Data Collection and Data Reduction Techniques for Modulated Structures

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Outline

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• An organic polycyclic compound
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Pseudoephedrine Hydrochloride in the literature


**The Crystal and Molecular Structures of (+)-Pseudoephedrine and (+)-Pseudoephedrine Hydrochloride**

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The crystal structures of (+)-pseudoephedrine, I, and (+)-pseudoephedrine hydrochloride, II, have been determined by X-ray diffraction techniques. Both compounds form orthorhombic crystals, with the space group $P2_12_12_1$ and four molecules per unit cell. The unit-cell dimensions are $a = 7.337 (4)$, $b = 8.646 (5)$ and $c = 16.113 (7)$ Å for I and $a = 25.358 (11)$, $b = 6.428 (5)$ and $c = 6.901 (5)$ Å for II. The structures were solved by direct methods and refined by least-squares techniques to $R$ values of 0.065 for I and 0.075 for II. We have demonstrated that protonation does not alter molecular shape since the conformations in I and II are virtually identical. Both molecules, I and II, are in an extended form which is similar to that found in various ephedrines and related phenethylamines.
Is this the whole story?

- What are these additional spots?
- No mentioning of additional reflections or satellites on Precession photographs
- Data were collected at room temperature

Preliminary precession photographs indicated orthorhombic symmetry. The systematic absences of \( h00 \) for \( h = 2n + 1 \), \( 0k0 \) for \( k = 2n + 1 \) and \( 00l \) for \( l = 2n + 1 \) indicated that the most probable space group was \( P2_12_12_1 \).
Pseudoephedrine at Low Temperature and at Room Temperature

- Problematic thermal ellipsoids at low temperature

-193 deg. C
R1 = 2.22%

23 deg. C
R1 = 2.82%
Single crystal experiments

- Data collection temperatures:
  53 °C, 23 °C, -73 °C, -123 °C, -173 °C and -193 °C

- Instrumentation:
  APEX DUO, Mo-radiation
  Cryostream 700+

- Data collection strategy:
  omega and phi scans, 0.3°, 10s

- Software:
  APEX2

-193 deg.C
Diffraction pattern at varying temperatures

- Diffraction patterns show two trends at lower temperatures
  - Diffraction to higher 2Theta angles
  - More (satellite) reflections

-193 deg. C
h0k layer – pseudo-precession frames

- Pseudo precession images reconstructed from complete data sets
- More satellites at lower temperature
- Almost no satellites detectable at high temperature
- Satellites are rather weak
- So where do all these additional spots come from?
A closer look at how the satellites change with temperature
Ratio of intensity of main reflection to satellites

- The relative intensity of the satellite reflections is the highest for the data collected at \(-123^\circ C\).
- Satellites become relatively weaker at lower temperatures.
- What would happen at \(-270^\circ C\)?
How to better describe the structure?

- Take the satellites into account and quadruple the a-axis
- Symmetry is now decreased from orthorhombic to monoclinic
- Spacegroup changes from P2₁2₁2₁ to P2₁
- Twinning is introduced as a 180° rotation about the c-axis
- Structure refines to R1=2.48%
- Modulation becomes quite obvious
How to even better describe the structure?

- Determine the q-vector
- Integrate main reflections with satellites using a q-vector concept
- Produce hkl 6 format files for data processing in Jana 2006
- Refine the structure as a modulated structure
Two-dimensional periodic arrangement
Diffraction pattern of a two-dimensional periodic arrangement
Two-dimensional periodic arrangement perturbed by a modulation
Diffraction pattern of a two-dimensional modulated arrangement
Defining the modulation vector $q$
The q-vector concept

These spots are regularly distributed and they can be indexed if one or more additional vectors are added to the reciprocal basis. The general diffraction spot at $Q$ can be expressed as

$$Q = h\mathbf{a}_1^* + k\mathbf{a}_2^* + l\mathbf{a}_3^* + mq$$

where the vector $\mathbf{q}$ is called the modulation vector. Reflections having index $m$ equal to zero are the main reflections, the others are satellite reflections. The modulation vector $\mathbf{q}$ can be expressed in the reciprocal basis:

$$\mathbf{q} = \alpha\mathbf{a}_1^* + \beta\mathbf{a}_2^* + \gamma\mathbf{a}_3^*$$
Types of Modulated Structures

**Commensurate cases**

If the superspots are located at simple fractions of the vectors of the reciprocal lattice of the substructure, e.g., at \( q=(\frac{1}{2},0,0) \), the resulting broken symmetry is a doubling of the unit cell along the \( a \) axis. Such a modulation is called a **commensurate** superstructure.

**Incommensurate cases**

In some materials, superspots will occur at positions that do not represent a simple fraction, say \( q=(0.5234,0,0) \). In such a case a structure results that strictly speaking has lost all translational symmetry in a particular direction. This is called an **incommensurate** structure.
Supercells

In the commensurate case, we can use a regular three-dimensional description as the basic vectors can be transformed into a proper supercell.

However, such an approach may not be convenient as satellites are often very weaker and the number of observable reflections may not be sufficient to solve and refine the structure in a supercell.
Identifying the main lattice (1)

- Harvested reflections from 300 frames using APEX2 software – about 4000 reflection
- Display reflections in RLATT
- Identify main lattice
- Select main lattice reflections
Identifying the main lattice (2)

- Harvested reflections from 300 frames using APEX2 software – about 4000 reflection
- Display reflections in RLATT
- Identify main lattice
- Select main lattice reflections
Identifying the main lattice (3)

- Harvested reflections from 300 frames using APEX2 software – about 4000 reflection
- Display reflections in RLATT
- Identify main lattice
- Select main lattice reflections
Identifying the main lattice (4)

- Harvested reflections from 300 frames using APEX2 software – about 4000 reflection
- Display reflections in RLATT
- Identify main lattice
- Select main lattice reflections
Indexing the main lattice

- Defined about 2,600 reflections belonging to the main lattice – gray group
- Indexing on the gray group only
- Refinement and Bravais proposes an orthorhombic cell
Defining the satellites – q vector (1)

- Reflection array aligned along a*
- Switch to “incommensurate mode”
Defining the satellites – q vector (2)

- Folding the main lattice on itself
- Removing three dimensions
Defining the satellites – q vector (3)

- Folding the main lattice on itself
- Removing three dimensions
- Setting the q-vector
Data integration

- The q-vector is written to APEX2's database and part of the p4p file
- SAINT automatically switches to “incommensurate mode” and generates a \texttt{hklf 6} type output file with a \texttt{.ram} extension
- Specify the Maximum Satellite Index in the integration options dialog
- SAINT refines the q-vector during data integration
- The q-vector refined to about 0.238 for all pseudoephedrine data sets
Data scaling

- SADABS was modified to handle the .ram files created by SAINT
- SADABS will create a hk6 file which can be used with Jana 2006
Structure refinement in Jana 2006

• Data were used for teaching purposes during the ACA Jana workshop
• The structure was refined in the super-spacegroup P212121(00g)000
• Several different models gave similar R-values which supports the fact that the modulation is not very strong
  • Modulated structure approach
  • Commensurate (supercell)
  • Incommensurate with overlap (of satellite reflections) option
Step-wise procedure for collecting and processing modulated structure data

- Collect hemisphere of high quality data
- Harvest large number of reflections with low I/sigma threshold (e.g., 1.75).
- Determine basic unit cell with very large I/sigma (e.g., 250) threshold.
- Use Incommensurate tool in RLATT to determine $q$-vector and number of satellite peaks.
- Integrate data to produce *.ram files.
- Scale the data to carry out absorption corrections on main reflections as well as satellites.
- Prepare JANA2006-compatible .hk6 file
- Input the corresponding .p4p and .hk6 files into JANA2006 to carry out solution and refinement of modulated structure.
Collection of Modulated Structure Data

Data Collection

- Data were collected at room temperature on a Bruker Kappa APEX II system equipped with a Mo fine-focus x-ray tube operated at 1,500 watts (50 kV, 30 mA).

- A total of 4,355 images were collected in 1024 x 1024 mode as phi or omega scans with 30-second exposure time at a detector distance of 60 mm. Total data collection time was 42 hours.
Collection of Modulated Structure Data
Reflections were harvested from the entire dataset with a very low threshold (e.g., 1.75)
Determination of the sub-cell – initial unit cell

• After harvesting, the threshold parameter was set to a very high value (e.g., 250) for indexing.

• The difference vector method produced a small triclinic cell with a high score.
Refinement of the initial unit cell

Unit Cell:
- \(a = 3.12 \text{Å}, \ c = 110.68^\circ, \ V = 38 \text{Å}^3\)
- \(b = 3.13 \text{Å}, \ \beta = 110.62^\circ\)
- \(c = 4.43 \text{Å}, \ y = 90.04^\circ\)

Parameters:

Unit cell
- \(a [\text{Å}]\): 3.12
- \(b [\text{Å}]\): 3.13
- \(c [\text{Å}]\): 4.43
- \(\alpha [^\circ]\): 110.68
- \(\beta [^\circ]\): 110.62
- \(\gamma [^\circ]\): 90.04
- \(V [\text{Å}^3]\): 38

Domain translation
- \(x [\text{mm}]\): 0.00
- \(y [\text{mm}]\): 0.00

Reflections:
- Group 0: 1774 reflections

Go to Image: C:\Frames\guest\...\mo_UWDF03A_01_0001.sfrm

More Reflections Fewer Reflections

Tolerance: 5.00

785 Reflections selected for Refinement
Determination of the Bravais lattice
I-centered orthorhombic
Refinement of the I-centered orthorhombic unit cell
RLATT view of the I-centered unit cell
RLATT view of the I-centered unit cell
Use of RLATT to determine q-vector for the I-centered unit cell
Integration of data with one q-vector, twinning and 4 orders of satellites
Creation of JANA2006-compatible .hk6 file
Format of JANA2006-compatible .hk6 file

```
3  2  -3  -4  0  0  9.93139  0.93847
3  2  -3  -3  0  0  0.45937  0.42944
3  2  -3  -2  0  0  4.99597  0.65284
3  2  -3  -1  0  0  0.1388  0.43648
3  2  -3  0  0  0  3416.04  50.8760
3  2  -3  1  0  0  0.6570  0.44759
3  2  -3  2  0  0  9.25200  0.83563
-3 -2  3  -2  0  0  10.3876  0.62885
-3 -2  3  -1  0  0  0.4724  0.33557
-3 -2  3  0  0  0  3521.40  39.4499
-3 -2  3  1  0  0  0.1642  0.32223
-3 -2  3  2  0  0  9.96444  0.57861
-3 -2  3  3  0  0  0.2452  0.30998
-3 -2  3  4  0  0  8.23304  0.72234
```
What’s wrong with it?

$R_1 = 22.23\%$; res. el. density $= 2.72 \text{ e}^- / \text{Å}^3$

Marilyn Olmstead
Pseudo precession image - h1l
Defining the satellites – q vector

- Folding the main lattice on itself
- Removing three dimensions
Defining the satellites – q vector

- Orientation along b*
- Measuring tool
- q vector 0.293 0.000 0.000
Defining the satellites – q vector

- Extended display for easier definition of satellite reflections
- Order of three was chosen to split the measuring tool into three segments
Defining the satellites – q vector

- Color coding the satellite reflections
Defining the satellites – q vector

- Unfolding the reflection array
Structure refinement

The structure was refined in the super space group: P212121(a00)s00

R factors : [16820=9856+6964/1609],  Damping factor:  1.0000
GOF(obs)=  1.61  GOF(all)=  1.30
R(obs)=  5.00  Rw(obs)=  5.79  R(all)=  8.90  Rw(all)=  6.30

R factors for main reflections : [3386=2579+807]
R(obs)=  3.48  Rw(obs)=  3.99  R(all)=  5.23  Rw(all)=  4.24

R factors for satellites of order 1 : [6704=4202+2502]
R(obs)=  4.97  Rw(obs)=  6.20  R(all)=  8.07  Rw(all)=  6.59

R factors for satellites of order 2 : [6730=3075+3655]
R(obs)=  7.21  Rw(obs)=  7.66  R(all)= 13.70  Rw(all)=  8.73

Maximal density : 0.45, minimal density : -0.32.

Trixie Wagner and Andreas Schönleber
Animated conformation changes

- Change of the molecular conformation as function of the phase of the modulation $t$, viewed along $c$
- The sequence along $t$ was calculated in steps of 0.1.
• Change of the molecular conformation as function of the phase of the modulation $t$, viewed along $a$
• The sequence along $t$ was calculated in steps of 0.1.

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Conclusion

- Powerful tools to identify incommensurate data are available
- Data collection at varying temperatures has been automated
- Indexing and q-vector determination has been greatly improved
- Data integration and scaling produces hkl 6 format data compatible with JANA 2006
Jana2006 Cookbook

Version December 2012

Solved examples on various topics covered by crystallographic computing system Jana2006. The cookbook cumulates examples from Jana workshops. The program Jana2006, the latest cookbook and data for examples are available in jana.fzu.cz.

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Importing of Bruker data into Jana2006

- Create new structure within JANA2006
Importing of Bruker data into Jana2006

- Browse to find .p4p file for project
Importing of Bruker data into Jana2006

- Specify data source

![Image of data import interface](image-url)
Importing of Bruker data into Jana2006

- Import data from .p4p file

![Diagram showing experimental parameters and polarization correction settings]
Importing of Bruker data into Jana2006

- Import data from .p4p and hk6 files

![Image of Jana2006 interface showing data import settings and a list of data files with information about file type and radiation.]
Importing of Bruker data into Jana2006

- Determine Bravais Lattice
Importing of Bruker data into Jana2006

- Determine Space Group and Superspace Group