1.684  0.48
 2 -2  2  1.261  0.43
-4  6  2  1.601  0.58

-4  0  6  1.417  0.66
-2 -4  2  1.225  0.45
-2  2 10  1.553  0.53
-6  6  2  1.458  0.58
-2  2  4  1.334  0.44

 2 -6  2  1.361  0.42
-2 -8  6  1.587  0.47
-6 -4  2  1.527  0.57
-4  4  4  1.171  0.51
```

Expected value of Sigma-1 = 0.516

Following phases held constant with unit weights for the initial 4 weighted tangent cycles (before phase annealing):

```
 h  k  l    E     Phase/Comment

-4  4  2  3.568    0   sigma-1 = 1.000
-2 -1  3  2.286   random phase
 0 -1  1  1.745   random phase
 2  0  1  2.202   random phase
-2  2  1  3.361   random phase
-3  0  1  1.801   random phase
 1  0  0  1.520   random phase
-2  0  3  1.743   random phase
 0  0  2  1.492   random phase
-1  6  2  1.703   random phase
 1 -3  2  1.487   random phase
-1  2  3  1.879   random phase
 0 -3  1  1.648   random phase
 2  0  0  1.528   random phase
```

All other phases random with initial weights of 0.200 replaced by 0.2*alpha (or 1 if less) during first 4 cycles - unit weights for all phases thereafter

```
   401 Unique NQR employed in phase annealing

   128 Parallel refinements,  highest memory =   17031 /   98531

     0.6 seconds elapsed time
```

STRUCTURE SOLUTION for 95adh06e in P-1

```
          Phase annealing cycle:    1   Beta =  0.05984
          Ralpha 0.211 0.193 0.596 0.029 0.157 0.612 0.332 0.200 0.388 0.186 0.458 0.286 0.365 0.448 0.032 0.219 0.625 0.229
0.238 0.618
          Nqual     -0.789-0.182-0.223-0.977-0.850-0.358-0.172-0.828-0.057-0.481-0.309-0.762-0.129-0.522-0.545-0.328-0.213-
0.765-0.843-0.378
          Mabs   0.792 0.796 0.589 1.148 0.851 0.581 0.688 0.793 0.659 0.814 0.637 0.726 0.684 0.642 1.131 0.774 0.582 0.776
0.761 0.580

          Phase annealing cycle:    2   Beta =  0.06649
          Ralpha 0.228 0.225 0.406 0.045 0.129 0.675 0.224 0.108 0.549 0.253 0.455 0.198 0.235 0.217 0.042 0.190 0.536 0.206
0.151 0.737
          Nqual     -0.946-0.720-0.770-0.992-0.933-0.767-0.920-0.944-0.816-0.863-0.823-0.938-0.850-0.973-0.992-0.926-0.883-
0.897-0.967-0.778
          Mabs   0.793 0.775 0.659 1.263 0.894 0.567 0.771 0.926 0.602 0.757 0.645 0.821 0.764 0.775 1.249 0.829 0.611 0.796
0.871 0.551

          Phase annealing cycle:    3   Beta =  0.07388
          Ralpha 0.175 0.218 0.317 0.045 0.137 0.600 0.209 0.081 0.518 0.279 0.438 0.192 0.179 0.134 0.045 0.190 0.362 0.204
0.138 0.664
          Nqual     -0.924-0.740-0.767-0.992-0.941-0.837-0.940-0.909-0.825-0.874-0.871-0.932-0.895-0.963-0.992-0.928-0.920-
0.889-0.973-0.817
          Mabs   0.851 0.781 0.715 1.263 0.886 0.592 0.799 0.985 0.612 0.743 0.654 0.836 0.830 0.897 1.263 0.825 0.682 0.800
0.898 0.570

          Phase annealing cycle:    4   Beta =  0.08208
          Ralpha 0.168 0.210 0.265 0.045 0.143 0.543 0.201 0.080 0.472 0.204 0.435 0.188 0.185 0.136 0.045 0.187 0.311 0.212
0.143 0.514
          Nqual     -0.920-0.830-0.894-0.992-0.950-0.805-0.939-0.906-0.818-0.974-0.878-0.941-0.914-0.971-0.992-0.939-0.898-
0.885-0.975-0.825
          Mabs   0.861 0.815 0.751 1.263 0.877 0.614 0.811 0.996 0.629 0.814 0.655 0.841 0.823 0.901 1.263 0.825 0.719 0.788
0.892 0.615

          Phase annealing cycle:    5   Beta =  0.09120
          Ralpha 0.167 0.201 0.249 0.045 0.140 0.612 0.198 0.077 0.465 0.131 0.412 0.190 0.185 0.137 0.045 0.197 0.227 0.221
0.142 0.462
          Nqual     -0.925-0.933-0.919-0.992-0.946-0.841-0.937-0.919-0.879-0.974-0.867-0.944-0.908-0.974-0.992-0.943-0.798-
0.889-0.974-0.818
          Mabs   0.863 0.823 0.772 1.263 0.879 0.589 0.810 0.992 0.630 0.903 0.666 0.832 0.824 0.898 1.263 0.812 0.778 0.779
0.893 0.634

          Phase annealing cycle:    6   Beta =  0.10134
          Ralpha 0.161 0.208 0.230 0.045 0.143 0.595 0.202 0.080 0.426 0.115 0.380 0.192 0.183 0.143 0.045 0.193 0.190 0.213
0.142 0.478
          Nqual     -0.923-0.937-0.928-0.992-0.950-0.855-0.941-0.921-0.855-0.974-0.871-0.945-0.909-0.975-0.992-0.943-0.922-
0.894-0.973-0.852
          Mabs   0.860 0.810 0.794 1.263 0.877 0.595 0.807 0.997 0.645 0.939 0.675 0.835 0.826 0.891 1.263 0.817 0.818 0.788
0.893 0.630

          Phase annealing cycle:    7   Beta =  0.11260
          Ralpha 0.165 0.206 0.229 0.045 0.140 0.604 0.201 0.080 0.426 0.115 0.365 0.200 0.183 0.140 0.045 0.194 0.201 0.210
0.140 0.490
          Nqual     -0.929-0.934-0.949-0.992-0.946-0.855-0.940-0.921-0.863-0.973-0.900-0.947-0.906-0.974-0.992-0.939-0.942-
0.891-0.974-0.855
          Mabs   0.855 0.812 0.797 1.263 0.879 0.592 0.807 0.997 0.644 0.939 0.686 0.826 0.825 0.894 1.263 0.817 0.817 0.793
0.894 0.624

          Phase annealing cycle:    8   Beta =  0.12511
          Ralpha 0.162 0.207 0.235 0.045 0.143 0.602 0.198 0.079 0.414 0.113 0.259 0.193 0.174 0.145 0.045 0.194 0.199 0.205
0.142 0.473
          Nqual     -0.931-0.951-0.949-0.992-0.950-0.843-0.937-0.919-0.852-0.971-0.868-0.942-0.903-0.975-0.992-0.939-0.937-
0.893-0.973-0.859
          Mabs   0.861 0.810 0.792 1.263 0.877 0.595 0.810 0.992 0.650 0.942 0.748 0.829 0.834 0.891 1.263 0.817 0.813 0.800
0.893 0.633

          Phase annealing cycle:    9   Beta =  0.13901
          Ralpha 0.172 0.221 0.232 0.045 0.143 0.587 0.203 0.080 0.414 0.114 0.060 0.186 0.187 0.142 0.045 0.185 0.204 0.194
0.140 0.474
          Nqual     -0.951-0.946-0.957-0.992-0.950-0.845-0.942-0.929-0.856-0.972-0.974-0.943-0.916-0.974-0.992-0.940-0.931-
0.878-0.974-0.878
          Mabs   0.849 0.803 0.797 1.263 0.877 0.597 0.806 0.992 0.650 0.946 0.965 0.835 0.822 0.893 1.263 0.823 0.816 0.806
```

```
0.894 0.633

          Phase annealing cycle:   10   Beta =  0.15445
          Ralpha 0.173 0.212 0.239 0.045 0.140 0.526 0.203 0.080 0.418 0.115 0.044 0.186 0.183 0.142 0.045 0.190 0.201 0.192
0.145 0.356
          Nqual     -0.955-0.947-0.955-0.992-0.946-0.856-0.942-0.921-0.853-0.973-0.992-0.932-0.914-0.974-0.992-0.941-0.945-
0.893-0.975-0.908
          Mabs   0.847 0.807 0.792 1.263 0.879 0.619 0.806 0.997 0.649 0.937 1.256 0.841 0.824 0.893 1.263 0.820 0.819 0.805
0.891 0.693

          Phase refinement cycle:  1
          Ralpha 1.172 1.287 1.328 0.158 0.956 2.829 1.288 0.753 2.806 0.860 0.158 1.279 1.217 0.983 0.158 1.365 1.264 1.392
0.983 1.895
          Nqual     -0.823-0.845-0.897-0.901-0.922-0.734-0.878-0.888-0.578-0.910-0.901-0.871-0.772-0.926-0.901-0.861-0.841-
0.821-0.926-0.878
          Mabs   0.476 0.462 0.457 0.771 0.508 0.349 0.461 0.543 0.351 0.524 0.771 0.462 0.471 0.503 0.771 0.453 0.465 0.450
0.503 0.405

           Try    Ralpha Nqual Sigma-1 M(abs) CFOM   Seminvariants

          422517. 0.267 -0.912  0.377  0.757  0.268  +---- -+-++ -++-+ -+--- -++++ +---- -+--+ ++++- -++++ -++-
           15433. 0.282 -0.935  0.258  0.748  0.282  +++-- --+-+ +-+++ ++--- +---- ++++- +---+ --++- -++-+ ++--
           77165. 0.295 -0.961  0.361  0.747  0.295  +++++ +++-- ++-+- -+++- ++--+ +---+ -+++- -+-++ +---+ --+-
          385825. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
         1929125. 0.198 -0.966  0.194  0.844  0.198  +++++ +---- -+--- ---+- +---- +++-- +++-- --+-- ++-+- +++-
         1257017. 0.518 -0.891  0.246  0.619  0.521  +--++ --+-+ +-++- ----- +---+ ++++- +-++- -+-+- +---+ +---
         2090781. 0.291 -0.947  0.594  0.749  0.291  +---- --+-- +-+++ --+-- +++-- +-+++ -+--- +-+-+ -+++- --+-
         2065297. 0.170 -0.920  0.361  0.852  0.171  +--++ +++-- +---+- +--+- -+-++ +---+ --+-+ +-+++ ++---+ ----
         1937877. 0.669 -0.785  0.365  0.567  0.696  +--++ +--++ ----- +++-- -++-+ -+-+- +---+ +---+ +--+- +---
         1300777. 0.194 -0.961  0.496  0.830  0.194  +--++ -+--- --+++ ----+ ---++ ----+ +---- ---++ +--++ +--+
          212429. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
         1062145. 0.317 -0.965  0.405  0.728  0.317  +++-- ---++ --+++ -+--+ ++--- -++-+ --++- +++-+ -+--- ---+
         1116421. 0.267 -0.898  0.553  0.768  0.270  +---- --+-- ++++- --++- -++-- +-+++ -+--- +-+-+ -++++ --+-
         1387801. 0.210 -0.970  0.315  0.818  0.210  +++-- +--+- -++-+ +--+- ----+ +--++ -+-++ -+-+- ----+ -+--
          647549. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
         1140593. 0.325 -0.935  0.487  0.720  0.325  +--++ --+-- +++++ --+-+ ----- ++---+ -+--- ----+ +---- -+++
         1508661. 0.282 -0.935  0.258  0.748  0.282  +++-- --+-+ +-+++ ++--- +---- ++++- +---+ --++- -++-+ ++--
         1251849. 0.359 -0.955  0.443  0.704  0.359  +--++ +--+- -++++ +-++- -++-+ -+-+- +++++ +--+- --+-+ ----
         2064941. 0.210 -0.970  0.315  0.818  0.210  +++-- +--+- -++-+ +--+- ----+ +--++ -+-++ -+-+- ----+ -+--
         1936097. 0.407 -0.952  0.389  0.668  0.407  +++++ ++++- +-+-+ +-++- ++-++ -+++- ---++ +++-- ++--- -+-+
         1291877. 0.208 -0.932  0.295  0.820  0.208  +++++ --+-+ +-+++ ++--- ----+ ++--- +-+-+ -+-+- ++-++ +-+-
          167929. 0.513 -0.884  0.365  0.622  0.517  +--++ --+++ --+-+ -++-- ++--- +++++ ----- +---+ ---+- -++-
          839645. 0.210 -0.654  0.369  0.779  0.298  +++-- +++-+ ++-+- -+++- -+-+- -+-+- ++--- +++-- -+--- +--+
            3921. 0.265 -0.862  0.480  0.760  0.273  +---- --+-- ++++- +-+-- -++-- +--++ -+--- --+-+ -++++ --++
           19605. 0.280 -0.894  0.476  0.752  0.283  +++-+ -+-+- +---+ +-++- --+-- --+-- --++- -+++- --+-- -+--
           98025. 0.209 -0.920  0.253  0.824  0.210  +++++ --+-+ +--+- ++--- -+--+ +---- +-+-+ ++++- +--++ +-+-
          490125. 0.170 -0.920  0.361  0.852  0.171  +--++ +++-- +--+- +--+- -+-++ +---+ --+-+ +-+++ ++---+ ----
          353473. 0.228 -0.943  0.464  0.799  0.228  +---- ++--- ---+- ++-++ +-++- -++++ --+-+ -+-++ --+++ ---+
         1767365. 0.420 -0.639  0.368  0.651  0.516  +---- +--++ +-+-+ -++-- +++-- +-+-+ --++- ++-++ +-+-- ++--
          448217. 0.272 -0.953  0.264  0.750  0.272  +++++ ---+- -++-+ +---+ ++--- --++- ++-++ +-++- +---+ +-++
          143933. 0.196 -0.922  0.362  0.839  0.197  +--++ +++-+ +---- ++-+- -+++- -+--- +---+ ++--- ++++- +---
          719665. 0.170 -0.920  0.361  0.852  0.171  +--++ +++-- +--+- +--+- -+-++ +---+ --+-+ +-+++ ++---+ ----
         1360801. 0.243 -0.951  0.234  0.775  0.243  +---- --+++ +---- +++-+ +-++- +-+-+ +--++ --+++ -+++- ++++
         1650613. 0.325 -0.957  0.281  0.720  0.325  +---- --+-+ ++++- +++-+ +-+-+ +-+-+ -+-++ --+-+ -+++- -+++
         1419437. 0.213 -0.961  0.360  0.816  0.213  +++-- ++--+ -++++ ++++- ---+- -+--- -++-+ --+-- -+-+- ----
         1576021. 0.198 -0.957  0.194  0.839  0.198  +++++ +---- -+--- ---+- +---- +++-- +++-- --+-- ++-+- +++-
         1762225. 0.292 -0.907  0.319  0.726  0.294  +++++ -++++ ++-+- -++-- +-+++ +--++ ++++- -++-- +-+-- +-+-
         1512769. 0.200 -0.957  0.194  0.842  0.200  +++++ +---- -+--- ---+- +---- +++-- +++-- --+-- ++-+- +++-
         1268857. 0.170 -0.920  0.361  0.852  0.171  +--++ ++++- +--+- +--+- -+-++ +---+ --+-+ +-+++ ++---+ ----
          952729. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
         1490557. 0.461 -0.862  0.388  0.637  0.469  +++++ ++--- ----- ---+- --+-- -+--+ ----- -++++ +++-+ -+--
         1499689. 0.366 -0.883  0.390  0.689  0.371  +++++ -++++ ++-+- -++-+ +-++- +--++ ++-+- -+--+ +-+-- +-+-
          677769. 0.394 -0.754  0.306  0.668  0.432  +++++ ++--+ -+-+- -+++- +--++ -+--- ++--- -++-- ++-+- +++-
          262809. 0.261 -0.847  0.320  0.755  0.272  +---- +---+ ----- +++++ +-+-- +++++ ----+ --+++ --+++ ---+
         1310853. 0.170 -0.920  0.361  0.852  0.171  +--++ +++-- +--+- +--+- -+-++ +---+ --+-+ +-+++ ++---+ ----
         1612341. 0.055 -0.617  0.372  1.161  0.166  +++++ +++++ +++++ ++++- +++++ ++-++ +++++ +++++ +++++ ++++
         1195533. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
         1012913. 0.064 -0.753  0.280  1.110  0.103  +++++ +++++ +++++ ++++- ++-+- ++--+ +++++ +++++ +++++ ++++
         1787041. 0.282 -0.952  0.262  0.742  0.282  +++++ ---+- -++-+ +---+ ++--- -+++- ++-++ +-++- +---+ +-++
          331385. 0.346 -0.783  0.354  0.694  0.374  +++-- +-+-- ++--- ---++ -+-++ ---++ -+++- +--++ ---+- ++-+
```

```
199025. 0.338 -0.846  0.418  0.706  0.349  +---- --+-- +++++ +-+-+ +-+-- +++-+ -+---+ --+-+ -++-- -+++
597109. 0.170 -0.936  0.358  0.853  0.171  +--++ +++-- +--+- +--+- -+-++ -+---+ ----+ +-+++ -+--+ ----
  7961. 0.202 -0.932  0.311  0.826  0.202  +++++ --+-+ +-+++ ++--- ----+ ++--- +-+-+ -+-+- +--++ +-+-
1238305. 0.205 -0.968  0.337  0.823  0.205  +++-- +--+- -++-+ +--+- ----+ +--+- -+-++ -+-+- ----+ -+--
 997013. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
1656925. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
1500549. 0.268 -0.952  0.262  0.751  0.268  +++++ ---+- -++-+ +---+ ++--- -+++- ++-++ +-+++- +---+ +-++
1722341. 0.261 -0.847  0.320  0.755  0.272  +---- +---+ ----- +++++ +-+-- +++++ ----+ --+++ --+++ ---+
 657725. 0.200 -0.957  0.194  0.842  0.200  +++++ +---- -+--- ---+- +---- +++-- +++-- --+-- ++-+- +++-
 223097. 0.220 -0.952  0.273  0.816  0.220  +--++ -+--+ -++-+ ++-++ +--+- +++-- +++-+ ----- +--+- ---+
 672141. 0.222 -0.735  0.386  0.771  0.268  +++-- +++-+ ++-+- -++++ -+-++ ++-+- ++--- ++--- --+-- +--+
1754165. 0.316 -0.959  0.574  0.727  0.316  +--+- --+-- +++++ --+-+ --+-- ++--+ -+--- ----+ +---- -+++
1079609. 0.182 -0.932  0.314  0.843  0.183  +++++ --+-+ +-+++ ++--- ----+ +---- +-+-+ -+-+- +--++ +-+-
1115485. 0.064 -0.759  0.319  1.153  0.100  +++++ +++++ +++++ ++++- +++++ +++-+ +++++ +++++ +++++ +-++
1187989. 0.296 -0.941  0.463  0.736  0.296  +++++ -++++ ++-+- -+++- +++-+ +---+ -+++- -+--+ +-+-+ --+-
 403585. 0.265 -0.862  0.480  0.760  0.273  +---- --+-- ++++- +-+-- -++-- +--++ -+--- --+-+ -++++ --++
 435773. 0.357 -0.950  0.393  0.706  0.357  +--++ +--++ --+-+ -+++- --+-+ +-+-+ --++- -+--+ -+++ --++
 891201. 0.210 -0.970  0.315  0.818  0.210  +++-- +--+- -++-+ +--+- ----+ +--++ -+-++ -+-+- -----+ -+--
1597733. 0.202 -0.932  0.311  0.826  0.202  +++++ --+-+ +-+++ ++--- ----+ ++--- +-+-+ -+-+- +--++ +-+-
1495889. 0.064 -0.759  0.319  1.153  0.100  +++++ +++++ +++++ ++++- +++++ +++-+ +++++ +++++ +++++ +-++
  97437. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
1356785. 0.064 -0.759  0.319  1.153  0.100  +++++ +++++ +++++ ++++- +++++ +++-+ +++++ +++++ +++++ +-++
 768177. 0.261 -0.847  0.320  0.755  0.272  +---- +---+ ----- +++++ +-+-- +++++ ----+ --+++ --+++ ---+
1668333. 0.198 -0.966  0.194  0.844  0.198  +++++ +---- -+--- ---+- +---- +++-- +++-- --+-- ++-+- +++-
 911789. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
1959969. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
1769693. 0.068 -0.752  0.315  1.082  0.107  +++++ +++++ +++++ ++++- ++++- +++-+ +++++ +++++ +++++ +-++
1415681. 0.065 -0.765  0.306  1.092  0.100  +++++ +++++ +++++ ++++- ++++- +++-+ +++++ +++++ +++++ ++++
1304217. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
 727417. 0.057 -0.722  0.258  1.113  0.109  +++++ +++++ +++++ ++++- ++-+- +++-+ +++++ +++++ +++++ ++++
  84941. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
 561829. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
1785309. 0.170 -0.920  0.361  0.852  0.171  +--++ +++-- +--+- +--+- -+-++ +---+ --+-+ +-+++ ++--+ ----
1458705. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
1022609. 0.064 -0.759  0.319  1.153  0.100  +++++ +++++ +++++ ++++- +++++ +++-+ +++++ +++++ +++++ +-++
1429461. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
  26373. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
1803061. 0.064 -0.753  0.280  1.110  0.103  +++++ +++++ +++++ ++++- ++-+- ++--+ +++++ +++++ +++++ ++++
1174305. 0.286 -0.924  0.433  0.745  0.286  +++-- +++-+ ++-+- -+++- -+-++ ++++- ++--- +++-- +-+-- +-++
1166729. 0.064 -0.759  0.319  1.153  0.100  +++++ +++++ +++++ ++++- +++++ +++-+ +++++ +++++ +++++ +-++
1493881. 0.065 -0.765  0.306  1.092  0.100  +++++ +++++ +++++ ++++- ++++- +++-+ +++++ +++++ +++++ ++++
1585413. 0.064 -0.759  0.319  1.153  0.100  +++++ +++++ +++++ ++++- +++++ +++-+ +++++ +++++ +++++ +-++
 412089. 0.068 -0.752  0.315  1.082  0.107  +++++ +++++ +++++ ++++- ++++- +++-+ +++++ +++++ +++++ +-++
1697013. 0.064 -0.759  0.319  1.153  0.100  +++++ +++++ +++++ ++++- +++++ +++-+ +++++ +++++ +++++ +-++
1307797. 0.065 -0.765  0.306  1.092  0.100  +++++ +++++ +++++ ++++- ++++- +++-+ +++++ +++++ +++++ ++++
 942601. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
 193789. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
 230269. 0.053 -0.691  0.258  1.110  0.121  +++++ +++++ +++++ ++++- ++-+- +++-+ +++++ +++++ +++++ ++++
 652509. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
 876353. 0.064 -0.759  0.319  1.153  0.100  +++++ +++++ +++++ ++++- +++++ +++-+ +++++ +++++ +++++ +-++
1264801. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
1572017. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
 395769. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
1978845. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
1269393. 0.198 -0.966  0.194  0.844  0.198  +++++ +---- -+--- ---+- +---- +++-- ++++- --+-- ++-+- +++-
 862801. 0.332 -0.920  0.395  0.715  0.333  +--++ +--+- -++-+ --+++ --+-- +--+- -+++- --++- +++-+ ++-+
1912961. 0.170 -0.920  0.361  0.852  0.171  +--++ +++-- +--+- +--+- -+-++ +---+ --+-+ +-+++ ++--+ ----
 601621. 0.194 -0.961  0.496  0.830  0.194  +--++ -+--- --+++ ----+ ---++ ----+ +---- ---++ +--++ +--+
1574417. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
 277545. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
1561953. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
 910953. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
 344949. 0.198 -0.966  0.194  0.844  0.198  +++++ +---- -+--- ---+- +---- +++-- +++-- --+-- ++-+- +++-
1175585. 0.195 -0.950  0.380  0.839  0.195  +++-- +---+ ---+- -+-++ +-++- -++++ --+-+ -++++ -++++ ---+
 155293. 0.236 -0.908  0.274  0.787  0.237  +---- -+-++ -++-+ ++--- ---++ +---- -+-++ -+++- -+-++ -++-
1321909. 0.202 -0.932  0.311  0.826  0.202  +++++ --+-+ +-+++ ++--- ----+ ++--- +-+-+ -+-+- +--++ +-+-
 508701. 0.182 -0.932  0.314  0.843  0.183  +++++ --+-+ +-+++ ++--- ----+ +---- +-+-+ -+-+- +--++ +-+-
 318089. 0.064 -0.759  0.319  1.153  0.100  +++++ +++++ +++++ ++++- +++++ +++-+ +++++ +++++ +++++ +-++
 235117. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
1522673. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
```

```
 672937. 0.261 -0.847  0.320  0.755  0.272  +---- +---+ ----- +++++ +-+-- +++++ ----+ --+++ --+++ ---+
 633353. 0.326 -0.887  0.388  0.712  0.330  +++++ -++++ ++-+- -++-- +++-+ +---+ ++++- -+--+ +-+-- --+-
 641553. 0.194 -0.961  0.496  0.830  0.194  +--++ -+--- --+++ ----+ ---++ ----+ +---- ---++ +--++ +--+
 231045. 0.168 -0.934  0.358  0.856  0.168  +--++ +++-- +--+- +--+- -+-++ -+--+ ----+ +-+++ -+--+ ----
1057885. 0.064 -0.759  0.319  1.153  0.100  +++++ +++++ +++++ ++++- +++++ +++-+ +++++ +++++ +++++ +-++
1585261. 0.064 -0.759  0.319  1.153  0.100  +++++ +++++ +++++ ++++- +++++ +++-+ +++++ +++++ +++++ +-++
 602457. 0.081 -0.944  0.596  1.351  0.081  +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
1155913. 0.081 -0.944  0.596  1.351  0.081* +---- ++++- +-+++ ---+- ++-+- +++-- ---+- +---- ---+- -++-
```

***[Note added to the XS output by ADH**: The Direct methods calculations in **XS** does not just find one solution, it finds a large number that are listed near the middle of the **name.lst** output file for **XS** (i.e., in this spot in the file). **XS** chooses the "best" solution number (indicated by a * after its CFOM value, in the case of the above example # 1155913 with a CFOM = 0.0806) for its subsequent analyses (i.e., it chooses the one with the best CFOM and semi-invariants). [Note: here this is the last solution shown above and is shaded in dark.] However, typically several other solutions have almost as good of CFOM values (e.g., solutions 602457, 1522673, and 235117 shaded in light, above). One can often use one of these other solutions to get a better initial model.]*

CFOM Range	Frequency
0.000 - 0.020	0
0.020 - 0.040	0
0.040 - 0.060	0
0.060 - 0.080	0
0.080 - 0.100	34
0.100 - 0.120	16
0.120 - 0.140	1
0.140 - 0.160	0
0.160 - 0.180	10
0.180 - 0.200	14
0.200 - 0.220	11
0.220 - 0.240	2
0.240 - 0.260	1
0.260 - 0.280	11
0.280 - 0.300	10
0.300 - 0.320	2
0.320 - 0.340	4
0.340 - 0.360	3
0.360 - 0.380	2
0.380 - 0.400	0
0.400 - 0.420	1
0.420 - 0.440	1
0.440 - 0.460	0
0.460 - 0.480	1
0.480 - 0.500	0
0.500 - 0.520	2
0.520 - 0.540	1
0.540 - 0.560	0
0.560 - 0.580	0
0.580 - 0.600	0
0.600 - 9.999	1

```
   128. Phase sets refined - best is code  1155913.  with CFOM =  0.0806

    9.7 seconds elapsed time

Tangent expanded to 2586  out of 2586  E greater than  1.000
Highest memory used = 10458 /  7639

    3.5 seconds elapsed time
```

FMAP and GRID set by program

FMAP 8 1 23
GRID -2.500 -2 -2 2.500 2 2

E-Fourier for 95adh06e in P-1

Maximum = 738.91, minimum = -114.20 highest memory used = 8798 / 18472

0.8 seconds elapsed time

Heavy-atom assignments:

x y z s.o.f. Height

CR1 0.1500 0.2203 0.8268 1.0000 738.9

Peak list optimization
RE = 0.168 for 23 surviving atoms and 2586 E-values Highest memory used = 1613 / 23274

1.0 seconds elapsed time

E-Fourier for 95adh06e in P-1

Maximum = 733.45, minimum = -139.47 highest memory used = 8806 / 18472

0.8 seconds elapsed time

Peak list optimization
RE = 0.166 for 23 surviving atoms and 2586 E-values Highest memory used = 1621 / 23274

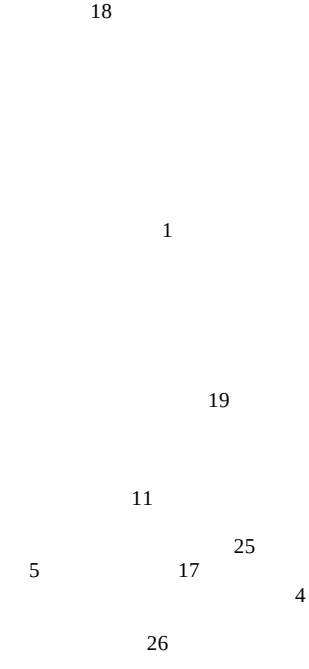
1.0 seconds elapsed time

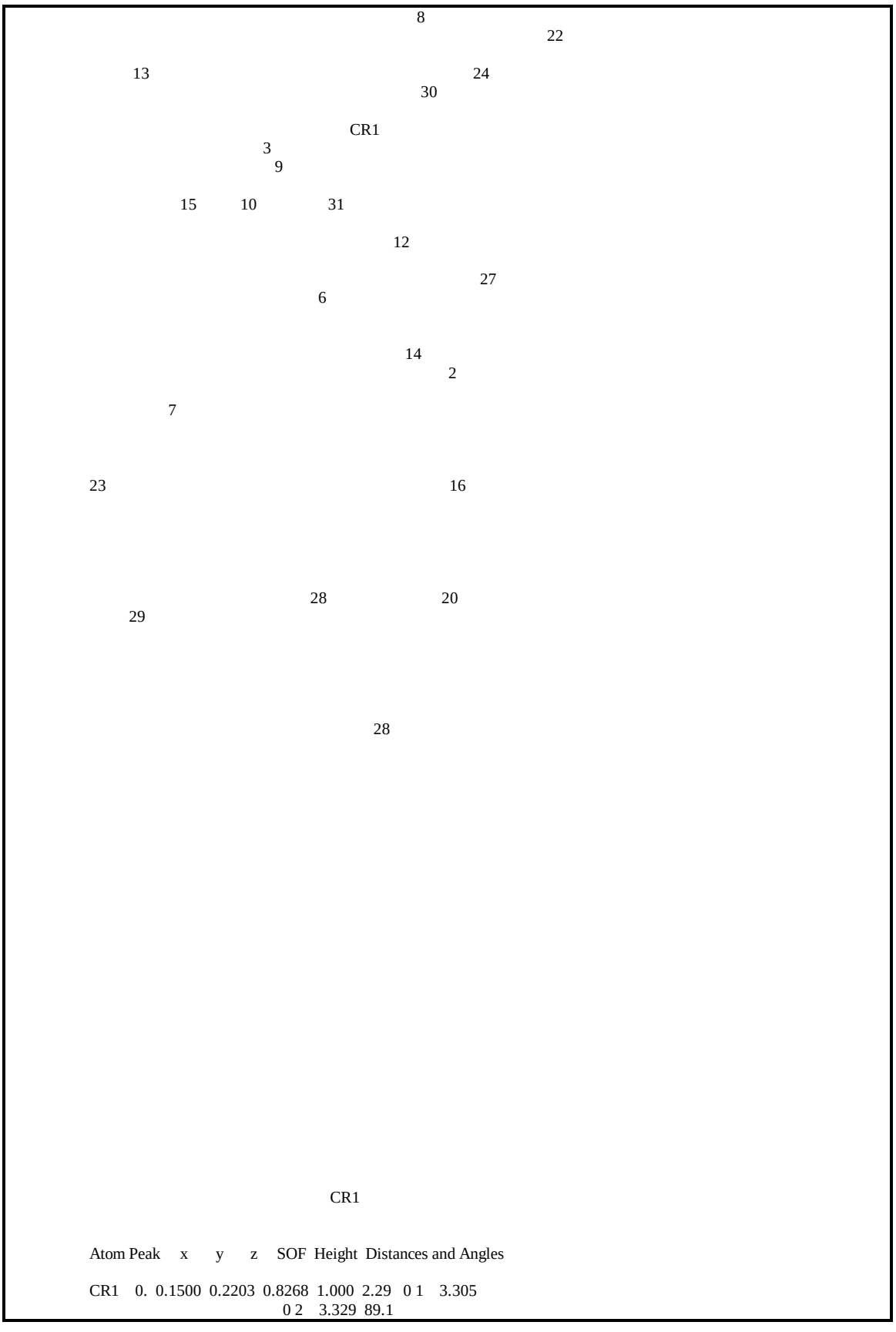
E-Fourier for 95adh06e in P-1

Maximum = 730.81, minimum = -88.13 highest memory used = 8806 / 18472

0.8 seconds elapsed time

Molecule 1 scale 0.870 inches = 2.209 cm per Angstrom





Atom Peak x y z SOF Height Distances and Angles

CR1 0. 0.1500 0.2203 0.8268 1.000 2.29 0 1 3.305
0 2 3.329 89.1

```
                              0 3   2.184  81.6  81.4
                              0 4   3.337  46.1  48.5  95.8
                              0 5   2.254  47.0  95.4  37.6  79.4
                              0 6   2.226  95.6  46.7  37.7  80.8  67.5
                              0 8   2.286  44.9  44.3  79.1  16.9  66.6  66.2
                              0 9   1.855 123.9 143.3  87.8 168.1  97.1 108.5 163.7
                              0 10  2.993 123.9 143.4  88.0 168.0  97.2 108.7 163.8   0.2
                              0 11  2.291  17.7  77.6  66.8  43.9  37.3  77.8  35.7 129.4 129.5
                              0 12  2.279  78.2  17.5  66.7  46.2  78.0  36.8  35.7 144.4 144.6  64.0
                              0 14  1.820 138.5  73.7 130.5  98.5 166.4  99.0 108.3  87.6  87.4 142.4  90.8
                              0 15  3.267  96.5  97.5  21.8 117.6  49.5  50.8 100.9  66.2  66.4  84.7  85.3
                              0 16  2.972 137.9  73.6 131.0  98.0 166.7  99.3 108.0  88.0  87.9 141.8  90.8
                              0 17  1.864  67.4 125.2 136.9  83.9 101.3 162.4  97.2  85.7  85.6  85.1 129.8
                              0 19  3.008  67.3 123.6 138.0  82.7 102.1 161.8  96.2  87.0  86.9  85.0 128.5
                              0 24  2.856  56.0  36.0  90.8  12.6  82.0  70.2  15.4 178.6 178.8  50.1  34.4
                              0 25  2.997  35.4  54.4  84.1  14.4  65.0  76.2  11.0 158.7 158.8  29.9  46.7
                              0 26  2.115  36.4  57.4  62.4  35.1  46.2  61.2  20.5 143.2 143.3  20.8  43.1
                              0 27  3.456  78.2  13.5  87.9  35.4  93.5  56.8  33.9 156.4 156.5  69.1  21.3
                              0 30  1.709  55.7  37.2  92.4  11.4  82.9  71.9  16.3 179.5 179.3  50.4  36.0
                              0 31  1.546  87.4  61.4  20.8  85.7  52.0  17.1  69.3 101.1 101.4  70.1  48.1
                              2 28  3.356 177.3  92.9  96.9 136.5 130.9  84.5 137.2  53.6  53.6 162.0 103.4

1   186.  0.0212  0.4553  0.6493  1.000  0.98   0 CR1  3.305
                              0 11  1.322  31.8
                              0 18  1.450 111.8 119.2
                              0 25  1.936  63.6  51.7 169.6
                              0 26  2.037  38.1  13.7 132.5  38.1

2   175. -0.3111  0.0821  0.7628  1.000  0.19   0 CR1  3.329
                              0 12  1.342  30.7
                              0 20  1.412 108.5 117.6
                              0 24  1.965  58.8  54.6 166.3
                              0 27  0.810  92.2  90.2 151.6  36.1

3   168.  0.0992  0.3597  0.9790  1.000  0.97   0 CR1  2.184
                              0 5   1.431  73.9
                              0 6   1.427  72.7 121.1
                              0 15  1.482 124.9 117.3 121.5
                              0 31  0.921  36.6  96.2  36.4 136.1

4   160. -0.2432  0.2300  0.5786  1.000  0.49   0 CR1  3.337
                              0 8   1.327  30.0
                              0 22  1.435  92.0 118.2
                              0 24  0.830  48.5  41.2  92.0
                              0 25  0.864  59.8  40.3 149.1  78.7
                              0 26  2.016  37.1  14.2 128.9  54.9  26.3
                              0 30  1.695  11.4  27.5  90.9  37.2  64.0  38.7

5   158.  0.1269  0.4391  0.8824  1.000  1.07   0 CR1  2.254
                              0 3   1.431  68.6
                              0 11  1.455  72.7 117.4
                              0 26  1.718  62.6  89.6  28.2
                              0 31  1.783  43.1  30.9  89.2  63.5

6   158. -0.0482  0.2375  0.9417  1.000  0.68   0 CR1  2.226
                              0 3   1.427  69.6
                              0 12  1.424  73.6 118.8
                              0 31  0.876  31.3  38.6  92.0

7   151.  0.1841  0.3296  1.1967  1.000  1.03   0 15   1.310
                              0 23  1.495 114.8
                              0 29  1.524 153.8  50.9

8   146. -0.1356  0.2643  0.7067  1.000  0.66   0 CR1  2.286
                              0 4   1.327 133.2
                              0 11  1.403  72.3 116.0
                              0 12  1.400  71.9 124.2 119.4
                              0 24  0.890 121.7  37.9 153.9  86.6
                              0 25  0.871 138.9  39.9  80.5 149.2  75.2
                              0 26  0.800  67.7 141.7  30.0  90.8 168.7 102.0
```

```
                                0 27   2.012 106.9  73.2 168.5  51.0  36.1 105.7 138.7
                                0 30   0.803  36.6 102.7 104.4  69.5  85.3 131.8 104.2  79.0

 9   141.  0.3947  0.2368  0.9464  1.000  3.40   0 CR1  1.855
                                0 10   1.138 179.4

10   140.  0.5452  0.2464  1.0189  1.000  4.10   0 CR1  2.993
                                0 9    1.138   0.4

11   138.  0.0032  0.3880  0.7443  1.000  0.90   0 CR1  2.291
                                0 1    1.322 130.4
                                0 5    1.455  70.0 120.9
                                0 8    1.403  72.0 117.7 121.5
                                0 25   1.524 101.7  85.4 151.8  34.3
                                0 26   0.815  67.3 143.7  94.1  29.4  58.5
                                0 30   1.781  47.6 122.9 109.8  25.9  54.4  39.6

12   134. -0.1657  0.1934  0.8050  1.000  0.51   0 CR1  2.279
                                0 2    1.342 131.9
                                0 6    1.424  69.6 122.3
                                0 8    1.400  72.4 116.1 121.6
                                0 24   1.615  92.7  82.7 154.9  33.4
                                0 26   1.623  63.0 144.2  92.9  29.5  62.6
                                0 27   1.570 126.8  31.1 153.2  85.1  51.9 113.3
                                0 30   1.348  48.2 111.3 115.8  33.9  44.5  49.4  87.3
                                0 31   1.697  42.7 147.8  31.0  93.3 124.9  67.4 168.8  85.3

13   130.  0.3643  0.5079  1.1548  1.000  1.51   0 15   1.214

14   128.  0.1270  0.0348  0.8014  1.000  2.99   0 CR1  1.820
                                0 16   1.152 178.3

15   127.  0.2315  0.4082  1.1185  1.000  1.21   0 CR1  3.267
                                0 3    1.482  33.3
                                0 7    1.310 109.3 110.7
                                0 13   1.214 116.4 124.4 125.0

16   123.  0.1108 -0.0828  0.7820  1.000  3.44   0 CR1  2.972
                                0 14   1.152   1.0

17   116.  0.2680  0.2359  0.6987  1.000  3.30   0 CR1  1.864
                                0 19   1.146 175.8

18   113.  0.1756  0.5758  0.6821  1.000  1.34   0 1    1.450

19   110.  0.3308  0.2400  0.6145  1.000  3.90   0 CR1  3.008
                                0 17   1.146   2.6

20   107. -0.3245 -0.0057  0.8538  1.000  0.23   0 2    1.412
                                0 28   1.315 137.7

22    77. -0.2419  0.1011  0.5046  1.000  1.24   0 4    1.435
                                0 24   1.683  29.5

23    76.  0.3085  0.3707  1.3403  1.000  1.24   0 7    1.495
                                0 29   1.297  65.7

24    52. -0.2292  0.1984  0.6479  1.000  0.52   0 CR1  2.856
                                0 2    1.965  85.2
                                0 4    0.830 118.9 154.7
                                0 8    0.890  42.9 102.5 100.8
                                0 12   1.615  52.9  42.6 159.6  60.0
                                0 22   1.683 105.3 110.4  58.4 131.7 138.6
                                0 25   1.075  86.9 144.4  52.0  51.5 107.6 105.1
                                0 26   1.682  47.3 101.1 101.3   5.4  58.9 136.4  50.6
                                0 27   1.395 103.4  20.0 134.8 121.8  62.4  97.1 152.1 119.8
                                0 30   1.149   2.6  86.9 116.9  44.2  55.3 102.8  86.8  48.7 104.7

25    43. -0.1816  0.3027  0.6389  1.000  0.40   0 CR1  2.997
                                0 1    1.936  81.0
```

```
                              0 4    0.864 105.7 132.5
                              0 8    0.871  30.1 106.0  99.8
                              0 11   1.524  48.5  42.9 150.5  65.2
                              0 24   1.075  72.1 150.7  49.2  53.2 117.8
                              0 26   1.300  37.3  75.1 136.6  37.0  32.3  89.7
                              0 30   1.528  23.5 103.6  85.5  23.1  71.4  48.6  52.4

26    43. -0.0684  0.3292  0.7625  1.000  0.65   0 CR1  2.115
                              0 1    2.037 105.5
                              0 4    2.016 107.7  79.8
                              0 5    1.718  71.2  79.6 158.1
                              0 8    0.800  91.9 101.5  24.1 162.5
                              0 11   0.815  91.8  22.6 101.1  57.6 120.6
                              0 12   1.623  73.8 160.8  82.2 117.2  59.6 165.5
                              0 24   1.682  96.9 103.1  23.8 168.0   6.0 123.4  58.5
                              0 25   1.300 120.9  66.8  17.1 146.1  40.9  89.2  96.7  39.7
                              0 30   1.265  53.9 109.6  56.8 125.0  38.0 116.1  53.9  43.1  73.1
                              0 31   1.844  45.3 134.8 135.2  59.9 111.3 112.7  58.2 112.7 152.2  81.6

27    40. -0.3408  0.0986  0.6881  1.000  0.14   0 CR1  3.456
                              0 2    0.810  74.3
                              0 8    2.012  39.3 102.6
                              0 12   1.570  31.9  58.8  43.9
                              0 24   1.395  53.5 123.8  22.1  65.7
                              0 30   2.020  20.2  93.5  23.0  41.8  33.4

28    38. -0.2972  0.0064  0.9820  1.000  0.00   0 20   1.315

29    36.  0.1359  0.3036  1.3205  1.000  0.51   0 7    1.524
                              0 23   1.297  63.4

30    36. -0.0746  0.2058  0.7158  1.000  1.26   0 CR1  1.709
                              0 4    1.695 157.2
                              0 8    0.803 127.2  49.8
                              0 11   1.781  82.0  83.5  49.7
                              0 12   1.348  95.7 104.2  76.6 100.4
                              0 24   1.149 175.6  25.9  50.6  97.2  80.2
                              0 25   1.528 135.5  30.5  25.1  54.2  99.2  44.6
                              0 26   1.265  89.4  84.5  37.8  24.3  76.7  88.2  54.5
                              0 27   2.020 135.8  66.9  78.0 126.7  50.9  41.9  83.8 106.2

31    35.  0.0489  0.2764  0.9206  1.000  1.17   0 CR1  1.546
                              0 3    0.921 122.6
                              0 5    1.783  84.9  52.9
                              0 6    0.876 131.6 105.1 135.9
                              0 12   1.697  89.2 137.1 110.0  57.0
                              0 26   1.844  76.6 102.1  56.5 103.0  54.4

Atom Code   x       y       z     Height  Symmetry transformation

CR1   1 -0.1500 -0.2203  1.1732   1.34   0.0000-X    0.0000-Y    2.0000-Z
28    2  0.2972 -0.0064  1.0180   3.63   0.0000-X    0.0000-Y    2.0000-Z

Molecule  2

Atom Peak     x       y       z     SOF  Height  Distances and Angles

21    82.  0.4708  0.6713  0.4870  1.000

    0.0 seconds elapsed time

++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
+ calctest      finished at 18:59:56   Total elapsed time:      26.8 secs  +
++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
```

Using **XP** after this cycle allowed me to assign all 23 non-Hydrogen atoms (i.e., they were 23 of the 24 strongest Q peaks generated by XS) with confidence for use in the subsequent **XL** cycle. Note: In this particular case both *Direct methods* and the *Patterson method* could have been used as the starting point for **XL** with equal success. For the purposes of this manual (i.e., to make both *Direct methods* and the *Patterson method* solutions give rise to the same files in the next stage), I chose to only assign the Cr atom. In any case, this type of conservative assignment strategy, while slower, is more reliable as it is both more likely to lead you to a global minimum solution and to not lead you to incorrectly assigning any garbage peaks as real atoms.

B. THE 2ND CYCLE: FINDING A TRIAL SOLUTION WITH XS AND THE PATTERSON METHOD

In general, one would use the *Patterson method* to find a trial solution via **XS** only if the *Direct methods* route fails. It requires the following **calctest.ins** input file and produces the following **calctest.res** and **calctest.lst** output files.

1. CALCTEST.INS Input File for 2nd Cycle: XS with the Patterson Method

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR    2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50
PATT
HKLF 4
END
```

[Note: the 'Patt' card is what tells the XS program to run *Patterson Methods*.] On a Gateway2000® Pentium computer running at 166 MHz and with 32 MB of RAM, this **XS** calculation look a total of 10 seconds.

2. CALCTEST.RES Output File for 2nd Cycle: XS with the Patterson Method

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR    2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50

L.S. 4
BOND
FMAP 2
PLAN 20

CR1    4  0.64993  0.72080  0.82771 11.00000   0.04
O2     3  0.59938  0.86042  0.97906 11.00000   0.04
O3     3  0.62753  0.93893  0.88188 11.00000   0.04
O4     3  0.52284  0.95461  0.64941 11.00000   0.04
O5     3  0.18878  0.58080  0.76327 11.00000   0.04
O6     3  0.25629  0.73048  0.57824 11.00000   0.04
O7     3  0.45116  0.73817  0.94133 11.00000   0.04
```

```
O8    3  0.36393  0.76364  0.70582 11.00000   0.04
HKLF 4
END
```

3. CALCTEST.LST Output File for 2nd Cycle: XS with the Patterson Method

```
++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
+ XS -  CRYSTAL STRUCTURE SOLUTION  - SIEMENS SHELXTL - Ver. 5.03  +
+ Copyright(c) 1994 Siemens Analytical X-ray - All Rights Reserved  +
+ calctest                started at 19:11:38 on 23 Mar 1997  +
++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR   2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2

V =     747.07     At vol =    16.2     F(000) =     372.0     mu =   0.81 mm-1
Max single Patterson vector = 179.2    cell wt =    724.50    rho =  1.610

TEMP -50
PATT
HKLF 4

  8074  Reflections read, of which     0  rejected
  Maximum h, k, l and 2-Theta =   11.   15.   16.   66.00
  5627  Unique reflections, of which   4360  observed
  R(int) = 0.0226     R(sigma) = 0.0488      Friedel opposites merged

NUMBER OF UNIQUE DATA AS A FUNCTION OF RESOLUTION IN ANGSTROMS

Resolution  Inf    5.00   3.50   2.50   2.00   1.70   1.50   1.40   1.30   1.20   1.10   1.00   0.90   0.80
N(observed)     11.    24.    59.    94.   121.   130.   103.   129.   181.   236.   345.   509.   729.
N(measured)     11.    24.    61.    98.   127.   138.   114.   137.   192.   270.   390.   584.   924.
N(theory)       11.    24.    61.    98.   127.   138.   114.   137.   192.   270.   390.   586.   924.
Two-theta   0.0    8.2   11.7   16.3   20.5   24.1   27.4   29.4   31.7   34.5   37.7   41.6   46.5   52.7

Highest memory for sort/merge = 11708 / 28135

Observed E .GT. 1.000 1.100 1.200 1.300 1.400 1.500 1.600 1.700 1.800 1.900

Number         2586  2199  1889  1590  1330  1093   886   710   549   435

               Centric Acentric   0kl     h0l     hk0     Rest

Mean Abs(E*E-1)    0.968    0.736    0.807    0.872    0.831    0.835

     5.7 seconds elapsed time

   SUMMARY OF PARAMETERS FOR  95adh06e in P-1

ESEL  Emin  1.000    Emax  5.000    DelU 0.005    renorm 0.700    axis 0
OMIT  s  4.00    2theta(lim)  180.0
PATT  nv  1  dmin  1.80  resl  0.65  Nsup  111  Zmin  4.80  maxat  8
FMAP  code  6
PLAN  npeaks   80    del1 0.500    del2 1.500
MORE  verbosity  1
TIME  t    9999999.

FMAP and GRID set by program
```

```
FMAP   6   1  23
GRID   -2.500  -2  -2     2.500   2   2

Super-sharp Patterson for  95adh06e in P-1

Maximum =  999.10,  minimum =  -89.70       highest memory used =  9198 / 18566

     1.0 seconds elapsed time

        X       Y       Z     Weight  Peak  Length

 1    0.0000  0.0000  0.0000    2.   999.   0.00
 2    0.3095  0.4437  0.6555    1.   261.   6.71
 3    0.1813  0.6784  0.4781    1.    99.   6.33
 4    0.1305  0.7645  0.1785    1.    94.   3.32
 5    0.4649  0.1384  0.0672    1.    88.   3.35
 6    0.0237  0.7812  0.9443    1.    88.   2.26
 7    0.1525  0.6948  0.4069    1.    87.   5.60
 8    0.2512  0.5803  0.8055    1.    87.   5.35
 9    0.0229  0.4861  0.5352    1.    87.   7.43
10    0.4045  0.9939  0.2538    1.    86.   3.41
11    0.0935  0.5506  0.5985    1.    86.   6.13
12    0.0503  0.8604  0.8473    1.    84.   2.19
13    0.1681  0.6160  0.5791    1.    83.   6.14
14    0.1986  0.9819  0.8845    1.    82.   2.24
15    0.2780  0.6587  0.7087    1.    82.   5.45
16    0.1496  0.8331  0.0826    1.    80.   2.29
17    0.9941  0.4192  0.6370    1.    80.   6.09
18    0.0986  0.9767  0.2322    1.    80.   2.43
19    0.1019  0.4573  0.7683    1.    79.   5.55
20    0.2888  0.9578  0.1229    1.    79.   2.31
21    0.3880  0.0226  0.1876    1.    75.   2.94
22    0.1692  0.1908  0.9454    1.    75.   2.36
23    0.2362  0.0151  0.1142    1.    75.   1.79
24    0.3471  0.5568  0.0301    1.    74.   5.53
25    0.3156  0.0291  0.0212    1.    74.   2.28
26    0.4839  0.2558  0.0074    1.    74.   4.06
27    0.4453  0.5384  0.2250    1.    73.   6.46
28    0.0367  0.3017  0.0400    1.    73.   2.96
29    0.0236  0.1035  0.3685    1.    72.   3.90
30    0.3036  0.5342  0.1541    1.    72.   5.76
31    0.2617  0.1608  0.1731    1.    71.   2.41
32    0.2070  0.2815  0.3236    1.    69.   3.89
33    0.0728  0.1841  0.2886    1.    68.   3.24
34    0.2722  0.1417  0.6154    1.    66.   5.39
35    0.3819  0.6285  0.9447    1.    65.   5.17
36    0.0254  0.1811  0.0249    1.    65.   1.77
37    0.0529  0.5970  0.9177    1.    63.   4.15
38    0.4154  0.4547  0.5245    1.    63.   8.23
39    0.2765  0.2560  0.6297    1.    62.   5.72
40    0.4805  0.4601  0.4390    1.    60.   5.91
41    0.0933  0.0073  0.8673    1.    59.   1.78
42    0.1267  0.3362  0.5446    1.    59.   6.50
43    0.1686  0.0157  0.7883    1.    59.   2.94
44    0.1281  0.0455  0.1426    1.    58.   1.50
45    0.0270  0.3584  0.8544    1.    57.   4.10
46    0.3554  0.1312  0.4017    1.    57.   4.21
47    0.1746  0.7872  0.3195    1.    56.   4.25
48    0.0336  0.0809  0.8975    1.    55.   1.51
49    0.3284  0.7980  0.5083    1.    54.   6.73
50    0.3892  0.1220  0.3215    1.    54.   3.66
51    0.0217  0.0017  0.9173    1.    53.   0.95
52    0.0786  0.6754  0.6620    1.    53.   4.81
53    0.1518  0.1270  0.0381    1.    52.   1.48
54    0.2955  0.5347  0.4853    1.    50.   7.52
55    0.0598  0.9731  0.0826    1.    49.   0.96
56    0.2193  0.7896  0.8579    1.    49.   3.39
57    0.0282  0.3634  0.3067    1.    46.   4.53
58    0.0163  0.0981  0.0057    1.    44.   0.96
59    0.1485  0.1438  0.5088    1.    43.   6.02
```

```
60   0.4577  0.5859  0.1631    1.    43.   5.94
61   0.0553  0.1447  0.8022    1.    43.   2.82
62   0.0601  0.0838  0.0649    1.    42.   0.96
63   0.1288  0.0237  0.0597    1.    42.   0.95
64   0.2833  0.4729  0.5806    1.    41.   7.44
65   0.1266  0.8244  0.6263    1.    40.   4.62
66   0.1431  0.4082  0.4407    1.    38.   5.55
67   0.0720  0.0051  0.9402    1.    37.   0.96
68   0.3186  0.7686  0.0930    1.    37.   3.63
69   0.0207  0.3021  0.4011    1.    37.   4.89
70   0.1867  0.9384  0.4581    1.    37.   4.83
71   0.2028  0.0044  0.3624    1.    36.   3.70
72   0.1066  0.0864  0.0275    1.    35.   1.02
73   0.0748  0.9420  0.9869    1.    34.   0.90
74   0.0466  0.0211  0.0971    1.    34.   0.97
75   0.4306  0.3604  0.1166    1.    34.   4.19
76   0.2118  0.5645  0.2552    1.    34.   5.65
77   0.0685  0.2193  0.7077    1.    33.   4.17
78   0.0925  0.0511  0.9876    1.    32.   0.85
79   0.2829  0.2408  0.0782    1.    32.   2.78
80   0.2314  0.0829  0.2678    1.    31.   2.79

Vectors selected for Patterson superposition:

Vector  X      Y      Z     Weight  Peak  Length

1    0.3095  0.4437  0.6555    1.    261.   6.71

FMAP and GRID set by program

FMAP   6   1  23
GRID   -2.500  -2  -2    2.500   2   2

Patterson vector superposition minimum function for  95adh06e in P-1

Patt. sup. on vector 1     0.3095  0.4437  0.6555   Height 261.   Length  6.71

Maximum =  256.33,  minimum =  -88.93       highest memory used = 12247 / 36736

     1.7 seconds elapsed time

  75 Superposition peaks employed, maximum height  35.4  and minimum height   1.9  on atomic number scale

Heavy-Atom Location for  95adh06e in P-1

  4360 reflections used for structure factor sums

Solution   1    CFOM = 39.10    PATFOM = 99.9    Corr. Coeff. = 62.5    SYMFOM = 99.9

Shift to be added to superposition coordinates:  0.5000  0.5000  0.5000

Name  At.No.  x      y      z    s.o.f.  Minimum distances / PATSMF (self first)

CR1   25.6  0.6499  0.7208  0.8277  1.0000    6.67
                                  315.5
O2    11.0  0.5994  0.8604  0.9791  1.0000    3.44    2.18
                                   32.7    91.9
O3    10.8  0.6275  0.9389  0.8819  1.0000    3.83    2.24  1.43
                                   20.3    92.1  58.9
O4    10.7  0.5228  0.9546  0.6494  1.0000    3.38    3.30  3.68  2.41
                                   25.7   108.7  30.4  28.3
O5    10.6  0.1888  0.5808  0.7633  1.0000    6.79    3.33  3.71  4.20  4.67
                                    9.2   103.8  31.0  33.3  30.6
O6    10.4  0.2563  0.7305  0.5782  1.0000    6.74    3.35  4.18  3.67  2.60  2.76
                                    6.9   105.1  47.6  27.2  25.6  36.1
O7    10.3  0.4512  0.7382  0.9413  1.0000    5.22    2.22  1.43  2.49  4.15  2.43  3.70
                                   24.1    87.4  57.5  30.6  37.5  21.3  41.5
O8     9.6  0.3639  0.7636  0.7058  1.0000    7.35    2.29  2.86  2.50  2.33  2.34  1.32  2.47
                                   41.5    89.5  32.1  36.0   2.9  15.8  22.8  35.5
```

```
Maximum memory for Patterson interpretation =  1984 /   748

    1.9 seconds elapsed time

++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
+ calctest     finished at 19:11:47   Total elapsed time:     10.3 secs  +
++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
```

Using **XP** after this cycle allowed me to assign the Cr atom as the only non-Hydrogen atom (out of a total of 23) with confidence for use in the subsequent **XL** cycle. Note: As stated above, in this particular case both *Direct methods* and the *Patterson method* could have been used as the starting point for **XL** with success. However, as is usual for most small molecules, *Direct methods* gets you off to a quicker start. For the purposes of this manual (i.e., to make both the both *Direct methods* and the *Patterson method* solutions give rise to the same files in the next stage), I chose to only assign the Cr atom with both methods..

C. THE 3RD CYCLE: USING XL AND FINDING MOST NON-HYDROGEN ATOMS WITH XP

This sections involves the first refinement cycle by **XL**. This takes the preliminary atom position(s) and isotropic displacement parameters derived from **XS/XP** and uses least squares refinement to improve them. It then calculates a residual electron density map (i.e., the Q peaks) which one uses **XP** to either confidently assign as atoms or delete from the list. It requires the following **calctest.ins** input file and produces the following **calctest.res** and **calctest.lst** output files.

1. CALCTEST.INS Input File for 3rd Cycle: Using XL to Find Most Non-Hydrogen Atoms

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR    2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50

L.S. .4
BOND
FMAP 2
PLAN 20

FVAR       1.00000
CR    4   0.64993   0.72080   0.82771  11.00000   0.04000

HKLF 4
END
```

[Note: the **LS** program is being asked to do 4 least squares cycles, the **LS** program is being asked to generate 20 Q peaks, and only the Cr atom is assigned and being fed into the **LS** program to generate trial phases at this stage.] On a Gateway2000® Pentium computer running at 166 MHz and with 32 MB of RAM, this **XL** calculation look a total of 15 seconds for 5 parameters.

After the refinement, the R factor for the 4360 reflections having Fo > 4 sigma (Fo) (i.e., the first R that **XL** lists) was 0.460, the observed R and wR factors for all of the data were 0.505 and 0.810, respectively, and the GOOF value was 7.694. In the final cycle, the largest shift for any atom (in this case Cr) was 0.003Å.

2. CALCTEST.RES Output File for 3rd Cycle: Using XL to Find Most Non-Hydrogen Atoms

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR   2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50

L.S. 4
BOND
FMAP 2
PLAN 20

WGHT    0.100000
FVAR      0.41077
CR     4   0.65424   0.72253   0.82907  11.00000   0.01023
HKLF 4
END

WGHT     0.8584     43.7763
Q1   1   0.6508  0.7206  0.7795  11.00000  0.05   25.23
Q2   1   0.1867  0.5834  0.7879  11.00000  0.05   12.85
Q3   1   0.5216  0.9552  0.5655  11.00000  0.05   12.83
Q4   1   0.2601  0.7302  0.6092  11.00000  0.05   12.37
Q5   1   1.0451  0.7449  1.0200  11.00000  0.05   11.91
Q6   1   0.6861  0.8332  1.1658  11.00000  0.05   10.83
Q7   1   0.6146  0.4173  0.7327  11.00000  0.05   10.81
Q8   1   0.8973  0.7380  0.9294  11.00000  0.05   10.79
Q9   1   0.8606  1.0101  1.1445  11.00000  0.05   10.77
Q10  1   0.8337  0.7412  0.6034  11.00000  0.05   10.21
Q11  1   0.6283  0.5345  0.7560  11.00000  0.05    9.93
Q12  1   0.7668  0.7346  0.6715  11.00000  0.05    9.68
Q13  1   0.5994  0.8585  0.9301  11.00000  0.05    9.47
Q14  1   0.3664  0.7613  0.7417  11.00000  0.05    9.33
Q15  1   0.6284  0.9380  0.8361  11.00000  0.05    9.10
Q16  1   0.8325  0.5194  1.1425  11.00000  0.05    9.05
Q17  1   0.4534  0.7359  1.0013  11.00000  0.05    8.91
Q18  1   0.7401  0.9121  1.0907  11.00000  0.05    8.87
Q19  1   0.3321  0.6918  0.8384  11.00000  0.05    8.02
Q20  1   0.5039  0.8874  0.6655  11.00000  0.05    7.68
```

3. CALCTEST.LST Output File for 3rd Cycle: Using XL to Find Most Non-Hydrogen Atoms

After this 3rd cycle this calctest.lst file is six pages long and is shown below for you to become familiar with the format for the listing of XL results. For subsequent cycles these files are typically much longer and for space reason they are not included in this manual (except for that for the 8th cycle). However, they are available on disk if you want to view them.

```
++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

+  XL - CRYSTAL STRUCTURE REFINEMENT - SIEMENS SHELXTL - Ver. 5.03  +
+  Copyright(c) 1994 Siemens Analytical Xray - All Rights Reserved  +
+  calctest                started at 19:17:50 on 23-Mar-1997  +
++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
```

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR    2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2

V =      747.07     F(000) =     372.0     Mu =   0.81 mm-1      Cell Wt =      724.50    Rho =  1.610

TEMP -50

L.S. 4
BOND
FMAP 2
PLAN 20

FVAR       1.00000
CR    4   0.64993   0.72080   0.82771  11.00000   0.04000

HKLF 4


Covalent radii and connectivity table for  95adh06e in P-1

C    0.770
H    0.320
O    0.660
CR   1.240

Cr - no bonds found


  8074  Reflections read, of which     0  rejected

 -1 =< h =< 11,    -15 =< k =< 15,    -16 =< l =< 16,   Max. 2-theta =   66.00

     0  Systematic absence violations

     0  Inconsistent equivalents

  5627  Unique reflections, of which      0  suppressed

R(int) = 0.0231     R(sigma) = 0.0490      Friedel opposites merged

Maximum memory for data reduction =   318 /   56289


 ** Cell contents from UNIT instruction and atom list do not agree **


Unit-cell contents from UNIT instruction and atom list resp.

C       28.00      0.00
H       28.00      0.00
O       16.00      0.00
CR       2.00      2.00

     6.1 seconds elapsed time


Least-squares cycle   1      Maximum vector length =  511      Memory required =    328 /   27619

wR2 =  0.8229 before cycle   1 for   5627 data and     5 /     5 parameters

GooF = S =     9.534;     Restrained GooF =      9.534  for      0 restraints

Weight = 1 / [ sigma^2(Fo^2) + ( 0.1000 * P )^2 +   0.00 * P ]   where  P = ( Max ( Fo^2, 0 ) + 2 * Fc^2 ) / 3
```

```
Shifts scaled down to reduce maximum shift/esd from  18.13  to  15.00


   N     value       esd    shift/esd  parameter

   1    0.58999    0.01667   -24.594    OSF
   2    0.65157    0.00036     4.553    x  Cr
   5    0.02470    0.00102   -15.000    U11 Cr

Mean shift/esd =   9.761    Maximum = -24.594 for  OSF

Max. shift = 0.013 A for Cr      Max. dU =-0.015 for Cr

     0.3 seconds elapsed time


Least-squares cycle  2     Maximum vector length =  511     Memory required =    328 /   27619

wR2 =  0.8098 before cycle  2 for  5627 data and     5 /     5 parameters

GooF = S =     7.774;     Restrained GooF =      7.774  for     0 restraints

Weight = 1 / [ sigma^2(Fo^2) + ( 0.1000 * P )^2 +   0.00 * P ]   where  P = ( Max ( Fo^2, 0 ) + 2 * Fc^2 ) / 3


   N     value       esd    shift/esd  parameter

   1    0.45449    0.01079   -12.563    OSF
   2    0.65302    0.00038     3.784    x  Cr
   5    0.01457    0.00089   -11.356    U11 Cr

Mean shift/esd =   6.279    Maximum = -12.563 for  OSF

Max. shift = 0.011 A for Cr      Max. dU =-0.010 for Cr

     0.4 seconds elapsed time


Least-squares cycle  3     Maximum vector length =  511     Memory required =    328 /   27619

wR2 =  0.8082 before cycle  3 for  5627 data and     5 /     5 parameters

GooF = S =     7.567;     Restrained GooF =      7.567  for     0 restraints

Weight = 1 / [ sigma^2(Fo^2) + ( 0.1000 * P )^2 +   0.00 * P ]   where  P = ( Max ( Fo^2, 0 ) + 2 * Fc^2 ) / 3


   N     value       esd    shift/esd  parameter

   1    0.42149    0.00869    -3.800    OSF
   5    0.01119    0.00081    -4.151    U11 Cr

Mean shift/esd =   2.393    Maximum =  -4.151 for  U11 Cr

Max. shift = 0.006 A for Cr      Max. dU =-0.003 for Cr

     0.4 seconds elapsed time


Least-squares cycle  4     Maximum vector length =  511     Memory required =    328 /   27619

wR2 =  0.8096 before cycle  4 for  5627 data and     5 /     5 parameters

GooF = S =     7.682;     Restrained GooF =      7.682  for     0 restraints

Weight = 1 / [ sigma^2(Fo^2) + ( 0.1000 * P )^2 +   0.00 * P ]   where  P = ( Max ( Fo^2, 0 ) + 2 * Fc^2 ) / 3


   N     value       esd    shift/esd  parameter
```

```
  1    0.41077    0.00819   -1.308   OSF
  2    0.65424    0.00039    1.039    x  Cr
  5    0.01023    0.00080   -1.206   U11 Cr

Mean shift/esd =   0.883    Maximum =  -1.308 for  OSF

Max. shift = 0.003 A for Cr      Max. dU =-0.001 for Cr


Largest correlation matrix elements

   0.882 U11 Cr / OSF

    0.3 seconds elapsed time



 95adh06e in P-1

ATOM         x       y       z        sof       U11      U22      U33      U23      U13      U12       Ueq

Cr         0.65424   0.72253   0.82907     1.00000     0.01023
          0.00039   0.00029   0.00029     0.00000     0.00080



Final Structure Factor Calculation for  95adh06e in P-1

Total number of l.s. parameters =     5     Maximum vector length =  511      Memory required =    323 /   22484

wR2 =  0.8104 before cycle   5 for   5627 data and     0 /     5 parameters

GooF = S =     7.694;     Restrained GooF =      7.694  for      0 restraints

Weight = 1 / [ sigma^2(Fo^2) + ( 0.1000 * P )^2 +   0.00 * P ]   where  P = ( Max ( Fo^2, 0 ) + 2 * Fc^2 ) / 3

R1 =  0.4597 for   4360 Fo > 4.sigma(Fo)  ).  and  0.5048 for all   5627 data
wR2 =  0.8104,  GooF = S =   7.694,  Restrained GooF =    7.694  for all data

    0.6 seconds elapsed time


Analysis of variance for reflections employed in refinement      K = Mean[Fo^2] / Mean[Fc^2]  for group

Fc/Fc(max)      0.000    0.051    0.098    0.142    0.182    0.215    0.239    0.271    0.321    0.416    1.000

Number in group      573.     555.     568.     556.     579.     542.     562.     569.     556.     567.

       GooF     6.604    7.024    6.604    6.949    6.046    6.087    6.944    8.002    9.417   11.237

       K      48.611   10.521    3.774    3.123    1.921    1.700    1.939    2.133    2.512    3.052


Resolution(A)   0.65     0.68     0.70     0.74     0.77     0.82     0.89     0.97     1.12     1.41     inf

Number in group      570.     569.     557.     555.     564.     566.     563.     560.     558.     565.

       GooF     3.136    3.555    3.880    4.729    5.688    6.029    7.766   10.010   10.861   13.393

       K       1.246    1.345    1.424    1.576    1.646    1.635    2.148    2.544    2.680    3.978

       R1      0.397    0.421    0.389    0.419    0.440    0.421    0.437    0.515    0.526    0.601


Recommended weighting scheme:  WGHT     0.8584     43.7763


Most Disagreeable Reflections (* if suppressed)
```

h	k	l	Fo^2	Fc^2	Delta(F^2)/esd	Fc/Fc(max)	Resolution(A)
0	-1	3	8784.70	13.64	3.69	0.084	3.36
-1	2	3	10563.09	42.85	3.65	0.150	2.73
-1	2	0	6705.29	118.91	3.52	0.249	4.48
-2	2	1	43725.24	1490.57	3.49	0.882	3.22
2	0	1	16190.28	628.33	3.39	0.573	2.99
-4	4	2	17493.97	631.84	3.32	0.574	1.61
-2	1	4	3765.24	18.80	3.30	0.099	2.38
3	4	4	3359.93	94.68	3.27	0.222	1.14
0	7	5	1905.99	28.19	3.26	0.121	1.05
2	0	0	8156.41	211.46	3.24	0.332	3.49
0	-3	1	8843.23	440.01	3.23	0.479	3.27
0	-10	3	1119.03	1.61	3.21	0.029	0.99
0	6	0	5774.79	201.51	3.19	0.324	1.62
-2	3	6	4782.66	169.84	3.17	0.298	1.49
0	0	2	9167.26	573.69	3.16	0.547	5.01
-7	-2	7	1250.15	8.55	3.16	0.067	0.95
-2	0	3	9957.32	277.80	3.14	0.381	2.97
-5	2	11	1727.32	16.44	3.14	0.093	0.90
-2	1	1	1813.53	3.14	3.14	0.040	3.67
-2	-2	3	2426.19	13.62	3.12	0.084	2.51
-2	-8	4	1395.46	7.34	3.11	0.062	1.10
7	-1	1	1416.83	42.63	3.11	0.149	0.98
0	-5	1	2818.70	44.70	3.10	0.153	1.98
-1	4	0	2449.45	10.10	3.10	0.073	2.47
3	-6	7	4072.43	251.22	3.10	0.362	1.01
-2	2	2	3384.27	113.48	3.09	0.243	2.95
-3	-7	5	3365.03	190.39	3.06	0.315	1.11
1	-11	3	997.61	27.73	3.05	0.120	0.91
-4	6	6	1787.01	46.50	3.05	0.156	1.10
-3	0	1	8609.34	569.17	3.05	0.545	2.46
1	-1	4	4884.29	0.18	3.04	0.010	2.20
-2	-6	4	3083.52	127.97	3.04	0.258	1.38
-3	-6	5	3114.86	154.08	3.03	0.284	1.22
-3	-3	1	3708.11	90.41	3.03	0.217	1.80
-2	3	1	5178.15	196.41	3.02	0.320	2.67
2	-1	5	1926.64	10.12	3.02	0.073	1.57
4	-1	7	1066.09	28.91	3.01	0.123	0.98
-3	-6	6	2089.76	84.72	2.99	0.210	1.17
-4	-1	2	3766.65	154.17	2.99	0.284	1.77
0	-4	4	10255.42	795.91	2.99	0.644	1.94
-1	1	5	2560.62	53.61	2.97	0.167	2.02
1	0	0	10369.17	675.73	2.97	0.594	6.97
3	-5	6	1889.99	81.96	2.97	0.207	1.14
1	0	2	3705.98	241.13	2.97	0.355	3.54
-2	-1	3	15305.87	1324.96	2.96	0.831	2.82
-3	4	2	9067.43	696.70	2.95	0.603	1.86
0	3	9	2126.08	138.70	2.95	0.269	1.00
6	0	2	3710.79	252.35	2.93	0.363	1.06
3	-1	3	1733.26	16.86	2.92	0.094	1.71
0	5	1	9539.74	812.90	2.91	0.651	1.84

5.4 seconds elapsed time

FMAP and GRID set by program

FMAP 2 1 24
GRID -2.381 -2 -2 2.381 2 2

R1 = 0.5054 for 5627 unique reflections after merging

Electron density synthesis with coefficients Fo-Fc

Maximum = 25.23, Minimum = -4.12 e/A^3, Highest memory used = 995 / 27387
Mean = 0.00, Rms deviation from mean = 1.31 e/A^3

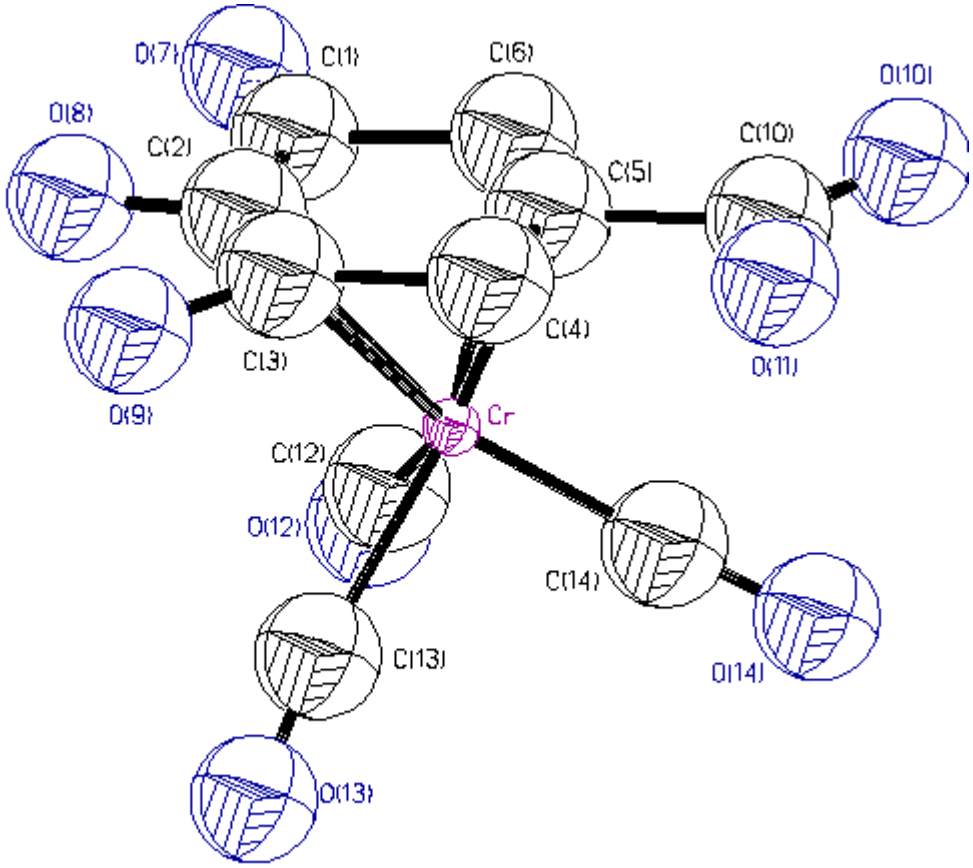
```
Fourier peaks appended to .res file

        x      y      z      sof    U      Peak   Distances to nearest atoms (including symmetry equivalents)

Q1    1  0.6508 0.7206 0.7795  1.00000 0.05  25.23  0.52 CR  7.07 CR
Q2    1  0.1867 0.5834 0.7879  1.00000 0.05  12.85  3.43 CR  5.40 CR
Q3    1  0.5216 0.9552 0.5655  1.00000 0.05  12.83  3.90 CR  5.63 CR
Q4    1  0.2601 0.7302 0.6092  1.00000 0.05  12.37  3.19 CR  6.38 CR
Q5    1  1.0451 0.7449 1.0200  1.00000 0.05  11.91  2.97 CR  5.75 CR
Q6    1  0.6861 0.8332 1.1658  1.00000 0.05  10.83  3.57 CR  5.52 CR
Q7    1  0.6146 0.4173 0.7327  1.00000 0.05  10.81  3.04 CR  5.90 CR
Q8    1  0.8973 0.7380 0.9294  1.00000 0.05  10.79  1.78 CR  6.52 CR
Q9    1  0.8606 1.0101 1.1445  1.00000 0.05  10.77  3.87 CR  4.06 CR
Q10   1  0.8337 0.7412 0.6034  1.00000 0.05  10.21  3.13 CR  5.91 CR
Q11   1  0.6283 0.5345 0.7560  1.00000 0.05   9.93  1.90 CR  6.17 CR
Q12   1  0.7668 0.7346 0.6715  1.00000 0.05   9.68  2.12 CR  8.47 CR
Q13   1  0.5994 0.8585 0.9301  1.00000 0.05   9.47  1.82 CR  5.58 CR
Q14   1  0.3664 0.7613 0.7417  1.00000 0.05   9.33  2.20 CR  7.13 CR
Q15   1  0.6284 0.9380 0.8361  1.00000 0.05   9.10  2.20 CR  5.76 CR
Q16   1  0.8325 0.5194 1.1425  1.00000 0.05   9.05  4.14 CR  4.16 CR
Q17   1  0.4534 0.7359 1.0013  1.00000 0.05   8.91  2.73 CR  5.19 CR
Q18   1  0.7401 0.9121 1.0907  1.00000 0.05   8.87  3.01 CR  5.25 CR
Q19   1  0.3321 0.6918 0.8384  1.00000 0.05   8.02  2.43 CR  5.81 CR
Q20   1  0.5039 0.8874 0.6655  1.00000 0.05   7.68  2.69 CR  6.92 CR

Shortest distances between peaks (including symmetry equivalents)

  10  12  1.01    7  11  1.15    9  18  1.16    5   8  1.21    6  18  1.30    2  19  1.32    2  16  1.36
   4  14  1.36    3  20  1.37   14  19  1.39   13  15  1.41    1  12  1.66   17  19  1.66   13  18  1.68
  15  20  1.74    3   3  1.74    1  11  1.83   13  17  1.90   14  20  1.92    1   8  2.01    6  17  2.05
   4  20  2.08    6   9  2.11    1  13  2.17    1  14  2.17   13  14  2.20    1  15  2.24   13  19  2.24
   2  14  2.26   14  15  2.28   16  19  2.34   17  18  2.39    1  20  2.42    4  19  2.45    6  13  2.47
  11  12  2.51    9  13  2.60    2  17  2.61    8  12  2.63    1  19  2.64    8  11  2.65   15  18  2.66
   1  10  2.67   12  20  2.69    2   4  2.70   14  17  2.71    8  13  2.73   13  20  2.77    3  15  2.80
   3   4  2.92   16  17  2.94    8  18  2.95    1   4  2.97    1   7  2.98

    1.4 seconds elapsed time

++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
+ calctest     finished at 19:18:04   Total elapsed time:     14.9 secs  +
++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
```

Using **XP** after this cycle allowed me to assign 18 additional non-Hydrogen atoms (for a total of 19 out of 23) with confidence for use in isotropic refinement during the following **XL** cycle. [Note: these were 18 of the 20 strongest Q peaks.] A displacement ellipsoid plot (Note: this is still isotropic) of this molecule at this stage of refinement is shown on the following page. For this and the subsequent five plots in this chapter the plotting parameters are:

telp 0 –75 0.04 0 [ent]

4. Plot calctest.3, After The 3rd Cycle

(i.e., When Most Non-Hydrogen Atoms Have Been Found.)



[Note: Made with graphics file CALCTEST.3hc.GIF]

D. THE 4TH CYCLE: USING XL AND FINDING THE REMAINING NON-HYDROGEN ATOMS WITH XP

This sections involves the second refinement cycle by **XL**. This takes the atom positions and isotropic displacement parameters from the first **XL** cycle (i.e., which produced most non-Hydrogen atoms) and uses least squares refinement to improve them. It then calculates a residual electron density map (i.e., the Q peaks) which one uses **XP** to either confidently assign as atoms or delete from the list. It requires the following **calctest.ins** input file and produces the following **calctest.res** and **calctest.lst** output files.

1. CALCTEST.INS Input File for 4th Cycle: Using XL to Find the Remaining Non-Hydrogen Atoms

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR    2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50

L.S. 4
BOND
FMAP 2
PLAN 20

WGHT    0.100000
FVAR       0.41077
CR    4   0.65424   0.72253   0.82907  11.00000   0.01023
O9    3   0.18670   0.58340   0.78790  11.00000   0.05000
O7    3   0.52160   0.95520   0.56550  11.00000   0.05000
O8    3   0.26010   0.73020   0.60920  11.00000   0.05000
O14   3   1.04510   0.74490   1.02000  11.00000   0.05000
O11   3   0.68610   0.83320   1.16580  11.00000   0.05000
O13   3   0.61460   0.41730   0.73270  11.00000   0.05000
C14   1   0.89730   0.73800   0.92940  11.00000   0.05000
O10   3   0.86060   1.01010   1.14450  11.00000   0.05000
O12   3   0.83370   0.74120   0.60340  11.00000   0.05000
C13   1   0.62830   0.53450   0.75600  11.00000   0.05000
C12   1   0.76680   0.73460   0.67150  11.00000   0.05000
C5    1   0.59940   0.85850   0.93010  11.00000   0.05000
C2    1   0.36640   0.76130   0.74170  11.00000   0.05000
C6    1   0.62840   0.93800   0.83610  11.00000   0.05000
C4    1   0.45340   0.73590   1.00130  11.00000   0.05000
C10   1   0.74010   0.91210   1.09070  11.00000   0.05000
C3    1   0.33210   0.69180   0.83840  11.00000   0.05000
C1    1   0.50390   0.88740   0.66550  11.00000   0.05000
```

```
HKLF 4
END
```

[Note: the **LS** program is still being asked to do 4 least squares cycles, the **LS** program is still being asked to generate 20 Q peaks, but now 19 atoms from Cr on the top of the list to C1 on the bottom of the list are assigned and being fed into the **LS** program to generate trial phases.] On a Gateway2000® Pentium computer running at 166 MHz and with 32 MB of RAM, this **XL** calculation look a total of 22 seconds for 77 parameters.

After the refinement, the R factor for the 4360 reflections having Fo > 4 sigma (Fo) (i.e., the first R that **XL** lists) was 0.242, the observed R and wR factors for all of the data were 0.279 and 0.582, respectively, and the GOOF value was 4.434. In the final cycle, the largest shift for any atom (in this case O7) was 0.333Å.

2. CALCTEST.RES Output File for 4th Cycle: Using XL to Find the Remaining Non-Hydrogen Atoms

```
TITL 95adh06e in P-1
CELL  0.71073     7.5265    10.0508    10.7429    97.271  108.116
99.782
ZERR    2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50

L.S. 4
BOND
FMAP 2
PLAN 20

WGHT    0.100000
FVAR      0.56033
CR     4  0.65426   0.72247   0.82856  11.00000   0.01807
O9     3  0.18990   0.58074   0.76094  11.00000   0.03472
O7     3  0.53819   0.96543   0.64061  11.00000   0.16682
O8     3  0.25828   0.73191   0.57773  11.00000   0.03555
O14    3  1.04713   0.74591   1.02038  11.00000   0.03616
O11    3  0.68319   0.82822   1.20140  11.00000   0.03887
O13    3  0.61346   0.41352   0.78450  11.00000   0.05001
C14    1  0.89672   0.73739   0.94578  11.00000   0.02270
O10    3  0.86008   1.00396   1.15422  11.00000   0.04363
O12    3  0.82670   0.74237   0.61502  11.00000   0.04687
C13    1  0.62919   0.53717   0.80128  11.00000   0.02503
C12    1  0.76117   0.73130   0.69436  11.00000   0.02955
C5     1  0.59873   0.85801   0.97874  11.00000   0.02331
C2     1  0.37152   0.76542   0.70561  11.00000   0.02701
C6     1  0.62901   0.93834   0.88163  11.00000   0.02886
C4     1  0.45896   0.73211   0.94420  11.00000   0.04435
C10    1  0.73534   0.91033   1.12162  11.00000   0.02739
C3     1  0.33417   0.69133   0.80758  11.00000   0.02690
C1     1  0.49573   0.93760   0.66294  11.00000   0.10842
HKLF 4
END

WGHT     0.4592     16.5984
Q1   1  0.5037  0.8878  0.7295  11.00000  0.05   10.10
Q2   1  0.1641  0.4874  0.8463  11.00000  0.05    8.54
Q3   1  0.6778  1.0770  0.6708  11.00000  0.05    8.38
```

Q4	1	0.8083	0.8707	1.3330	11.00000	0.05	7.58
Q5	1	0.2540	0.6007	0.5079	11.00000	0.05	6.90
Q6	1	0.6837	0.7245	0.8111	11.00000	0.05	5.60
Q7	1	0.3536	0.7644	0.7296	11.00000	0.05	2.29
Q8	1	0.8956	0.9922	1.1362	11.00000	0.05	2.22
Q9	1	0.8416	1.0331	1.1537	11.00000	0.05	2.12
Q10	1	0.7701	0.7210	0.5722	11.00000	0.05	1.96
Q11	1	0.1721	0.6000	0.7058	11.00000	0.05	1.77
Q12	1	0.1819	0.6639	0.6067	11.00000	0.05	1.46
Q13	1	1.0769	0.7472	1.0029	11.00000	0.05	1.33
Q14	1	0.7965	0.4955	1.0123	11.00000	0.05	1.30
Q15	1	0.7244	0.9437	0.5317	11.00000	0.05	1.24
Q16	1	0.6276	0.8785	0.9499	11.00000	0.05	1.18
Q17	1	0.2111	0.9346	0.6274	11.00000	0.05	1.18
Q18	1	0.7929	0.5484	0.8927	11.00000	0.05	1.15
Q19	1	0.4941	0.4214	0.6910	11.00000	0.05	1.15
Q20	1	1.0468	0.8487	1.1612	11.00000	0.05	1.10

3. CALCTEST.LST Output File for 4th Cycle: Using XL to Find the Remaining Non-Hydrogen Atoms

15 pages of text. See the computer copies of these files.

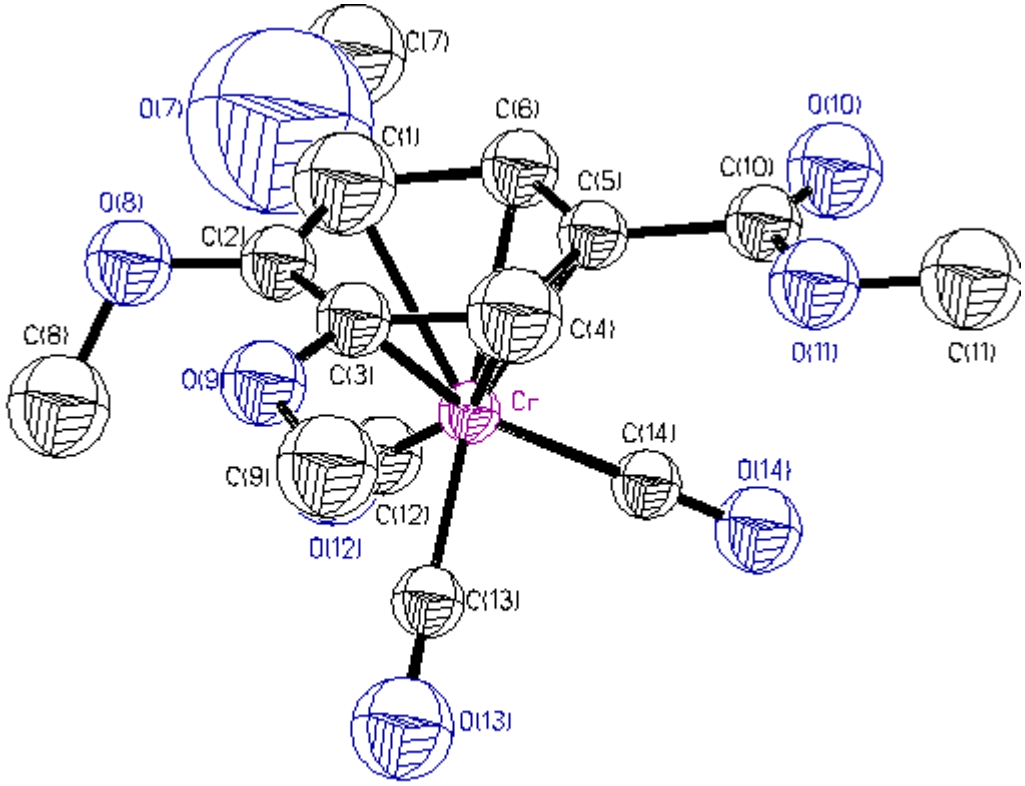
Using **XP** after this cycle allowed me to assign the remaining 5 additional non-Hydrogen atoms (i.e., the last 4 that were previously unassigned out of a total of 23).

Note: inspection of these tables and the graphical data often indicates problems with the model. In this case, one atom, C1, had moved to a bad position (i.e., out of the aromatic ring to a point only 0.5Å away from O7, an obvious chemical impossibility) and both C1 and O7 had bad displacement parameters (i.e., in the table above one can see that they are five times larger than those of their neighbors and in the plot **calctest.4** they are also obviously outsized). As was described in chapter VI(B), above, in such cases one has several good options. For this particular example, we chose the first suggested "fix." Thus, the "bad" C1 was deleted and Q1 (which was where C1 was expected to be) was successfully assigned as C1 (see the next section).

A displacement ellipsoid plot (Note: this is still isotropic) of this molecule at this stage of refinement is shown on the following page.

4. Plot calctest.4, After The 4th Cycle

(i.e., When all Remaining Non-Hydrogen Atoms Have Been Found.)



[Note: Made with graphics file CALCTEST.4hc.GIF]

E. THE 5TH CYCLE: USING XL AND REFINING ALL NON-HYDROGEN ATOMS TO THEIR BEST ISOTROPIC VALUES

This sections involves the third refinement cycle by **XL**. This takes the atom positions and isotropic displacement parameters from the second **XL** cycle just described above (i.e., which produced all of the non-Hydrogen atoms) and uses least squares refinement to improve them to the best values that could be found with this limited model (i.e., it unrealistically assumes *spherical* displacement parameters). It then calculates a residual electron density map (i.e., the Q peaks) which one uses **XP** to ensure that no non-Hydrogen atom assignments are bad. Note: at this point one can typically identify at least some of the Hydrogen atoms amongst the Q peaks but these should not be assigned until the non-Hydrogen atoms have been given an anisotropic refinement. It requires the following **calctest.ins** input file and produces the following **calctest.res** and **calctest.lst** output files.

1. CALCTEST.INS Input File for 5th Cycle: Using XL to Obtain the Best Isotropic displacement Parameters

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR    2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50

L.S. 4
BOND
FMAP 2
PLAN 20

WGHT    0.100000
FVAR      0.56033
CR    4   0.65426   0.72247   0.82856  11.00000   0.01807
O7    3   0.53819   0.96543   0.64061  11.00000   0.16682
O8    3   0.25828   0.73191   0.57773  11.00000   0.03555
O9    3   0.18990   0.58074   0.76094  11.00000   0.03472
O10   3   0.86008   1.00396   1.15422  11.00000   0.04363
O11   3   0.68319   0.82822   1.20140  11.00000   0.03887
O12   3   0.82670   0.74237   0.61502  11.00000   0.04687
O13   3   0.61346   0.41352   0.78450  11.00000   0.05001
O14   3   1.04713   0.74591   1.02038  11.00000   0.03616
C1    1   0.50370   0.88780   0.72950  11.00000   0.05000
C2    1   0.37152   0.76542   0.70561  11.00000   0.02701
C3    1   0.33417   0.69133   0.80758  11.00000   0.02690
C4    1   0.45896   0.73211   0.94420  11.00000   0.04435
C5    1   0.59873   0.85801   0.97874  11.00000   0.02331
C6    1   0.62901   0.93834   0.88163  11.00000   0.02886
```

```
C7    1   0.67780   1.07700   0.67080  11.00000   0.05000
C8    1   0.25400   0.60070   0.50790  11.00000   0.05000
C9    1   0.16410   0.48740   0.84630  11.00000   0.05000
C10   1   0.73534   0.91033   1.12162  11.00000   0.02739
C11   1   0.80830   0.87070   1.33300  11.00000   0.05000
C12   1   0.76117   0.73130   0.69436  11.00000   0.02955
C13   1   0.62919   0.53717   0.80128  11.00000   0.02503
C14   1   0.89672   0.73739   0.94578  11.00000   0.02270

HKLF 4
END
```

[Note: the small changes/improvements in values for the atomic coordinates and isotropic displacement parameters compared to those in the last section.] On a Gateway2000® Pentium computer running at 166 MHz and with 32 MB of RAM, this **XL** calculation look a total of 26 seconds for 93 parameters.

After the refinement, the R factor for the 4360 reflections having Fo > 4 sigma (Fo) (i.e., the first R that **XL** lists) was 0.0984, the observed R and wR factors for all of the data were 0.120 and 0.277, respectively, and the GOOF value was 1.853. In the final cycle, the largest shift for any atom (in this case O12) was 0.003Å and the largest shift/standard uncertainty for any parameter was less than 0.01.

Remember from the last section (where the "bad" C1 was deleted and Q1 (which was where C1 was expected to be) was assigned as C1. After the 5th cycle, both C1 and O7 are in reasonable positions and in the calctest.res file, below, it can be seen that they both have small and reasonable displacement parameters (these have been shaded).

2. CALCTEST.RES Output File for 5th Cycle: Using XL to Obtain the Best Isotropic displacement Parameters

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR   2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50

L.S. 4
BOND
FMAP 2
PLAN 20

WGHT    0.100000
FVAR      0.61864
CR    4   0.65442   0.72257   0.82861  11.00000   0.02089
O7    3   0.52392   0.95672   0.64835  11.00000   0.02992
O8    3   0.25566   0.72934   0.57790  11.00000   0.03320
O9    3   0.18829   0.58203   0.76054  11.00000   0.03199
O10   3   0.86333   1.00651   1.15356  11.00000   0.04120
O11   3   0.68465   0.82987   1.19973  11.00000   0.03747
```

```
O12    3  0.82541  0.73869  0.61191 11.00000  0.05086
O13    3  0.61189  0.41788  0.78577 11.00000  0.04656
O14    3  1.04726  0.74434  1.02053 11.00000  0.04038
C1     1  0.51006  0.89160  0.74837 11.00000  0.02489
C2     1  0.36919  0.76592  0.70811 11.00000  0.02504
C3     1  0.33457  0.69407  0.80677 11.00000  0.02548
C4     1  0.45278  0.73789  0.94165 11.00000  0.02462
C5     1  0.59849  0.85894  0.97813 11.00000  0.02282
C6     1  0.62715  0.93760  0.88191 11.00000  0.02473
C7     1  0.67748  1.07612  0.68055 11.00000  0.03852
C8     1  0.25526  0.60042  0.50569 11.00000  0.05106
C9     1  0.17061  0.48972  0.85023 11.00000  0.03428
C10    1  0.73205  0.90838  1.11880 11.00000  0.02751
C11    1  0.80670  0.86844  1.33980 11.00000  0.04568
C12    1  0.76067  0.73183  0.69516 11.00000  0.03044
C13    1  0.62656  0.53544  0.80118 11.00000  0.02931
C14    1  0.89508  0.73681  0.94554 11.00000  0.02707
HKLF 4
END

WGHT     0.1434     2.7443
Q1    1  0.5954  0.7142  0.8121  11.00000  0.05    2.92
Q2    1  0.7189  0.7327  0.8339  11.00000  0.05    2.75
Q3    1  0.9068  0.9804  1.1381  11.00000  0.05    1.49
Q4    1  0.3147  0.6163  0.5070  11.00000  0.05    1.27
Q5    1  0.6723  0.4214  0.7925  11.00000  0.05    1.21
Q6    1  0.8120  1.0246  1.1566  11.00000  0.05    1.21
Q7    1  0.6405  1.1059  0.6924  11.00000  0.05    1.20
Q8    1  0.6485  0.8549  1.1922  11.00000  0.05    1.18
Q9    1  0.7326  1.0587  0.6750  11.00000  0.05    1.15
Q10   1  0.3054  0.7254  0.5673  11.00000  0.05    1.14
Q11   1  0.5720  0.9435  0.6319  11.00000  0.05    1.13
Q12   1  0.8125  0.9183  1.3370  11.00000  0.05    1.08
Q13   1  0.4736  0.9676  0.6692  11.00000  0.05    1.07
Q14   1  0.5447  0.4139  0.7517  11.00000  0.05    1.06
Q15   1  0.1473  0.6038  0.7821  11.00000  0.05    1.02
Q16   1  0.8877  0.7681  0.6381  11.00000  0.05    1.02
Q17   1  0.7578  0.7095  0.5752  11.00000  0.05    1.01
Q18   1  0.7426  0.8108  1.1947  11.00000  0.05    1.01
Q19   1  0.7960  0.8223  1.3364  11.00000  0.05    0.98
Q20   1  1.0854  0.7591  1.0018  11.00000  0.05    0.92
```

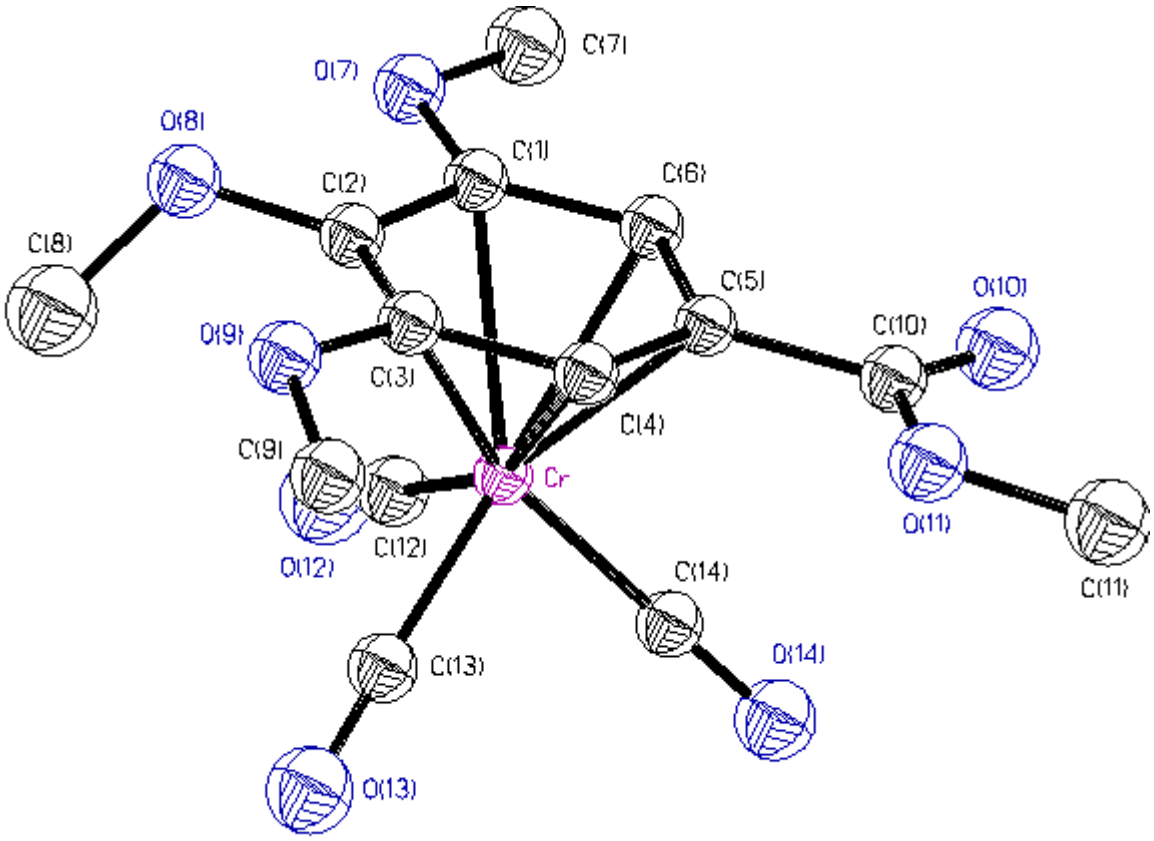
3. CALCTEST.LST Output File for 5th Cycle: Using XL to Obtain the Best Isotropic displacement Parameters

14 pages of text. See the computer copies of these files.

Using **XP** after this cycle allowed me to test the assignment of all of the non-Hydrogen atoms which have now been assigned for use in the next anisotropic refinement **XL** cycle that follows. In this case no Hydrogen atoms were apparent in the 'proj' view of **XP**. A displacement ellipsoid plot (Note: this is still isotropic) of this molecule at this stage of refinement is shown on the following page.

4. Plot calctest.5, After The 5th Cycle

(i.e., When all Non-Hydrogen Atoms Have Been Refined to Their Best Isotropic Values.)



[Note: Made with graphics file CALCTEST.5hc.GIF]

F. THE 6TH CYCLE: USING XL AND REFINING ALL NON-HYDROGEN ATOMS USING ANISOTROPIC DISPLACEMENT PARAMETERS

This sections involves the fourth refinement cycle by **XL**. This takes the atom positions and isotropic displacement parameters from the third **XL**, converts them to anisotropic values, and then uses least squares refinement to improve the atomic positions and give more realistic anisotropic displacement parameters (i.e., these are shaped like footballs or pancakes). It then calculates a residual electron density map (i.e., the Q peaks) which one uses **XP** to assign as many Hydrogen atoms as possible. It requires the following **calctest.ins** input file and produces the following **calctest.res** and **calctest.lst** output files.

To convert the assigned non-Hydrogen atoms to anisotropic displacement parameters one must edit the **name.ins** file and add a line that reads 'ANIS' after the line containing the command 'PLAN', e.g.

edit calctest.ins [ent] (this is done in **DOS**)

Then, add the line **ANIS** as outlined below and save the result and exit from this **calctest.ins** file. *[Note: it is very critical that you add this line in here!!! If you put it in earlier in this file then **XL** will almost always crash.]*

1. CALCTEST.INS Input File for 6th Cycle: Using XL to Refine Anisotropic displacement Parameters and Assign Most of the Hydrogen Atoms

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR    2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50

L.S. 4
BOND
FMAP 2
PLAN 20

ANIS

WGHT    0.100000
FVAR      0.61864
CR    4   0.65442   0.72257   0.82861  11.00000   0.02089
O7    3   0.52392   0.95672   0.64835  11.00000   0.02992
O8    3   0.25566   0.72934   0.57790  11.00000   0.03320
O9    3   0.18829   0.58203   0.76054  11.00000   0.03199
```

```
O10   3   0.86333   1.00651   1.15356  11.00000   0.04120
O11   3   0.68465   0.82987   1.19973  11.00000   0.03747
O12   3   0.82541   0.73869   0.61191  11.00000   0.05086
O13   3   0.61189   0.41788   0.78577  11.00000   0.04656
O14   3   1.04726   0.74434   1.02053  11.00000   0.04038
C1    1   0.51006   0.89160   0.74837  11.00000   0.02489
C2    1   0.36919   0.76592   0.70811  11.00000   0.02504
C3    1   0.33457   0.69407   0.80677  11.00000   0.02548
C4    1   0.45278   0.73789   0.94165  11.00000   0.02462
C5    1   0.59849   0.85894   0.97813  11.00000   0.02282
C6    1   0.62715   0.93760   0.88191  11.00000   0.02473
C7    1   0.67748   1.07612   0.68055  11.00000   0.03852
C8    1   0.25526   0.60042   0.50569  11.00000   0.05106
C9    1   0.17061   0.48972   0.85023  11.00000   0.03428
C10   1   0.73205   0.90838   1.11880  11.00000   0.02751
C11   1   0.80670   0.86844   1.33980  11.00000   0.04568
C12   1   0.76067   0.73183   0.69516  11.00000   0.03044
C13   1   0.62656   0.53544   0.80118  11.00000   0.02931
C14   1   0.89508   0.73681   0.94554  11.00000   0.02707

HKLF 4
END
```

On a Gateway2000® Pentium computer running at 166 MHz and with 32 MB of RAM, this **XL** calculation look a total of 58 seconds for 208 parameters.

After the refinement, the R factor for the 4360 reflections having Fo > 4 sigma (Fo) (i.e., the first R that **XL** lists) was 0.052, the observed R and wR factors for all of the data were 0.073 and 0.174, respectively, and the GOOF value was 1.153. In the final cycle, the largest shift for any atom (in this case C11) was 0.000 and the largest shift/standard uncertainty for any parameter was substantially less than 0.01.

[Note: that the single number representing the isotropic displacement parameters in the previous calctest.res file or in the calctest.ins file to start this cycle has now been converted to a set of six numbers for each atom, the anisotropic displacement parameters.]

2. CALCTEST.RES Output File for 6th Cycle: Using XL to Refine Anisotropic displacement Parameters and Assign Most of the Hydrogen Atoms

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR   2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50

L.S. 4
BOND
FMAP 2
PLAN 20
```

```
WGHT    0.100000
FVAR      0.62287
CR     4  0.65442  0.72256  0.82864 11.00000  0.02633  0.01993 =
     0.01661  0.00344  0.00673  0.00556
O7     3  0.52384  0.95653  0.64844 11.00000  0.03778  0.02878 =
     0.02116  0.01126  0.00462  0.00389
O8     3  0.25569  0.72944  0.57773 11.00000  0.03788  0.03530 =
     0.01928  0.00543 -0.00179  0.00552
O9     3  0.18846  0.58229  0.76086 11.00000  0.03031  0.03181 =
     0.02869  0.00767  0.00485 -0.00192
O10    3  0.86349  1.00645  1.15330 11.00000  0.04752  0.04101 =
     0.02393  0.00237  0.00134 -0.00721
O11    3  0.68441  0.82987  1.20000 11.00000  0.04498  0.04672 =
     0.01874  0.01030  0.00698  0.00329
O12    3  0.82539  0.73856  0.61165 11.00000  0.07345  0.06393 =
     0.04246  0.02005  0.03871  0.02571
O13    3  0.61228  0.41766  0.78574 11.00000  0.07264  0.02423 =
     0.05677  0.00725  0.03156  0.01135
O14    3  1.04740  0.74466  1.02050 11.00000  0.03245  0.04439 =
     0.04057  0.00516 -0.00009  0.01111
C1     1  0.51004  0.89173  0.74838 11.00000  0.03203  0.02408 =
     0.01938  0.00672  0.00700  0.00886
C2     1  0.36909  0.76565  0.70800 11.00000  0.02795  0.02566 =
     0.01854  0.00420  0.00368  0.00642
C3     1  0.33472  0.69419  0.80682 11.00000  0.02626  0.02496 =
     0.02379  0.00471  0.00656  0.00579
C4     1  0.45282  0.73796  0.94143 11.00000  0.02749  0.02591 =
     0.02186  0.00636  0.00898  0.00692
C5     1  0.59841  0.85917  0.97811 11.00000  0.02949  0.02294 =
     0.01660  0.00258  0.00723  0.00679
C6     1  0.62741  0.93762  0.88216 11.00000  0.03249  0.02243 =
     0.01874  0.00502  0.00825  0.00783
C7     1  0.67809  1.07595  0.68080 11.00000  0.04379  0.04004 =
     0.03032  0.01584  0.00634 -0.00416
C8     1  0.25718  0.60033  0.50581 11.00000  0.06373  0.05306 =
     0.02630 -0.00853  0.00181  0.01117
C9     1  0.17027  0.48996  0.85013 11.00000  0.03837  0.03151 =
     0.03555  0.01152  0.01067  0.00160
C10    1  0.73194  0.90819  1.11869 11.00000  0.03179  0.02935 =
     0.01877  0.00426  0.00738  0.00862
C11    1  0.80745  0.86813  1.33983 11.00000  0.04978  0.07211 =
     0.01835  0.01318  0.00478  0.01466
C12    1  0.76155  0.73223  0.69527 11.00000  0.04125  0.03205 =
     0.02601  0.00898  0.01422  0.01225
C13    1  0.62657  0.53566  0.80107 11.00000  0.03394  0.02683 =
     0.02840  0.00603  0.01256  0.00728
C14    1  0.89536  0.73641  0.94589 11.00000  0.03261  0.02320 =
     0.02650  0.00297  0.00909  0.00734
HKLF 4
END

WGHT     0.0911     0.4011
Q1   1   0.2819  0.4555  0.8822  11.00000  0.05    0.85
Q2   1   0.7203  1.0132  0.8980  11.00000  0.05    0.82
Q3   1   0.6661  1.1058  0.5975  11.00000  0.05    0.73
Q4   1   0.4336  0.6853  1.0033  11.00000  0.05    0.72
Q5   1   0.1396  0.5425  0.9414  11.00000  0.05    0.70
Q6   1   0.6556  1.1481  0.7376  11.00000  0.05    0.68
Q7   1   0.7910  1.0560  0.7184  11.00000  0.05    0.67
Q8   1   0.9262  0.8458  1.3589  11.00000  0.05    0.64
Q9   1   0.0635  0.4170  0.8012  11.00000  0.05    0.59
Q10  1   0.2181  0.6015  0.4216  11.00000  0.05    0.59
Q11  1   0.8123  0.9473  1.3785  11.00000  0.05    0.54
Q12  1   0.7301  0.8242  1.3781  11.00000  0.05    0.51
Q13  1   0.2807  0.5359  0.5620  11.00000  0.05    0.50
Q14  1   0.2160  0.5165  0.5416  11.00000  0.05    0.50
Q15  1   0.3822  0.5839  0.5229  11.00000  0.05    0.47
Q16  1   0.3485  0.6342  0.5026  11.00000  0.05    0.45
Q17  1   0.6202  0.9044  0.9374  11.00000  0.05    0.44
Q18  1   0.7645  0.8607  1.3182  11.00000  0.05    0.39
```

```
Q19   1   0.6633  0.8814  1.0374  11.00000  0.05    0.39
Q20   1   0.3321  0.7323  0.7625  11.00000  0.05    0.34
```

3. CALCTEST.LST Output File for 6th Cycle: Using XL to Refine Anisotropic Displacement Parameters and Assign Most of the Hydrogen Atoms

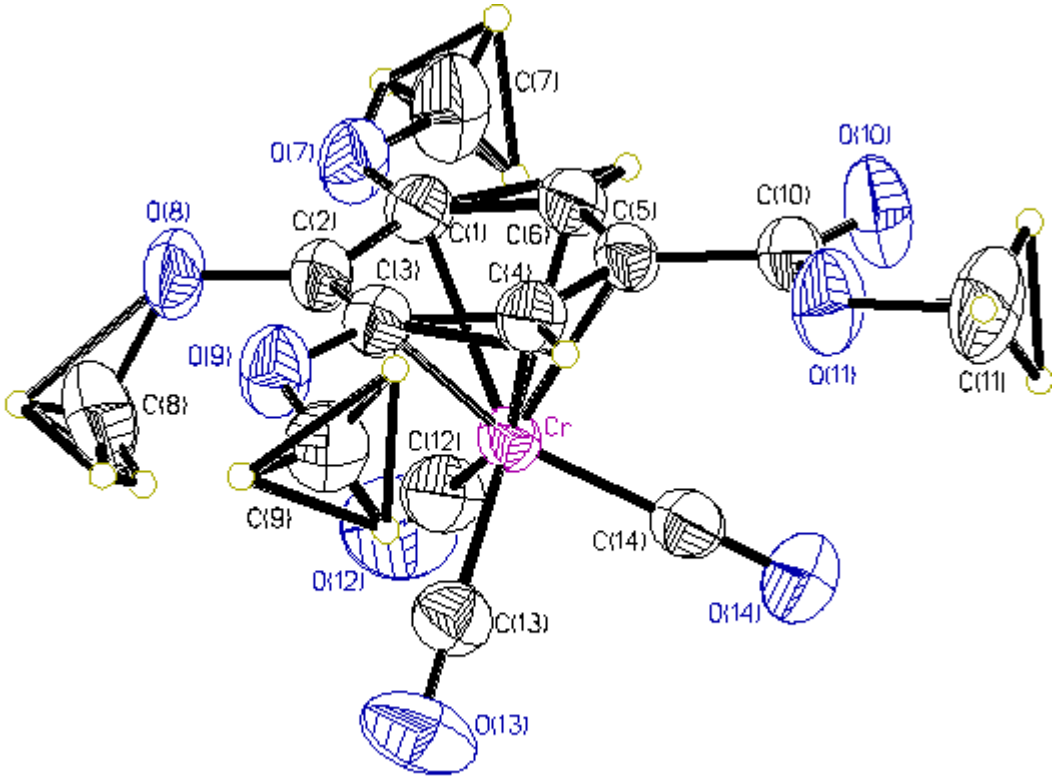
17 pages of text. See the computer copies of these files.

Using **XP** after this cycle allowed me to assign all 14 Hydrogen atoms. For many samples, the rest will need to be assigned in the next cycle. A displacement ellipsoid plot (**telp 0 -75 0.04 0 [ent] calctest.6 [ent]**) (Note: this plot is now anisotropic of this molecule at this stage of refinement is included in the following page.

Note: The extra H-H "bonds" between the methyl hydrogens are typical for cases when hydrogen atoms that have just been assigned on the same CH_2 or CH_3 group but have not yet been refined. These extra "bonds" will disappear upon refinement. They are due the default values used by XP for recognizing contacts being chosen for non-hydrogen atoms. If one desires to do so, one can use the 'undo' command to remove these "ghost" bonds.

4. Plot calctest.6, After The 6th Cycle

(i.e., When All Non-Hydrogen Atoms Have Been Refined Using Anisotropic Displacement Parameters.)



[Note: Made with graphics file CALCTEST.6hc.GIF]

G. THE 7TH CYCLE: USING XL AND REFINING ANISOTROPIC NON-HYDROGEN ATOMS AND THE FIRST SET OF ISOTROPIC HYDROGEN ATOMS

This sections involves the fifth refinement cycle by **XL**. This takes the atom positions and anisotropic displacement parameters for non-Hydrogen atoms and the first set of isotropic Hydrogen atoms from the fourth **XL** and then uses least squares refinement to improve the atomic positions and displacement parameters. It then calculates a residual electron density map (i.e., the Q peaks) which one uses **XP** to assign as many of the remaining Hydrogen atoms as possible (in this example all of them). It requires the following **calctest.ins** input file and produces the following **calctest.res** and **calctest.lst** output files.

[Note: the 'ANIS' command you added in the calctest.ins file in the previous cycle has disappeared (i.e., leaving the blank line shown shaded below) because its function (to convert any atoms after it to the anisotropic form) is complete.]

[Further note: As described in the earlier chapter on **XL**, I do not routinely use the powerful **AFIX** or **HFIX** commands (these are edited into the name.ins file). Their purpose is to fix the positional and/or displacement parameters of the specified atoms to idealized values (often with respect to the heavier atoms to which they are bonded). Because of the excellent data quality obtained from this crystal, leaving the hydrogen parameters free to refine eventually gave a quality solution, see below.]

1. CALCTEST.INS Input File for 7th Cycle: Using XL to do an Anisotropic Refinement of all Non-Hydrogen Atoms and the Isotropic Refinement of the First Set of Hydrogen Atoms

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR    2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50

L.S. 4
BOND
FMAP 2
PLAN 20


WGHT    0.100000
FVAR      0.62287
CR    4   0.65442   0.72256   0.82864  11.00000   0.02633   0.01993 =
     0.01661   0.00344   0.00673   0.00556
```

```
O7   3  0.52384  0.95653  0.64844 11.00000  0.03778  0.02878 =
     0.02116  0.01126  0.00462  0.00389
O8   3  0.25569  0.72944  0.57773 11.00000  0.03788  0.03530 =
     0.01928  0.00543 -0.00179  0.00552
O9   3  0.18846  0.58229  0.76086 11.00000  0.03031  0.03181 =
     0.02869  0.00767  0.00485 -0.00192
O10  3  0.86349  1.00645  1.15330 11.00000  0.04752  0.04101 =
     0.02393  0.00237  0.00134 -0.00721
O11  3  0.68441  0.82987  1.20000 11.00000  0.04498  0.04672 =
     0.01874  0.01030  0.00698  0.00329
O12  3  0.82539  0.73856  0.61165 11.00000  0.07345  0.06393 =
     0.04246  0.02005  0.03871  0.02571
O13  3  0.61228  0.41766  0.78574 11.00000  0.07264  0.02423 =
     0.05677  0.00725  0.03156  0.01135
O14  3  1.04740  0.74466  1.02050 11.00000  0.03245  0.04439 =
     0.04057  0.00516 -0.00009  0.01111
C1   1  0.51004  0.89173  0.74838 11.00000  0.03203  0.02408 =
     0.01938  0.00672  0.00700  0.00886
C2   1  0.36909  0.76565  0.70800 11.00000  0.02795  0.02566 =
     0.01854  0.00420  0.00368  0.00642
C3   1  0.33472  0.69419  0.80682 11.00000  0.02626  0.02496 =
     0.02379  0.00471  0.00656  0.00579
C4   1  0.45282  0.73796  0.94143 11.00000  0.02749  0.02591 =
     0.02186  0.00636  0.00898  0.00692
H4   2  0.43360  0.68530  1.00330 11.00000  0.05000
C5   1  0.59841  0.85917  0.97811 11.00000  0.02949  0.02294 =
     0.01660  0.00258  0.00723  0.00679
C6   1  0.62741  0.93762  0.88216 11.00000  0.03249  0.02243 =
     0.01874  0.00502  0.00825  0.00783
H6   2  0.72030  1.01320  0.89800 11.00000  0.05000
C7   1  0.67809  1.07595  0.68080 11.00000  0.04379  0.04004 =
     0.03032  0.01584  0.00634 -0.00416
H7C  2  0.66610  1.10580  0.59750 11.00000  0.05000
H7B  2  0.65560  1.14810  0.73760 11.00000  0.05000
H7A  2  0.79100  1.05600  0.71840 11.00000  0.05000
C8   1  0.25718  0.60033  0.50581 11.00000  0.06373  0.05306 =
     0.02630 -0.00853  0.00181  0.01117
H8C  2  0.21810  0.60150  0.42160 11.00000  0.05000
H8B  2  0.28070  0.53590  0.56200 11.00000  0.05000
H8A  2  0.21600  0.51650  0.54160 11.00000  0.05000
C9   1  0.17027  0.48996  0.85013 11.00000  0.03837  0.03151 =
     0.03555  0.01152  0.01067  0.00160
H9C  2  0.28190  0.45550  0.88220 11.00000  0.05000
H9B  2  0.13960  0.54250  0.94140 11.00000  0.05000
H9A  2  0.06350  0.41700  0.80120 11.00000  0.05000
C10  1  0.73194  0.90819  1.11869 11.00000  0.03179  0.02935 =
     0.01877  0.00426  0.00738  0.00862
C11  1  0.80745  0.86813  1.33983 11.00000  0.04978  0.07211 =
     0.01835  0.01318  0.00478  0.01466
H11C 2  0.92620  0.84580  1.35890 11.00000  0.05000
H11B 2  0.81230  0.94730  1.37850 11.00000  0.05000
H11A 2  0.73010  0.82420  1.37810 11.00000  0.05000
C12  1  0.76155  0.73223  0.69527 11.00000  0.04125  0.03205 =
```

```
     0.02601   0.00898   0.01422   0.01225
C13  1  0.62657  0.53566  0.80107  11.00000  0.03394  0.02683 =
     0.02840   0.00603   0.01256   0.00728
C14  1  0.89536  0.73641  0.94589  11.00000  0.03261  0.02320 =
     0.02650   0.00297   0.00909   0.00734

HKLF 4
END
```

On a Gateway2000® Pentium computer running at 166 MHz and with 32 MB of RAM, this **XL** calculation look a total of 86 seconds for 264 parameters.

After the refinement, the R factor for the 4360 reflections having Fo > 4 sigma (Fo) (i.e., the first R that **XL** lists) was 0.0417, the observed R and wR factors for all of the data were 0.0623 and 0.139, respectively, and the GOOF value was 0.920. In the final cycle, the largest shift for any atom (in this case H8B) was 0.210Å and the largest shift/standard uncertainty for any parameter was substantially more than 0.1 for several hydrogen atoms (they were substantially smaller for all non-hydrogen atoms).

[Note: in the following calctest.res output file you can clearly see in the darkened text the distinction between the non-Hydrogen atoms that are anisotropic and the isotropic Hydrogen atoms as the latter each have many fewer displacement parameters.]

2. CALCTEST.RES Output File for 7th Cycle: Using XL to do an Anisotropic Refinement of all Non-Hydrogen Atoms and the Isotropic Refinement of the First Set of Hydrogen Atoms

```
TITL 95adh06e in P-1
CELL 0.71073  7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR   2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50

L.S. 4
BOND
FMAP 2
PLAN 20

WGHT    0.100000
FVAR      0.62761
CR    4  0.65440  0.72254  0.82867  11.00000  0.02659  0.02019 =
     0.01688   0.00352   0.00683   0.00563
O7    3  0.52391  0.95662  0.64835  11.00000  0.03841  0.02887 =
     0.02153   0.01117   0.00512   0.00400
O8    3  0.25581  0.72953  0.57765  11.00000  0.03865  0.03619 =
     0.01938   0.00492  -0.00155   0.00605
O9    3  0.18823  0.58253  0.76081  11.00000  0.03108  0.03206 =
     0.02837   0.00759   0.00467  -0.00190
O10   3  0.86343  1.00617  1.15328  11.00000  0.04806  0.04149 =
     0.02468   0.00248   0.00183  -0.00674
O11   3  0.68509  0.83015  1.20028  11.00000  0.04485  0.04710 =
     0.01854   0.01023   0.00677   0.00347
O12   3  0.82505  0.73845  0.61180  11.00000  0.07314  0.06383 =
```

```
      0.04186   0.01911   0.03844   0.02436
O13    3  0.61300  0.41786  0.78536 11.00000  0.07202  0.02400 =
     0.05807   0.00665   0.03182   0.01110
O14    3  1.04761  0.74487  1.02005 11.00000  0.03273  0.04390 =
     0.04098   0.00584   0.00020   0.01046
C1     1  0.50999  0.89148  0.74815 11.00000  0.03269  0.02471 =
     0.01956   0.00691   0.00735   0.00919
C2     1  0.36916  0.76568  0.70792 11.00000  0.02798  0.02611 =
     0.01837   0.00420   0.00350   0.00659
C3     1  0.33493  0.69422  0.80665 11.00000  0.02663  0.02485 =
     0.02417   0.00482   0.00668   0.00593
C4     1  0.45293  0.73826  0.94123 11.00000  0.02857  0.02583 =
     0.02204   0.00692   0.00965   0.00716
H4     2  0.44605  0.68617  1.01092 11.00000  0.02263
C5     1  0.59867  0.85880  0.97806 11.00000  0.02994  0.02323 =
     0.01645   0.00244   0.00716   0.00740
C6     1  0.62711  0.93742  0.88225 11.00000  0.03194  0.02128 =
     0.01918   0.00437   0.00790   0.00639
H6     2  0.72001  1.01290  0.90558 11.00000  0.02575
C7     1  0.67793  1.07571  0.68083 11.00000  0.04413  0.03904 =
     0.02888   0.01453   0.00689  -0.00102
H7C    2  0.67300  1.09880  0.59829 11.00000  0.03254
H7B    2  0.65551  1.14752  0.74090 11.00000  0.04051
H7A    2  0.78986  1.05269  0.71452 11.00000  0.04687
C8     1  0.25741  0.60036  0.50591 11.00000  0.06612  0.05310 =
     0.02544  -0.00593   0.00116   0.01225
H8C    2  0.19469  0.58906  0.41479 11.00000  0.10224
H8B    2  0.35402  0.56250  0.52043 11.00000  0.15001
H8A    2  0.21005  0.52184  0.54436 11.00000  0.11119
C9     1  0.17013  0.48995  0.84946 11.00000  0.03779  0.03119 =
     0.03693   0.01068   0.01106   0.00158
H9C    2  0.28780  0.45769  0.87892 11.00000  0.03267
H9B    2  0.13681  0.54024  0.92725 11.00000  0.07106
H9A    2  0.07112  0.41509  0.80792 11.00000  0.04563
C10    1  0.73262  0.90843  1.11884 11.00000  0.03202  0.02908 =
     0.01912   0.00402   0.00760   0.00846
C11    1  0.80566  0.86740  1.33914 11.00000  0.04885  0.07198 =
     0.01916   0.01251   0.00518   0.01459
H11C   2  0.91206  0.84274  1.35464 11.00000  0.06396
H11B   2  0.83570  0.96603  1.36615 11.00000  0.07090
H11A   2  0.72394  0.81729  1.38243 11.00000  0.07281
C12    1  0.76103  0.73192  0.69507 11.00000  0.04194  0.03217 =
     0.02588   0.00855   0.01431   0.01221
C13    1  0.62647  0.53558  0.80079 11.00000  0.03440  0.02704 =
     0.02914   0.00577   0.01327   0.00712
C14    1  0.89604  0.73694  0.94599 11.00000  0.03315  0.02323 =
     0.02638   0.00324   0.00912   0.00712
HKLF 4
END

WGHT     0.0440     0.2400
Q1   1  0.6187  0.9038  0.9379  11.00000  0.05   0.42
Q2   1  0.6621  0.8812  1.0379  11.00000  0.05   0.41
Q3   1  0.3319  0.7351  0.7621  11.00000  0.05   0.37
Q4   1  0.3986  0.6385  0.4821  11.00000  0.05   0.37
Q5   1  0.5633  0.9255  0.8179  11.00000  0.05   0.33
Q6   1  0.5480  0.7846  0.9378  11.00000  0.05   0.29
Q7   1  0.6861  0.7454  0.7380  11.00000  0.05   0.28
Q8   1  0.4508  0.8211  0.7422  11.00000  0.05   0.28
Q9   1  0.7503  0.7238  0.7581  11.00000  0.05   0.28
Q10  1  0.2626  0.6145  0.4419  11.00000  0.05   0.27
Q11  1  0.6716  0.8628  1.1779  11.00000  0.05   0.26
Q12  1  0.8144  0.7633  0.8982  11.00000  0.05   0.25
Q13  1  0.8969  0.9594  1.1384  11.00000  0.05   0.25
Q14  1  0.7091  0.9020  1.3980  11.00000  0.05   0.24
Q15  1  0.9359  0.9199  1.3385  11.00000  0.05   0.24
Q16  1  0.8398  0.7640  1.3783  11.00000  0.05   0.23
Q17  1  0.2577  0.6403  0.8019  11.00000  0.05   0.23
Q18  1  0.5492  0.6769  0.8178  11.00000  0.05   0.23
Q19  1  0.7514  0.9801  1.0981  11.00000  0.05   0.23
```

```
Q20   1   0.8456  0.9808  0.6383  11.00000  0.05    0.22
```

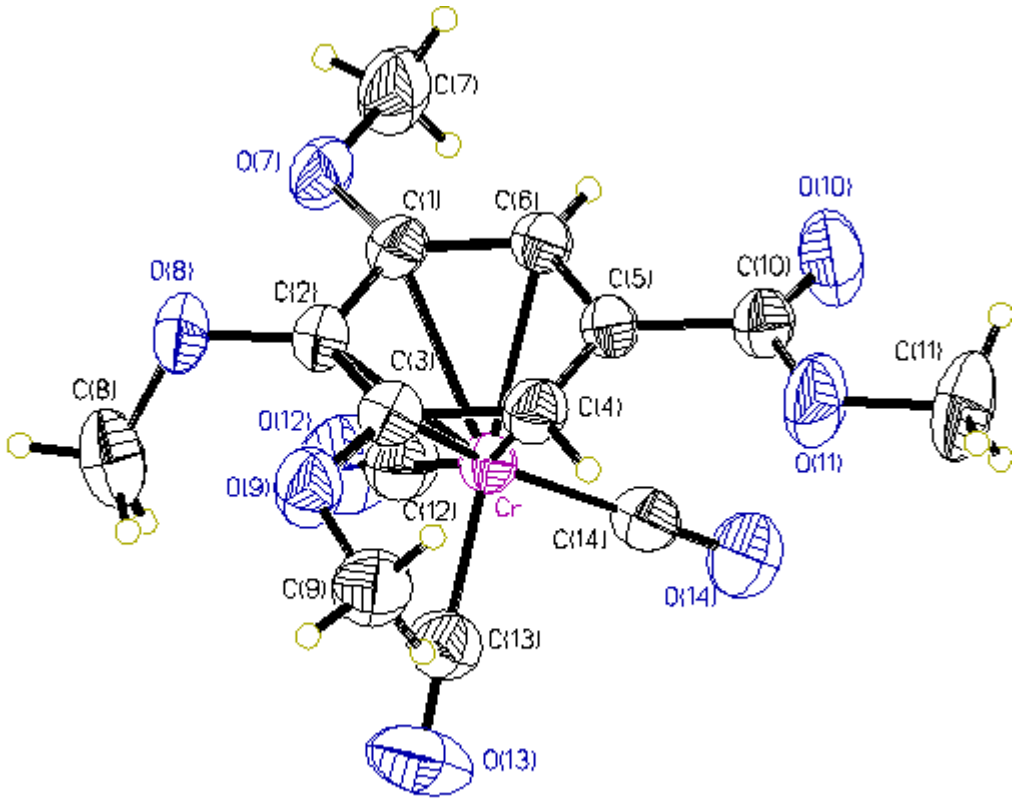
3. CALCTEST.LST Output File for 7th Cycle: Using XL to do an Anisotropic Refinement of all Non-Hydrogen Atoms and the Isotropic Refinement of the First Set of Hydrogen Atoms

17 pages of text. See the computer copies of these files.

Using **XP** after this cycle allowed me to check to assignments of the 14 Hydrogen atoms using 'proj' and 'bang'. A displacement ellipsoid plot (**telp 0 -75 0.04 0 [ent] calctest.7 [ent]**) (Note: this plot is now anisotropic) of this molecule at this stage of refinement is included in the following section: Displacement Ellipsoid Plots of the Output from the Various Stages in the refinement of calctest, (η^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$Cr(CO)_3$.

4. Plot calctest.7, After The 7th Cycle

(i.e., When all Non-Hydrogen Atoms Have Been Refined Using Anisotropic Displacement Parameters and the First Set of Hydrogen Atoms Have Been Refined Using Isotropic Displacement Parameters.)



[Note: Made with graphics file CALCTEST.7hc.GIF]

H. THE 8TH CYCLE: USING XL AND DOING THE FINAL REFINEMENT OF ALL ATOMS INCLUDING REFINEMENT OF EXTINCTION AND THE USE OF THE WEIGHTING FUNCTION

This sections involves the sixth refinement cycle by **XL**. This takes the atom positions and anisotropic displacement parameters for non-Hydrogen atoms and the isotropic displacement parameters for Hydrogen atoms from the fifth **XL** and then uses least squares refinement to improve the atomic positions and displacement parameters and to refine a few additional parameters such as extinction and the weighting function. It then calculates a residual electron density map (i.e., the Q peaks) which one uses **XP** to check the results and prepare the final plots and then uses **XCIF** to prepare the tables. It requires the following **calctest.ins** input file and produces the following **calctest.res** and **calctest.lst** output files.

The various things you have to do to the **calctest.ins** file (by editing it in **DOS**) are outlined below (save the result and exit from this **calctest.ins** file when you are done). The numbers put into the WGHT command line were taken from the calctest.res file.

[Note: again it is very important that the two new lines added go in the specified positions (i.e., to prevent XL from crashing) and that the $H is added in the 'BOND' line (i.e., so that the software will save the details on the Hydrogen atom positions).]

1. CALCTEST.INS Input File for 8th Cycle: Using XL to do the Final Refinement Cycles

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR   2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50

L.S. 4
BOND $H
FMAP 2
PLAN 20

ACTA
EXTI

WGHT    0.0440  0.2400
FVAR       0.62761
CR    4   0.65440   0.72254   0.82867  11.00000   0.02659   0.02019 =
     0.01688   0.00352   0.00683   0.00563
O7    3   0.52391   0.95662   0.64835  11.00000   0.03841   0.02887 =
     0.02153   0.01117   0.00512   0.00400
```

```
O8   3  0.25581  0.72953  0.57765 11.00000  0.03865  0.03619 =
     0.01938  0.00492 -0.00155  0.00605
O9   3  0.18823  0.58253  0.76081 11.00000  0.03108  0.03206 =
     0.02837  0.00759  0.00467 -0.00190
O10  3  0.86343  1.00617  1.15328 11.00000  0.04806  0.04149 =
     0.02468  0.00248  0.00183 -0.00674
O11  3  0.68509  0.83015  1.20028 11.00000  0.04485  0.04710 =
     0.01854  0.01023  0.00677  0.00347
O12  3  0.82505  0.73845  0.61180 11.00000  0.07314  0.06383 =
     0.04186  0.01911  0.03844  0.02436
O13  3  0.61300  0.41786  0.78536 11.00000  0.07202  0.02400 =
     0.05807  0.00665  0.03182  0.01110
O14  3  1.04761  0.74487  1.02005 11.00000  0.03273  0.04390 =
     0.04098  0.00584  0.00020  0.01046
C1   1  0.50999  0.89148  0.74815 11.00000  0.03269  0.02471 =
     0.01956  0.00691  0.00735  0.00919
C2   1  0.36916  0.76568  0.70792 11.00000  0.02798  0.02611 =
     0.01837  0.00420  0.00350  0.00659
C3   1  0.33493  0.69422  0.80665 11.00000  0.02663  0.02485 =
     0.02417  0.00482  0.00668  0.00593
C4   1  0.45293  0.73826  0.94123 11.00000  0.02857  0.02583 =
     0.02204  0.00692  0.00965  0.00716
H4   2  0.44605  0.68617  1.01092 11.00000  0.02263
C5   1  0.59867  0.85880  0.97806 11.00000  0.02994  0.02323 =
     0.01645  0.00244  0.00716  0.00740
C6   1  0.62711  0.93742  0.88225 11.00000  0.03194  0.02128 =
     0.01918  0.00437  0.00790  0.00639
H6   2  0.72001  1.01290  0.90558 11.00000  0.02575
C7   1  0.67793  1.07571  0.68083 11.00000  0.04413  0.03904 =
     0.02888  0.01453  0.00689 -0.00102
H7C  2  0.67300  1.09880  0.59829 11.00000  0.03254
H7B  2  0.65551  1.14752  0.74090 11.00000  0.04051
H7A  2  0.78986  1.05269  0.71452 11.00000  0.04687
C8   1  0.25741  0.60036  0.50591 11.00000  0.06612  0.05310 =
     0.02544 -0.00593  0.00116  0.01225
H8C  2  0.19469  0.58906  0.41479 11.00000  0.10224
H8B  2  0.35402  0.56250  0.52043 11.00000  0.15001
H8A  2  0.21005  0.52184  0.54436 11.00000  0.11119
C9   1  0.17013  0.48995  0.84946 11.00000  0.03779  0.03119 =
     0.03693  0.01068  0.01106  0.00158
H9C  2  0.28780  0.45769  0.87892 11.00000  0.03267
H9B  2  0.13681  0.54024  0.92725 11.00000  0.07106
H9A  2  0.07112  0.41509  0.80792 11.00000  0.04563
C10  1  0.73262  0.90843  1.11884 11.00000  0.03202  0.02908 =
     0.01912  0.00402  0.00760  0.00846
C11  1  0.80566  0.86740  1.33914 11.00000  0.04885  0.07198 =
     0.01916  0.01251  0.00518  0.01459
H11C 2  0.91206  0.84274  1.35464 11.00000  0.06396
H11B 2  0.83570  0.96603  1.36615 11.00000  0.07090
H11A 2  0.72394  0.81729  1.38243 11.00000  0.07281
C12  1  0.76103  0.73192  0.69507 11.00000  0.04194  0.03217 =
     0.02588  0.00855  0.01431  0.01221
C13  1  0.62647  0.53558  0.80079 11.00000  0.03440  0.02704 =
```

```
      0.02914   0.00577   0.01327   0.00712
C14   1   0.89604   0.73694   0.94599  11.00000   0.03315   0.02323 =
      0.02638   0.00324   0.00912   0.00712

HKLF 4
END
```

On a Gateway2000® Pentium computer running at 166 MHz and with 32 MB of RAM, this **XL** calculation look a total of 87 seconds for 265 parameters.

After the refinement, the R factor for the 4360 reflections having Fo > 4 sigma (Fo) (i.e., the first R that **XL** lists) was 0.0.0404, the observed R and wR factors for all of the data were 0.0611 and 0.106, respectively, and the GOOF value was 1.028. In the final cycle, the largest shift for any atom (in this case H8B) was 0.062 and the largest shift/standard uncertainty for any parameter was still greater than 0.1 for several hydrogen atoms (they were substantially smaller values for all non-hydrogen atoms).

[Note: that the 'EXTI' command moves after it starts being refined.]

2. CALCTEST.RES Output File for 8th Cycle: Using XL to do the Final Refinement Cycles

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR   2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50

L.S. 4
BOND $H
FMAP 2
PLAN 20


ACTA

WGHT    0.044000    0.240000
EXTI    0.006399
FVAR       0.62922
CR    4   0.65437   0.72254   0.82866  11.00000   0.02686   0.02032 =
      0.01698   0.00354   0.00689   0.00573
O7    3   0.52386   0.95642   0.64831  11.00000   0.03809   0.02893 =
      0.02133   0.01097   0.00482   0.00394
O8    3   0.25572   0.72963   0.57763  11.00000   0.03831   0.03702 =
      0.01937   0.00480  -0.00189   0.00601
O9    3   0.18826   0.58267   0.76084  11.00000   0.03140   0.03220 =
      0.02845   0.00737   0.00476  -0.00208
O10   3   0.86346   1.00601   1.15333  11.00000   0.04785   0.04182 =
      0.02479   0.00247   0.00242  -0.00658
O11   3   0.68504   0.83020   1.20010  11.00000   0.04469   0.04742 =
      0.01855   0.01029   0.00669   0.00319
O12   3   0.82516   0.73861   0.61183  11.00000   0.07339   0.06521 =
      0.04150   0.01914   0.03837   0.02448
O13   3   0.61275   0.41774   0.78541  11.00000   0.07164   0.02394 =
      0.05839   0.00682   0.03170   0.01105
```

```
O14    3  1.04765  0.74498  1.02004 11.00000  0.03260  0.04401 =
     0.04113  0.00576  0.00012  0.01038
C1     1  0.50983  0.89156  0.74810 11.00000  0.03314  0.02478 =
     0.01958  0.00712  0.00767  0.00937
C2     1  0.36934  0.76566  0.70802 11.00000  0.02782  0.02659 =
     0.01837  0.00392  0.00333  0.00668
C3     1  0.33500  0.69418  0.80655 11.00000  0.02701  0.02501 =
     0.02450  0.00488  0.00713  0.00598
C4     1  0.45316  0.73843  0.94132 11.00000  0.02898  0.02616 =
     0.02169  0.00689  0.00974  0.00731
H4     2  0.44138  0.68516  1.00913 11.00000  0.02351
C5     1  0.59866  0.85867  0.97794 11.00000  0.02973  0.02340 =
     0.01670  0.00236  0.00726  0.00753
C6     1  0.62719  0.93751  0.88232 11.00000  0.03200  0.02098 =
     0.01975  0.00413  0.00766  0.00630
H6     2  0.71900  1.01411  0.90463 11.00000  0.02664
C7     1  0.67806  1.07571  0.68085 11.00000  0.04522  0.03907 =
     0.02878  0.01450  0.00748 -0.00108
H7C    2  0.67009  1.10120  0.59892 11.00000  0.03488
H7B    2  0.65602  1.14848  0.73957 11.00000  0.04080
H7A    2  0.80170  1.05097  0.71989 11.00000  0.04636
C8     1  0.25717  0.60017  0.50600 11.00000  0.06470  0.05252 =
     0.02561 -0.00588  0.00123  0.00986
H8C    2  0.18548  0.58902  0.41984 11.00000  0.09167
H8B    2  0.38670  0.60641  0.50058 11.00000  0.12526
H8A    2  0.24218  0.52729  0.54745 11.00000  0.10411
C9     1  0.17005  0.48994  0.84953 11.00000  0.03753  0.03139 =
     0.03690  0.01079  0.01094  0.00113
H9C    2  0.28316  0.45400  0.87675 11.00000  0.03532
H9B    2  0.14351  0.53556  0.92949 11.00000  0.05603
H9A    2  0.06863  0.41714  0.80400 11.00000  0.04964
C10    1  0.73279  0.90833  1.11897 11.00000  0.03239  0.02933 =
     0.01920  0.00397  0.00784  0.00889
C11    1  0.80591  0.86732  1.33921 11.00000  0.04920  0.07185 =
     0.01951  0.01271  0.00529  0.01437
H11C   2  0.91698  0.84345  1.35439 11.00000  0.06447
H11B   2  0.83137  0.95907  1.36722 11.00000  0.07514
H11A   2  0.72682  0.81937  1.38454 11.00000  0.07329
C12    1  0.76065  0.73155  0.69504 11.00000  0.04194  0.03197 =
     0.02627  0.00832  0.01389  0.01236
C13    1  0.62637  0.53553  0.80089 11.00000  0.03479  0.02735 =
     0.02870  0.00605  0.01342  0.00738
C14    1  0.89574  0.73695  0.94584 11.00000  0.03366  0.02368 =
     0.02632  0.00322  0.00980  0.00718
HKLF 4
END

WGHT     0.0356     0.3014
Q1   1  0.6192  0.9035  0.9378  11.00000  0.05   0.44
Q2   1  0.6621  0.8812  1.0379  11.00000  0.05   0.42
Q3   1  0.3314  0.7350  0.7620  11.00000  0.05   0.39
Q4   1  0.5626  0.9245  0.8178  11.00000  0.05   0.35
Q5   1  0.5498  0.7835  0.9378  11.00000  0.05   0.31
Q6   1  0.4499  0.8210  0.7423  11.00000  0.05   0.31
Q7   1  0.6822  0.7431  0.7380  11.00000  0.05   0.31
Q8   1  0.7479  0.7223  0.7581  11.00000  0.05   0.30
Q9   1  0.8082  0.7600  0.8783  11.00000  0.05   0.26
Q10  1  0.2580  0.6408  0.8019  11.00000  0.05   0.26
Q11  1  0.2610  0.6147  0.4419  11.00000  0.05   0.26
Q12  1  0.5461  0.6761  0.8177  11.00000  0.05   0.25
Q13  1  0.3917  0.7180  0.8822  11.00000  0.05   0.25
Q14  1  0.1894  0.5547  0.7817  11.00000  0.05   0.25
Q15  1  0.5983  0.7992  1.1778  11.00000  0.05   0.24
Q16  1  0.7528  0.9803  1.0982  11.00000  0.05   0.24
Q17  1  0.8981  0.9622  1.1385  11.00000  0.05   0.24
Q18  1  0.3135  0.6404  0.4820  11.00000  0.05   0.24
Q19  1  0.6723  0.8646  1.1779  11.00000  0.05   0.23
Q20  1  0.9617  1.0309  1.1987  11.00000  0.05   0.23
```

3. CALCTEST.LST Output File for 8th Cycle: Using XL to do the Final Refinement Cycles

After this 8th cycle this calctest.lst file is six pages long and is shown below for you to become familiar with the format for the listing of XL results. As noted above, these files are typically very longer and for space reason they are not included in this manual (except for that for the 3rd cycle). However, they are available on disk if you want to view them.

```
++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

+ XL - CRYSTAL STRUCTURE REFINEMENT - SIEMENS SHELXTL - Ver. 5.03 +

+ Copyright(c) 1994 Siemens Analytical Xray - All Rights Reserved +

+ calctest                started at 20:28:08 on 23-Mar-1997 +
++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++

TITL 95adh06e in P-1
CELL 0.71073  7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR   2.00  0.0003  0.0005  0.0005  0.004  0.004  0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2

V =    747.07    F(000) =    372.0    Mu =  0.81 mm-1    Cell Wt =    724.50   Rho =  1.610

TEMP -50

L.S. 4
BOND $H
FMAP 2
PLAN 20

ACTA
EXTI

WGHT    0.0440  0.2400
FVAR      0.62761
CR   4  0.65440  0.72254  0.82867  11.00000  0.02659  0.02019 =
     0.01688  0.00352  0.00683  0.00563
O7   3  0.52391  0.95662  0.64835  11.00000  0.03841  0.02887 =
     0.02153  0.01117  0.00512  0.00400
O8   3  0.25581  0.72953  0.57765  11.00000  0.03865  0.03619 =
     0.01938  0.00492 -0.00155  0.00605
O9   3  0.18823  0.58253  0.76081  11.00000  0.03108  0.03206 =
     0.02837  0.00759  0.00467 -0.00190
O10  3  0.86343  1.00617  1.15328  11.00000  0.04806  0.04149 =
     0.02468  0.00248  0.00183 -0.00674
O11  3  0.68509  0.83015  1.20028  11.00000  0.04485  0.04710 =
     0.01854  0.01023  0.00677  0.00347
O12  3  0.82505  0.73845  0.61180  11.00000  0.07314  0.06383 =
     0.04186  0.01911  0.03844  0.02436
O13  3  0.61300  0.41786  0.78536  11.00000  0.07202  0.02400 =
     0.05807  0.00665  0.03182  0.01110
O14  3  1.04761  0.74487  1.02005  11.00000  0.03273  0.04390 =
     0.04098  0.00584  0.00020  0.01046
C1   1  0.50999  0.89148  0.74815  11.00000  0.03269  0.02471 =
     0.01956  0.00691  0.00735  0.00919
C2   1  0.36916  0.76568  0.70792  11.00000  0.02798  0.02611 =
```

```
     0.01837   0.00420   0.00350   0.00659
C3   1  0.33493  0.69422  0.80665  11.00000  0.02663  0.02485 =
     0.02417   0.00482   0.00668   0.00593
C4   1  0.45293  0.73826  0.94123  11.00000  0.02857  0.02583 =
     0.02204   0.00692   0.00965   0.00716
H4   2  0.44605  0.68617  1.01092  11.00000  0.02263
C5   1  0.59867  0.85880  0.97806  11.00000  0.02994  0.02323 =
     0.01645   0.00244   0.00716   0.00740
C6   1  0.62711  0.93742  0.88225  11.00000  0.03194  0.02128 =
     0.01918   0.00437   0.00790   0.00639
H6   2  0.72001  1.01290  0.90558  11.00000  0.02575
C7   1  0.67793  1.07571  0.68083  11.00000  0.04413  0.03904 =
     0.02888   0.01453   0.00689  -0.00102
H7C  2  0.67300  1.09880  0.59829  11.00000  0.03254
H7B  2  0.65551  1.14752  0.74090  11.00000  0.04051
H7A  2  0.78986  1.05269  0.71452  11.00000  0.04687
C8   1  0.25741  0.60036  0.50591  11.00000  0.06612  0.05310 =
     0.02544  -0.00593   0.00116   0.01225
H8C  2  0.19469  0.58906  0.41479  11.00000  0.10224
H8B  2  0.35402  0.56250  0.52043  11.00000  0.15001
H8A  2  0.21005  0.52184  0.54436  11.00000  0.11119
C9   1  0.17013  0.48995  0.84946  11.00000  0.03779  0.03119 =
     0.03693   0.01068   0.01106   0.00158
H9C  2  0.28780  0.45769  0.87892  11.00000  0.03267
H9B  2  0.13681  0.54024  0.92725  11.00000  0.07106
H9A  2  0.07112  0.41509  0.80792  11.00000  0.04563
C10  1  0.73262  0.90843  1.11884  11.00000  0.03202  0.02908 =
     0.01912   0.00402   0.00760   0.00846
C11  1  0.80566  0.86740  1.33914  11.00000  0.04885  0.07198 =
     0.01916   0.01251   0.00518   0.01459
H11C 2  0.91206  0.84274  1.35464  11.00000  0.06396
H11B 2  0.83570  0.96603  1.36615  11.00000  0.07090
H11A 2  0.72394  0.81729  1.38243  11.00000  0.07281
C12  1  0.76103  0.73192  0.69507  11.00000  0.04194  0.03217 =
     0.02588   0.00855   0.01431   0.01221
C13  1  0.62647  0.53558  0.80079  11.00000  0.03440  0.02704 =
     0.02914   0.00577   0.01327   0.00712
C14  1  0.89604  0.73694  0.94599  11.00000  0.03315  0.02323 =
     0.02638   0.00324   0.00912   0.00712

HKLF 4


Covalent radii and connectivity table for  95adh06e in P-1

C    0.770
H    0.320
O    0.660
CR   1.240

Cr - C13 C14 C12 C5 C6 C4 C2 C1 C3
O7 - C1 C7
O8 - C2 C8
O9 - C3 C9
O10 - C10
O11 - C10 C11
O12 - C12
O13 - C13
O14 - C14
C1 - O7 C6 C2 Cr
C2 - O8 C3 C1 Cr
C3 - O9 C4 C2 Cr
C4 - C3 C5 Cr
C5 - C4 C6 C10 Cr
C6 - C1 C5 Cr
C7 - O7
C8 - O8
C9 - O9
C10 - O10 O11 C5
C11 - O11
```

```
C12 - O12 Cr
C13 - O13 Cr
C14 - O14 Cr


  8074  Reflections read, of which     0  rejected

 -1 =< h =< 11,    -15 =< k =< 15,    -16 =< l =< 16,   Max. 2-theta =   66.00

     0  Systematic absence violations

     0  Inconsistent equivalents

  5627  Unique reflections, of which      0  suppressed

R(int) = 0.0231     R(sigma) = 0.0490      Friedel opposites merged

Maximum memory for data reduction =  1994 /   56289


     6.8 seconds elapsed time


Least-squares cycle   1      Maximum vector length =  511      Memory required =   2582 /  329089

wR2 =  0.1076 before cycle   1 for   5627 data and   265 /   265 parameters

GooF = S =     1.045;     Restrained GooF =      1.045  for      0 restraints

Weight = 1 / [ sigma^2(Fo^2) + ( 0.0440 * P )^2 +   0.24 * P ]   where  P = ( Max ( Fo^2, 0 ) + 2 * Fc^2 ) / 3


   N      value       esd    shift/esd  parameter

   1    0.62895    0.00103     1.305    OSF
   2    0.00599    0.00158     3.797   EXTI
 181    0.58815    0.00604     4.247     y  H8B

Mean shift/esd =   0.461    Maximum =   4.247 for   y  H8B

Max. shift = 0.284 A for H8B      Max. dU =-0.011 for H9B

    18.4 seconds elapsed time


Least-squares cycle   2      Maximum vector length =  511      Memory required =   2582 /  329089

wR2 =  0.1064 before cycle   2 for   5627 data and   265 /   265 parameters

GooF = S =     1.031;     Restrained GooF =      1.031  for      0 restraints

Weight = 1 / [ sigma^2(Fo^2) + ( 0.0440 * P )^2 +   0.24 * P ]   where  P = ( Max ( Fo^2, 0 ) + 2 * Fc^2 ) / 3


   N      value       esd    shift/esd  parameter

   1    0.62916    0.00104     0.201    OSF
   2    0.00639    0.00178     0.223   EXTI

Mean shift/esd =   0.087    Maximum =  -1.964 for   z  H8B

Max. shift = 0.153 A for H8B      Max. dU =-0.012 for H8B

    18.4 seconds elapsed time


Least-squares cycle   3      Maximum vector length =  511      Memory required =   2582 /  329089

wR2 =  0.1062 before cycle   3 for   5627 data and   265 /   265 parameters
```

GooF = S = 1.029; Restrained GooF = 1.029 for 0 restraints

Weight = 1 / [sigma^2(Fo^2) + (0.0440 * P)^2 + 0.24 * P] where P = (Max (Fo^2, 0) + 2 * Fc^2) / 3

N	value	esd	shift/esd	parameter
1	0.62921	0.00104	0.048	OSF
2	0.00640	0.00179	0.007	EXTI

Mean shift/esd = 0.056 Maximum = 1.469 for y H8B

Max. shift = 0.101 A for H8B Max. dU =-0.005 for H8A

18.4 seconds elapsed time

Least-squares cycle 4 Maximum vector length = 511 Memory required = 2582 / 329089

wR2 = 0.1062 before cycle 4 for 5627 data and 265 / 265 parameters

GooF = S = 1.028; Restrained GooF = 1.028 for 0 restraints

Weight = 1 / [sigma^2(Fo^2) + (0.0440 * P)^2 + 0.24 * P] where P = (Max (Fo^2, 0) + 2 * Fc^2) / 3

N	value	esd	shift/esd	parameter
1	0.62922	0.00104	0.010	OSF
2	0.00640	0.00179	-0.001	EXTI

Mean shift/esd = 0.034 Maximum = 0.910 for x H8A

Max. shift = 0.062 A for H8B Max. dU =-0.004 for H8A

Largest correlation matrix elements

0.629 U13 O12 / U11 O12	0.535 U33 Cr / OSF	0.528 z O12 / x O12
0.612 U13 O12 / U33 O12	0.534 U11 Cr / OSF	0.518 U13 O13 / U11 O13
0.555 U12 O12 / U23 O12	0.534 U22 Cr / OSF	0.513 U13 O13 / U33 O13

18.4 seconds elapsed time

95adh06e in P-1

ATOM	x	y	z	sof	U11	U22	U33	U23	U13	U12	Ueq
Cr	0.65437	0.72254	0.82866	1.00000	0.02686	0.02032	0.01698	0.00354	0.00689	0.00573	0.02146
	0.00004	0.00003	0.00003	0.00000	0.00013	0.00012	0.00011	0.00008	0.00009	0.00009	0.00008
O7	0.52386	0.95642	0.64831	1.00000	0.03809	0.02893	0.02133	0.01097	0.00482	0.00394	0.03058
	0.00019	0.00013	0.00012	0.00000	0.00068	0.00059	0.00054	0.00046	0.00049	0.00051	0.00027
O8	0.25572	0.72963	0.57763	1.00000	0.03831	0.03702	0.01937	0.00480	-0.00189	0.00601	0.03472
	0.00020	0.00015	0.00013	0.00000	0.00071	0.00069	0.00055	0.00049	0.00050	0.00057	0.00030
O9	0.18826	0.58267	0.76084	1.00000	0.03140	0.03220	0.02845	0.00737	0.00476	-0.00208	0.03299
	0.00019	0.00014	0.00013	0.00000	0.00064	0.00064	0.00062	0.00050	0.00051	0.00052	0.00028
O10	0.86346	1.00601	1.15333	1.00000	0.04785	0.04182	0.02479	0.00247	0.00242	-0.00658	0.04299
	0.00023	0.00016	0.00014	0.00000	0.00085	0.00079	0.00063	0.00056	0.00059	0.00066	0.00036
O11	0.68504	0.83020	1.20010	1.00000	0.04469	0.04742	0.01855	0.01029	0.00669	0.00319	0.03838
	0.00022	0.00016	0.00013	0.00000	0.00079	0.00082	0.00055	0.00053	0.00053	0.00064	0.00032
O12	0.82516	0.73861	0.61183	1.00000	0.07339	0.06521	0.04150	0.01914	0.03837	0.02448	0.05353
	0.00029	0.00020	0.00017	0.00000	0.00120	0.00113	0.00088	0.00080	0.00087	0.00095	0.00044

```
O13     0.61275  0.41774  0.78541   1.00000   0.07164  0.02394  0.05839  0.00682  0.03170  0.01105   0.04907
       0.00027  0.00015  0.00018   0.00000   0.00114  0.00066  0.00101  0.00064  0.00090  0.00070   0.00040

O14     1.04765  0.74498  1.02004   1.00000   0.03260  0.04401  0.04113  0.00576  0.00012  0.01038   0.04221
       0.00021  0.00016  0.00016   0.00000   0.00072  0.00083  0.00080  0.00064  0.00061  0.00062   0.00035

C1      0.50983  0.89156  0.74810   1.00000   0.03314  0.02478  0.01958  0.00712  0.00767  0.00937   0.02551
       0.00025  0.00017  0.00016   0.00000   0.00082  0.00071  0.00066  0.00055  0.00061  0.00063   0.00031

C2      0.36934  0.76566  0.70802   1.00000   0.02782  0.02659  0.01837  0.00392  0.00333  0.00668   0.02531
       0.00024  0.00017  0.00016   0.00000   0.00077  0.00074  0.00064  0.00054  0.00057  0.00062   0.00031

C3      0.33500  0.69418  0.80655   1.00000   0.02701  0.02501  0.02450  0.00488  0.00713  0.00598   0.02586
       0.00024  0.00017  0.00017   0.00000   0.00076  0.00072  0.00073  0.00057  0.00061  0.00060   0.00031

C4      0.45316  0.73843  0.94132   1.00000   0.02898  0.02616  0.02169  0.00689  0.00974  0.00731   0.02497
       0.00025  0.00017  0.00016   0.00000   0.00078  0.00073  0.00069  0.00057  0.00060  0.00061   0.00030

H4      0.44138  0.68516  1.00913   1.00000   0.02351
       0.00297  0.00214  0.00215   0.00000   0.00492

C5      0.59866  0.85867  0.97794   1.00000   0.02973  0.02340  0.01670  0.00236  0.00726  0.00753   0.02336
       0.00024  0.00016  0.00015   0.00000   0.00077  0.00068  0.00062  0.00051  0.00056  0.00059   0.00029

C6      0.62719  0.93751  0.88232   1.00000   0.03200  0.02098  0.01975  0.00413  0.00766  0.00630   0.02444
       0.00026  0.00017  0.00016   0.00000   0.00081  0.00068  0.00066  0.00053  0.00060  0.00062   0.00030

H6      0.71900  1.01411  0.90463   1.00000   0.02664
       0.00315  0.00235  0.00219   0.00000   0.00524

C7      0.67806  1.07571  0.68085   1.00000   0.04522  0.03907  0.02878  0.01450  0.00748 -0.00108   0.03949
       0.00034  0.00023  0.00021   0.00000   0.00115  0.00103  0.00090  0.00080  0.00083  0.00088   0.00046

H7C     0.67009  1.10120  0.59892   1.00000   0.03488
       0.00327  0.00243  0.00245   0.00000   0.00599

H7B     0.65602  1.14848  0.73957   1.00000   0.04080
       0.00360  0.00275  0.00267   0.00000   0.00652

H7A     0.80170  1.05097  0.71989   1.00000   0.04636
       0.00402  0.00280  0.00275   0.00000   0.00698

C8      0.25717  0.60017  0.50600   1.00000   0.06470  0.05252  0.02561 -0.00588  0.00123  0.00986   0.05265
       0.00046  0.00030  0.00024   0.00000   0.00167  0.00142  0.00097  0.00092  0.00103  0.00124   0.00063

H8C     0.18548  0.58902  0.41984   1.00000   0.09167
       0.00566  0.00408  0.00431   0.00000   0.01194

H8B     0.38670  0.60641  0.50058   1.00000   0.12526
       0.00748  0.00492  0.00497   0.00000   0.01712

H8A     0.24218  0.52729  0.54745   1.00000   0.10411
       0.00622  0.00480  0.00451   0.00000   0.01480

C9      0.17005  0.48994  0.84953   1.00000   0.03753  0.03139  0.03690  0.01079  0.01094  0.00113   0.03611
       0.00032  0.00022  0.00022   0.00000   0.00102  0.00090  0.00099  0.00076  0.00083  0.00079   0.00041

H9C     0.28316  0.45400  0.87675   1.00000   0.03532
       0.00352  0.00251  0.00237   0.00000   0.00599

H9B     0.14351  0.53556  0.92949   1.00000   0.05603
       0.00417  0.00304  0.00303   0.00000   0.00801

H9A     0.06863  0.41714  0.80400   1.00000   0.04964
       0.00400  0.00294  0.00280   0.00000   0.00741

C10     0.73279  0.90833  1.11897   1.00000   0.03239  0.02933  0.01920  0.00397  0.00784  0.00889   0.02700
       0.00026  0.00018  0.00016   0.00000   0.00083  0.00078  0.00067  0.00057  0.00061  0.00065   0.00032
```

```
C11       0.80591  0.86732  1.33921    1.00000    0.04920  0.07185  0.01951  0.01271  0.00529  0.01437   0.04790
       0.00040  0.00034  0.00021    0.00000    0.00134  0.00176  0.00082  0.00095  0.00084  0.00125   0.00057

H11C      0.91698  0.84345  1.35439    1.00000    0.06447
       0.00494  0.00332  0.00320    0.00000    0.00933

H11B      0.83137  0.95907  1.36722    1.00000    0.07514
       0.00482  0.00397  0.00352    0.00000    0.01076

H11A      0.72682  0.81937  1.38454    1.00000    0.07329
       0.00479  0.00352  0.00346    0.00000    0.00990

C12       0.76065  0.73155  0.69504    1.00000    0.04194  0.03197  0.02627  0.00832  0.01389  0.01236   0.03206
       0.00029  0.00020  0.00018    0.00000    0.00100  0.00086  0.00079  0.00066  0.00073  0.00076   0.00037

C13       0.62637  0.53553  0.80089    1.00000    0.03479  0.02735  0.02870  0.00605  0.01342  0.00738   0.02953
       0.00027  0.00018  0.00018    0.00000    0.00089  0.00078  0.00080  0.00063  0.00070  0.00068   0.00034

C14       0.89574  0.73695  0.94584    1.00000    0.03366  0.02368  0.02632  0.00322  0.00980  0.00718   0.02803
       0.00027  0.00017  0.00017    0.00000    0.00086  0.00072  0.00076  0.00059  0.00066  0.00064   0.00033



Final Structure Factor Calculation for  95adh06e in P-1

Total number of l.s. parameters =   265     Maximum vector length =  511      Memory required =   2317 /   22484

wR2 =  0.1061 before cycle   5 for   5627 data and     0 /   265 parameters

GooF = S =     1.028;     Restrained GooF =      1.028  for      0 restraints

Weight = 1 / [ sigma^2(Fo^2) + ( 0.0440 * P )^2 +   0.24 * P ]   where  P = ( Max ( Fo^2, 0 ) + 2 * Fc^2 ) / 3

R1 =  0.0404 for   4360 Fo > 4.sigma(Fo)  ).  and  0.0611 for all   5627 data
wR2 =  0.1061,  GooF = S =   1.028,  Restrained GooF =    1.028  for all data

    2.0 seconds elapsed time



Principal mean square atomic displacements U

 0.0274   0.0201   0.0168   Cr
 0.0459   0.0294   0.0164   O7
 0.0504   0.0373   0.0165   O8
 0.0472   0.0276   0.0242   O9
 0.0693   0.0372   0.0225   O10
 0.0576   0.0407   0.0169   O11
 0.0805   0.0574   0.0227   O12
 0.0753   0.0487   0.0232   O13
 0.0572   0.0433   0.0261   O14
 0.0345   0.0245   0.0175   C1
 0.0321   0.0263   0.0175   C2
 0.0287   0.0250   0.0239   C3
 0.0292   0.0259   0.0199   C4
 0.0308   0.0231   0.0162   C5
 0.0330   0.0207   0.0196   C6
 0.0620   0.0345   0.0220   C7
 0.0773   0.0588   0.0218   C8
 0.0469   0.0359   0.0255   C9
 0.0342   0.0277   0.0191   C10
 0.0720   0.0540   0.0177   C11
 0.0427   0.0294   0.0240   C12
 0.0352   0.0271   0.0263   C13
 0.0341   0.0274   0.0226   C14



Analysis of variance for reflections employed in refinement      K = Mean[Fo^2] / Mean[Fc^2]  for group
```

Fc/Fc(max) 0.000 0.010 0.019 0.027 0.036 0.045 0.056 0.068 0.090 0.128 1.000

Number in group 582. 607. 506. 593. 563. 568. 519. 580. 548. 561.

GooF 1.024 1.068 1.022 1.045 1.110 0.990 1.084 0.997 1.026 0.898

K 1.103 1.069 1.063 1.030 1.027 1.015 1.002 1.005 0.998 1.000

Resolution(A) 0.65 0.68 0.70 0.74 0.77 0.82 0.89 0.97 1.12 1.41 inf

Number in group 570. 569. 557. 555. 564. 566. 563. 560. 558. 565.

GooF 0.954 0.972 0.969 0.917 0.909 1.010 0.836 0.935 0.884 1.649

K 1.011 1.010 1.010 1.012 1.017 1.003 0.996 0.990 0.990 1.007

R1 0.161 0.149 0.117 0.095 0.081 0.066 0.041 0.034 0.028 0.030

Recommended weighting scheme: WGHT 0.0356 0.3014

Most Disagreeable Reflections (* if suppressed)

h	k	l	Fo^2	Fc^2	Delta(F^2)/esd	Fc/Fc(max)	Resolution(A)
7	-4	4	22.89	96.47	9.59	0.067	0.86
1	4	1	122.38	64.26	8.16	0.055	1.99
1	0	4	76.83	39.45	7.04	0.043	2.14
-2	-2	5	128.61	74.57	6.93	0.059	1.95
-1	-4	5	59.43	30.01	6.83	0.038	1.72
-1	-3	4	235.27	152.85	6.25	0.085	2.19
0	-3	4	21.26	6.30	5.68	0.017	2.20
2	1	8	198.45	273.60	4.85	0.113	1.04
0	1	4	175.20	116.67	4.73	0.074	2.32
-2	3	0	9.36	0.62	4.67	0.005	2.69
1	-1	1	152.21	104.91	4.60	0.070	4.98
-2	-4	1	50.35	31.70	4.57	0.039	1.89
2	-6	3	22.68	8.88	4.54	0.020	1.47
0	1	5	309.19	231.02	4.36	0.104	1.89
-1	-2	5	136.72	183.15	4.26	0.093	2.05
-3	1	3	88.18	61.13	4.12	0.054	2.30
-3	1	0	71.44	50.80	3.98	0.049	2.38
0	-4	5	27.26	11.18	3.93	0.023	1.72
1	2	4	166.24	216.71	3.91	0.101	1.81
-2	1	2	197.14	254.86	3.88	0.109	3.36
-2	-2	2	216.60	164.84	3.86	0.088	2.71
2	-4	4	22.01	9.79	3.84	0.021	1.64
-4	-6	1	34.14	19.24	3.68	0.030	1.11
0	-5	2	5.31	14.29	3.65	0.026	1.94
-2	5	0	16.17	4.42	3.59	0.014	1.89
1	-3	5	97.60	74.74	3.56	0.059	1.73
-3	-8	10	49.33	26.40	3.53	0.035	0.84
-1	4	0	1040.57	863.10	3.52	0.201	2.47
2	8	9	4.98	32.44	3.49	0.039	0.69
-2	-3	1	344.62	276.61	3.48	0.114	2.26
3	3	0	21.78	11.84	3.44	0.024	1.72
2	2	2	144.89	183.62	3.41	0.093	2.02
-1	-1	2	318.17	256.88	3.40	0.110	4.46
2	1	3	118.54	150.98	3.38	0.084	1.94
0	2	3	266.08	213.72	3.31	0.100	2.54
2	-3	3	32.56	46.04	3.29	0.047	2.00
-1	12	4	13.99	1.31	3.24	0.008	0.75
-3	-5	9	16.70	32.12	3.19	0.039	1.05
-1	1	2	297.80	239.78	3.19	0.106	4.35
1	5	0	256.90	203.14	3.14	0.098	1.77
3	3	11	20.69	2.58	3.11	0.011	0.71
5	-6	10	46.65	26.11	3.04	0.035	0.72

-8	-3	9	56.68	35.88	3.03	0.041	0.80
-1	7	1	35.69	20.65	3.03	0.031	1.39
0	-2	2	636.02	539.42	3.02	0.159	3.88
-2	-2	1	41.50	30.43	3.00	0.038	2.74
4	-8	1	15.26	4.91	2.97	0.015	1.11
3	1	1	74.28	58.56	2.94	0.052	1.97
2	2	0	533.30	447.28	2.92	0.145	2.58
-5	0	1	138.79	169.63	2.92	0.089	1.45

Bond lengths and angles

Cr -	Distance	Angles						
C13	1.830 (0.002)							
C14	1.830 (0.002)	88.11 (0.08)						
C12	1.852 (0.002)	90.17 (0.08)	87.95 (0.08)					
C5	2.163 (0.002)	130.05 (0.07)	89.22 (0.07)	139.56 (0.07)				
C6	2.225 (0.002)	165.35 (0.08)	98.41 (0.07)	103.11 (0.07)	37.71 (0.06)			
C4	2.226 (0.002)	98.28 (0.07)	109.43 (0.07)	160.80 (0.07)	37.33 (0.06)	67.20 (0.06)		
C2	2.280 (0.002)	107.01 (0.08)	164.50 (0.07)	95.21 (0.07)	78.53 (0.06)	66.10 (0.06)	65.86 (0.06)	
C1	2.288 (0.002)	141.82 (0.08)	129.41 (0.07)	85.13 (0.07)	66.14 (0.06)	36.24 (0.06)	77.56 (0.06)	36.34 (0.06)
C3	2.305 (0.002)	89.60 (0.07)	144.55 (0.07)	127.44 (0.08)	65.81 (0.06)	77.46 (0.06)	36.20 (0.06)	35.96 (0.06)
	Cr -	C13	C14	C12	C5	C6	C4	C2

O7 -	Distance	Angles
C1	1.345 (0.002)	
C7	1.441 (0.002)	117.29 (0.14)
	O7 -	C1

O8 -	Distance	Angles
C2	1.359 (0.002)	
C8	1.429 (0.003)	117.14 (0.16)
	O8 -	C2

O9 -	Distance	Angles
C3	1.349 (0.002)	
C9	1.434 (0.002)	118.07 (0.15)
	O9 -	C3

O10 -	Distance	Angles
C10	1.192 (0.002)	
	O10 -	

O11 -	Distance	Angles
C10	1.333 (0.002)	
C11	1.449 (0.002)	116.26 (0.18)
	O11 -	C10

O12 -	Distance	Angles
C12	1.146 (0.002)	
	O12 -	

O13 -	Distance	Angles
C13	1.157 (0.002)	
	O13 -	

O14 -	Distance	Angles
C14	1.155 (0.002)	
	O14 -	

C1 -	Distance	Angles		
O7	1.345 (0.002)			
C6	1.405 (0.002)	124.37 (0.16)		
C2	1.424 (0.002)	115.00 (0.14)	120.58 (0.14)	
Cr	2.288 (0.002)	130.01 (0.12)	69.45 (0.09)	71.54 (0.09)
	C1 -	O7	C6	C2

C2 -	Distance	Angles
O8	1.359 (0.002)	

C3 1.415 (0.002) 122.45 (0.15)
C1 1.424 (0.002) 117.64 (0.15) 119.27 (0.14)
Cr 2.280 (0.002) 134.27 (0.13) 72.96 (0.10) 72.11 (0.09)
C2 - O8 C3 C1

C3 - Distance Angles
O9 1.349 (0.002)
C4 1.410 (0.002) 124.35 (0.15)
C2 1.415 (0.002) 115.31 (0.15) 120.32 (0.15)
Cr 2.305 (0.002) 131.99 (0.12) 68.88 (0.10) 71.08 (0.10)
C3 - O9 C4 C2

C4 - Distance Angles
C3 1.410 (0.002)
C5 1.406 (0.002) 119.31 (0.15)
Cr 2.226 (0.002) 74.92 (0.10) 68.87 (0.09)
H4 0.974 (0.021) 121.69 (1.30) 118.91 (1.28) 124.85 (1.23)
C4 - C3 C5 Cr

C5 - Distance Angles
C4 1.406 (0.002)
C6 1.419 (0.002) 121.36 (0.15)
C10 1.500 (0.002) 121.71 (0.14) 116.92 (0.15)
Cr 2.163 (0.002) 73.80 (0.09) 73.52 (0.09) 124.14 (0.12)
C5 - C4 C6 C10

C6 - Distance Angles
C1 1.405 (0.002)
C5 1.419 (0.002) 118.78 (0.15)
Cr 2.225 (0.002) 74.31 (0.10) 68.76 (0.09)
H6 0.893 (0.023) 119.18 (1.40) 122.02 (1.41) 127.27 (1.40)
C6 - C1 C5 Cr

C7 - Distance Angles
O7 1.441 (0.002)
H7C 0.935 (0.024) 104.54 (1.48)
H7B 0.975 (0.027) 108.98 (1.54) 110.30 (2.07)
H7A 0.983 (0.028) 109.94 (1.61) 109.76 (2.10) 112.99 (2.21)
C7 - O7 H7C H7B

C8 - Distance Angles
O8 1.429 (0.003)
H8C 0.896 (0.042) 110.28 (2.58)
H8B 0.986 (0.051) 107.30 (2.89) 101.59 (3.65)
H8A 0.913 (0.047) 115.37 (2.85) 117.34 (3.78) 103.18 (3.67)
C8 - O8 H8C H8B

C9 - Distance Angles
O9 1.434 (0.002)
H9C 0.958 (0.024) 109.71 (1.42)
H9B 1.013 (0.030) 111.79 (1.65) 111.15 (2.17)
H9A 0.919 (0.029) 108.51 (1.72) 107.58 (2.22) 107.96 (2.32)
C9 - O9 H9C H9B

C10 - Distance Angles
O10 1.192 (0.002)
O11 1.333 (0.002) 124.85 (0.16)
C5 1.500 (0.002) 123.98 (0.16) 111.17 (0.15)
C10 - O10 O11

C11 - Distance Angles
O11 1.449 (0.002)
H11C 0.881 (0.035) 113.15 (2.14)
H11B 0.901 (0.038) 110.20 (2.18) 107.07 (3.01)
H11A 0.983 (0.036) 103.22 (2.06) 112.41 (2.74) 110.83 (2.93)
C11 - O11 H11C H11B

C12 - Distance Angles
O12 1.146 (0.002)
Cr 1.852 (0.002) 179.03 (0.17)

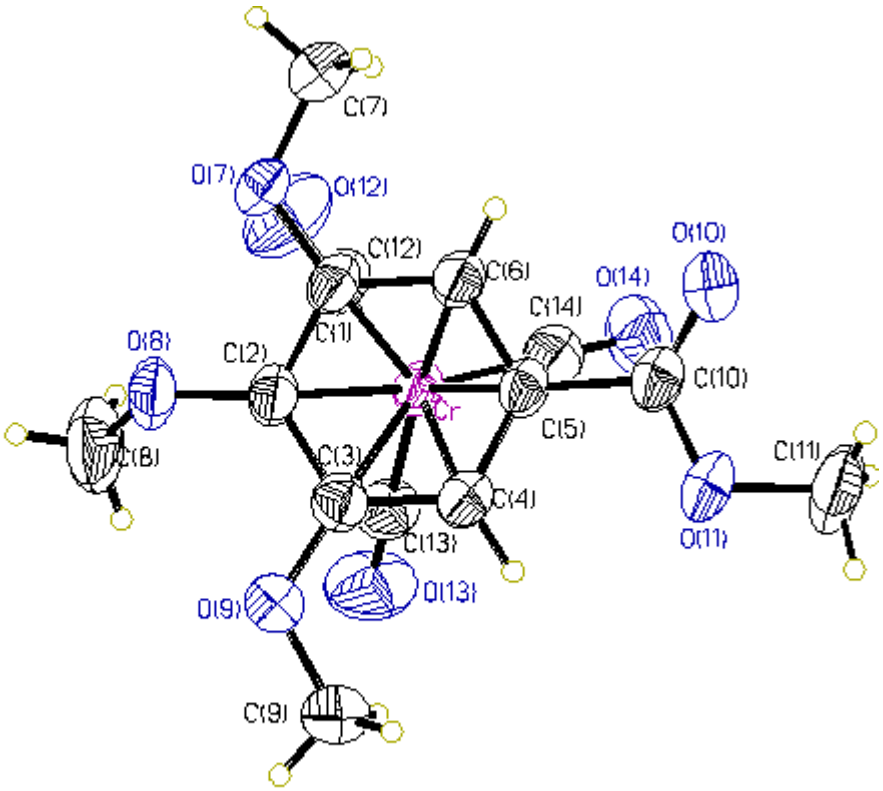
```
          C12 -        O12

C13 -      Distance      Angles
O13        1.157 (0.002)
Cr         1.830 (0.002)   178.46 (0.18)
          C13 -        O13

C14 -      Distance      Angles
O14        1.155 (0.002)
Cr         1.830 (0.002)   179.43 (0.16)
          C14 -        O14

    2.4 seconds elapsed time


FMAP and GRID set by program

FMAP   2   1  24
GRID   -2.381  -2  -2     2.381   2   2

R1 =  0.0597 for   5627 unique reflections after merging


Electron density synthesis with coefficients Fo-Fc

Maximum =    0.44,     Minimum =   -0.39 e/A^3,     Highest memory used =  1319 / 27387
Mean =    0.00,    Rms deviation from mean =    0.07 e/A^3


Fourier peaks appended to .res file

          x      y      z      sof     U      Peak   Distances to nearest atoms (including symmetry equivalents)

Q1    1   0.6192  0.9035  0.9378   1.00000  0.05    0.44   0.69 C5  0.74 C6  1.38 H6  1.86 C10
Q2    1   0.6621  0.8812  1.0379   1.00000  0.05    0.42   0.66 C5  0.85 C10  1.79 O10  1.79 C6
Q3    1   0.3314  0.7350  0.7620   1.00000  0.05    0.39   0.67 C3  0.79 C2  1.71 O9  1.85 C4
Q4    1   0.5626  0.9245  0.8178   1.00000  0.05    0.35   0.69 C6  0.73 C1  1.35 H6  1.83 O7
Q5    1   0.5498  0.7835  0.9378   1.00000  0.05    0.31   0.79 C5  0.80 C4  1.59 H4  1.71 CR
Q6    1   0.4499  0.8210  0.7423   1.00000  0.05    0.31   0.71 C2  0.76 C1  1.75 C3  1.79 C6
Q7    1   0.6822  0.7431  0.7380   1.00000  0.05    0.31   0.87 C12  1.09 CR  1.98 O12  2.15 C1
Q8    1   0.7479  0.7223  0.7581   1.00000  0.05    0.30   0.73 C12  1.18 CR  1.85 O12  1.95 C14
Q9    1   0.8082  0.7600  0.8783   1.00000  0.05    0.26   0.90 C14  1.09 CR  1.86 C12  2.01 O14
Q10   1   0.2580  0.6408  0.8019   1.00000  0.05    0.26   0.70 C3  0.71 O9  1.75 C9  1.77 C4
Q11   1   0.2610  0.6147  0.4419   1.00000  0.05    0.26   0.54 H8C  0.73 C8  0.98 H8B  1.55 H8A
Q12   1   0.5461  0.6761  0.8177   1.00000  0.05    0.25   0.83 CR  1.60 C3  1.64 C13  1.78 C4
Q13   1   0.3917  0.7180  0.8822   1.00000  0.05    0.25   0.64 C4  0.77 C3  1.40 H4  1.84 C5
Q14   1   0.1894  0.5547  0.7817   1.00000  0.05    0.25   0.38 O9  1.06 C9  1.56 C3  1.61 H9A
Q15   1   0.5983  0.7992  1.1778   1.00000  0.05    0.24   0.63 O11  1.68 C10  1.89 C11  1.92 H4
Q16   1   0.7528  0.9803  1.0982   1.00000  0.05    0.24   0.79 C10  0.83 O10  1.64 C5  2.06 O11
Q17   1   0.8981  0.9622  1.1385   1.00000  0.05    0.24   0.58 O10  1.21 C10  2.22 O11  2.34 H7A
Q18   1   0.3135  0.6404  0.4820   1.00000  0.05    0.24   0.67 C8  0.69 H8B  0.99 H8C  1.49 O8
Q19   1   0.6723  0.8646  1.1779   1.00000  0.05    0.23   0.45 O11  0.99 C10  1.71 C11  1.95 O10
Q20   1   0.9617  1.0309  1.1987   1.00000  0.05    0.23   0.73 O10  1.82 C10  2.08 H7A  2.44 H11B

Shortest distances between peaks (including symmetry equivalents)

  11  18  0.49     7   8  0.56    15  19  0.78    17  20  0.84    10  14  0.89     1   2  1.09     2  16  1.10
  16  17  1.10    10  13  1.18     5  13  1.18     3  10  1.21     8   9  1.21     3   6  1.22     1   5  1.23
   4   6  1.23     3  13  1.27     1   4  1.28     2   5  1.31     7   9  1.48     2  19  1.51    16  20  1.56
   5  12  1.56    12  13  1.61     7  12  1.64    16  19  1.67     1  16  1.70     2  17  1.75     3  12  1.77
   8  12  1.84     9  12  1.88     6  12  1.90     2  15  1.95    13  14  1.96    17  19  2.00     3  14  2.01
   3   5  2.02     6  13  2.04     4   5  2.04     6   7  2.04     1   6  2.06    10  12  2.09     5   6  2.11
   1  13  2.18     3   4  2.23     5   9  2.27     5  10  2.33     4   7  2.35     1   9  2.35     1  12  2.36
   2   4  2.37     2  13  2.38     5  16  2.38    15  16  2.39     6  10  2.40     1  17  2.42     5  19  2.43
  19  20  2.44     5  15  2.47     2  20  2.47     4  12  2.48     4  13  2.54     1   3  2.55     6   8  2.57
   1  19  2.58     2   9  2.59    12  14  2.64     5   7  2.65     4   9  2.67     3   7  2.72     1   7  2.73
  15  17  2.73     2  12  2.73     4   8  2.77     4  16  2.84     6   9  2.85     5   8  2.85     9  20  2.86
   8  20  2.90     6  18  2.91     1  15  2.94     5  17  2.94     1   8  2.98     4  19  2.99     3  18  2.99

    2.2 seconds elapsed time
```

```
++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
+ calctest     finished at 20:29:34   Total elapsed time:     87.0 secs  +
          ++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++++
```

Using **XP** after this cycle allows one to check that all the bond lengths and angles are reasonable and to look for disorder etc. [Note: the Hydrogens on carbon 8 have large displacement parameters that are about twice those of the other Hydrogens (i.e., seen from 'info'), probably reflecting greater motion.] A displacement ellipsoid plot (**telp 0 -75 0.04 0 [ent] calctest.8 [ent]**) (Note: this plot is now anisotropic) of this molecule at this stage of refinement is plotted on the following page. For some structures, this cycle will have to be repeated before the refinement goes to final convergence (i.e., the atoms aren't shifting any more). In the chapter after this one (i.e., Tables for calctest, (η^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$Cr(CO)_3$), the Tables for this example are presented. For some structures, this cycle will have to be repeated before the refinement goes to final convergence (i.e., the atoms aren't shifting any more).

4. Plot calctest.8, After The 8th Cycle

(i.e., When all Non-Hydrogen Atoms Have Been Refined Using Anisotropic Displacement Parameters, all Hydrogen Atoms Have Been Refined Using Isotropic Displacement Parameters, and Extinction and the Weighting Function have Been Added to the Refinement.)



[Note: Made with graphics file CALCTEST.8hc.GIF]

I. THE 9TH CYCLE: USING XL TO DRIVE THE SOLUTION TO CONVERGENCE

This sections involves the seventh refinement cycle by **XL**. This takes the atom positions and anisotropic displacement parameters for non-Hydrogen atoms and the isotropic displacement parameters for Hydrogen atoms from the sixth **XL** and then uses least squares refinement to improve the atomic positions and displacement parameters and to refine a few additional parameters such as extinction. It then calculates a residual electron density map (i.e., the Q peaks) which one uses **XP** to check the results and prepare the final plots and then uses **XCIF** to prepare the tables. It requires the following **calctest.ins** input file and produces the following **calctest.res** and **calctest.lst** output files.

We often change the L.S. command in **calctest.ins** file (by editing it in **DOS**) to about 10 or 15 to ensure that refinement is complete.

1. CALCTEST.INS Input File for 9th Cycle: Using XL to do the Final Refinement Cycles

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR   2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50

L.S. .10
BOND $H
FMAP 2
PLAN 20

ACTA

WGHT    0.044000    0.240000
EXTI    0.006399
FVAR       0.62922
CR    4   0.65437   0.72254   0.82866  11.00000   0.02686   0.02032 =
     0.01698   0.00354   0.00689   0.00573
O7    3   0.52386   0.95642   0.64831  11.00000   0.03809   0.02893 =
     0.02133   0.01097   0.00482   0.00394
O8    3   0.25572   0.72963   0.57763  11.00000   0.03831   0.03702 =
     0.01937   0.00480  -0.00189   0.00601
O9    3   0.18826   0.58267   0.76084  11.00000   0.03140   0.03220 =
     0.02845   0.00737   0.00476  -0.00208
O10   3   0.86346   1.00601   1.15333  11.00000   0.04785   0.04182 =
     0.02479   0.00247   0.00242  -0.00658
O11   3   0.68504   0.83020   1.20010  11.00000   0.04469   0.04742 =
```

```
     0.01855   0.01029   0.00669   0.00319
O12  3  0.82516  0.73861  0.61183 11.00000  0.07339  0.06521 =
     0.04150   0.01914   0.03837   0.02448
O13  3  0.61275  0.41774  0.78541 11.00000  0.07164  0.02394 =
     0.05839   0.00682   0.03170   0.01105
O14  3  1.04765  0.74498  1.02004 11.00000  0.03260  0.04401 =
     0.04113   0.00576   0.00012   0.01038
C1   1  0.50983  0.89156  0.74810 11.00000  0.03314  0.02478 =
     0.01958   0.00712   0.00767   0.00937
C2   1  0.36934  0.76566  0.70802 11.00000  0.02782  0.02659 =
     0.01837   0.00392   0.00333   0.00668
C3   1  0.33500  0.69418  0.80655 11.00000  0.02701  0.02501 =
     0.02450   0.00488   0.00713   0.00598
C4   1  0.45316  0.73843  0.94132 11.00000  0.02898  0.02616 =
     0.02169   0.00689   0.00974   0.00731
H4   2  0.44138  0.68516  1.00913 11.00000  0.02351
C5   1  0.59866  0.85867  0.97794 11.00000  0.02973  0.02340 =
     0.01670   0.00236   0.00726   0.00753
C6   1  0.62719  0.93751  0.88232 11.00000  0.03200  0.02098 =
     0.01975   0.00413   0.00766   0.00630
H6   2  0.71900  1.01411  0.90463 11.00000  0.02664
C7   1  0.67806  1.07571  0.68085 11.00000  0.04522  0.03907 =
     0.02878   0.01450   0.00748  -0.00108
H7C  2  0.67009  1.10120  0.59892 11.00000  0.03488
H7B  2  0.65602  1.14848  0.73957 11.00000  0.04080
H7A  2  0.80170  1.05097  0.71989 11.00000  0.04636
C8   1  0.25717  0.60017  0.50600 11.00000  0.06470  0.05252 =
     0.02561  -0.00588   0.00123   0.00986
H8C  2  0.18548  0.58902  0.41984 11.00000  0.09167
H8B  2  0.38670  0.60641  0.50058 11.00000  0.12526
H8A  2  0.24218  0.52729  0.54745 11.00000  0.10411
C9   1  0.17005  0.48994  0.84953 11.00000  0.03753  0.03139 =
     0.03690   0.01079   0.01094   0.00113
H9C  2  0.28316  0.45400  0.87675 11.00000  0.03532
H9B  2  0.14351  0.53556  0.92949 11.00000  0.05603
H9A  2  0.06863  0.41714  0.80400 11.00000  0.04964
C10  1  0.73279  0.90833  1.11897 11.00000  0.03239  0.02933 =
     0.01920   0.00397   0.00784   0.00889
C11  1  0.80591  0.86732  1.33921 11.00000  0.04920  0.07185 =
     0.01951   0.01271   0.00529   0.01437
H11C 2  0.91698  0.84345  1.35439 11.00000  0.06447
H11B 2  0.83137  0.95907  1.36722 11.00000  0.07514
H11A 2  0.72682  0.81937  1.38454 11.00000  0.07329
C12  1  0.76065  0.73155  0.69504 11.00000  0.04194  0.03197 =
     0.02627   0.00832   0.01389   0.01236
C13  1  0.62637  0.53553  0.80089 11.00000  0.03479  0.02735 =
     0.02870   0.00605   0.01342   0.00738
C14  1  0.89574  0.73695  0.94584 11.00000  0.03366  0.02368 =
     0.02632   0.00322   0.00980   0.00718

HKLF 4
END
```

On a Gateway2000® Pentium computer running at 166 MHz and with 32 MB of RAM, this **XL** calculation look a total of 197 seconds for 265 parameters.

After the refinement, there is no significant change in any of the R values, etc. In the final cycle, the largest shift for any atom (in this case H8A) was 0.002 and the largest shift in a displacement parameter was 0.000 for H8A and the largest shift/standard uncertainty for any parameter was now less than 0.01 for all atoms.

2. CALCTEST.RES Output File for 9th Cycle: Using XL to do the Final Refinement Cycles

```
TITL 95adh06e in P-1
CELL 0.71073   7.5265  10.0508  10.7429  97.271 108.116  99.782
ZERR   2.00   0.0003   0.0005   0.0005   0.004   0.004   0.004
LATT  1
SFAC C H O CR
UNIT 28 28 16 2
TEMP -50

L.S. 10
BOND $H
FMAP 2
PLAN 20

ACTA

WGHT    0.044000    0.240000
EXTI    0.006355
FVAR       0.62919
CR    4  0.65437  0.72254  0.82866  11.00000   0.02686   0.02032 =
     0.01697  0.00354  0.00689  0.00573
O7    3  0.52386  0.95643  0.64833  11.00000   0.03809   0.02892 =
     0.02133  0.01098  0.00482  0.00396
O8    3  0.25571  0.72963  0.57765  11.00000   0.03828   0.03704 =
     0.01936  0.00482 -0.00186  0.00603
O9    3  0.18825  0.58267  0.76084  11.00000   0.03143   0.03223 =
     0.02844  0.00735  0.00473 -0.00206
O10   3  0.86345  1.00601  1.15335  11.00000   0.04784   0.04181 =
     0.02478  0.00247  0.00245 -0.00658
O11   3  0.68506  0.83021  1.20009  11.00000   0.04464   0.04743 =
     0.01856  0.01028  0.00669  0.00314
O12   3  0.82516  0.73862  0.61183  11.00000   0.07336   0.06531 =
     0.04149  0.01914  0.03838  0.02446
O13   3  0.61277  0.41774  0.78541  11.00000   0.07166   0.02393 =
     0.05842  0.00685  0.03178  0.01103
O14   3  1.04766  0.74498  1.02004  11.00000   0.03260   0.04404 =
     0.04110  0.00577  0.00012  0.01041
C1    1  0.50984  0.89157  0.74810  11.00000   0.03314   0.02479 =
     0.01958  0.00712  0.00764  0.00938
C2    1  0.36932  0.76566  0.70802  11.00000   0.02782   0.02657 =
     0.01837  0.00392  0.00334  0.00666
C3    1  0.33499  0.69418  0.80655  11.00000   0.02703   0.02501 =
     0.02449  0.00489  0.00715  0.00597
C4    1  0.45318  0.73844  0.94132  11.00000   0.02900   0.02619 =
     0.02167  0.00689  0.00974  0.00734
H4    2  0.44108  0.68494  1.00927  11.00000   0.02389
C5    1  0.59866  0.85866  0.97793  11.00000   0.02974   0.02341 =
     0.01669  0.00236  0.00726  0.00757
C6    1  0.62718  0.93750  0.88232  11.00000   0.03202   0.02097 =
     0.01975  0.00411  0.00766  0.00628
H6    2  0.71844  1.01387  0.90473  11.00000   0.02661
C7    1  0.67805  1.07572  0.68084  11.00000   0.04517   0.03907 =
```

```
     0.02880   0.01449   0.00745  -0.00106
H7C    2   0.67004   1.10138   0.59847  11.00000   0.03451
H7B    2   0.65605   1.14812   0.73989  11.00000   0.04071
H7A    2   0.80150   1.05101   0.72024  11.00000   0.04679
C8     1   0.25710   0.60015   0.50600  11.00000   0.06528   0.05221 =
     0.02548  -0.00570   0.00106   0.01003
H8C    2   0.18358   0.58779   0.42071  11.00000   0.09233
H8B    2   0.38881   0.61360   0.49524  11.00000   0.12818
H8A    2   0.25598   0.52894   0.54903  11.00000   0.09593
C9     1   0.17004   0.48995   0.84951  11.00000   0.03749   0.03135 =
     0.03689   0.01077   0.01089   0.00109
H9C    2   0.28311   0.45401   0.87659  11.00000   0.03538
H9B    2   0.14351   0.53546   0.92953  11.00000   0.05520
H9A    2   0.06925   0.41706   0.80381  11.00000   0.04979
C10    1   0.73278   0.90833   1.11897  11.00000   0.03241   0.02930 =
     0.01919   0.00397   0.00784   0.00890
C11    1   0.80592   0.86730   1.33922  11.00000   0.04924   0.07181 =
     0.01952   0.01268   0.00530   0.01439
H11C   2   0.91747   0.84378   1.35466  11.00000   0.06470
H11B   2   0.83140   0.95842   1.36755  11.00000   0.07589
H11A   2   0.72703   0.81890   1.38472  11.00000   0.07287
C12    1   0.76062   0.73155   0.69503  11.00000   0.04199   0.03199 =
     0.02625   0.00828   0.01388   0.01237
C13    1   0.62639   0.53553   0.80090  11.00000   0.03480   0.02736 =
     0.02871   0.00605   0.01343   0.00738
C14    1   0.89572   0.73695   0.94584  11.00000   0.03362   0.02368 =
     0.02634   0.00321   0.00980   0.00716
HKLF 4
END

WGHT     0.0362     0.2614
Q1   1   0.6191  0.9034  0.9379  11.00000  0.05   0.44
Q2   1   0.6622  0.8812  1.0379  11.00000  0.05   0.42
Q3   1   0.3316  0.7350  0.7621  11.00000  0.05   0.39
Q4   1   0.5624  0.9245  0.8178  11.00000  0.05   0.35
Q5   1   0.5500  0.7833  0.9378  11.00000  0.05   0.31
Q6   1   0.4501  0.8211  0.7423  11.00000  0.05   0.31
Q7   1   0.6822  0.7430  0.7380  11.00000  0.05   0.31
Q8   1   0.7477  0.7222  0.7581  11.00000  0.05   0.31
Q9   1   0.2599  0.6146  0.4419  11.00000  0.05   0.26
Q10  1   0.2581  0.6407  0.8019  11.00000  0.05   0.26
Q11  1   0.8083  0.7601  0.8783  11.00000  0.05   0.26
Q12  1   0.5459  0.6761  0.8177  11.00000  0.05   0.26
Q13  1   0.1903  0.5551  0.7818  11.00000  0.05   0.25
Q14  1   0.3920  0.7179  0.8822  11.00000  0.05   0.25
Q15  1   0.5989  0.7993  1.1778  11.00000  0.05   0.24
Q16  1   0.7526  0.9802  1.0982  11.00000  0.05   0.24
Q17  1   0.8979  0.9625  1.1385  11.00000  0.05   0.24
Q18  1   0.6762  0.8604  1.1579  11.00000  0.05   0.23
Q19  1   0.9618  1.0309  1.1987  11.00000  0.05   0.23
Q20  1   0.7689  0.7729  0.8182  11.00000  0.05   0.23
```

3. CALCTEST.LST Output File for 9th Cycle: Using XL to do the Final Refinement Cycles

18 pages of text. See the computer copies of these files.

The Structure has now converged and the bond lengths and angle won't improve with further refinement *of this model*. [Note: the plots from this molecule at the end of this 9th cycle of refinement are visually indistinguishable from those after the last cycle shown in Plot calctest.8, above

CHAPTER X. EXAMPLES OF MOLECULAR PLOTS GENERATED USING XP FOR THE TEST DATA SET "PLOTTEST", (h^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$CR(CO)_3$)

There are an almost limitless number of ways one can use **XP** to illustrate a least squares planes calculated by XP. Some of the most common are described in the following section with a series of examples of such plots for one molecule (95ADH06e referred to as "plottest", (η^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$Cr(CO)_3$). The setting up of these plots are described in detail in chapter VII above. The refinement of this structure is also illustrated in chapter IX, above (i.e., as the **calctest.*** input and output files).

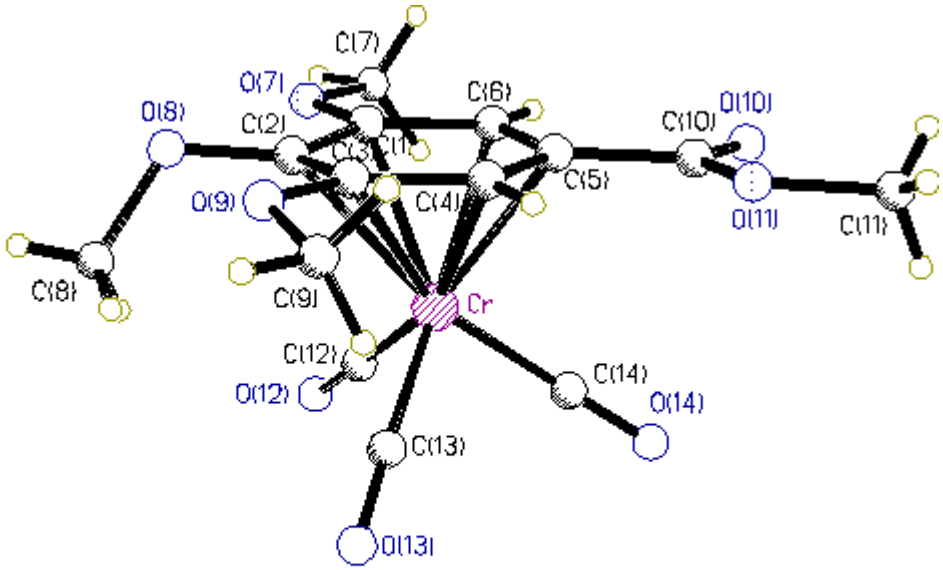
Plot Name	Plot Features
plottest.a	**telp [ent]** A standard ball and stick plot.
plottest.b	**telp 0 -50 0.04 0 [ent]** A displacement ellipsoid view with 50% ellipsoids.
plottest.c	**telp 0 -100 0.04 0 [ent]** A displacement ellipsoid view with 100% ellipsoids.
plottest.d	**telp 0 -75 0.04 0 [ent]** A displacement ellipsoid view with 75% ellipsoids.
plottest.e	**proj cell [ent] telp 0 -75 0.04 0 CELL [ent]** This gives a displacement ellipsoid plot of the molecule in the orientation chosen in 'proj' with 75% ellipsoids.
plottest.f	**telp 0 -75 0.04 0 less $H [ent]** A displacement ellipsoid view with 75% ellipsoids and without Hydrogens.
plottest.g	**telp 3 50 0.08 50 [ent]** A *stereo* view of the molecule.
plottest.h	**proj cell [ent] telp 3 50 0.08 50 CELL [ent]** This gives a *stereo* view of the molecule and the unit cell.
plottest.i	**telp 3 -50 0.08 50 [ent]** A *stereo* displacement ellipsoid view with 50% ellipsoids and with "fatter" bonds
plottest.j	**prun Cr [ent] telp 0 -75 0.04 0 [ent]**

	After all bonds to the Cr atom removed. A displacement ellipsoid view with 75% ellipsoids.
plottest.k	**join Cr C12 [ent] join Cr C13 [ent] join Cr C14 [ent] telp 0 -75 0.04 0 [ent]** After the bonds to the carbonyl carbons are added back. A displacement ellipsoid view with 75% ellipsoids.
plottest.l	**cent/x C1 to C6 [ent] join Cr X1A [ent] telp 0 -75 0.04 0 [ent]** After a dummy atom has been added in the centroid of the arene ring (i.e., X1A) and connected to the Cr atom. A displacement ellipsoid view with 75% ellipsoids.
plottest.m	**invt [ent] proj [ent] telp 0 -75 0.04 0 [ent]** This gives a displacement ellipsoid plot of the inverted molecule having 75% ellipsoids.
plottest.n	**pbox 5 5 [ent] pack [ent] proj [ent] telp CELL [ent]** A view of the packing with a orientation chosen in 'proj'.
plottest.o	**pbox 5 5 [ent] pack [ent] matr 1 [ent] telp CELL [ent]** A view chosen down the a axis of the unit cell.
plottest.p	**pbox 5 5 [ent] pack [ent] matr 2 [ent] telp CELL [ent]** A view chosen down the b axis of the unit cell.
plottest.q	**pbox 5 5 [ent] pack [ent] matr 3 [ent] telp CELL [ent]** A view chosen down the c axis of the unit cell.
plottest.r	**sfil [ent]** A 'SFIL' space filling plot.
plottest.s	**sfil 3 50 [ent]** A *stereo* 'SFIL' space filling plot.

Note: Because of difficulties I have had as yet in importing the graphics into this Microsoft Word/.pdf file, all of the following plots are at substantially lower resolution than they are when produced directly by XP and also are approximately 40% smaller.

A. PLOTTEST.A A STANDARD BALL AND STICK PLOT.

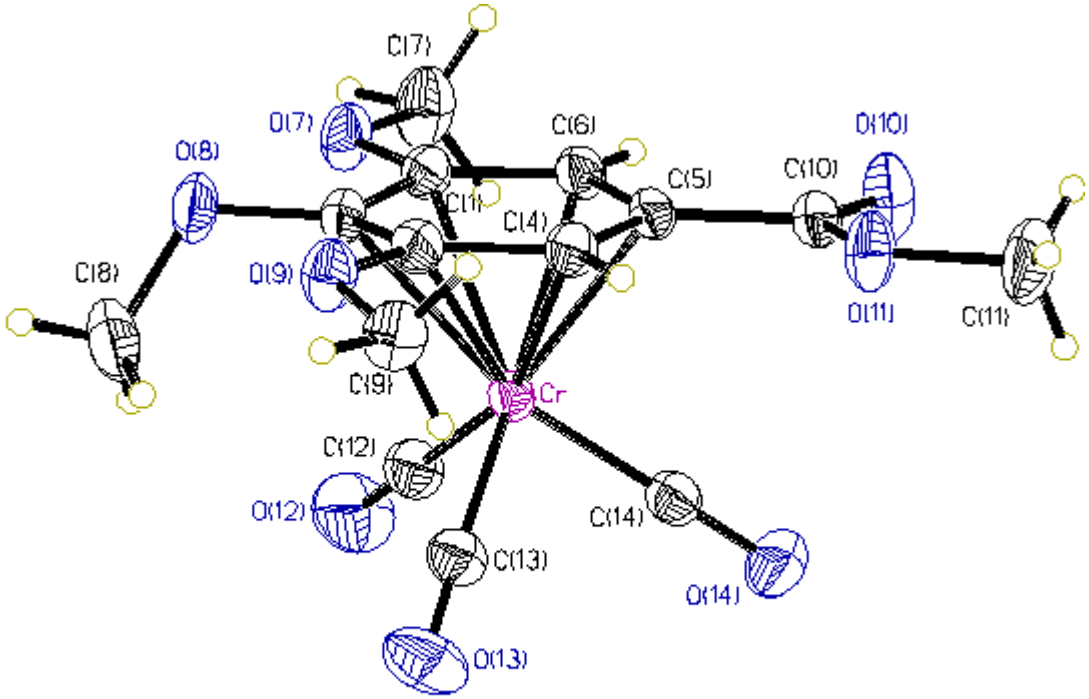
telp [ent]



[Note: Made with graphics file PLOTTEST.Ahc.GIF]

B. PLOTTEST.B A DISPLACEMENT ELLIPSOID VIEW WITH 50% ELLIPSOIDS.

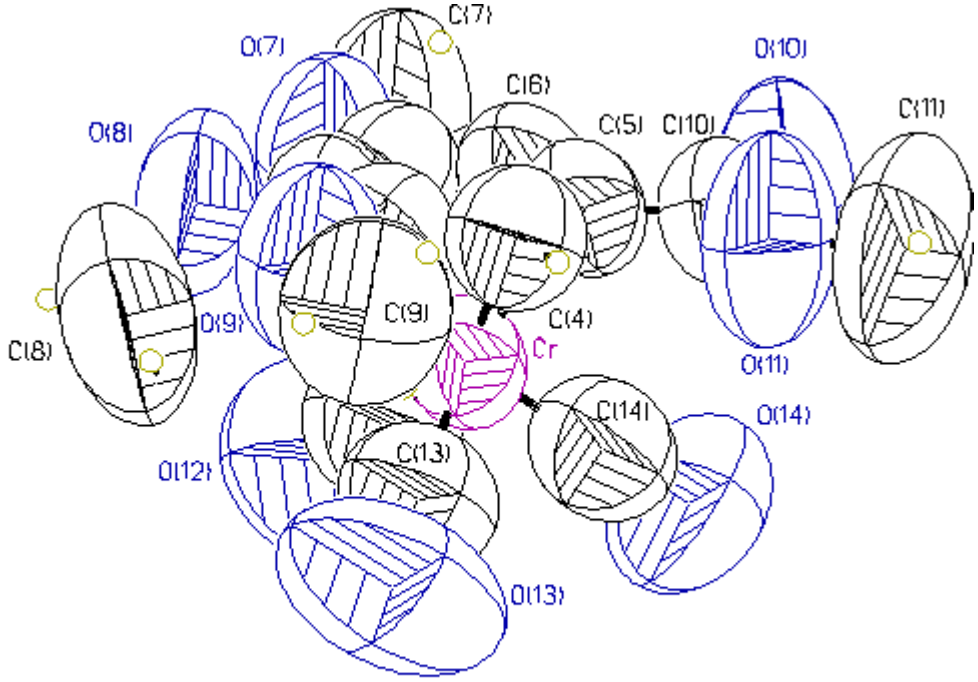
telp 0 -50 0.04 0 [ent]



[Note: Made with graphics file PLOTTEST.Bhc.GIF]

C. PLOTTEST.C A DISPLACEMENT ELLIPSOID VIEW WITH 100% ELLIPSOIDS.

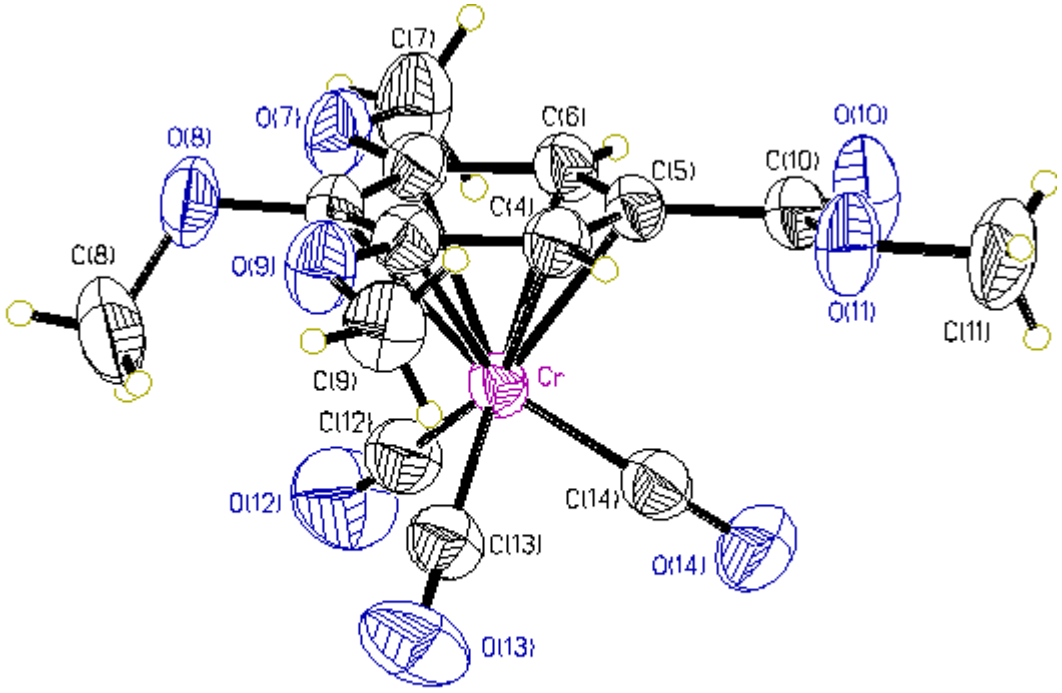
telp 0 -100 0.04 0 [ent]



[Note: Made with graphics file PLOTTEST.Chc.GIF]

D. PLOTTEST.D A DISPLACEMENT ELLIPSOID VIEW WITH 75% ELLIPSOIDS.

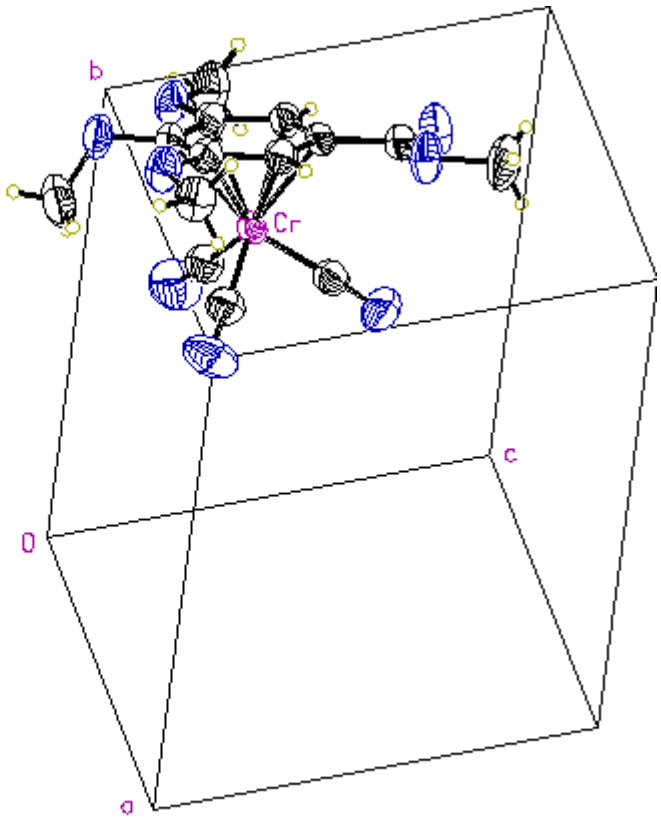
telp 0 -75 0.04 0 [ent]



[Note: Made with graphics file PLOTTEST.Dhc.GIF]

E. PLOTTEST.E THIS GIVES A DISPLACEMENT ELLIPSOID PLOT OF THE MOLECULE IN THE ORIENTATION CHOSEN IN 'PROJ' WITH 75% ELLIPSOIDS.

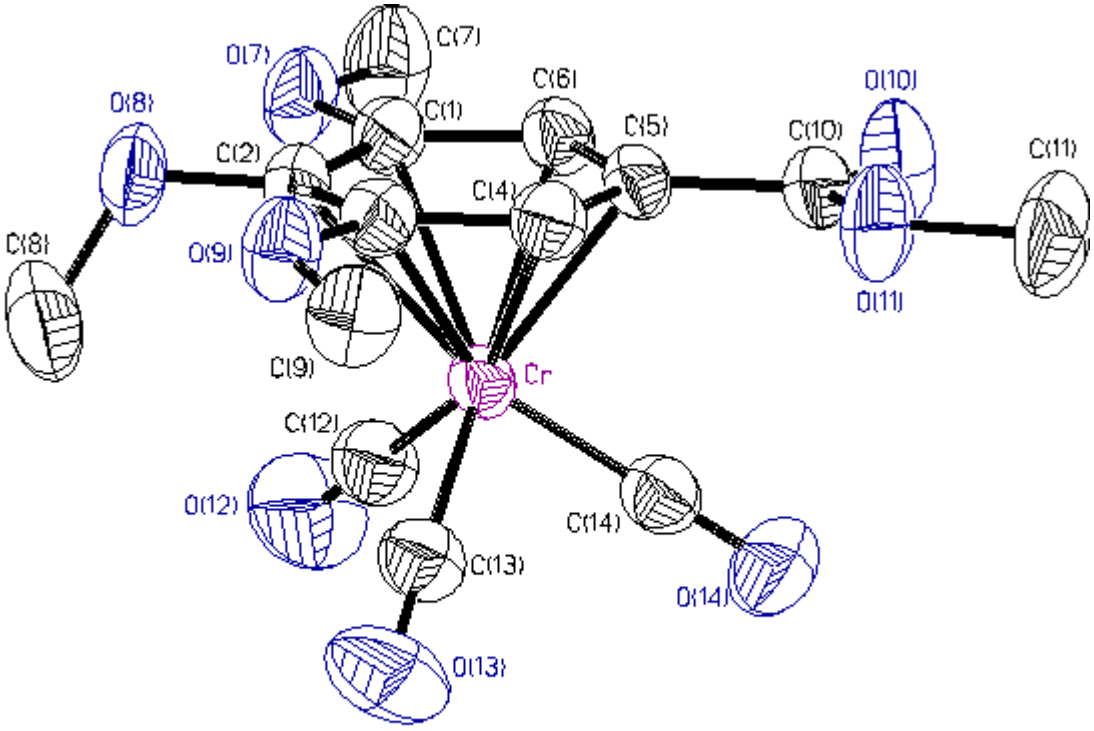
proj cell [ent] telp 0 -75 0.04 0 CELL [ent]



[Note: Made with graphics file PLOTTEST.Ehc.GIF]

F. PLOTTEST.F A DISPLACEMENT ELLIPSOID VIEW WITH 75% ELLIPSOIDS AND WITHOUT HYDROGENS.

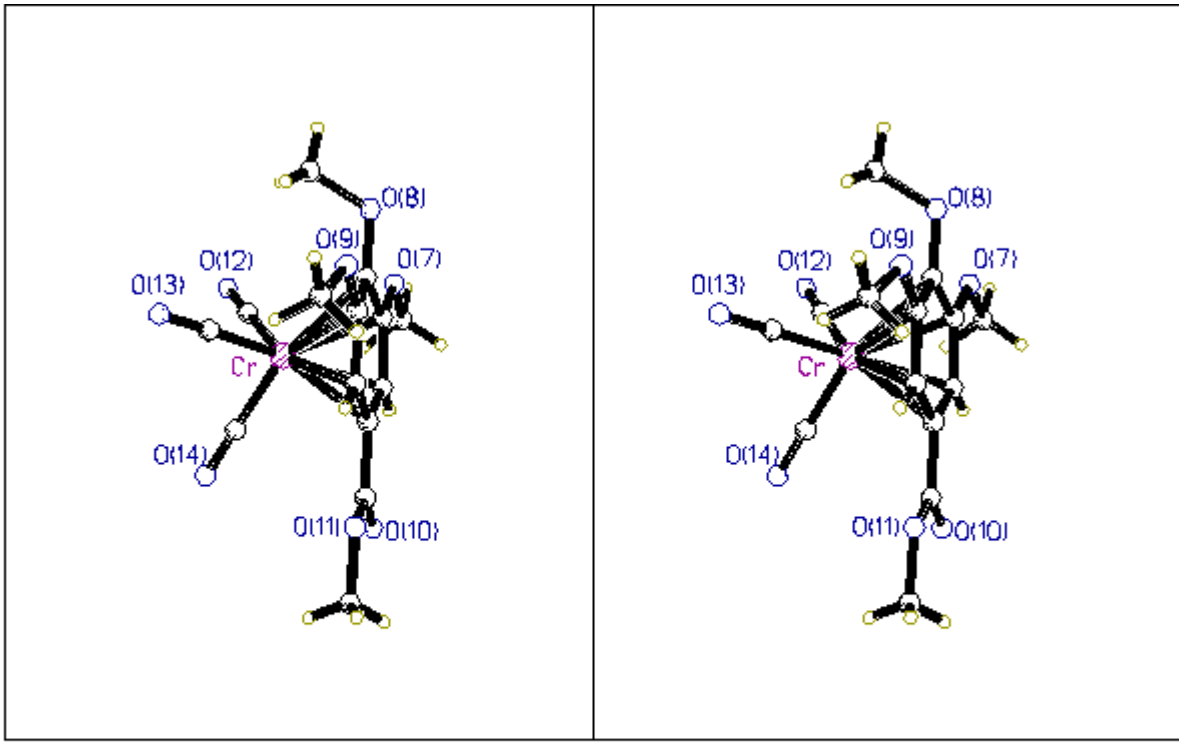
telp 0 -75 0.04 0 less $H [ent]



[Note: Made with graphics file PLOTTEST.Fhc.GIF]

G. PLOTTEST.G A *STEREO* VIEW OF THE MOLECULE.

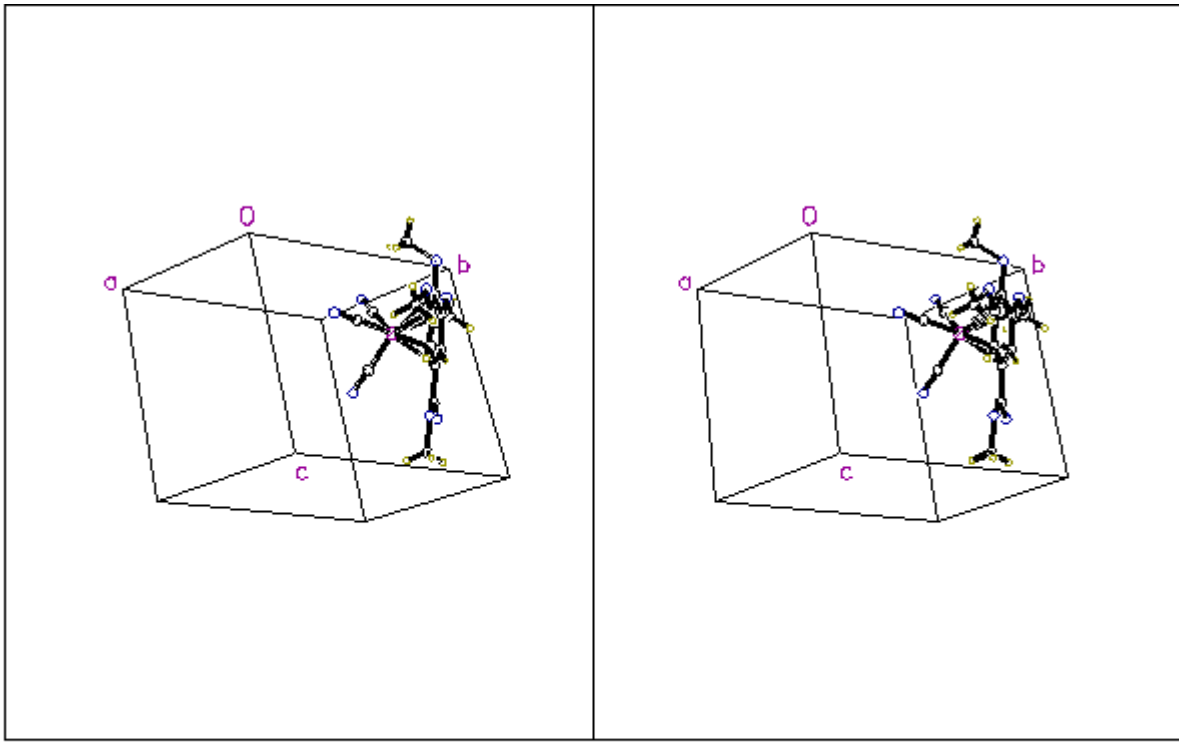
telp 3 50 0.08 50 [ent]



[Note: Made with graphics file PLOTTEST.Ghc.GIF]

H. PLOTTEST.H THIS GIVES A *STEREO* VIEW OF THE MOLECULE AND THE UNIT CELL.

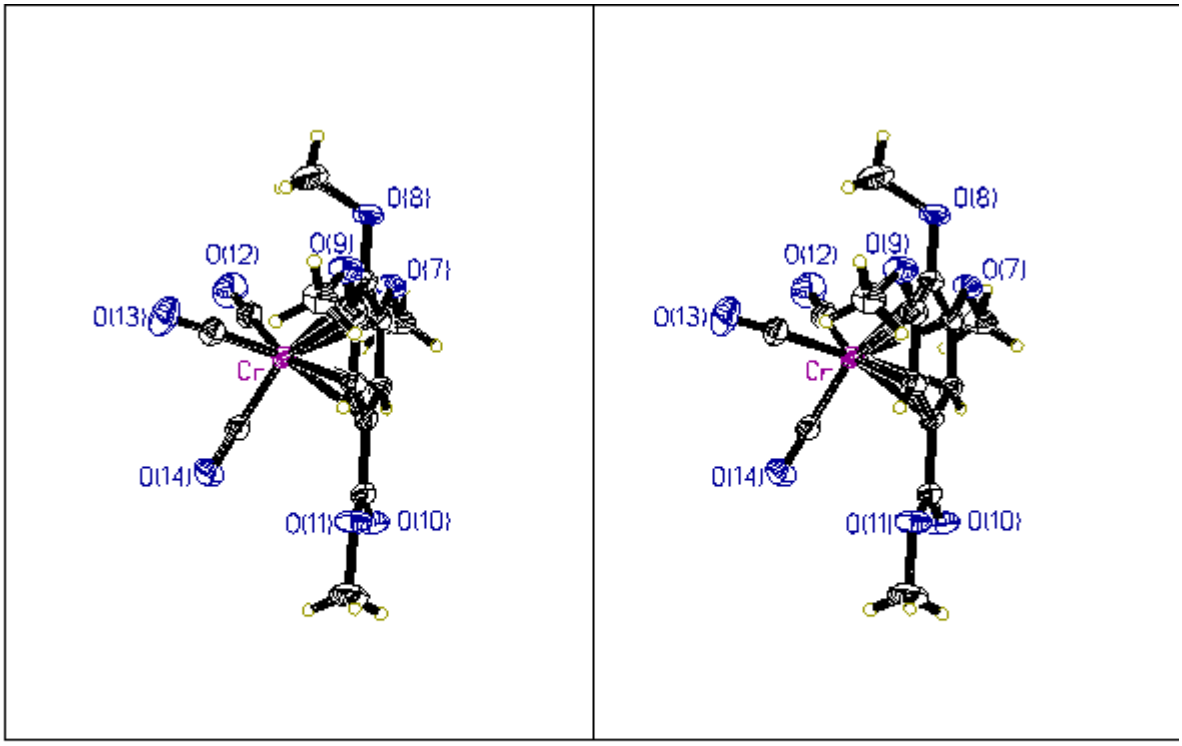
proj cell [ent]
telp 3 50 0.08 50 CELL [ent]



[Note: Made with graphics file PLOTTEST.Hhc.GIF]

I. PLOTTEST.I A S*TEREO* DISPLACEMENT ELLIPSOID VIEW OF THE MOLECULE WITH 50% ELLIPSOIDS AND WITH "FATTER" BONDS.

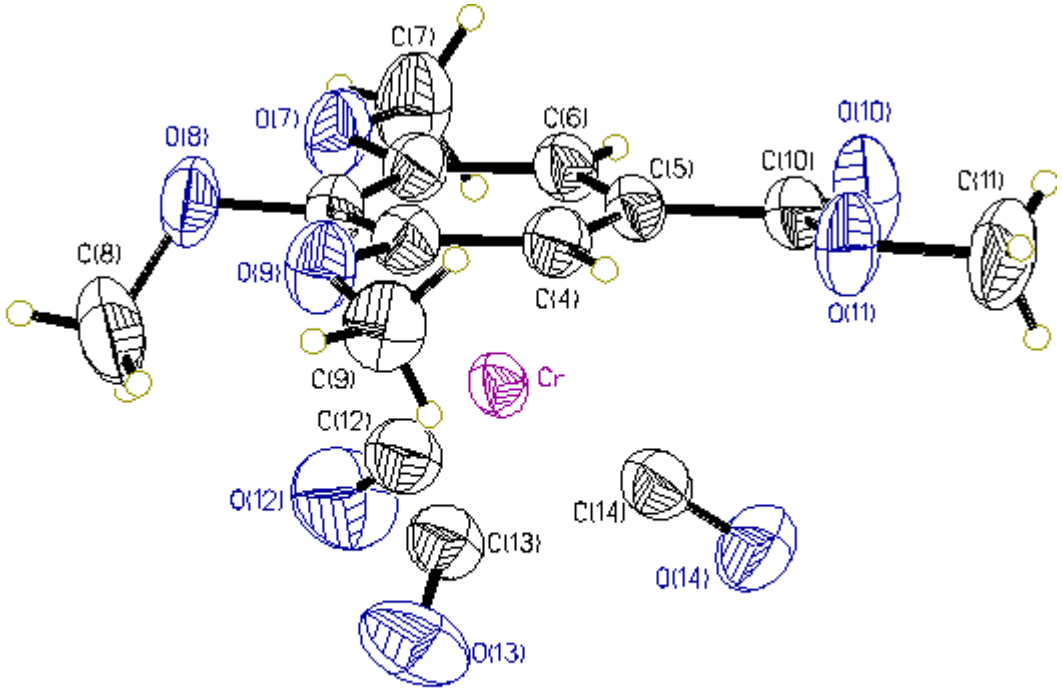
telp 3 -50 0.08 50 [ent]



[Note: Made with graphics file PLOTTEST.Ihc.GIF]

J. PLOTTEST.J AFTER ALL BONDS TO THE CR ATOM REMOVED. A DISPLACEMENT ELLIPSOID VIEW WITH 75% ELLIPSOIDS.

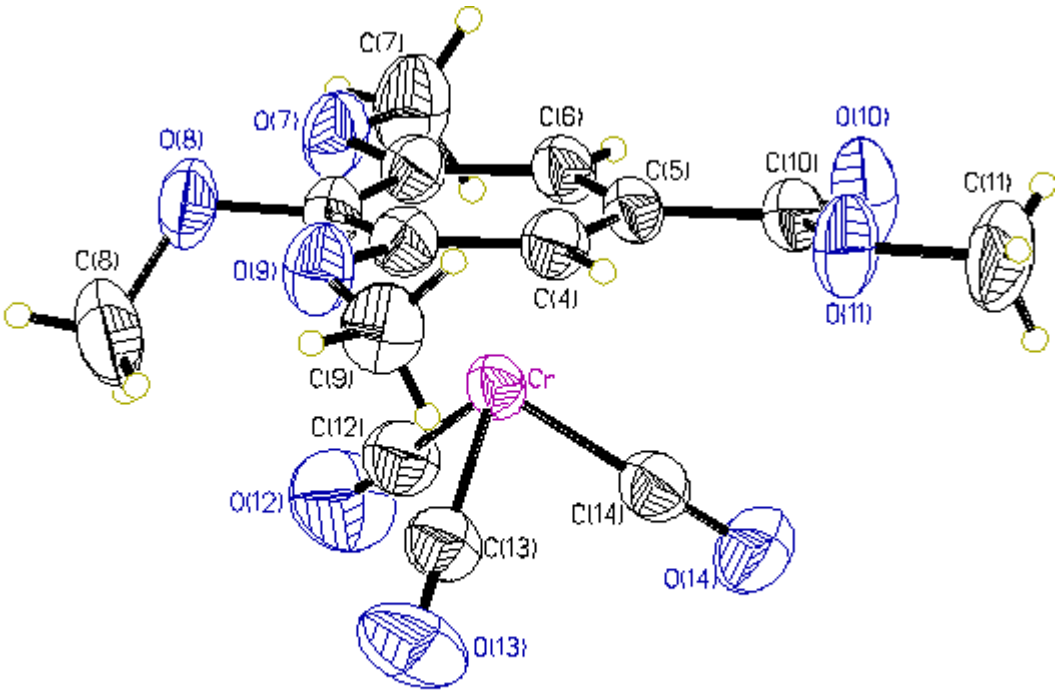
prun Cr [ent] telp 0 -75 0.04 0 [ent]



[Note: Made with graphics file PLOTTEST.Jhc.GIF]

K. PLOTTEST.K AFTER THE BONDS TO THE CARBONYL CARBONS ARE ADDED BACK. A DISPLACEMENT ELLIPSOID VIEW WITH 75% ELLIPSOIDS.

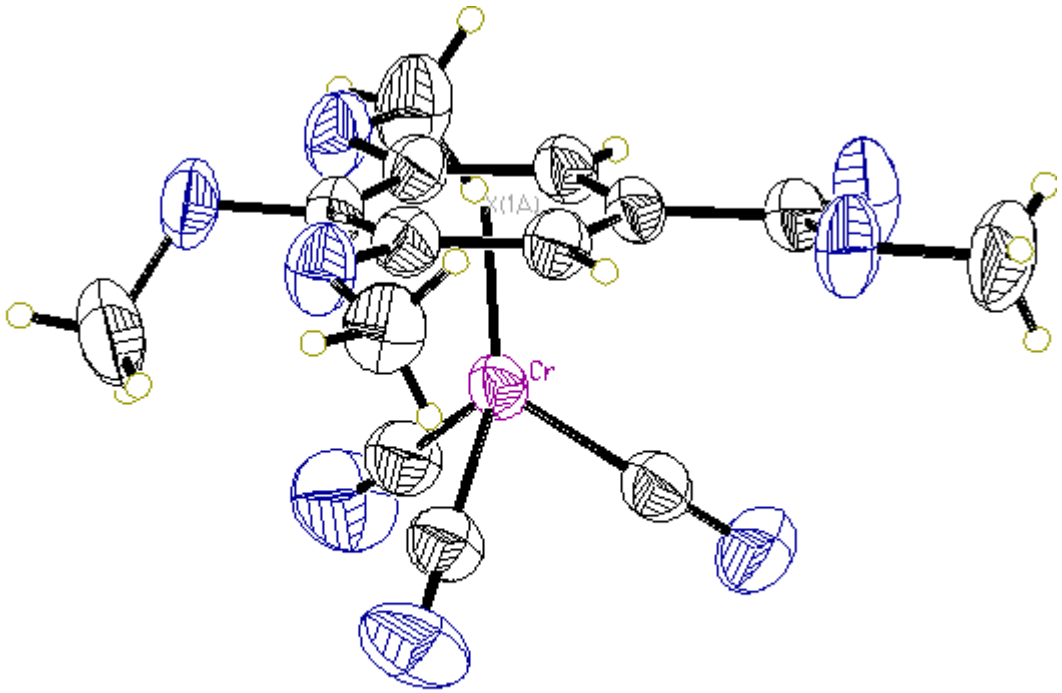
join Cr C12 [ent] join Cr C13 [ent] join Cr C14 [ent] telp 0 -75 0.04 0 [ent]



[Note: Made with graphics file PLOTTEST.Khc.GIF]

L. PLOTTEST.L AFTER A DUMMY ATOM HAS BEEN ADDED IN THE CENTROID OF THE ARENE RING (I.E., X1A) AND CONNECTED TO THE CR ATOM. A DISPLACEMENT ELLIPSOID VIEW WITH 75% ELLIPSOIDS.

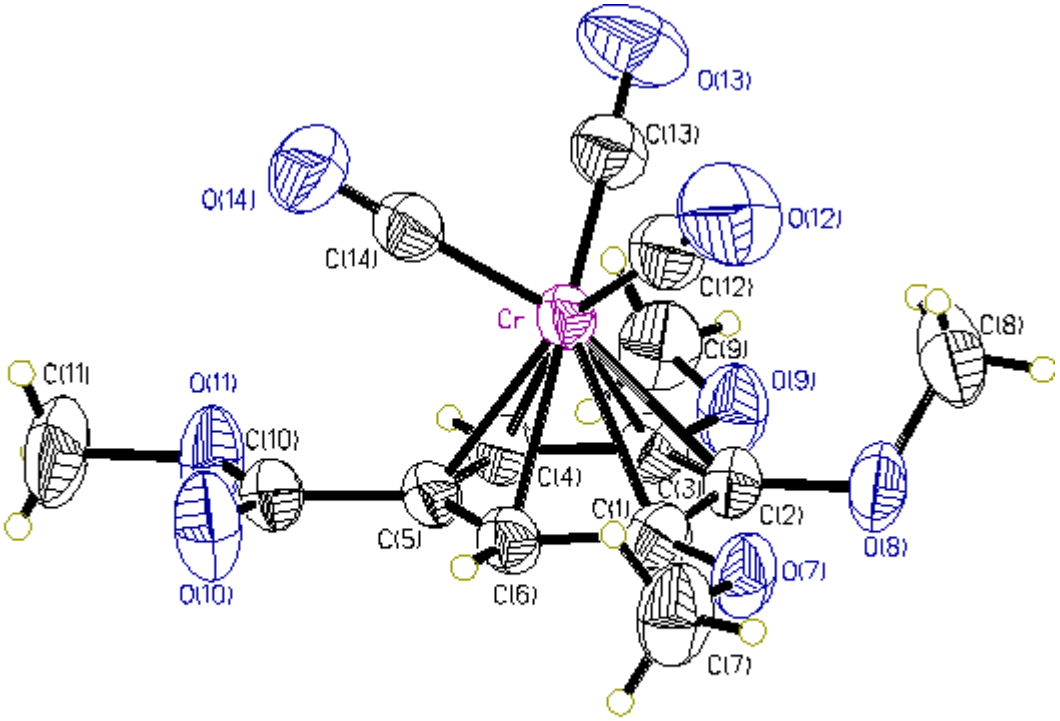
cent/x C1 to C6 [ent] join Cr X1A [ent] telp 0 -75 0.04 0 [ent]



[Note: Made with graphics file PLOTTEST.Lhc.GIF]

M. PLOTTEST.M THIS GIVES AND DISPLACEMENT ELLIPSOID PLOT OF THE INVERTED MOLECULE HAVING 75% ELLIPSOIDS.

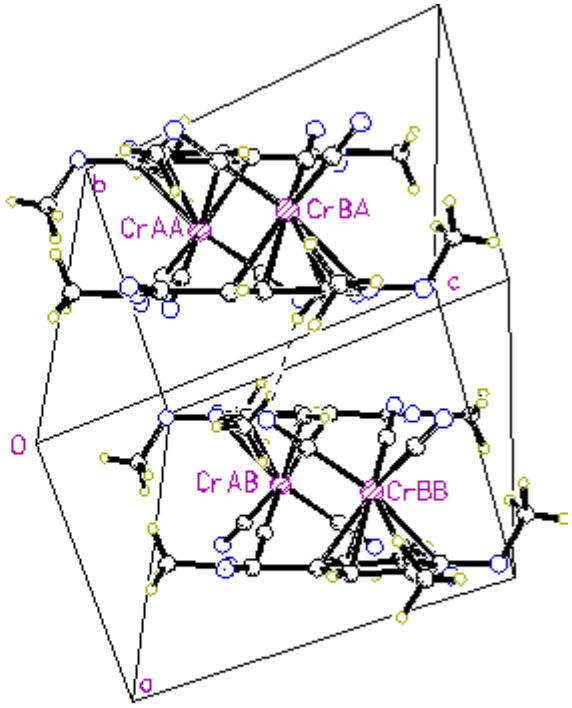
invt [ent] proj [ent] telp 0 -75 0.04 0 [ent]



[Note: Made with graphics file PLOTTEST.Mhc.GIF]

N. PLOTTEST.N A VIEW OF THE PACKING WITH A ORIENTATION CHOSEN IN 'PROJ'.

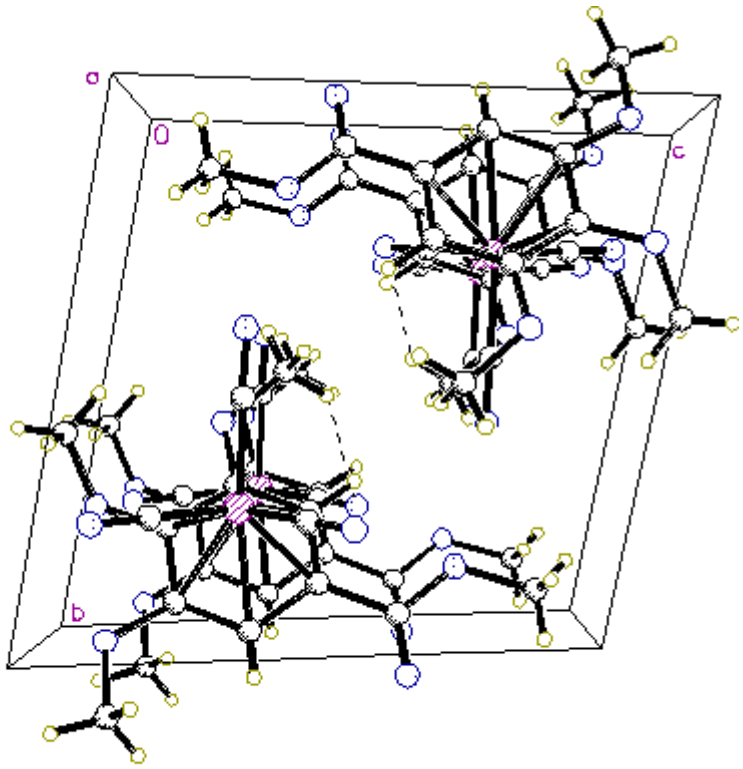
pbox 5 5 [ent] pack [ent] proj [ent] telp CELL [ent]



[Note: Made with graphics file PLOTTEST.Nhc.GIF]

O. PLOTTEST.O A VIEW CHOSEN DOWN THE A AXIS OF THE UNIT CELL..

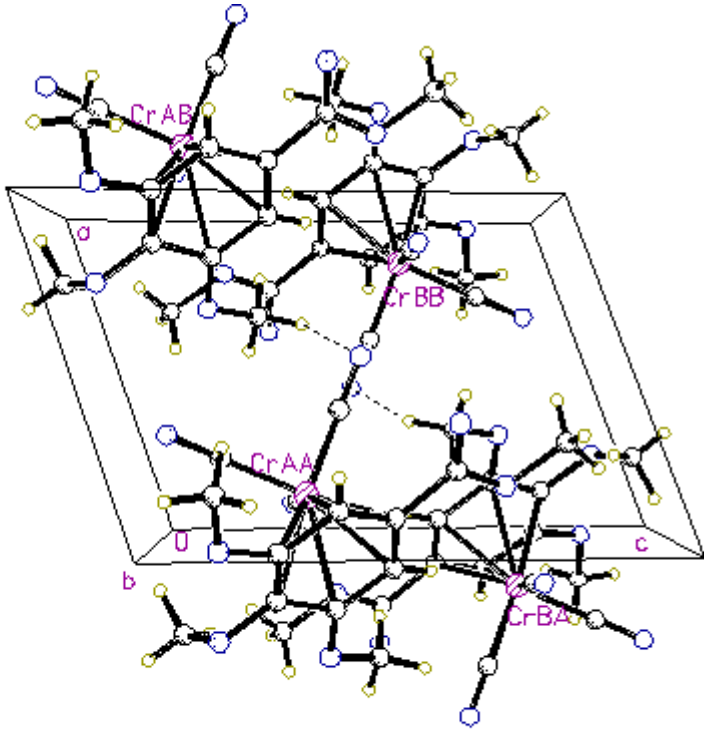
pbox 5 5 [ent] pack [ent] matr 1 [ent] telp CELL [ent]



[Note: Made with graphics file PLOTTEST.Ohc.GIF]

P. PLOTTEST.P A VIEW CHOSEN DOWN THE B AXIS OF THE UNIT CELL..

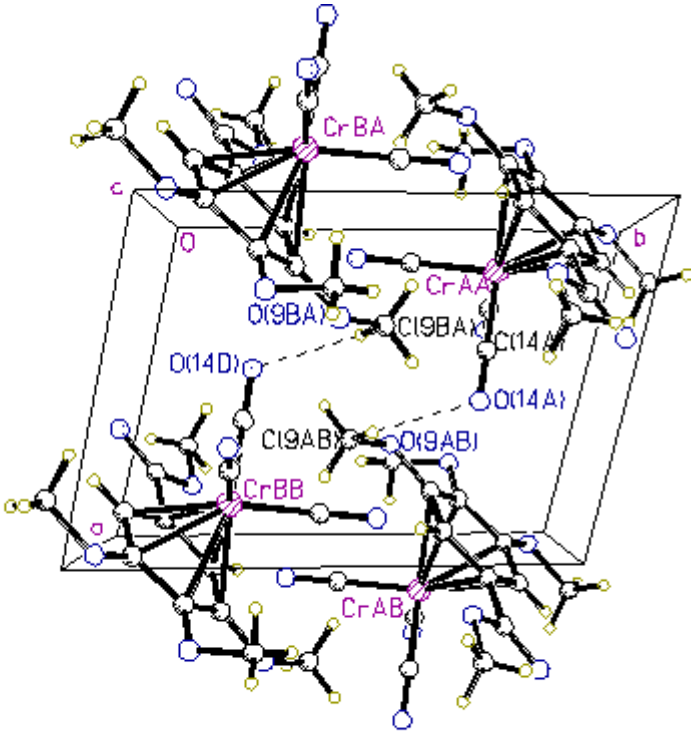
pbox 5 5 [ent] pack [ent] matr 2 [ent] telp CELL [ent]



[Note: Made with graphics file PLOTTEST.Phc.GIF]

Q. PLOTTEST.Q A VIEW CHOSEN DOWN THE C AXIS OF THE UNIT CELL..

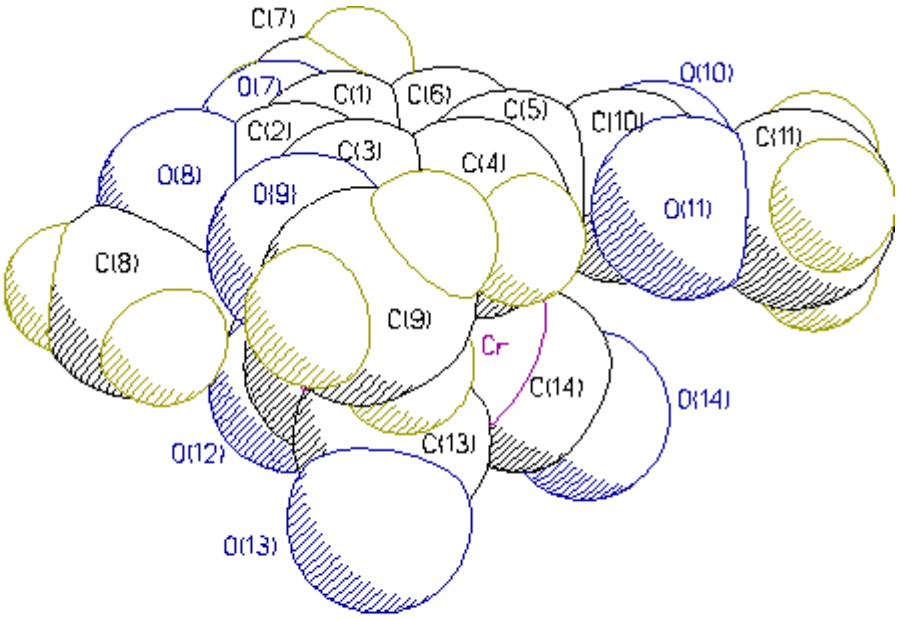
pbox 5 5 [ent] pack [ent] matr 3 [ent] telp CELL [ent]



[Note: Made with graphics file PLOTTEST.Qhc.GIF]

R. PLOTTEST.R A 'SFIL' SPACE FILLING PLOT.

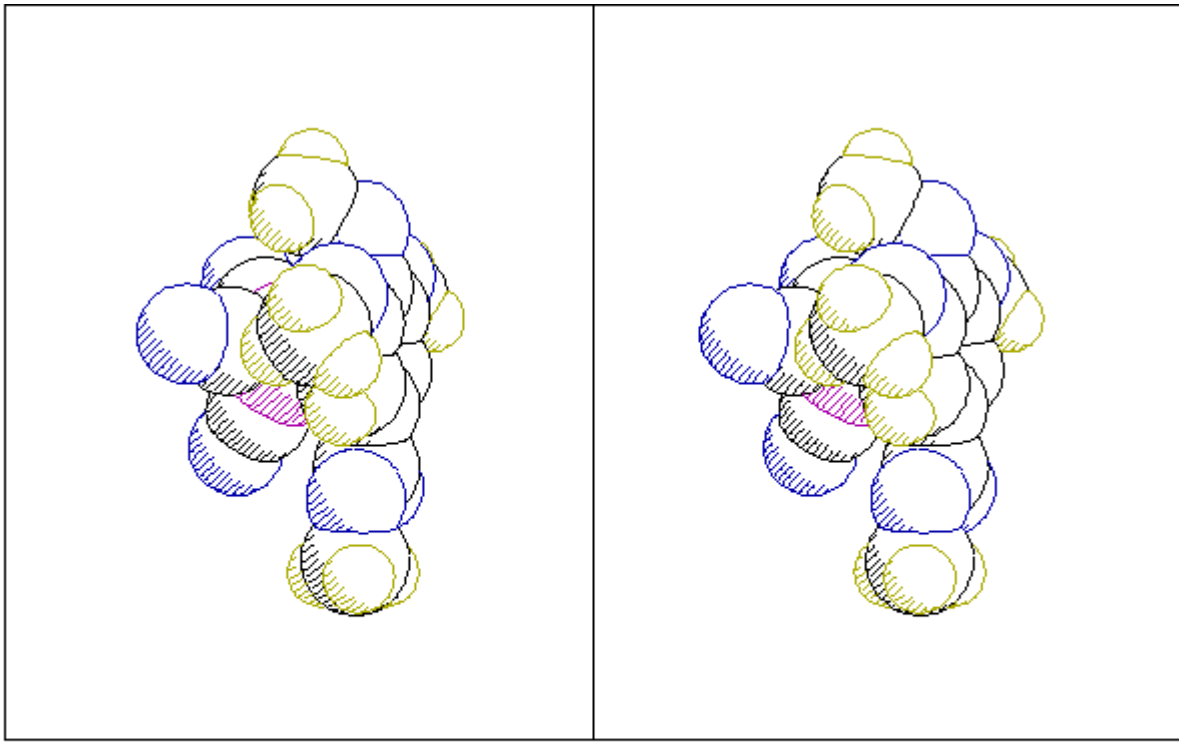
sfil [ent]



[Note: Made with graphics file PLOTTEST.Rhc.GIF]

S. PLOTTEST.S A *STEREO* 'SFIL' SPACE FILLING PLOT.

sfil 3 50 [ent]



[Note: Made with graphics file PLOTTEST.Shc.GIF]

CHAPTER XI. EXAMPLES OF TABLES GENERATED USING XCIF FOR THE TEST DATA SET "CALCTEST", (h^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$CR(CO)_3$)

The following are the standard tables of final results for the test structure "calctest," (η^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$Cr(CO)_3$ that are produced by **XCIF**. They are in a form suitable for publication.

A. TABLE 1. CRYSTAL DATA AND STRUCTURE REFINEMENT FOR "CALCTEST", (h^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$CR(CO)_3$)

Table 1. Crystal data and structure refinement for 1.

Identification code	calctest
Empirical formula	C14 H14 Cr O8
Formula weight	362.25
Temperature	223(2) K
Wavelength	0.71073 A
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 7.5265(3) A alpha = 97.271(4) deg. b = 10.0508(5) A beta = 108.116(4) deg. c = 10.7429(5) A gamma = 99.782(4) deg.
Volume, Z	747.07(6) A^3, 2
Density (calculated)	1.610 Mg/m^3
Absorption coefficient	0.806 mm^-1
F(000)	372
Crystal size	.12 x .28 x .36 mm
Theta range for data collection	2.03 to 33.00 deg.
Limiting indices	-1≤h≤11, -15≤k≤15, -16≤l≤16
Reflections collected	8074
Independent reflections	5627 [R(int) = 0.0231]
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	0.7232 and 0.6426
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5627 / 0 / 265
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0404, wR2 = 0.0961
R indices (all data)	R1 = 0.0610, wR2 = 0.1061
Extinction coefficient	0.006(2)
Largest diff. peak and hole	0.439 and -0.388 e.A^-3

[Note: This table and the others that follow were originally in courier font.]

B. TABLE 2. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS FOR "CALCTEST", (h^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$CR(CO)_3$)

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 1. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor .

	x	y	z	U(eq)
Cr	6544(1)	7225(1)	8287(1)	21(1)
O(7)	5239(2)	9564(1)	6483(1)	31(1)
O(8)	2557(2)	7296(2)	5777(1)	35(1)
O(9)	1883(2)	5827(1)	7608(1)	33(1)
O(10)	8634(2)	10060(2)	11534(1)	43(1)
O(11)	6851(2)	8302(2)	12001(1)	38(1)
O(12)	8252(3)	7386(2)	6118(2)	54(1)
O(13)	6128(3)	4177(2)	7854(2)	49(1)
O(14)	10477(2)	7450(2)	10200(2)	42(1)
C(1)	5098(3)	8916(2)	7481(2)	26(1)
C(2)	3693(2)	7657(2)	7080(2)	25(1)
C(3)	3350(2)	6942(2)	8065(2)	26(1)
C(4)	4532(2)	7384(2)	9413(2)	25(1)
C(5)	5987(2)	8587(2)	9779(2)	23(1)
C(6)	6272(3)	9375(2)	8823(2)	24(1)
C(7)	6780(3)	10757(2)	6808(2)	40(1)
C(8)	2571(5)	6002(3)	5060(2)	53(1)
C(9)	1700(3)	4900(2)	8495(2)	36(1)
C(10)	7328(3)	9083(2)	11190(2)	27(1)
C(11)	8059(4)	8673(3)	13392(2)	48(1)
C(12)	7606(3)	7315(2)	6950(2)	32(1)
C(13)	6264(3)	5355(2)	8009(2)	30(1)
C(14)	8957(3)	7370(2)	9458(2)	28(1)

TABLE 3. BOND LENGTHS AND ANGLES FOR "CALCTEST", (h^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$CR(CO)_3$)

Table 3. Bond lengths [A] and angles [deg] for 1.

Cr-C(14)	1.830(2)
Cr-C(13)	1.831(2)
Cr-C(12)	1.852(2)
Cr-C(5)	2.163(2)
Cr-C(6)	2.225(2)
Cr-C(4)	2.226(2)
Cr-C(2)	2.280(2)
Cr-C(1)	2.288(2)
Cr-C(3)	2.305(2)
O(7)-C(1)	1.345(2)
O(7)-C(7)	1.441(2)
O(8)-C(2)	1.359(2)
O(8)-C(8)	1.429(3)
O(9)-C(3)	1.349(2)
O(9)-C(9)	1.434(2)
O(10)-C(10)	1.192(2)
O(11)-C(10)	1.333(2)
O(11)-C(11)	1.449(2)
O(12)-C(12)	1.146(2)
O(13)-C(13)	1.157(2)
O(14)-C(14)	1.156(2)
C(1)-C(6)	1.405(2)
C(1)-C(2)	1.425(2)
C(2)-C(3)	1.415(2)
C(3)-C(4)	1.410(2)
C(4)-C(5)	1.406(2)
C(4)-H(4)	0.98(2)
C(5)-C(6)	1.419(2)
C(5)-C(10)	1.500(2)
C(6)-H(6)	0.89(2)
C(7)-H(7C)	0.94(2)
C(7)-H(7B)	0.97(3)
C(7)-H(7A)	0.98(3)
C(8)-H(8C)	0.89(4)
C(8)-H(8B)	1.02(5)
C(8)-H(8A)	0.90(4)
C(9)-H(9C)	0.96(2)
C(9)-H(9B)	1.01(3)
C(9)-H(9A)	0.92(3)
C(11)-H(11C)	0.88(3)
C(11)-H(11B)	0.90(4)
C(11)-H(11A)	0.99(4)
C(14)-Cr-C(13)	88.10(8)
C(14)-Cr-C(12)	87.96(8)
C(13)-Cr-C(12)	90.16(8)
C(14)-Cr-C(5)	89.21(7)
C(13)-Cr-C(5)	130.05(7)
C(12)-Cr-C(5)	139.56(7)
C(14)-Cr-C(6)	98.41(7)
C(13)-Cr-C(6)	165.35(8)
C(12)-Cr-C(6)	103.11(7)
C(5)-Cr-C(6)	37.71(6)
C(14)-Cr-C(4)	109.42(7)

C(13)-Cr-C(4)	98.29(7)
C(12)-Cr-C(4)	160.80(7)
C(5)-Cr-C(4)	37.32(6)
C(6)-Cr-C(4)	67.19(6)
C(14)-Cr-C(2)	164.50(7)
C(13)-Cr-C(2)	107.02(8)
C(12)-Cr-C(2)	95.21(7)
C(5)-Cr-C(2)	78.53(6)
C(6)-Cr-C(2)	66.10(6)
C(4)-Cr-C(2)	65.86(6)
C(14)-Cr-C(1)	129.41(7)
C(13)-Cr-C(1)	141.83(8)
C(12)-Cr-C(1)	85.12(7)
C(5)-Cr-C(1)	66.14(6)
C(6)-Cr-C(1)	36.24(6)
C(4)-Cr-C(1)	77.56(6)
C(2)-Cr-C(1)	36.34(6)
C(14)-Cr-C(3)	144.55(7)
C(13)-Cr-C(3)	89.60(7)
C(12)-Cr-C(3)	127.43(8)
C(5)-Cr-C(3)	65.81(6)
C(6)-Cr-C(3)	77.46(6)
C(4)-Cr-C(3)	36.20(6)
C(2)-Cr-C(3)	35.96(6)
C(1)-Cr-C(3)	64.50(6)
C(1)-O(7)-C(7)	117.30(14)
C(2)-O(8)-C(8)	117.2(2)
C(3)-O(9)-C(9)	118.1(2)
C(10)-O(11)-C(11)	116.3(2)
O(7)-C(1)-C(6)	124.4(2)
O(7)-C(1)-C(2)	115.00(14)
C(6)-C(1)-C(2)	120.57(14)
O(7)-C(1)-Cr	130.01(12)
C(6)-C(1)-Cr	69.45(9)
C(2)-C(1)-Cr	71.54(9)
O(8)-C(2)-C(3)	122.4(2)
O(8)-C(2)-C(1)	117.6(2)
C(3)-C(2)-C(1)	119.27(14)
O(8)-C(2)-Cr	134.27(13)
C(3)-C(2)-Cr	72.96(10)
C(1)-C(2)-Cr	72.11(9)
O(9)-C(3)-C(4)	124.4(2)
O(9)-C(3)-C(2)	115.3(2)
C(4)-C(3)-C(2)	120.3(2)
O(9)-C(3)-Cr	131.99(12)
C(4)-C(3)-Cr	68.87(10)
C(2)-C(3)-Cr	71.08(10)
C(5)-C(4)-C(3)	119.3(2)
C(5)-C(4)-Cr	68.88(9)
C(3)-C(4)-Cr	74.92(10)
C(5)-C(4)-H(4)	119.0(13)
C(3)-C(4)-H(4)	121.6(13)
Cr-C(4)-H(4)	124.9(12)
C(4)-C(5)-C(6)	121.4(2)
C(4)-C(5)-C(10)	121.71(14)
C(6)-C(5)-C(10)	116.9(2)
C(4)-C(5)-Cr	73.80(9)
C(6)-C(5)-Cr	73.53(9)
C(10)-C(5)-Cr	124.15(12)
C(1)-C(6)-C(5)	118.8(2)
C(1)-C(6)-Cr	74.31(10)
C(5)-C(6)-Cr	68.76(9)
C(1)-C(6)-H(6)	119.3(14)
C(5)-C(6)-H(6)	121.9(14)
Cr-C(6)-H(6)	127.4(14)
O(7)-C(7)-H(7C)	105(2)
O(7)-C(7)-H(7B)	109(2)

H(7C)-C(7)-H(7B)	111(2)
O(7)-C(7)-H(7A)	110(2)
H(7C)-C(7)-H(7A)	110(2)
H(7B)-C(7)-H(7A)	113(2)
O(8)-C(8)-H(8C)	111(3)
O(8)-C(8)-H(8B)	105(3)
H(8C)-C(8)-H(8B)	99(4)
O(8)-C(8)-H(8A)	117(3)
H(8C)-C(8)-H(8A)	120(4)
H(8B)-C(8)-H(8A)	103(4)
O(9)-C(9)-H(9C)	109.7(14)
O(9)-C(9)-H(9B)	112(2)
H(9C)-C(9)-H(9B)	111(2)
O(9)-C(9)-H(9A)	108(2)
H(9C)-C(9)-H(9A)	107(2)
H(9B)-C(9)-H(9A)	108(2)
O(10)-C(10)-O(11)	124.8(2)
O(10)-C(10)-C(5)	124.0(2)
O(11)-C(10)-C(5)	111.2(2)
O(11)-C(11)-H(11C)	113(2)
O(11)-C(11)-H(11B)	111(2)
H(11C)-C(11)-H(11B)	107(3)
O(11)-C(11)-H(11A)	103(2)
H(11C)-C(11)-H(11A)	112(3)
H(11B)-C(11)-H(11A)	111(3)
O(12)-C(12)-Cr	179.0(2)
O(13)-C(13)-Cr	178.5(2)
O(14)-C(14)-Cr	179.4(2)

Symmetry transformations used to generate equivalent atoms:

TABLE 4. ANISOTROPIC DISPLACEMENT PARAMETERS FOR "CALCTEST", (h^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$CR(CO)_3$)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 1.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Cr	27(1)	20(1)	17(1)	4(1)	7(1)	6(1)
O(7)	38(1)	29(1)	21(1)	11(1)	5(1)	4(1)
O(8)	38(1)	37(1)	19(1)	5(1)	-2(1)	6(1)
O(9)	31(1)	32(1)	28(1)	7(1)	5(1)	-2(1)
O(10)	48(1)	42(1)	25(1)	2(1)	2(1)	-7(1)
O(11)	45(1)	47(1)	19(1)	10(1)	7(1)	3(1)
O(12)	73(1)	65(1)	42(1)	19(1)	38(1)	24(1)
O(13)	72(1)	24(1)	58(1)	7(1)	32(1)	11(1)
O(14)	33(1)	44(1)	41(1)	6(1)	0(1)	10(1)
C(1)	33(1)	25(1)	20(1)	7(1)	8(1)	9(1)
C(2)	28(1)	27(1)	18(1)	4(1)	3(1)	7(1)
C(3)	27(1)	25(1)	24(1)	5(1)	7(1)	6(1)
C(4)	29(1)	26(1)	22(1)	7(1)	10(1)	7(1)
C(5)	30(1)	23(1)	17(1)	2(1)	7(1)	8(1)
C(6)	32(1)	21(1)	20(1)	4(1)	8(1)	6(1)
C(7)	45(1)	39(1)	29(1)	14(1)	7(1)	-1(1)
C(8)	65(2)	52(1)	26(1)	-6(1)	1(1)	10(1)
C(9)	38(1)	31(1)	37(1)	11(1)	11(1)	1(1)
C(10)	32(1)	29(1)	19(1)	4(1)	8(1)	9(1)
C(11)	49(1)	72(2)	20(1)	13(1)	5(1)	14(1)
C(12)	42(1)	32(1)	26(1)	8(1)	14(1)	12(1)
C(13)	35(1)	27(1)	29(1)	6(1)	13(1)	7(1)
C(14)	34(1)	24(1)	26(1)	3(1)	10(1)	7(1)

C. TABLE 5. HYDROGEN COORDINATES AND ISOTROPIC DISPLACEMENT PARAMETERS FOR "CALCTEST", (h^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$CR(CO)_3$)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for 1.

	x	y	z	U(eq)
H(4)	4411(30)	6849(21)	10093(22)	24(5)
H(6)	7184(31)	10139(24)	9047(22)	27(5)
H(7C)	6700(33)	11014(24)	5985(24)	35(6)
H(7B)	6560(36)	11481(27)	7399(27)	41(7)
H(7A)	8015(40)	10510(28)	7202(28)	47(7)
H(8C)	1836(57)	5878(41)	4207(43)	92(12)
H(8B)	3888(75)	6136(50)	4952(50)	128(17)
H(8A)	2560(58)	5289(44)	5490(42)	96(13)
H(9C)	2831(35)	4540(25)	8766(24)	35(6)
H(9B)	1435(41)	5355(30)	9295(30)	55(8)
H(9A)	692(40)	4171(29)	8038(28)	50(7)
H(11C)	9175(49)	8438(33)	13547(32)	65(9)
H(11B)	8314(49)	9584(40)	13675(35)	76(11)
H(11A)	7270(48)	8189(35)	13847(34)	73(10)

Table 6. Table of Structure Factors for "calctest", (η^6-1,2,3-$(OMe)_3$-5-$(CO_2Me)C_6H_2$)$Cr(CO)_3$)

Table 7. Observed and calculated structure factors for 1 Page 1

h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s	h	k	l	10Fo	10Fc	10s
1	0	0	679	677	5	5	4	0	20	25	8	-3	9	0	126	125	2	5-14	1	115	121	4	6	-8	1	106	104	3
2	0	0	594	599	5	6	4	0	0	10	1	-2	9	0	78	78	3	6-14	1	37	30	8	7	-8	1	86	84	3
3	0	0	244	248	4	7	4	0	59	60	4	-1	9	0	209	209	3	-3-13	1	63	65	5	8	-8	1	46	40	5
4	0	0	255	254	4	8	4	0	66	72	5	0	9	0	267	267	2	-2-13	1	41	41	8	9	-8	1	73	76	5
5	0	0	11	6	11	9	4	0	13	6	12	1	9	0	0	8	1	-1-13	1	20	2	10	10	-8	1	63	61	5
6	0	0	201	203	3	-10	5	0	50	53	6	2	9	0	108	110	2	0-13	1	76	79	3	-8	-7	1	55	47	5
7	0	0	163	163	2	-9	5	0	0	11	1	3	9	0	132	136	3	1-13	1	81	84	3	-7	-7	1	44	33	6
8	0	0	48	38	4	-8	5	0	113	117	2	4	9	0	81	80	3	2-13	1	11	8	11	-6	-7	1	25	31	13
9	0	0	26	20	12	-7	5	0	96	98	2	5	9	0	64	62	4	3-13	1	115	111	3	-5	-7	1	95	91	3
10	0	0	64	63	5	-6	5	0	94	99	2	6	9	0	70	67	4	4-13	1	108	116	4	-4	-7	1	21	5	7
-10	1	0	36	33	8	-5	5	0	110	116	2	7	9	0	36	34	10	5-13	1	0	9	1	-3	-7	1	86	89	2
-9	1	0	0	4	1	-4	5	0	86	88	1	-9	10	0	31	34	11	6-13	1	59	65	6	-2	-7	1	75	79	3
-8	1	0	65	63	4	-3	5	0	191	179	3	-8	10	0	81	69	4	7-13	1	51	43	6	-1	-7	1	57	52	2
-7	1	0	48	44	2	-2	5	0	40	21	3	-7	10	0	0	4	1	-5-12	1	19	14	18	0	-7	1	23	22	6
-6	1	0	34	33	3	-1	5	0	231	242	5	-6	10	0	42	43	6	-4-12	1	29	21	14	1	-7	1	252	258	7
-5	1	0	423	431	3	0	5	0	332	329	3	-5	10	0	153	151	3	-3-12	1	14	21	13	2	-7	1	407	413	3
-4	1	0	183	189	3	1	5	0	160	143	3	-4	10	0	74	73	3	-2-12	1	22	23	22	3	-7	1	102	102	1
-3	1	0	85	73	1	2	5	0	158	164	3	-3	10	0	50	50	3	-1-12	1	70	70	2	4	-7	1	266	262	3
-2	1	0	64	64	1	3	5	0	218	211	3	-2	10	0	72	73	2	0-12	1	97	102	2	5	-7	1	111	106	2
-1	1	0	207	206	2	4	5	0	0	14	1	-1	10	0	192	195	6	1-12	1	78	78	2	6	-7	1	14	16	13
0	1	0	148	147	1	5	5	0	163	161	4	0	10	0	19	16	11	2-12	1	43	33	5	7	-7	1	47	49	5
1	1	0	559	559	2	6	5	0	86	88	3	1	10	0	197	204	1	3-12	1	58	55	4	8	-7	1	58	64	4
2	1	0	320	319	3	7	5	0	83	77	3	2	10	0	169	171	3	4-12	1	96	94	3	9	-7	1	42	35	7
3	1	0	83	91	1	8	5	0	52	53	6	3	10	0	21	29	20	5-12	1	109	105	3	10	-7	1	10	8	9

[Note: To save space, only part of the first page of structure factors is printed out.]

PART III: APPENDICES

CHAPTER XII. REFERENCE MATERIALS CONCERNING X-RAY DIFFRACTION ANALYSIS

I have prepared a list of many excellent reference materials on different aspects of X-ray crystallography that I have consulted, purchased, and/or are available in the YSU or comparable libraries.

A. CRYSTALLOGRAPHY TEXTS

1. Text Which Are Particularly Suitable for the Novice Crystallographer

(1) G. Rhodes, "Crystallography Made Crystal Clear: A Guide for Users of Macromolecular Models", 1993, Academic Press, San Diego. QP 551.R48 1993
(2) J. P. Glusker, M Lewis, and M. Rossi, "Crystal Structure Analysis for Chemists and Biologists", 1994, VCH, NY. QD 945.G583 1994 **[Note: This is the text for the lecture component of Chemistry 832: Solid State Structural Methods.]**
(3) C. P. Brock, B. M. Craven, B. A. Frenz, E. Gabe, R. A. Sparks, C. E. Strouse, K. N. Trueblood, and B. C. Wang, Notes from the ACA "Course for Crystallographers," "Structure Analysis by X-ray Crystallography," 3rd Ed., 1995.

2. The International Tables

The single most important resource guide is the "International Tables of X-ray Crystallography." Current Volumes in X-ray Lab. Old Edition: QD 945.I55 1965 V.1 V.2 V.3

3. General Crystallography Texts

(1) A. Hauptman, "Crystal Structure Determination: the Role of the Cosine Semi-Invariants",
(2) A. Holden and P. Singer, "Crystals and Crystal Growing", Anchor Books-Doubleday, NT, 1960.
(3) B. Carpenter, "Principles of Crystal Structure Determination", 1969, W. A. Benjamin, NY. QD 945.C35
(4) Coppens, "X-ray Charge Densities and Chemical Bonding".
(5) D. Cullity, "Elements of X-ray Diffraction",
(6) Drenth, "Principles of Protein X-ray Crystallography",
(7) E. Alexander, "Diffraction Methods in Polymer Science", 1969, Wiley-Interscience, NY. QD 945.A365
(8) E. Warren, "X-ray Diffraction", 1969, Addison-Wesley, Reading, MA. QD 945.W33
(9) F. C. Ladd and R. A. Palmer, "Structure Determination by X-ray Diffraction", 3rd Edition, 1993, Plenum, NY. [1st edition: QD 945.L32 (1977). 2nd edition: QD 945.L32 1985.]

(10) G. H. W. Milburn, "X-ray Crystallography; An Introduction to the Theory and Practice of Single Crystal Structure Analysis", 1973, CRC Press, Cleveland, OH. QD 945.M5 1973.
(11) G. Rhodes, "Crystallography Made Crystal Clear: A Guide for Users of Macromolecular Models", 1993, Academic Press, San Diego. QP 551.R48 1993
(12) Guinier, "X-ray Diffraction in Crystals, Imperfect Crystals, and Amorphous Bodies", 1963, W. H. Freeman, San Francisco. QD 945.G943
(13) H. Brumberger, "Small-Angle X-ray Scattering; Proceedings of the Conference held at Syracuse University, June 1965", 1967, Gordon and Breach, NY. QC 482.S52
(14) H. S. Lipson, "Crystals and X-rays", 1970, Wykeham, London. QD 945.L522
(15) H. S. Lipson, "Interpretation of X-ray Powder Diffraction Patterns", 1970, St. Martin's Press, NY. QD 945.L52
(16) H. Stout and L. H. Jensen, "X-ray Structure Determination; A Practical Guide", 1968, Macmillan, NY. QD 945.S8 Note: There is also a 2nd edition published in 1989.
(17) H. W. Wyckoff, C. H. W. Hirs, and Serge N. Timasheff, "Diffraction Methods for Biological Macromolecules/Part A", 1985, Academic Press, Orlando, FL. QP 601.M49 vol. 114
(18) H. W. Wyckoff, C. H. W. Hirs, and Serge N. Timasheff, "Diffraction Methods for Biological Macromolecules/Part B" 1985, Academic Press, Orlando, FL. QP 601.M49 vol. 115
(19) Hammond, "The Basics of Crystallography and Diffraction",
(20) Hargittai and M. Hargittai, "Symmetry Through the Eyes of a Chemist", 1995, Plenum, NY. QD 461.H268 1995.
(21) J. C. Wilson, "Elements of X-ray Crystallography",
(22) J. Cochran Wilson, "Elements of X-ray Crystallography", 1970, Addison-Wesley, Reading, MA. QD 945.W49
(23) J. L. Amoros, M. J. Buerger, and M. C. De Amoros, "The Laue Method",
(24) J. P. Glusker and K. N. Trueblood "Crystal Structure Analysis: A Primer", 1st Edition, 1972. QD 945.G58
(25) J. P. Glusker, "Crystal Structure Analysis: A Primer", 2nd Edition, 1985, Oxford University Press, NY. QD 945.G58 1985.
(26) J. P. Glusker, Editor, "Structural Crystallography in Chemistry and Biology", 1981, Hutchinson Ross Pub. Co., Stroudsburg, PA. QD 945.S87
(27) J. P. Glusker, M Lewis, and M. Rossi, "Crystal Structure Analysis for Chemists and Biologists", 1994, VCH, NY. QD 945.G583 1994
(28) J. R. Helliwell and P. M. Rentizepis, "Time Resolved Diffraction",
(29) J. R. Wormald, "Diffraction Methods", 1973, Claredon Press, Oxford. QD 945.W63
(30) J. W. Jeffery, "Methods in X-ray Crystallography", 1971, Academic Press, NY. QD 945.J36 1971
(31) K. Tanner, "X-ray Diffraction Topography", 1976, Pergamon Press, NY. QD 945.T36 1976
(32) L. V. Azaroff et al, "X-ray Diffraction", 1974, McGraw-Hill, NY. QC 482.D5 X7 1974
(33) L. V. Azaroff, "Elements of X-ray Crystallography", 1968, McGraw-Hill, NY. QD 945.A85
(34) M. J. Buerger, "The Precession Method in X-ray Crystallography", 1964, Wiley, NY. QD 945.B79

(35) M. M. Woolfson, "An Introduction to X-ray Crystallography", 1970, Cambridge University Press, Cambridge. QD 945.W58
(36) McPherson, "Preparation and Analysis of Protein Crystals", 1982, Wiley, NY. QP 551.M364 1982
(37) R. Jenkins and R. Snyder, "Introduction to X-ray Powder Diffractometry", 1993, Wiley, NY. QD 482.D5 J46 1996
(38) R. Rudman, "Low-temperature X-ray Diffraction: Apparatus and Techniques", 1976, Plenum Press, NY. QD 945.R77
(39) R. A. Laudise, "The Growth of Single Crystals", Solid State Physics Series, N. Holonyak, Jr. Ed., Prentice-Hall, 1970.
(40) S. Zevin and G. Kimmel, "Quantitative X-ray Diffractometry",
(41) Sherwood, "Crystals, X-rays, and Proteins", 1976, Wiley, NY. QD 945.S46 1976
(42) W. Mak and G. D. Zhou, "Crystallography in Modern Chemistry: A Resource Book of….",
(43) W. Nuffield, "X-ray Diffraction Methods", 1966, Wiley, NY. QD 945.N83
(44)

B. REVIEW ARTICLES AND CHAPTERS ON CRYSTALLOGRAPHY

(1) E. A. V. Ebsworth, D. W. H. Rankin, & S. Cradock, "Structural Methods in Inorganic Chemistry", Second Edition, 1991, CRC Press, Boca Raton, Florida, QD 95.E29.1991b [1st edition, 1987, QD 95.E29 1987] ($69.95 from Bookstore)
(2)

In most polymer characterization textbooks there is a section or chapter on X-ray characterization methods. A listing of some of these books can be found on my WEB page (as of December, 1998) at (http://www.as.ysu.edu/~adhunter/Teaching/Chem824/index.html).

C. JOURNALS

1. Educational and General Interest Journals Which Regularly Publish Articles on X-ray Diffraction Methods

(1) The Journal Of Chemical Education
(2) Chemical and Engineering News
(3) Science
(4) Nature
(5) Physics Today

2. Journals Devoted Largely to X-ray Crystallography

(1) Acta Crystallographica. Section A. Foundation of Crystallography. QD 901.A25
(2) Acta Crystallographica. Section B. Structural Science. QD 901.A26
(3) Acta Crystallographica. Section C. Crystal Structure Communications. QD 901.A27
(4) Acta Crystallographica. Section D. Biological Crystallography. QD 901.A28

3. Synthetic Chemistry Journals Which Deal With Crystallographic Results Particularly Rigorously

(1) Journal of the American Chemical Society
(2) Inorganic Chemistry
(3) Organometallics
(4) Science
(5) Nature
(6) Nature: Structural Biology

D. REFERENCES AND LITERATURE SOURCES ON X-RAY DIFFRACTION

1. Papers Discussing Teaching Methods in Crystallography

a) Interesting *Journal of Chemical Education* Papers

The best regular source of papers on the educational aspects of crystallography is the Journal of Chemical Education. Several of the most interesting of these are listed below:

(1) Hunter, A. D.: "Crystallographic Structure Determination: An Experiment for Organic Analysis and other Non-Traditional Venues," *Journal of Chemical Education*, **1998**, *75*, 1297-1299 (plus on-line supplementary materials at http://jchemed.chem.wisc.edu/Journal/issues/1998/Oct/abs1297.html).
(2)

b) *Journal of Chemical Education* Searches

If you go to their WEB site at (http://jchemed.chem.wisc.edu/Journal/) and their on-line index (http://jchemed.chem.wisc.edu/Journal/Search/index.html) and type in crystallography, X-ray, diffraction, crystal, etc., you can get an up to date listing of all papers they have published on this topic.

A listing of such a *JCE* search made for the "keyword" "crystallography" on October 28, 1998 looks as follows (two less relevant items have been deleted):

Search results 1 - 8 of 8 found

1. Teaching Protein Crystallization by the Gel Acupuncture Method J. Chem. Educ. 1998 75 442. (Apr 1998)
2.
3. Cady, Susan G. Use of Pom Pons To Illustrate Cubic Crystal Structures J. Chem. Educ. 1997 74 794. (Jul 1997)
4. Laing, Michael An Inexpensive Kit for Constructing Models of Crystals J. Chem. Educ. 1997 74 795. (Jul 1997)
5. Hardgrove, Jr., George L. Teaching Space Group Symmetry through Problems J. Chem. Educ. 1997 74 797. (Jul 1997)
6. Suh, Il-Hwan; Park, Koon Ha ; Jensen, William P.; Lewis, David E. Molecules, Crystals, and Chirality J. Chem. Educ. 1997 74 800. (Jul 1997)
7.
8. Masson, Bernard L. X-ray Powder Diffraction Simulation with a Microcomputer J. Chem. Educ. 1996 73 918. (Oct 1996)

A listing of such a search made for the "title" "crystallography" on October 28, 1998 looks as follows:

Search results 1 - 16 of 16 found

1. Bond, Marcus R.; Carrano, Carl J. Introductory Crystallography in the Advanced Inorganic Chemistry Laboratory. J. Chem. Educ. 1995 72 451.
2. Rudman, Reuben. Isidor Fankuchen and crystallography (LTE). J. Chem. Educ. 1992 69 775.
3. Kettle, Sidney F. A.; Norrby, Lars J. The Brillouin zone--An interface between spectroscopy and crystallography. J. Chem. Educ. 1990 67 1022.
4. Glusker, Jenny P. Teaching crystallography to noncrystallographers (SYMP). J. Chem. Educ. 1988 65 474.
5. Wuenseh, Bernhardt J. The teaching of crystallography to materials scientists and engineers (SYMP). J. Chem. Educ.

1988 65 494.
6. Julian, Maureen M. Isabella L. Karle and a new mathematical breakthrough in crystallography (PROFILES). J. Chem. Educ. 1986 63 66.
7. Affholter, Kathleen A. Egg your optical crystallography students on. J. Chem. Educ. 1983 60 196.
8. Brady, K. T. Models as an aid to courses in crystallography and mineralogy. J. Chem. Educ. 1983 60 36.
9. Webster, M. An introduction to X-ray crystallography-two computer programs (CS). J. Chem. Educ. 1981 58 555.
10. March, Richard E.; Nordman, Christer E. Interpretation of a Patterson map-a dry-lab experiment in X-ray crystallography (IE). J. Chem. Educ. 1977 54 318.
11. Howald, James C.; Smith, Gerald D. Crystallography-a January term on the properties of crystals. J. Chem. Educ. 1976 53 224.
12. Kauffman, George B. Crystals as molecular compounds. Paul Pfeiffer's application of coordination theory to crystallography. J. Chem. Educ. 1973 50 277.
13. Allsobrook, A. J. R.; Brown, M. E.; Glasser, L. Xtal-line. A board game in crystallography. J. Chem. Educ. 1973 50 688.
14. Waser, Jurg. Pictorial representation of the Fourier method of X-ray crystallography. J. Chem. Educ. 1968 45 446.
15. Boer, F. Peter; Jordan, Truman H. X-ray crystallography "experiment." Powder patterns for alkali halides. J. Chem. Educ. 1965 42 76.
16. Macintyre, Walter M. X-ray crystallography as a tool for structural chemists. J. Chem. Educ. 1964 41 526.

A listing of such a *JCE* search made for the "title" "diffraction" on October 28, 1998 looks as follows (3 less relevant items have been deleted):

Search results 1 - 35 of 35 found

1. Butera, R. A.; Waldeck, D. H. X-ray Diffraction Investigation of Alloys J. Chem. Educ. 1997 74 115. (Jan 1997)
2. Pope, Christopher G. X-ray Diffraction and the Bragg

Equation J. Chem. Educ. 1997 74 129. (Jan 1997)
3. Masson, Bernard L. X-ray Powder Diffraction Simulation with a Microcomputer J. Chem. Educ. 1996 73 918. (Oct 1996)
4. Hanson, Robert M.; Bergman, Sara A. Data-Driven Chemistry: Building Models of Molecular Structure (Literally) from Electron Diffraction Data. J. Chem. Educ. 1994 71 150.
5.
6. Pu, Qian. Simulation of X-ray powder diffraction (CS). J. Chem. Educ. 1992 69 815.
7. Rosenthal, Jeffrey. Spreadsheet calculations for X-ray powder diffraction patterns (BULLETIN). J. Chem. Educ. 1991 68 A285.
8. Klier, Kamil; Taylor, J. Ashley. Diffraction of a laser light by a memory chip (TD). J. Chem. Educ. 1991 68 155.
9. Lisensky, George C.; Kelly, Thomas F.; Neu, Donald R.; Ellis, Arthur B. The optical transform: Simulating diffraction experiments in introductory courses. J. Chem. Educ. 1991 68 91.
10. Goldberg, Stephen Z. On an X-ray diffraction pattern simulator (LTE). J. Chem. Educ. 1991 68 969.
11. Rodriguez, Silvio. On an X-ray diffraction pattern simulator (LTE). J. Chem. Educ. 1991 68 969.
12. Spencer, Bertrand H.; Zare, Richard N. Direct visualization of Bragg diffraction with a He-Ne laser and an ordered suspension of charged microspheres. J. Chem. Educ. 1991 68 97.
13. Segschneider, Claudia; Versmold, Heiner. A simple Bragg diffraction experiment with harmless visible light. J. Chem. Educ. 1990 67 967.
14. Rodriguez, Gonzalo; Rodriguez, Silvio. An X-ray diffraction pattern simulator (CS). J. Chem. Educ. 1989 66 648.
15. Glasser, L. Diffraction at your finger tips. J. Chem. Educ. 1988 65 707.
16.
17. Speakman, J. C. The discovery of X-ray diffraction by crystals (SBS). J. Chem. Educ. 1980 57 489.
18. Goldberg, Stephen Z. Two computer programs for the simulation of X-ray diffraction phenomena. J. Chem. Educ. 1979 56 227.
19. Williams, Jack M. Combining residual entropy and diffraction results to understand crystal structure. J. Chem. Educ. 1975 52 210.

20. Brisse, F.; Sundararajan, P. K. A practical method of simulating X-ray diffraction. J. Chem. Educ. 1975 52 414.
21. Nathan, Lawrence C. Computer analysis of X-ray diffraction patterns of cubic substances. J. Chem. Educ. 1975 52 438.
22. Shields, K. G.; Kennard, C. H. L. A novel X-ray powder diffraction experiment. J. Chem. Educ. 1974 51 265.
23. Lippert, E. L., Jr. Ambiguous unknowns for X-ray diffraction identification. J. Chem. Educ. 1973 50 771.
24. Pavkovic, S. F. X-ray diffraction by crystal planes in real space and reciprocal space. J. Chem. Educ. 1972 49 237.
25. Knox, James R. Protein molecular weight by X-ray diffraction. J. Chem. Educ. 1972 49 476.
26. Wilson, F. C. Radiation safety in the X-ray diffraction lab (Safety). J. Chem. Educ. 1970 47 A97.
27. Rudman, Reuben. X-ray diffraction analysis (Chem Inst.) Part 1. Safety and generators. J. Chem. Educ. 1967 44 A7.
28. Rudman, Reuben. X-ray diffraction analysis (Chem Inst.) Part 2. X-ray tubes and monochromatization. J. Chem. Educ. 1967 44 A99.
29. Rudman, Reuben. X-ray diffraction analysis (Chem Inst.) Part 3. Detectors. J. Chem. Educ. 1967 44 A187.
30. Rudman, Reuben. X-ray diffraction analysis (Chem Inst.) Part 4. Powder cameras and techniques. J. Chem. Educ. 1967 44 A289.
31. Rudman, Reuben. X-ray diffraction analysis (Chem Inst.) Part 5. Single crystal methods. J. Chem. Educ. 1967 44 A399.
32. Rudman, Reuben. X-ray diffraction analysis (Chem Inst.) Part 6. Single crystal methods (continued) and miscellaneous methods. J. Chem. Educ. 1967 44 A499.
33. Rudman, Reuben. Laboratory experiments in low-temperature X-ray diffraction. J. Chem. Educ. 1967 44 331.
34. Ryland, Ada L. X-ray diffraction. J. Chem. Educ. 1958 35 80.
35.

A listing of such a *JCE* search made for the "keyword" "crystal" on October 28, 1998 looks as follows (the "title" search produced 220 entries, some less relevant items have been deleted):

Search results 1 - 48 of 48 found

1. Teaching Protein Crystallization by the Gel Acupuncture Method J. Chem. Educ. 1998 75 442. (Apr 1998)
2.
3. Cady, Susan G. Use of Pom Pons To Illustrate Cubic Crystal Structures J. Chem. Educ. 1997 74 794. (Jul 1997)
4. Laing, Michael An Inexpensive Kit for Constructing Models of Crystals J. Chem. Educ. 1997 74 795. (Jul 1997)
5. Hardgrove, Jr., George L. Teaching Space Group Symmetry through Problems J. Chem. Educ. 1997 74 797. (Jul 1997)
6. Suh, Il-Hwan; Park, Koon Ha ; Jensen, William P.; Lewis, David E. Molecules, Crystals, and Chirality J. Chem. Educ. 1997 74 800. (Jul 1997)
7.
8. Masson, Bernard L. X-ray Powder Diffraction Simulation with a Microcomputer J. Chem. Educ. 1996 73 918. (Oct 1996)
9.
10. Laporterie, A. The microscale organic laboratory: A very simple method of filtration and recrystallization (ML). J. Chem. Educ. 1992 69 A42.
11.
12. Ali, Saqib; Kalsoom, Abida. Selection of recrystallization solvent. J. Chem. Educ. 1991 68 877.
13. Qian, Chengyi. A useful method for obtaining crystals from viscous oils. J. Chem. Educ. 1990 67 355.
14.
15. Craig, Rhoda E. R. Rapid, efficient determination of recrystallization solvents at the microscale level. J. Chem. Educ. 1989 66 88.
16. Landgrebe, John A. Microscale recrystallizations with a disposable pipet. J. Chem. Educ. 1988 65 460.
17. Pyriadi, Thanun M. A simple and convenient method for crystallization of thermally unstable or highly soluble compounds. J. Chem. Educ. 1987 64 813.
18. Hiegel, Gene A. Selecting a solvent for recrystallization. J. Chem. Educ. 1986 63 273.
19.
20. Scaife, Charles W. J.; Dubs, Richard L. Association of ions and fractional crystallization: a general chemistry experiment. J. Chem. Educ. 1983 60 418.
21. Mroczkowski, Stanley. Needs and opportunities in crystal

growth. J. Chem. Educ. 1980 57 537.
22. Baumann, Jacob B. Solvent selection for recrystallization: An undergraduate organic experiment. J. Chem. Educ. 1979 56 64.
23. Chu, Samuel S.-T. Crystallization by the "gauze bandage" method. J. Chem. Educ. 1977 54 639.
24. Lewis, Dennis A. Oil formation. An "unexpected" difficulty in an elementary organic laboratory experiment. J. Chem. Educ. 1975 52 601.
25. Horak, V.; Crist, DeLanson R. Small scale organic techniques: Filtration and crystallization. J. Chem. Educ. 1975 52 664.
26.
27. Bierne, David; Smith, Steven; Hoogenboom, Bernard E. Recrystallization without tears. J. Chem. Educ. 1974 51 602.
28.
29. Caughlin, Charles. Theory of crystal growth. J. Chem. Educ. 1973 50 642.
30. Shaw, C. Frank III; Allred, A. L. Crystallization and filtration apparatus for low temperatures and inert atmosphere. J. Chem. Educ. 1970 47 164.
31.
32. Fischinger, Andrew J. A flotation method for growing large single crystals. J. Chem. Educ. 1969 46 486.
33. Gravatt, C. C.; Gross, Paul M. Apparatus for the purification and crystal growth of organic compounds. J. Chem. Educ. 1969 46 693.
34. Kaye, Irving Allan. Purification of low-melting compounds. J. Chem. Educ. 1969 46 696.
35. Giese, Roger. Low temperature recrystallization tube. J. Chem. Educ. 1968 45 610.
36. Bluhm, Aaron L. Apparatus for semimicro low temperature crystallizations. J. Chem. Educ. 1958 35 200.
37. Schoen, Herbert M.; Grove, C. S., Jr.; Palermo, Joseph A. The early history of crystallization. J. Chem. Educ. 1956 33 373.
38. Fehlner, Francis P. Growing crystals. J. Chem. Educ. 1956 33 449.
39. Svanoe, Hans. Crystallization of organic compounds from solution. J. Chem. Educ. 1950 27 549.
40. Stone, Charles H. Crystallization. J. Chem. Educ. 1946 23 404.
41. Devor, Arthur W. Agitation and crystallization: a practical laboratory experiment. J. Chem. Educ. 1945 22 200.

42. Fernelius, W. Conard; Detling, Kenneth D. Preparation of crystals of sparingly soluble salts. J. Chem. Educ. 1934 11 176.
43. Dunning, John; Pratt, Philip; Lowman, O. E. What starts precipitation from a supersaturated solution? J. Chem. Educ. 1934 11 624.
44. Stone, Charles H. Some experiments with crystals. J. Chem. Educ. 1932 9 1107.
45. Fliedner, Leonard J. The preparation and preservation of large crystals of chrome alum. J. Chem. Educ. 1932 9 1453.
46. Tauber, Henry; Kleiner, Israel S. A convenient method for the crystallization of sugars and other organic substances. J. Chem. Educ. 1932 9 1970.
47. Fisher, H. R. Crystallization. J. Chem. Educ. 1931 8 149.
48. Stone, Charles H. Some experiments in crystallization. J. Chem. Educ. 1930 7 2170.

c) Papers from other journals concerning the teaching of crystallography and/or general aspects of crystallography

General interest journals such as those listed above also regularly publish interesting an enlightening papers. A selection of ones that I use for my class include:

(1) A Special Section in *Science*, August **1997**, pages 1213-1219, on synchrotron radiation sources.
(2) A Special Section in Physics Today, November 1995, pages 23 to 48, entitled "X-Rays 100 Years Later" on the history of X-ray diffraction.
(3) "Optical Transform Kit: Simulating Diffraction Experiments in Introductory Courses," 2nd Ed., 1994, Institute for Chemical Education.
(4)

2. Papers Discussing Strategies for Growing Crystals

Strategies for growing single crystals have been most systematically developed by people interested in macromolecular structures where the problem of growing quality single crystals are most severe. However, some relevant papers have been written on this topic.

(1) M. P. Byrn, 6 others, and C. E. Strouse, "Porphyrin Sponges: Conservation of Host Structure in over 200 Porphyrin-Based Lattice Clathrates," *JACS*, **1993**, *115*, 9480-9497.
(2) C. Reichardt, "*Solvents and Solvent Effects in Organic Chemistry*," 2nd Ed., VCH, NY, **1990**.

(3)

3. Papers on Technical Aspects of X-ray Crystallography

These is a massive literature on this topic but little of it is easily accessible to the crystallographic novice. Some of the more accessible papers, or at least the most valuable to brute ones way through, as listed below:

(1) R. E. Marsh, "Some Thoughts on Choosing the Correct Space Group," Acta. Cryst. B, 1995, B51, 897-907. **[Note: This is a very important paper on determining space groups as Professor Marsh is the world expert on this topic and if you aren't careful, one day one of your papers might be "Marshed."**
(2) N. Niimura, et. al., "Neutron Laue Diffractometry with an imaging plate provides and effective data collection regime for neutron protein crystallography," *Nature Structural Biology*, **1997**, *4*, 909-914.
(3) T. Koritsanszky, et. al., "Accurate Experimental Electronic Properties of DL-Proline Monohydrate Obtained within 1 Day," *Science*, **1998**, *279*, 356-358.
(4) S. Borman, "New Class of Diffractometer Speeds X-ray Crystal Structure Determinations," Chemical and Engineering News, March 11, 1996, 30-32.
(5) W. Roush, "Analyzing Molecular Structure With Astronomical Speed," Science, February 23, 1996, 1060.
(6)

4. References on Mosaic Tiling, Escher Patterns, etc.

Understanding of repeating motifs, mosaic tiling, Escher patterns, etc., is very helpful in understanding the repeating units of solids. There are many resources for doing so. For example:

(1) Have you students identify the two dimensional unit cells in samples of wallpaper. From the discount bin, these can be purchased for a few dollars a roll.
(2) For a nice WEB page on complex two dimensional tiling patterns, including an introduction to M. C. Escher's work (http://hyperion.advanced.org/16661/index2.html).
(3) "The M. C. Escher Coloring Book," 1995, Harry N. Abrams, Inc.
(4)

5. Allen Hunter's Papers That Contain an X-ray Crystallographic Component

Most of my papers have had a substantial crystallographic component. My current CV is available from my WEB site (http://www.as.ysu.edu/~adhunter/Research/ADHpubs.html) and lists these comprehensively.

E. WEB BASED MATERIALS.

1. WEB Based Instructional Materials

(1) The IUCr Commission on Crystallographic Teaching WEB Site currently contain 19 html formatted pamphlets on crystallographic teaching that may be downloaded from (http://www.iucr.ac.uk/) and printed for individual study and use.
(2) The IUCr WEB Site contains detailed instructions on CIF files and their preparation that may be downloaded from (http://www.iucr.ac.uk/iucr-top/cif/index.html).
(3) Paul Boyle at North Carolina State University maintains a WEB page devoted to methods of growing singles crystals at (http://laue.chem.ncsu.edu/web/GrowXtal.html).
(4) Kevin Cowtan maintains an excellent WEB site for the interactive teaching of Fourier transforms relevant to crystallography at (http://www.yorvic.york.ac.uk/~cowtan/fourier/fourier.html).
(5) Kent Wilson at UCSD offers an excellent WEB site about diffraction and crystals at (http://sdchemw1.ucsd.edu/education/xraydiff/xraydiff.html).
(6)

2. WEB Sites Devoted to Various Aspects of X-ray Crystallography

(1) The American Crystallographic Association, ACA, home page has many valuable links at (http://www.hwi.buffalo.edu/aca/).
(2) Access to the Cambridge Structural Database, CCDB, for small molecules is essential to all chemists and it is located at (http://www.ccdc.cam.ac.uk/).
(3) The Protein Data Bank, PDB, is similarly essential for macromolecular crystallographers at (http://www.pdb.bnl.gov/pdb-bin/pdbmain).
(4) Tony Day has produced an excellent WEB site detailing the Source of Stability in Proteins at (http://www.cryst.bbk.ac.uk/PPS2/projects/day/TDayDiss/index.html).
(5) John C. Huffman at the Indiana University Molecular Structure Center has an *excellent set of links* on its WEB site and is a source of crystallographic data sets at (http://www.iumsc.indiana.edu).
(6)

3. WEB Sites on Diffraction Hardware and Software

(1) The IUCr maintains a comprehensive listing (currently 84 pages long) of software useful in X-ray crystallography, the SINCRIS list, at (http://www.iucr.ac.uk/).
(2) Bruker AXS (Siemens) has a useful home page at (http://www.siemens-xray.com/).
(3) The National University of Ireland at Galway has a freeware structure solution package including training tools at (http://www.ucg.ie/cryst/software.htm).
(4) Steffen Weber at NIRIM in Tsukuba Japan has an freeware structure solution package available at (http://www.nirim.go.jp/~weber/).

(5) The WebLab Viewer (and its free WebLab Viewer Lite version) from Molecular Simulations (i.e., at http://www.msi.com).
(6) RasMol and Chime are available from (http://klaatu.oit.umass.edu/microbio/rasmol/).
(7)

CHAPTER XIII. A QUICK INTRODUCTION TO DOS COMMANDS

DOS is the basic underlying operating system of IBM compatible computers(i.e., Wintel computers). On our Gateway2000® Pentium computers, **DOS** is the operating system used by **XSCANS** and **SHELXTL** (we are currently installing **SHELXTL** on our WINDOWS NT machines, **XSCANS** runs only under DOS).

Common Commands You'll Use

a: **[ent]** tells the CPU to read files, directories, etc., from the disk in the floppy drive which is designated as the "A" drive.

c: [ent] tells the CPU to read files, directories, etc., from the hard drive which is designated as the "C" drive.

cd c:\C832\YOURNAME\COMPOUND [ent] tells the CPU to change to the COMPOUND directory in the YOURNAME directory in the C832 directory.

cd \ [ent] tells the CPU to go back to the main directory on the current drive.

cd.. **[ent]** goes back one level.

cd name [ent] goes up one level to the file with the name "name".

Copy [ent] The copy command can be written with one or two arguments. If written with one, i.e., copy STUFF [ent] it tells the CPU to copy "STUFF" (which includes disk, directory, and filename info) to the current drive and directory, e.g., copy a:\HUNTER\pig.nut [ent] would copy the file pig.nut in the directory HUNTER in drive a to the current drive and directory. If written with two arguments, it copies from the first to the second, e.g., copy a:\pig.nut c:\NOSE* [ent] would copy the pig.nut file from drive a to the same name in directory NOSE on drive c. If the file names in the source and destination are different, the file is renamed while copying.

copy a:*.* [ent] tells the CPU to copy all of the files on the floppy drive to the current directory on the current (hard) drive.

copy a:\name.p4p [ent] tells the CPU to copy the file name.p4p (or any other designated file you put in) from the disk in the floppy drive to the current directory on the current (hard) drive.

copy name.* a:*.* [ent] tells the CPU to copy all of the files name.* (i.e., * is a wild card) to the disk in the floppy drive without changing their names.

copy name.ins a:\name.int [ent] tells the CPU to copy the designated file (in this case name.ins) from the current directory of the current (hard) drive to the disk in the floppy drive and to rename it (to name.int in this case) while doing so.

copy **name.p4p a:*.* [ent]** tells the CPU to copy the designated file (in this case name.p4p) from the current directory on the current (hard) drive to the disk in the floppy drive without changing its name.

dir [ent] tells the CPU to give you the contents of the current directory.

dir a: [ent] tells the CPU to give you the contents of the "a" drive.

dir name.* [ent] tells the CPU to give you the names of all files name.* in the current directory.

edit name.* [ent] tells the CPU to open the specified file so that you can edit its contents.

md c:\C832\YOURNAME\COMPOUND [ent] tells the CPU to make a directory (file folder) called COMPOUND in a directory called YOURNAME in a directory called C832 on drive "C". Each of these directory names can be up to eight alphanumeric characters long.

Print name.big [ent] tells the CPU to print the file name.big (for the old **Windows**/**DOS** machines).

Copy name.big Prn [ent] tells the CPU to print the file name.big (for **Windows** 95 machines even when they are running under **DOS**).

rd c:\C832\YOURNAME\COMPOUND [ent] tells the CPU to delete the directory (file folder) called COMPOUND in a directory called YOURNAME in a directory called C832 on drive "C". The directory must be empty first.

ren name1 name2 [ent] tells the CPU to rename the file name1 as name2.

CHAPTER XIV. GROWING SINGLE CRYSTALS SUITABLE FOR DIFFRACTION ANALYSIS

A. GENERAL PRINCIPLES OF GROWING SINGLE CRYSTALS

Most synthetic chemists consider the growing of quality single crystals to be more of an art form than a science. To support this belief, they will point to many things: most often the high degree of chance that seems to be involved in getting such crystals and the fact that some people just seem to have "green thumbs." There is much truth to these contentions but experience has shown that a fuller understanding of crystal growth and solvent properties and careful analysis of past successes and failures can lead to more consistently positive results. Indeed, protein crystallographers have achieved excellent levels success in this area and we synthetic chemists could learn a lot from their thinking process.

1. Rates of Crystal Growth

The laws of thermodynamics tell us that the slower a crystal grows the lower the levels of entropy induced defects to its perfection. Dramatic evidence for this can be seen in the nearly perfect crystals often observed for mineral which crystallize over periods measured in years and millennia. In a lab setting, experience has shown that crystals suitable for diffraction analysis typically grow best over periods of days. Occasionally a quality crystal will be found that formed accidentally while one was taking a solution quickly to dryness, but such cases are the happy exception. Typically when one sets up a crystallization, the best crystals will have formed between one day and a week later. In my experience, the probability of a crystallization proceeding successfully drops off dramatically after the first few weeks, although again I have seen happy exceptions to this.

2. General Conditions for Crystal Growth

Most types of crystallization proceed best in areas of the lab where the temperature remains relatively constant, vibration levels are minimal, and the samples are in the dark. This is often a little used cupboard, closet, or back room. Remember, convection is generally your enemy so try to keep the temperatures relatively constant. In addition, convection is naturally lower in more viscous solvents, ones with less dependence of their density on temperature, and in narrow containers. Since crystallization always takes time and chemists are an impatient lot, there is a tendency to check the samples too often. While hard to avoid, the handling which results is generally detrimental to optimum crystal growth. I therefore recommend that one doesn't check their samples more than once a day.

3. Solvent Properties and Saturated Solutions

Crystals must be grown from saturated solutions. For optimum crystal growth, the compound should be moderately soluble under the crystallization conditions. If it is too soluble then at saturation one will tend to get crystals growing together in clumps. If it is not soluble enough, then there is not enough solute around to supply the growing crystal surface and one tends to get small crystals. To get the correct solubilities one should carefully match the solute and solvent. One can start this process by consulting the literature for parameters like solvent polarity and dielectric constant as well as one's own experience. However, the best procedure is to systematically try different solvents and solvent combinations until you find a half dozen or so where your sample is moderately soluble. In my experience with neutral (and a few ionic) organometallic, inorganic, and organic compounds, the solvents of choice varied dramatically with the class of compounds. However, I typically had the most success at growing single crystals with combinations of three solvents, namely: CH_2Cl_2, toluene, hexanes with a few others being successful less often, namely: $CDCl_3$, CH_3CN, acetone, ethanol, methanol, THF, and ether. With experience and careful experimentation, you will find a good combination for your system!

4. Master Several Favorite Methods

To get really proficient at growing crystals takes sufficient practice with a method that one masters it. When this happens, one gets very attuned to subtle clues and the rate of ones success increases dramatically. Because of this phenomenon, skilled crystal gardeners will tend to have two or three techniques with which they will get almost all of their success.

B. PROVEN METHODS FOR GROWING CRYSTALS

In the following sections, are listed some of the most commonly used and/or most promising methods for growing single crystals that I have used or considered using in my research.

Safety Tip: Most crystallizations involve one or more components that are moderately or extremely flammable Although crystallizations typically involve only small solvent quantities, one must still use the best safety procedures and equipment. In particular, flammable materials must be handled with care.

1. Crystallization by Slow Evaporation

Perhaps the most widely used method for growing single crystals is this one in which one takes a solution of your target molecule that is not quite saturated and slowly allows the solvent to evaporate. Once saturation is reached, crystals start to form and the continued evaporation provides a continual source of solute molecules to add to the growing faces.

Typical experimental methods include:

- One places the solution in a vial or tube in which the lid is pierced by a small pinhole to allow the solvent vapors to slowly diffuse out.
- One places the solution in a vial or tube in which the lid is made of a material which is somewhat permeable to the solvent vapors.
- For air sensitive compounds, one can carry out these procedures in an inert atmosphere (i.e., a glove box, glove bag, or a larger container such as a large jar or dessicator).
-

2. Crystallization by Cooling

In almost all cases solubility decreases with temperature. One can take advantage of this by dissolving your solute in a solvent system to give a near saturated solution at one temperature and then letting the system cool to a lower temperature. If one is blessed with access to a water bath or crystal growing cabinet that has temperature ramp capabilities, cooling times of a day to a week or more are typically chosen. Surprisingly, the cooling times of only a few hours or over night which are all that one can normally get using "natural" thermal gradients are also often successful.

Typical experimental methods include:

- Dissolving the sample at some elevated temperature and then insulating the container (e.g., with cotton wool, metal foil, and/or a large thermal buffer) and letting the sample cool slowly to ambient temperatures.
- Dissolving the sample at or near room temperature and then placing the (perhaps) insulated container into an approved lab fridge or freezer.
-

3. Crystallization Using Mixed Solvents and Solvent Diffusion in the Gas Phase

In this method, one slowly adjusts the composition of a mixed solvent system having two solvents. The solute should be moderately soluble in the "good" solvent but mostly insoluble in the "poor" solvent.

Typical experimental methods include:

- In one variant, you first dissolve the solute in the better solvent and then add the poorer solvent slowly.
  - Sometimes this can be done by dropwise addition of the poorer solvent.
  - Sometimes this can be done by using an extremely low velocity solvent pumps (i.e., typically a syringe pump) to add the second solvent.
- In another variant, you remove the better solvent.

- This can be done by having the better solvent evaporate out of the system because it is more volatile.
- This process is aided if one adds a selective adsorbent to a container holding the sample vial.

- In the third variant, the better solvent is removed while the poorer is added. One sets up the apparatus so that the second solvent is transferred into the mixed system (and the first solvent commonly diffuses out as well) by diffusion through the gas phase.
  - In the first apparatus, one takes a sample vial containing the solute and good solvent and places it into a second larger container having the poorer solvent in its bottom or a second sample vial.
  - In the second apparatus, two tubes are connected by a bridge through which the solvents can diffuse (i.e., this apparatus is shaped somewhat like a capital "H").
-

4. Crystallization by Solvent Layering

An important variant to the previous technique relies on the fact that solvents of substantially different densities mix remarkably slowly when they are not stirred. One can take advantage of this by dissolving the solute in the better solvent and then adding a (bottom or preferably top) layer of the poorer solvent. If this system is not stirred, shaken, or vibrated too much I have seen it take several days for the two layers to mix. The resulting slow diffusion of solvents across the boundary layer often results in excellent crystals growing there.

Typical experimental methods include:

- I commonly dissolve compounds in dense chlorinated solvents such as CH_2Cl_2 and then carefully add a top layer of less polar and less dense solvents (e.g. hexanes, ether, toluene).
- If your compound is water soluble, you can vary the density and solvent properties of the two water layers by having very different salt concentrations in each. Protein crystallographers use this technique widely.
-

5. Crystallization by Diffusion Through Capillaries and Gels

Because of their inherent viscosities and in the absence of convection, solvents typically diffuse very slowly though narrow bore capillaries.

Typical experimental methods include:

- This general procedure can be done with equipment shaped either as a capital "H" with the capillary being the cross bar or as a vertical tube with a constriction in the middle. The second apparatus is generally easier to make and fill.

- I have typically dissolved my solute in a more dense solvent and placed this in the bottom half of the tube so that the solution just comes up to the middle of the constriction. I then add a second poorer solvent to the top.
- A major variant of this technique is to bridge the two solutions with a wider bore tube filled with a gel. This produces very slow diffusion and can be used to grow great crystals but tends to work very slowly.
-

6. Crystallization From Melts

If your compound is sufficiently thermally stable, one can often grow crystal from a homogeneous or even heterogeneous melt. Having careful control of the cooling rate is especially critical here. This method is widely used to grow crystals of high temperature solids such as metals and metal oxides and has recently become more popular for conventional ionic compound through the use of low temperature molten salts.

7. Crystallization by Sublimation

Compounds that are sufficiently volatile at accessible vacuums can be crystallized, often from crude mixtures, to give single crystals by sublimation. In my experience, I have only seen this work for relatively volatile solids like naphthalene, Ferrocene, $M(CO)_6$, and $(\eta^5\text{-}C_5H_5)M(CO)_2(NO)$ (where M = Cr, Mo, and W) but I understand it works well for many other relatively non-polar compounds.

8. Crystallization Using Combinations

When these individual methods don't work, try combos. I particularly like using combinations of mixed solvent methods with cooling but many of these methods can be made to work well together.

9. Syntheses In Situ

Reactions at the interface between two solutions (e.g., different layers or at a capillary junction) can be used to generate a new product that is less soluble than either starting material and hence precipitates out as single crystals. If the reaction is slow enough, this can even happen in a single phase system. I have seen such methods work with both bond forming reactions and with redox reactions. In the latter case, one can often prepare single crystals of compounds that decompose almost instantly in solution at ambient temperature.

10. The Magic of NMR Tubes

If you've had occasion to search the data bases for crystal structures you may have noticed that an amazingly large number of structures are reported with deuterated solvents. This is not because people set out to crystallize from them but rather that crystals often grow "spontaneously" in NMR tubes. [Note: This is aided by the fact that many people don't clean out their NMR tubes until no clean ones are left in the lab and this beaker or "discarded" tubes it set somewhere out of the way where the boss won't see them and/or they won't cause guilt. This gives the solutions large blocks of time with no one disturbing them to grow crystals.] Most commonly, this happens because the NMR solvents one uses (e.g., $CDCl_3$) slowly diffuse out through the plastic caps.

11. Other Chance Methods

If all else fails, don't sneer at chance. Single crystals are often found in "purification" crystallizations, dishes waiting to be washed, and other unexpected places.

C. WHAT TO DO WHEN PROVEN METHODS FAIL

When your attempts at crystallization fail, there are a number of things that you should try.

1. Purify Your Material

Many times materials that are "analytically pure," are not pure enough for single crystal growth to be successful. Try an additional round of purification as this often improves your chances of success.

2. Seed Crystals

Because growing crystals pattern themselves on their initial substrate, seed crystals of the same or similar materials will often induce the growth of single crystals of the desired size. Such seeds are often formed inadvertently from droplets of crystallizing solution splashed on the container walls. However, they can also be added on purpose. One often uses a few of the best formed crystals from previous attempts where the crystals were too small by themselves. In some cases, one can use an isomorphous seed.

3. The Role of Extraneous Materials

Crystal growth typically requires a nucleating agent. Sometimes this is a seed crystal but often it is extraneous materials like dust, container walls, etc. Having just the right amount of nucleating agent is required to get great crystals.

a) Dust, dandruff, and grease

Unless "clean room" procedures are followed, every crystallization attempt will be effected by the presence to dust, dandruff, and other random particulates. A little normal lab dust will sometimes seed a crystal. I have also seen crystals that apparently were seeded by traces of grease on the flask walls!

b) Scratches and defects in the container walls

Tiny scratches and defects on the container walls are often the nucleating site for crystal growth. Sometimes if you can't get single crystals in a new container it pays to scratch it up a little. Alternately, if you are getting too many tiny crystals to grow you should use a less scratched container.

c) Surface treatments of the container walls

One trick that I have seen reported for improving crystal growth is to treat the surface of the container to change its chemical nature. This is most often done by reacting the surface with reagents such as Me_3SiCl.

4. Try, Try Again

The most important ingredients in the growing of quality single crystals are perseverance and patience. It is not uncommon to spend months or even years growing important crystals and succeeding after dozens or hundreds of failures.

a) Sequential crystal growing strategies

Most chemists employ sequential strategies where they try one or a few things at a time and then use the results to modify the procedures the next time. This typically takes only a fraction of your efforts each week to do but can be slow in terms of the number of months that pass before one is successful.

b) Systematic approaches to growing crystals and the exploration of crystallization: the multiplex advantage

Protein crystallographers have developed systematic methods to enhance crystal growing success. These typically involve careful explorations of the compound's "crystallization space." By this I mean the effects of temperature, time, solvent, etc., on crystal growing success. A key feature in this method is to use parallel approaches to crystal growth. For a small molecule chemist, this might translate into identifying five promising candidate solvents, and then simultaneously setting up 125 crystallizations (i.e., a 5 by 5 array to test various solvent mixtures made up five times with five different pin hole sizes in the lid). This does require more sample than sequential methods but can be done on very small scales (i.e., you only need one good crystal and this can grow from a fraction of a milliliter of solution) and will tend to give you successful results months sooner.

5. Make Derivatives

If your chosen compound just won't crystallize, one should often make a derivative of it. For example, I have made an ethyl rather than a methyl compound, a anisole rather than a benzene derivative, and a PF_6 rather than a BF_4 salt.

6. Solvates and Crystallization Agents

Many substances crystallize best as solvates. One can therefore add solvent molecules that are prone to forming such solvates (e.g., chlorinated organics such as CH_2Cl2, aromatics such as benzene and toluene, and water) to induce crystallization.

7. Inclusion Compounds and Supramolecular Complexes

Thiourea tends to form hollow channels of defined size when it crystallizes and if one adds a suitably sized substrate, it will often crystallize into these channels. Similarly, many bulky porphyrin compounds, cyclodextrins, calixarenes, and related molecules don't crystallize well in the absence of potential guest molecules. One can therefore sometimes induce the formation of host/guest supramolecular complexes by the purposeful addition of such hosts. Similarly, molecules such as crown ethers and cryptands can be added to modify the crystallization of ionic compounds.

CHAPTER XV. INDEX

It indexes the most important and/or commonly sought items in the manual, including: terms, concepts, commands, and symbols.

Dear Readers: Please feel free to suggest additional entries that should be added to this list.

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