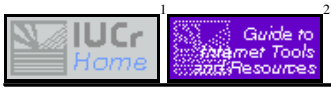
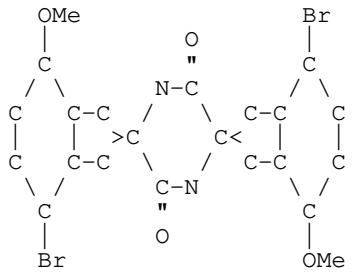


News Example: Help prevent ORTEP of the year

```
Newsgroups: sci.techniques.xtallography
From: mbruck@azstarnet.com (Mike Bruck)
Subject: help prevent ORTEP of the year
Date: Thu, 14 Mar 1996 03:10:26 GMT
Organization: Arizona Daily Star - AZSTARNET
```

I have a structure which is not behaving well and I would like some advice or assistance. The molecule is the meso form of Dimethoxy Dibromo Diketopiperazine



```
The unit cell is  8.2817    6.1031   21.7360
                 90.0000   97.2519   90.0000
```

There is an 0k0 k=2n+1 absence condition There are many exceptions to an h0l h+l=2n+1 condition so I have concluded that it is either P21 (#4) or P21/m (#11)

Surprizingly the Patterson shows a series of weak, monotonically decreasing peaks. There are no distinct Br vectors!

Direct Methods (Shelxs−93) gives a solution in P21, but not in P21/m.

The solution in P21 has TOTALLY disordered Br and OMe groups so that it is not possible to distinquish whether this is meso or a racemic d−l compound. The coordinates are appended to the bottom of this message for those who are interested.

Unfortunately it only refines to an R of 6% and what is worse(!) the ORTEP shows all the characteristics of an improperly solved structure.

Any suggestions or advice will be appreciated.

Mike Bruck
University of Arizona
Department of Chemistry
Tucson AZ 85721

mbruck@xray0.chem.arizona.edu

atoms.dat from Molen, (VAX/VMS version)

```
  Br5       0.128469 -0.471507  0.008544
  0.027163  0.045821  0.003037 -0.008107 -0.000228 -0.006707
  Br8       0.851728 -0.402233  0.178531
  0.017018  0.060790  0.005143  0.006661  0.003677 -0.007259
  Br15      0.365973  0.398590  0.492627
  0.022662  0.049764  0.003308 -0.008550  0.002012 -0.000845
```

[1] http://www.iucr.ac.uk/iucr−top/welcome.html
[2] int.index.html

```
  Br18     -0.349850  0.329514  0.317910
  0.022662  0.034667  0.007132  0.008754  0.006707 -0.006838
  O5        0.216013 -0.399334  0.024075
  5.291246  0.000000  0.000000  0.000000  0.000000  0.000000
  O8        0.756489 -0.376800  0.158928
  6.280622  0.000000  0.000000  0.000000  0.000000  0.000000
  O15       0.315678  0.301081  0.475958
  6.890503  0.000000  0.000000  0.000000  0.000000  0.000000
  O18      -0.314081  0.272711  0.337257
  4.934363  0.000000  0.000000  0.000000  0.000000  0.000000
  C5A       0.160286 -0.554202 -0.017289
 13.890241  0.000000  0.000000  0.000000  0.000000  0.000000
  C8A       0.932448 -0.522617  0.152742
 12.050902  0.000000  0.000000  0.000000  0.000000  0.000000
  C15A      0.327256  0.468537  0.534906
  7.281434  0.000000  0.000000  0.000000  0.000000  0.000000
  C18A     -0.396610  0.469593  0.339509
  5.042902  0.000000  0.000000  0.000000  0.000000  0.000000
  O1        0.330063  0.330823  0.190052
  0.042674  0.010281  0.004969  0.005982  0.018490  0.003096
  O11       0.166999 -0.388135  0.308109
  0.026009  0.014399  0.001743 -0.000858  0.006590  0.001528
  N1        0.288575 -0.241561  0.232677
  0.028239  0.009377  0.001721  0.007421  0.007517  0.000096
  N11       0.218433  0.169748  0.268218
  0.012730  0.013262  0.003025 -0.000046  0.006008 -0.000155
  C1        0.286521  0.160457  0.220380
  0.022497  0.006690  0.004030 -0.005519  0.011693 -0.003584
  C2        0.339585 -0.067213  0.192207
  0.027726  0.004049  0.002326 -0.000149  0.012429 -0.001685
  C3        0.257598 -0.093858  0.126123
  0.022852  0.029176  0.002291  0.017629 -0.000693  0.003769
  C4        0.362455 -0.246014  0.101100
  0.019074  0.013992  0.003251 -0.004032 -0.000107  0.001632
  C5        0.328710 -0.412091  0.053676
  0.013434  0.037925  0.002619 -0.001449  0.001165 -0.002472
  C6        0.455876 -0.570064  0.042223
  0.021542  0.015390  0.002074 -0.003415  0.003334 -0.004612
  C7        0.596182 -0.545046  0.076015
  0.038062  0.021064  0.003091 -0.006228  0.015521 -0.003311
  C8        0.636387 -0.390151  0.124722
  0.011330  0.041116  0.002367 -0.010377 -0.001363  0.004964
  C9        0.519831 -0.256081  0.140341
  0.009134  0.019729  0.003156 -0.008755  0.006535  0.002467
  C10       0.511464 -0.077406  0.190748
  0.017107  0.013267  0.002865 -0.003406  0.008159 -0.007461
  C11       0.201666 -0.228944  0.282632
  0.015021  0.020114  0.001250  0.012704  0.000677  0.004773
  C12       0.169209 -0.011933  0.303618
  0.009868  0.023692  0.002059  0.004163 -0.000636  0.001387
  C13       0.242529  0.035043  0.373245
  0.015767  0.010086  0.002570 -0.002117  0.008438  0.000072
  C14       0.122526  0.204556  0.395170
  0.016170  0.020013  0.000775  0.008643  0.006939  0.002802
  C15       0.142918  0.344224  0.442194
  0.021988  0.025402  0.001291 -0.004737  0.006385  0.001928
  C16       0.027875  0.462322  0.455081
  0.037018  0.032486  0.002710 -0.030589  0.011089 -0.008939
  C17      -0.126261  0.468957  0.421037
  0.011450  0.031638  0.003526  0.014387  0.004207 -0.003196
  C18      -0.153165  0.325269  0.370122
  0.022234  0.014197  0.003709  0.013014  0.010684 -0.003662
  C19      -0.023043  0.180242  0.362781
  0.027486  0.012583  0.001793  0.005638  0.005599 -0.001633
  C20      -0.026055  0.025355  0.311515
  0.013538  0.020609  0.002921 -0.001255  0.002358  0.002786
  H6        0.439777 -0.678942  0.010812
  5.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  H7        0.682121 -0.639956  0.068108
  5.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  H3A       0.243344  0.039122  0.103367
  5.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  H3B       0.154789 -0.161718  0.127279
  5.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  H10A      0.566168 -0.130925  0.228832
  5.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  H10B      0.559924  0.056482  0.180371
  5.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  H1        0.314219 -0.385776  0.220621
```

```
  5.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  H11       0.192953  0.312672  0.281382
  5.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  H13A      0.350329  0.090622  0.375872
  5.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  H13B      0.242121 -0.094759  0.397348
  5.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  H17      -0.210580  0.564684  0.430100
  5.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  H16       0.052721  0.558181  0.489407
  5.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  H20A     -0.068262 -0.109608  0.324308
  5.000000  0.000000  0.000000  0.000000  0.000000  0.000000
  H20B     -0.086663  0.070837  0.273638
  5.000000  0.000000  0.000000  0.000000  0.000000  0.000000
```

```
Newsgroups: sci.techniques.xtallography
From: fronz@chxray.dnet.lsu.edu (Frank Fronczek)
Subject: Re: help prevent ORTEP of the year
Date: Thu, 14 Mar 1996 04:17:07 -0600
Organization: Louisiana State University InterNetNews Site
```

Mike,
Translation of your coordinates by something like –0.249, 0.029, –0.249 places the molecule on a center in P2(1)/n with deviations on the order of a few tenths on an Angstrom across the center. You might want to try refinement of this centrosymmetric model on the hypothesis that the n–glide violations are spurious. The Br and OMe groups would still be disordered, of course. Good luck!

```
Newsgroups: sci.techniques.xtallography
From: GREGOR@unisi.it (Miguel Gregorkiewitz)
Subject: RE: stx2485 help prevent ORTEP of the year
Date: Thu, 14 Mar 1996 20:33:32 +0100 (WET)
Organization: Dip Scienze della Terra, Universita, SIENA, Europe
```

Date: Thu, 14 Mar 1996 03:54:42 CST
mbruck@azstarnet.com (Michael Bruck) wrote about an organic crystal stru (dipiperazine....) to behave crazy withpseudo–extinctions and the like.
We had similar problems with a metall–organic structure and zeolites, and found some help thru intensity statistics. There is even a program which does the job – oh, only half of the job, because I never had time to include the less original steps like space group selection. You may have a look at some aspect in Gregorkiewitz & Tudela, Acta Cryst (1990) C46: 210–213, if you think it is of interest for your case, I can send you an abstract with more exhaustive explanations presented at ECM–16 or so some year ago.
Best regards

Prof. Miguel Gregorkiewitz
Dip Scienze della Terra, Universita
Via delle Cerchia 3, I–53100 SIENA, Europe
fon +39’577’298823 fax 298815

```
Newsgroups: sci.techniques.xtallography
From: mbruck@azstarnet.com (Mike Bruck)
Subject: Re: help prevent ORTEP of the year
Date: Sat, 16 Mar 1996 13:19:12 GMT
Organization: Arizona Daily Star - AZSTARNET

Frank Fronczek <fronz@chxray.dnet.lsu.edu> wrote:

>Mike,
>Translation of your coordinates by something like -0.249, 0.029,
>-0.249 places the molecule on a center in P2(1)/n with deviations on
>the order of a few tenths on an Angstrom across the center. You might
>want to try refinement of this centrosymmetric model on the hypothesis
>that the n-glide violations are spurious. The Br and OMe groups would
```

```
>still be disordered, of course.
>Good luck!
>Frank Fronczek
```

THANKS to Frank, Fred Hollander, Larry Henling, Kris Tesh and A. Chandrasekaran!! The advice to ignore the h+l=2n+1 violations seems to be the answer. The structure solves quite nicely in P21/n. The final R−value is slightly lower than in P21, but the data:parameter ratio is much better! since the molecule now sits on an inversion center. The ORTEP no longer gives me nightmares!

Anyone have a good explanation for the h+l=2n+1 exceptions? Maybe the disorder of the Br isn't perfectly distributed? Might this be the source of anomolous reflection intensity? If I have the time and the crystal is stll mounted I'll try some psi−scans when the diffractometer is free.....

Thanks again
Mike

```
Newsgroups: sci.techniques.xtallography
From: boyle@laue.chem.ncsu.edu (Paul D. Boyle)
Subject: Re: help prevent ORTEP of the year
Date: 19 Mar 1996 14:04:39 GMT
Organization: North Carolina State University
```

Michael Bruck (mbruck@azstarnet.com) wrote:

```
: Anyone have a good explanation for the h+l=2n+1 exceptions?
: Maybe the disorder of the Br isn't perfectly distributed?  Might this
: be the source of anomolous reflection intensity?  If I have the time
: and the crystal is stll mounted I'll try some psi-scans when the
: diffractometer is free.....
```

These could be Renniger reflections. If your crystal is still on the difractometer, go to one of the "violations" and offset psi by couple of degrees and scan through the peak. If it's a Renniger affected reflection, the anomalous intensity should drop off.

You may also find it constructive to read Marsh's recent paper, "Some Thoughts on Choosing the Correct Space Group" in Acta. Cryst. (1995) B51, 897−907. It is a very worthwhile read.

later,

Paul

```
__
Paul D. Boyle                          |   boyle@laue.chem.ncsu.edu
Director, X-ray Structural Facility    |   phone: (919) 515-7362
Department of Chemistry - Box 8204     |   FAX:   (919) 515-5079
North Carolina State University        |
Raleigh, NC, 27695-8204
http://laue.chem.ncsu.edu/web/xray.welcome.html
```

```
Newsgroups: sci.techniques.xtallography
From: "Graheme J.B. Williams" <GRAHEME@enraf.delftny.com>
Subject: (Fwd) Spurious reflections
Date: Tue, 19 Mar 1996 15:56:38 EST
Organization: Enraf-Nonius, Kipp & Zonen
```

Mike,

Pleased to note that you will not be cited in The R Harlow Hall of Shame – this year or any other I am sure.

Obviously your respondents were right in suggesting that the violations of the h+l=2n rule were spurious. There are two main reasons for this.
1) Renninger reflections. These are "reflections which use a strong reflected beam as the x−ray source" They are common when the crystal is of high quality and good reflection power.

Perhaps they are the cause for you but I do not expect so since the sample is disordered.
2) Lambda/2 effects. In both a crystal–monochromated beam and in a filtered beam there exists significant contamination by the "half wavelength" component of the spectrum. This can give rise to spurious reflections and, of course, contamination of all reflections. If the doubled indices of the spurious reflections correspond to strong reflections then I think that this is a most likely cause. For example if your reflection 2.0.1 is present but should not be then look at 4.0.2 Is it strong? The diagnostic test for this phenomena is to look at a position in space where ONLY the lambda/2 reflection will occur. For example if your 1.1.1 is strong look for the reflection 1/2.1/2.1/2 If it's there then you have contamination. Of course in order to look for a reflection with fractional indices you need to have a CAD4 or some other diffractometer which has some sophistocated tools built in!

If this contamination exists then there are two "cures".
1) Don't worry about it.
2) Adjust the window of your Pulse Height Discriminator to reduce the observability of the double–energy peaks. Of course when you do this you also will reduce the observabilityof peaks which have double energy because of two normal pulses arriving at the same time. This should be too much of a problem however since at high count rates your diffractometer looks after you!


```
Cheers.  =Graheme=
EEEE N   N Graheme J. B. Williams:     || //   cc   cc  ddd    \\
E    NN  N 390 Central Ave,       :    ||//   c    c    d  d    \\
EEE  N N N Bohemia,NY 11716-3147 :    ||\\   c    c    d  d    //
E    N  NN Tel;(516)589-2885,X40 :     || \\   cc   cc  ddd    //
EEEE N   N Fax;(516)589-2068     :
           Williams@DelftNY.com  : HTTP://WWW.Enraf-Nonius.DelftNY.com
Comments on our WWW site are solicited
```

```
Newsgroups: sci.techniques.xtallography
From: swinnea@weiss.che.utexas.edu (J. Steven Swinnea)
Subject: Re: (Fwd) Spurious reflections
Date: 20 Mar 1996 16:31:48 GMT
Organization: Dept. Chem. Engr., Univ. of Texas at Austin

In article <7F29017BD0@enraf.delftny.com>,
Graheme J.B. Williams <williams@delftny.com> wrote:
>there then you have contamination.  Of course in order to look for a
>reflection with fractional indices you need to have a CAD4 or some
>other diffractometer which has some sophistocated tools built in!
```

Gee... I didn't know that doubling the unit–cell edges to make the 1/2.1/2.1/2 a 1.1.1 was all that sophisticated. :–)


```
Steve Swinnea
swinnea@che.utexas.edu
Department of Chemical Engineering
```

```
Newsgroups: sci.techniques.xtallography
From: Hakon Hope <hhope@ucdavis.edu>
Subject: Re: (Fwd) Spurious reflections
Date: Wed, 20 Mar 1996 17:05:18 -0800
Organization: University of California, Davis

:Steve Swinnea says: Gee...  I didn't know that doubling the
:unit-cell edges to make the
:1/2.1/2.1/2 a 1.1.1 was all that sophisticated.  :-)
```

The sophistication lies in *not* having to double the cell edges, but to go to fractional indices without further ado. Graheme Williams is quite justified in making fun of some well–known diffractometer software where you have to double, or triple, or quadruple or whatever, just to check some region with non–integer indices.

Hakon Hope

[Index[3]] – 10th Sept. 1996 – © Lachlan M. D. Cranswick[4] – **Not to be copied or reproduced without permission** – Author's current manuscript[5]

[3] int.index.html
[4] http://www.unige.ch/crystal/stxnews/stx/volnteer.htm
[5] http://www.unige.ch/crystal/stxnews/newsgrp/newsexm3.htm