Modulated organic compounds

Gervais Chapuis, LCr
Disclaimer and copyright notice

Copyright 2010 Gervais Chapuis for this compilation.

This compilation is the collection of sheets of a presentation at the “International School on Aperiodic Crystals,” 26 September – 2 October 2010 in Carqueiranne, France. Reproduction or redistribution of this compilation or parts of it are not allowed.

This compilation may contain copyrighted material. The compilation may not contain complete references to sources of materials used in it. It is the responsibility of the reader to provide proper citations, if he or she refers to material in this compilation.
Modulated structures in organic compounds

Examples of organic incommensurate structures

- 4-bromo-4’nitrobenzylidene aniline (BNBA)
- Quininium R mandelate (QuiRMa)
- HMT Resorcinol

Organic compounds with large Z’ treated as commensurately modulated structures

- Diaqua (15-crown-5 ether) copper(II) nitrate (crown ether)
4-bromo-4’nitrobenzylidene aniline (BNBA)

- second-order nonlinear optical material
- (3+1) dimensional incommensurately modulated structure

Alla Arakcheeva, private communication
### BNBA (2)

<table>
<thead>
<tr>
<th>Chemical formula</th>
<th>C_{13}H_9BrN_2O_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol. weight</td>
<td>305.1</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Group of symmetry (Space group)</td>
<td>A2(α0γ)0 / A2</td>
</tr>
<tr>
<td>Unit cell parameters</td>
<td>a = 10.5217(10), b = 16.2535(16), c = 7.4403(7) Å, β = 110.709(7), V = 1190.2(2) Å³</td>
</tr>
<tr>
<td></td>
<td>a = 10.6408(9), b = 16.2706(10), c = 7.5669(7) Å, β = 110.783(8), V = 1224.8(2) Å³</td>
</tr>
<tr>
<td>Modulation vector q</td>
<td>0.0658(1)a* -0.2658(1)c* / none</td>
</tr>
<tr>
<td>T, K</td>
<td>173 / 290</td>
</tr>
<tr>
<td>No. unique reflections: observed / total</td>
<td>4686 / 6701 / 1555 / 2557</td>
</tr>
<tr>
<td>No. main reflections: observed / total</td>
<td>1898 / 2228 / 1555 / 2557</td>
</tr>
<tr>
<td>No. satellite reflections: observed / total</td>
<td>2788 / 4473 / none</td>
</tr>
<tr>
<td>R_{obs}; R_{wobs}; R_{all}; R_{wall} (%)</td>
<td>main reflections 3.04; 3.06; 3.66; 3.13 / 7.01; 6.76; 11.22; 7.18</td>
</tr>
<tr>
<td></td>
<td>satellites 4.73; 4.48; 7.18; 4.71 / 4.76; 3.02; 4.88; 3.12</td>
</tr>
<tr>
<td></td>
<td>altogether 4.73; 4.48; 7.18; 4.71 / 4.76; 3.02; 4.88; 3.12</td>
</tr>
<tr>
<td>Residual electron density r_{max} and r_{min} e.Å⁻³</td>
<td>0.32 ; -0.30 / 0.28; -0.16</td>
</tr>
</tbody>
</table>
BNBA (3). Reconstructed $h0l$ layer showing the presence of main and satellites reflections. The crystal is obviously twinned.
BNBA (4). Simulated $h0l$ layer of a single twin component compared with the diffraction pattern.
BNBA (5). A single molecule with anisotropic displacement parameters (ADP’s)
BNBA (6). The packing of the molecules is subject to a network of H-bonds.
BNBA (7). 2D layers formed by non-periodic networks of H-bonded molecules.
BNBA (8). Sequence of different molecular conformations depending on the variable $t$
BNBA (9). Sequence of different molecular conformations depending on the variable $t$. 
BNBA (10). The displacement of the N atom is better represented by a combination of Crenel and modulation functions.
BNBA (11). The displacement of the C atom close to N is is also better represented by a combination of Crenel and modulation functions.
Modulated structures in organic compounds

Examples of organic incommensurate structures

- 4-bromo-4’nitrobenzylidene aniline (BNBA)
- Quinininium R mandelate (QuiRMa)
- HMT Resorcinol

Organic compounds with large Z’ treated as commensurately modulated structures

- Diaqua (15-crown-5 ether) copper(II) nitrate (crown ether)
**Quininium (R)-mandelate (QuiRMa)**

<table>
<thead>
<tr>
<th><strong>Chemical formula</strong></th>
<th>$\text{C}<em>{20}\text{H}</em>{25}\text{N}_2\text{O}_2^+ \text{C}_8\text{H}_7\text{O}_3^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>superspace group</strong></td>
<td>Monoclinic, $P2_1(\alpha\gamma)$</td>
</tr>
<tr>
<td><strong>a, b, c (Å)</strong></td>
<td>6.614, 18.552, 10.377</td>
</tr>
<tr>
<td><strong>$\beta (°)$</strong></td>
<td>107.47</td>
</tr>
<tr>
<td><strong>Modulation wavevector</strong></td>
<td>0.3329, 0, -0.2713</td>
</tr>
<tr>
<td><strong>No. of measured, independent and observed reflections ($&gt; 2\sigma$)</strong></td>
<td>204'354, 40'498, 12'714</td>
</tr>
<tr>
<td><strong>No. of independent and observed fifth-order satellites ($&gt; 2\sigma$)</strong></td>
<td>6936, 287</td>
</tr>
</tbody>
</table>

QuiRMa. The reciprocal space.

$h1l$ precession layer
QuiRMa. Resolution and refinement.

Structure solution
- charge flipping
- (a more elaborate resolution was used at the time of publication)

Structure refinement
- Introduction of rigid entities
- Four harmonic terms for displ. modul.
QuiRMa. Refinement results.
QuiRMa. Crenel and sawtooth functions refinements.
QuiRMa. Torsion angle of the vinyl group.
QuiRMa. The vinyl group.
QuiRMa. The vinyl group.
QuiRMa. Others functional groups.
QuiRMa. What about a commensurate approximation?

3x5 approximation?

3x6 approximation?
QuiRMs. What about a commensurate approximation?

Problems with commensurate approximations

- Requires often a very large number of closely identical molecules ($Z' > 10$ to $20$)
- Leads to ill defined refinement problems
- The commensurate model remains always an approximation
- The symmetry of the model depends on which rational approximation is used
- The number of refined parameters might greatly increase
- ...
Organic compounds with large $Z'$ treated in the superspace formalism

There are many advantages to treat this category of structures in the superspace formalism:

• Recall that $Z$ is the number of formula units in the unit cell and $Z'$ is the number of symmetry independent formula units.
• In general, a single superspace group is sufficient to describe all possible temperature of pressure dependent phases.
• Great help for solving cases of polymorphism.
• Tools for the resolution of the structure in superspace are more efficient than conventional ones.
Modulated structures in organic compounds

Examples of organic incommensurate structures

- 4-bromo-4’nitrobenzylidene aniline (BNBA)
- Quininium R mandelate (QuiRMa)
- HMT Resorcinol

Organic compounds with large $Z'$ treated as commensurately modulated structures

- Diaqua (15-crown-5 ether) copper(II) nitrate (crown ether)
Hexamine resorcinol, an organic incommensurate structure

hexamine resorcinol

projection along x

projection along y

The diffraction patterns

Room temperature

\[ \mathbf{q} = (0, 0.376, 0) \rightarrow 268\text{K} \]

Low temperature

\[ \mathbf{q} = (0\frac{1}{2}, \frac{1}{4}) \]
Possible C-H⋯O interactions and corresponding schemes

Example of neighbourhood of one resorcinol molecule.

The molecule at the centre can have two possible orientations.

The pictogram is used to characterise each possible H-bond environment.
Incommensurate refinement in superspace

\( o[A] \) and \( o[B] \) gives the occupancies of the central molecules A and B.

The orientations of the molecules in the neighbourhood is given by the pictograms.
Satellites and diffuse scattering

The example of HMT resorcinol illustrates many aspects encountered in organic compounds:

- Satellites are often observed with the presence of diffuse scattering.
- Diffuse scattering often converge to satellite reflections at phase transition.
- The interpretation of diffuse scattering can be facilitated by using pseudo satellite reflections and solving the structure with the superspace formalism.
Modulated structures in organic compounds

Examples of organic incommensurate structures

- 4-bromo-4’nitrobenzylidene aniline (BNBA)
- Quinininium R mandelate (QuiRMa)
- HMT Resorcinol

Organic compounds with large $Z'$ treated as commensurately modulated structures

- Diaqua (15-crown-5 ether) copper(II) nitrate (crown ether)
Crown ether

\[ [\text{Cu(H}_2\text{O)}_2(\text{C}_{10}\text{H}_{20}\text{O}_5)](\text{NO}_3)_2 \]

(15-crown-5 ether) copper(II)

Schönleber et al., Ferroelectrics, 2004)
Crown ether

$$[\text{Cu(H}_2\text{O})_2(\text{C}_{10}\text{H}_{20}\text{O}_5)](\text{NO}_3)_2$$

Diaqua
(15-crown-5 ether)
copper(II) nitrate
Crown ether

<table>
<thead>
<tr>
<th></th>
<th>[1]</th>
<th>[2a]</th>
<th>[2b]</th>
<th>[3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z, Z'</td>
<td>2, 1/2</td>
<td>20, 10</td>
<td>20, 10</td>
<td>2, 1</td>
</tr>
<tr>
<td>space group</td>
<td>P2\textsubscript{1}/c</td>
<td>Pc</td>
<td>Pn</td>
<td>Pc(0\textgamma)s</td>
</tr>
<tr>
<td>a (Å)</td>
<td>7.375(3)</td>
<td>14.758(5)</td>
<td>14.7668(9)</td>
<td>7.3820(8)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>13.981(4)</td>
<td>13.978(4)</td>
<td>13.9749(7)</td>
<td>13.9705(13)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>8.657(3)</td>
<td>43.914(13)</td>
<td>43.3500(30)</td>
<td>8.6690(10)</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>97.35(3)</td>
<td>102.19(3)</td>
<td>97.369(5)</td>
<td>97.371(7)</td>
</tr>
<tr>
<td>q</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(0.5, 0, -0.4)</td>
</tr>
</tbody>
</table>

[2a] Dejehet et al. (1987)
[2b] Pc \rightarrow Pn
TWO CLOSELY RELATED POLYMORPHS (Z'\(=\)1/2 AND Z'\(=\)10) THAT SEEM TO CO-EXIST

C. P. Brock X. Hao S. Parkin
University Of Kentucky Department Of Chemistry Rose Street At Funkhouser Drive
LEXINGTON KY 40506-0055 USA

The compound [Cu(H\(_2\)O\(_2\))(15-crown-5)](NO\(_3\))\(_2\) (CSD refcode GAVPEY) is reported to have two polymorphs: one with Z'\(=\)10 (1) and a second with Z'\(=\)1/2 (2). If the former is transformed from \(Pc\) to \(Pn\). The larger \(Pn\) cell is related to the smaller \(P2_1/c\) cell by the transformation 200/010/005. The dimensions near 295 K of the two cells are indistinguishable if \(a\) and \(c\) for the larger cell are divided by 2 and 5, respectively. In the Z'\(=\)1/2 polymorph the cations are disordered around inversion centers, but in the Z'\(=\)10 structure the cations are ordered.

(…)

TWO CLOSELY RELATED POLYMORPHS (Z'=1/2 AND Z'=10) THAT SEEM TO CO-EXIST

C. P. Brock X. Hao S. Parkin
University Of Kentucky Department Of Chemistry Rose Street At Funkhouser Drive
LEXINGTON KY 40506-0055 USA

(…) A partially disordered Z'=5 structure in P2_1/n seems reasonable, but preliminary results suggest that the noncentrosymmetric Pn description is preferable. Phase transitions from disordered to ordered structures are usually associated with a decrease in molar volume, but this one is not. Careful examination of diffraction patterns suggests that most 'single' crystals contain more than one phase. The diffraction patterns for most crystals are best indexed using the larger cell, but the relative intensities of the substructure and superstructure reflections are highly variable. For some crystals the superstructure reflections (h.ne.2n and l.ne.5m) are only ca. 10x weaker than the reflections that correspond to the smaller cell, but for other crystals the superstructure reflections are too weak to measure reliably.

The structure with $Z' = 1/2$
The structure with \( Z' = 10 \) (SG: \( Pc \))
Crown ether
The motif

A sequence of 10 successive molecules, 5 in one orientation and 5 in the other can be defined as the motif, *i.e.* the distinct repeat unit.
$h11$ zoom
Reciprocal Space

$Z' = 10$

$Z' = 1/2$

$P_c$

$P_n$
Superspace groups

- Reflection conditions
  - $0k00$: $k = 2n$
  - $h0l0$: $l = 2n$
  - $h0lm$: $l+m = 2n$

- Possible superspace groups
  - $P2_1/c(\alpha0\gamma)0s$
  - $Pc(\alpha0\gamma)s$

\[ \{ \text{3D supercell symmetry: Pn} \]
Superspace structure in $Pc(\alpha0\gamma)s$

- The starting model (fractional coordinates) is derived from the molecules of the $Z' = 10$ superstructure with one formula unit for each orientation.

- For each of the orientations the width of the crenels is set to $\Delta x_4 = 1/2$.

- Main and 1$^{st}$ order satellite reflections are used in the refinement.
Superspace structure in $Pc(\alpha 0 \gamma)_s$

- Fourier maps of corresponding Cu atoms in the $x_1$-$x_4$ plane
Superspace structure in $Pc(\alpha 0 \gamma)s$

- Fourier maps of corresponding O atoms in the $x_1$-$x_4$ plane
Superspace structure in $Pc(\alpha 0 \gamma)s$

- Cu – O distances in the crown-ether (5) and with water (2)
Crown ether
The conventional refinement with $Z' = 10$
What did we gain by using the superspace formalism?

• The structure model derived from the superspace is more plausible from the crystal chemical point of view
  - It contains essentially two types of molecules with the same geometry
  - This is a more plausible model than the classical model with \( Z' = 10 \) containing 10 independent molecules each with its own independant geometry.

• The unique model can also be applied to homologous series of this compound.