Modulated organic compounds

Gervais Chapuis, LCr

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Modulated structures in organic compounds

Examples of organic incommensurate structures

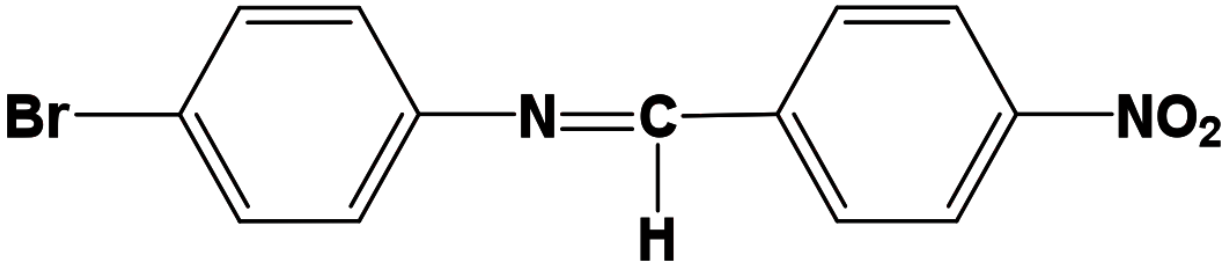
- 4-bromo-4'nitrobenzylidene aniline (BNBA)
- Quininium R mandelate (QuiRMa)
- HMT Resorcinol

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



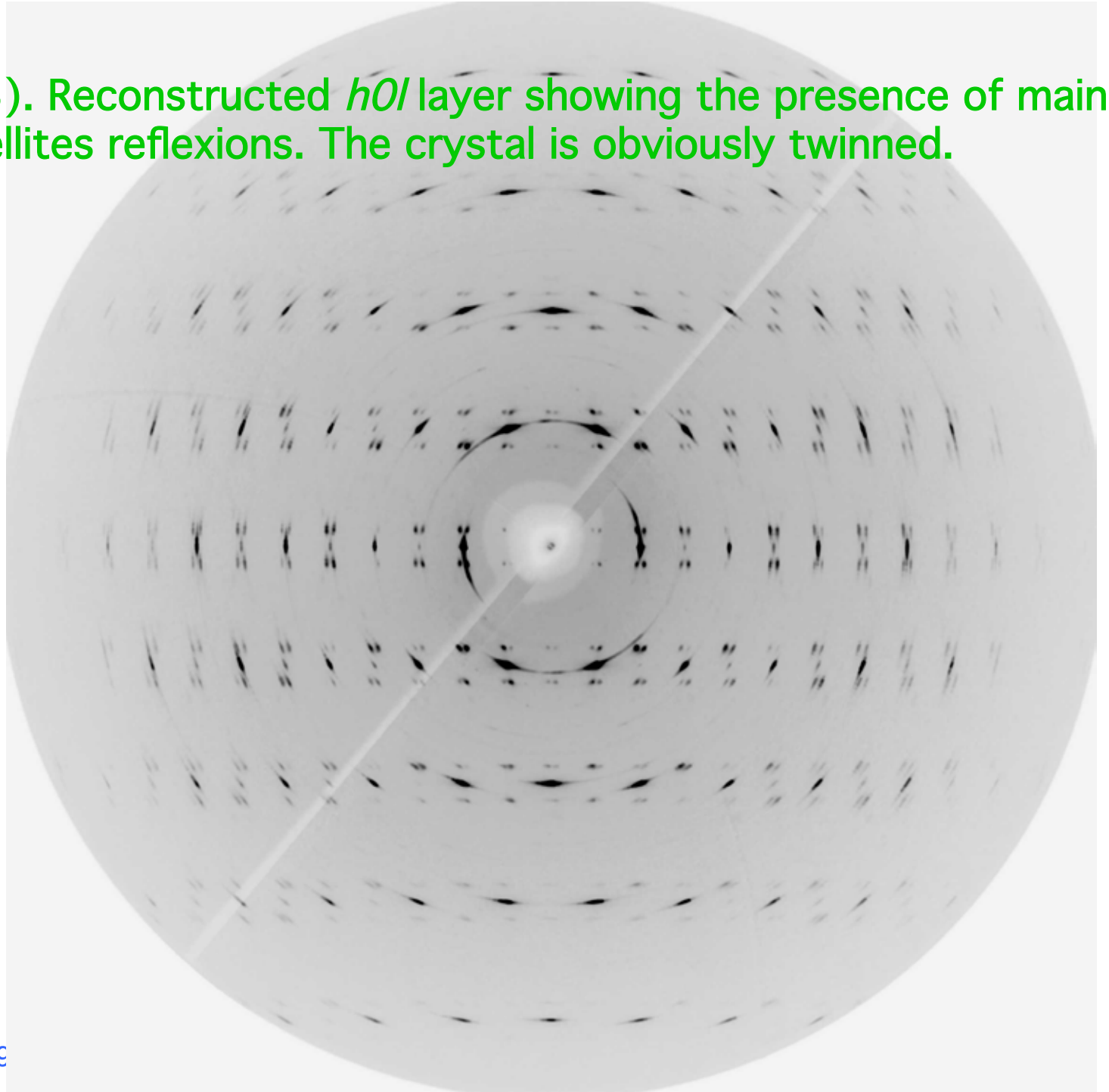
BNBA

Alla Arakcheeva, private communication

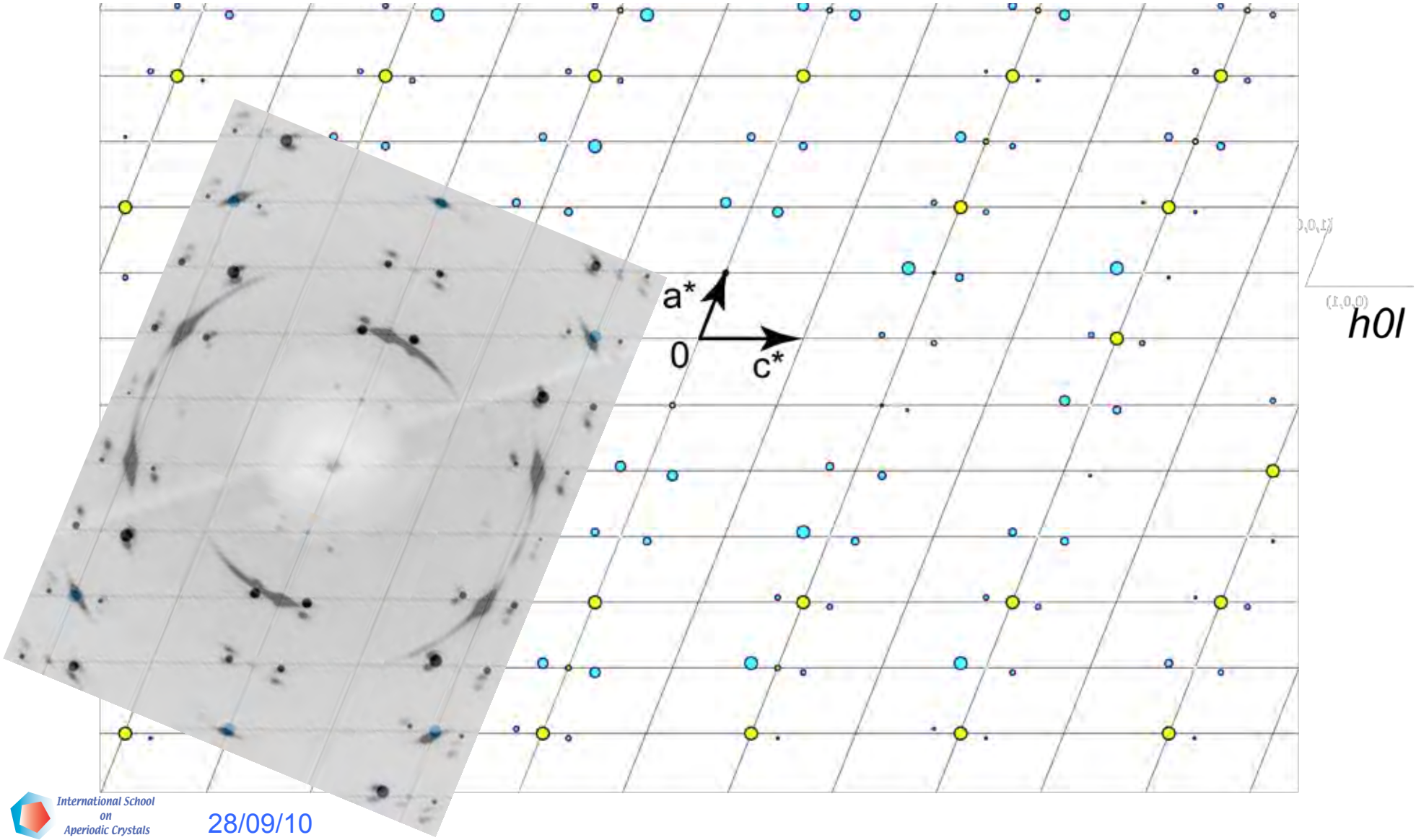
BNBA (2)

Chemical formula	$C_{13}H_9BrN_2O_2$	
Mol. weight	305.1	
Crystal System	Monoclinic	
Group of symmetry (Space group)	A2(α0γ)0	A2
Unit cell parameters	a = 10.5217(10), b = 16.2535(16), c = 7.4403(7) Å, β = 110.709(7); V = 1190.2(2) Å^3	a = 10.6408(09), b = 16.2706(10), c = 7.5669(7) Å, β = 110.783(8); V = 1224.8(2) Å^3
Modulation vector **q**	0.0658(1)**a*** -0.2658(1)**c***	none
T, K	173	290
No. unique reflections: observed / total	4686 / 6701	1555 / 2557
No. main reflections: observed / total	1898 / 2228	1555 / 2557
No. satellite reflections: observed / total	2788 / 4473	none
R_{obs}; Rw_{obs}; R_{all}; Rw_{all} (%): main reflections satellites altogether	 3.04; 3.06; 3.66; 3.13 7.01; 6.76; 11.22; 7.18 4.73; 4.48; 7.18; 4.71	 2.96; 3.02; 4.88; 3.12
Residual electron density r_{max} and r_{min} e.Å^{-3}	0.32 ; -0.30	0.28; -0.16

BNBA (3). Reconstructed *h0l* layer showing the presence of main and satellites reflexions. The crystal is obviously twinned.

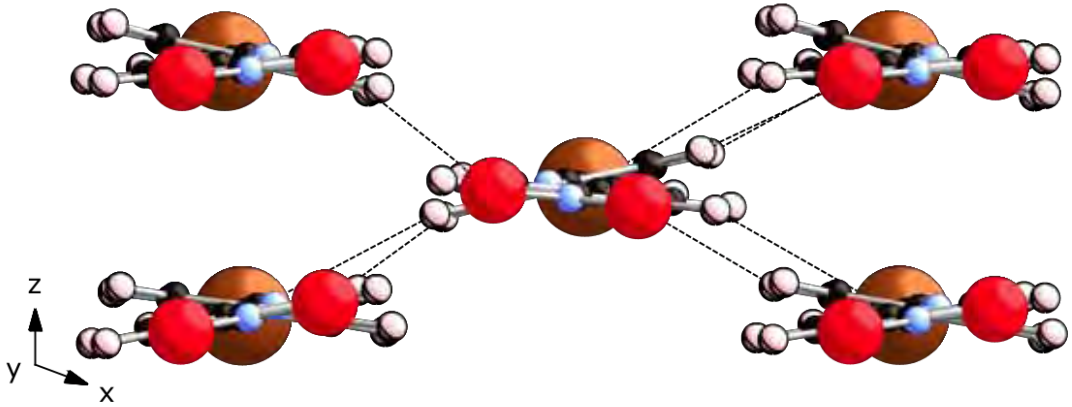


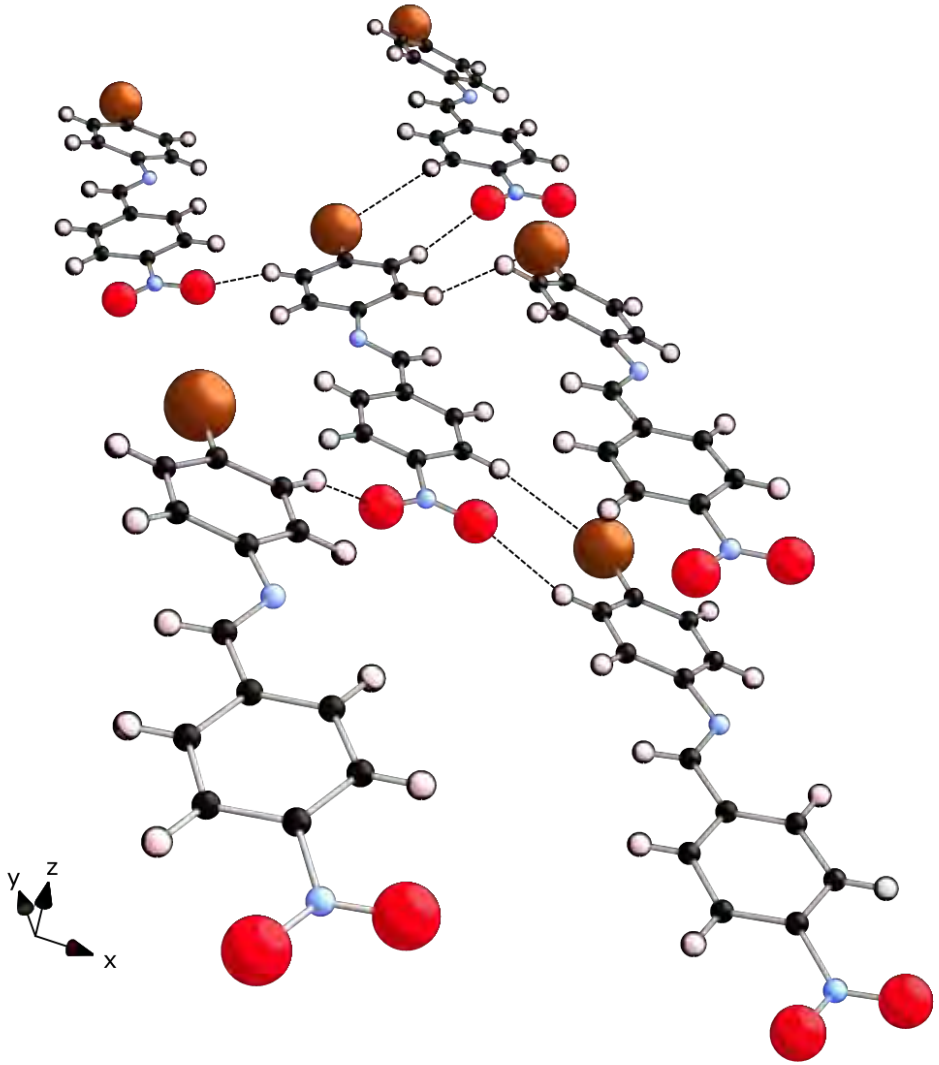
BNBA (4). Simulated *h0l* layer of a single twin component compared with the diffraction pattern.



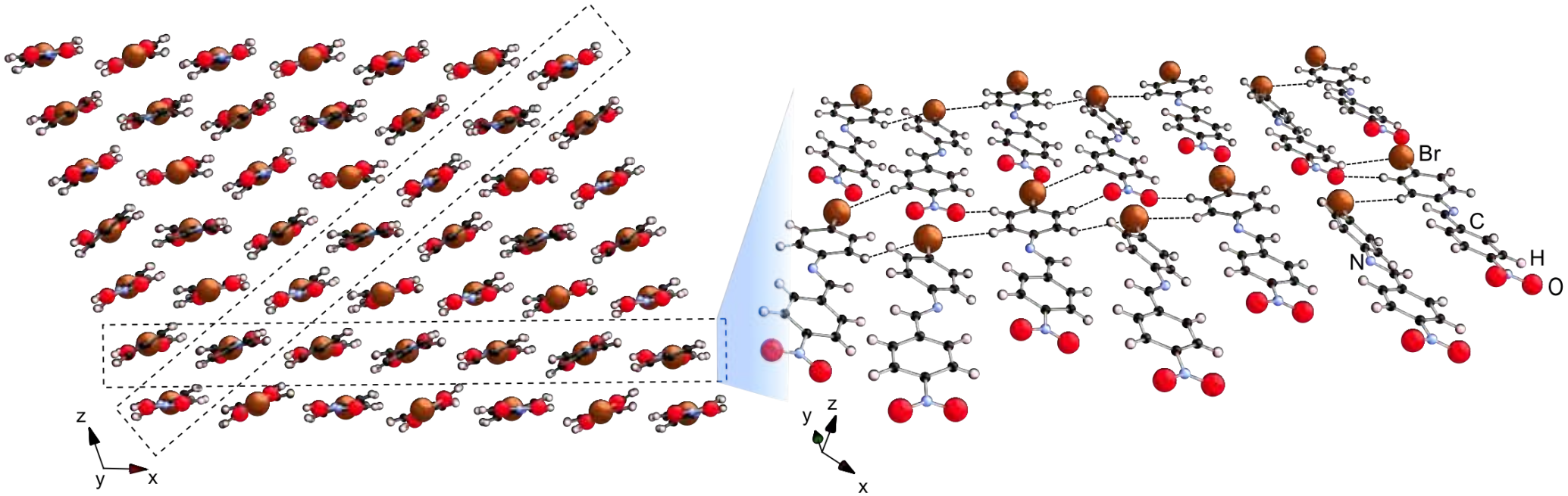
BNBA (5). A single molecule with anisotropic dsiplacement parameters (ADP's)

BNBA (6). The packing of the molecules is subject to a network of H-bonds

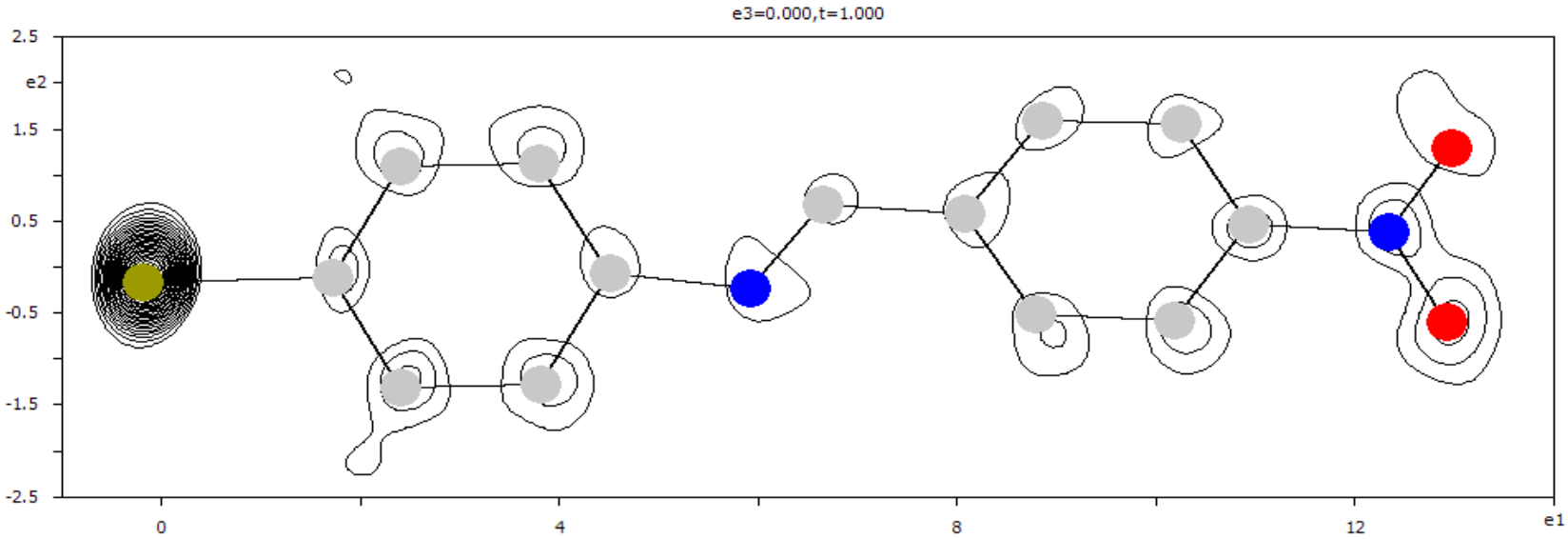




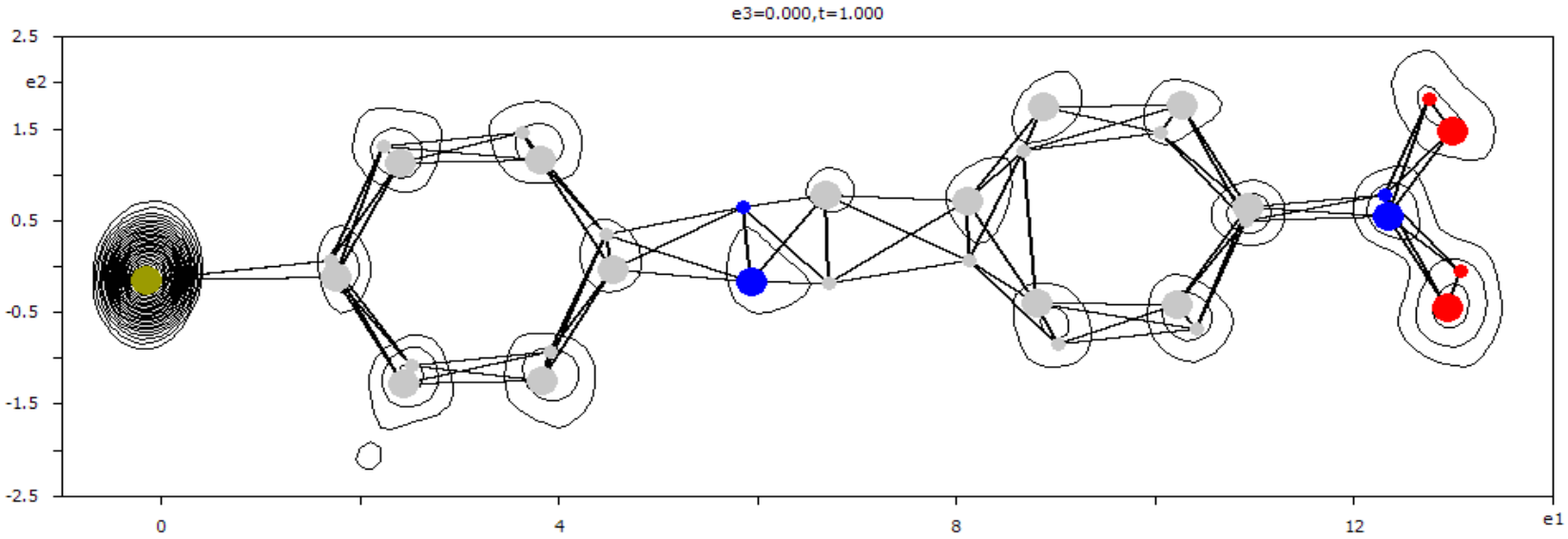
BNBA (7). 2D layers formed by non-periodic networks of H-bonded molecules.



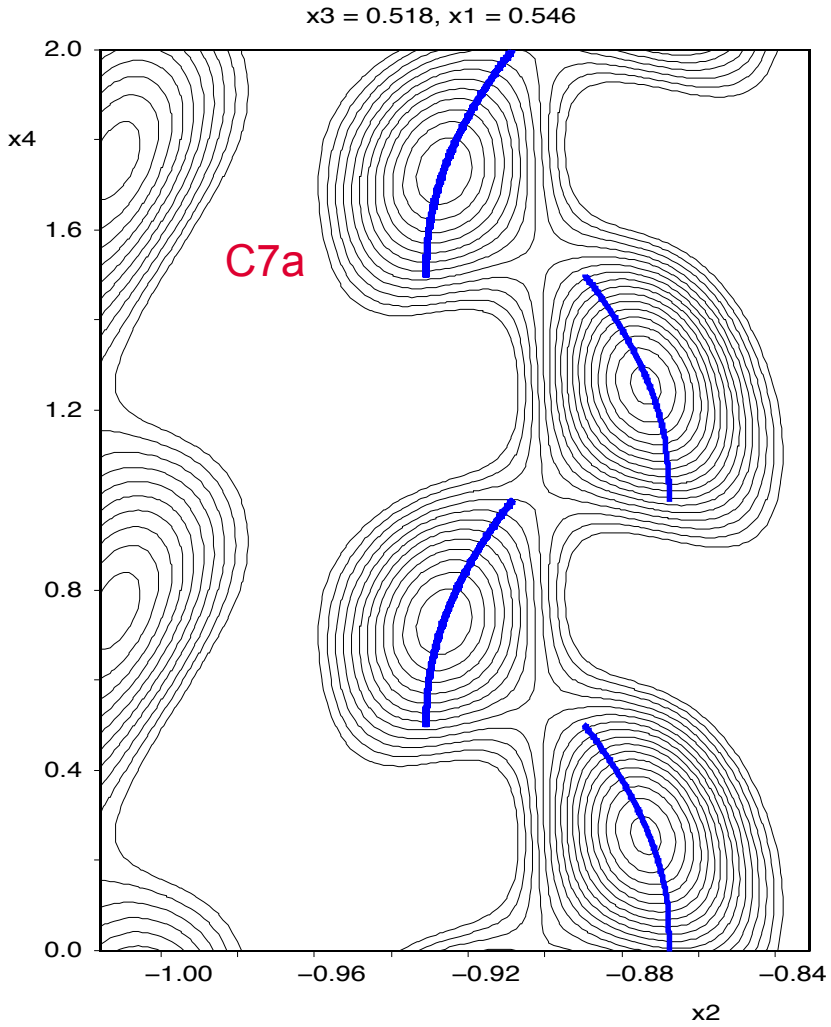
BNBA (8). Sequence of different molecular conformations depending on the variable *t*

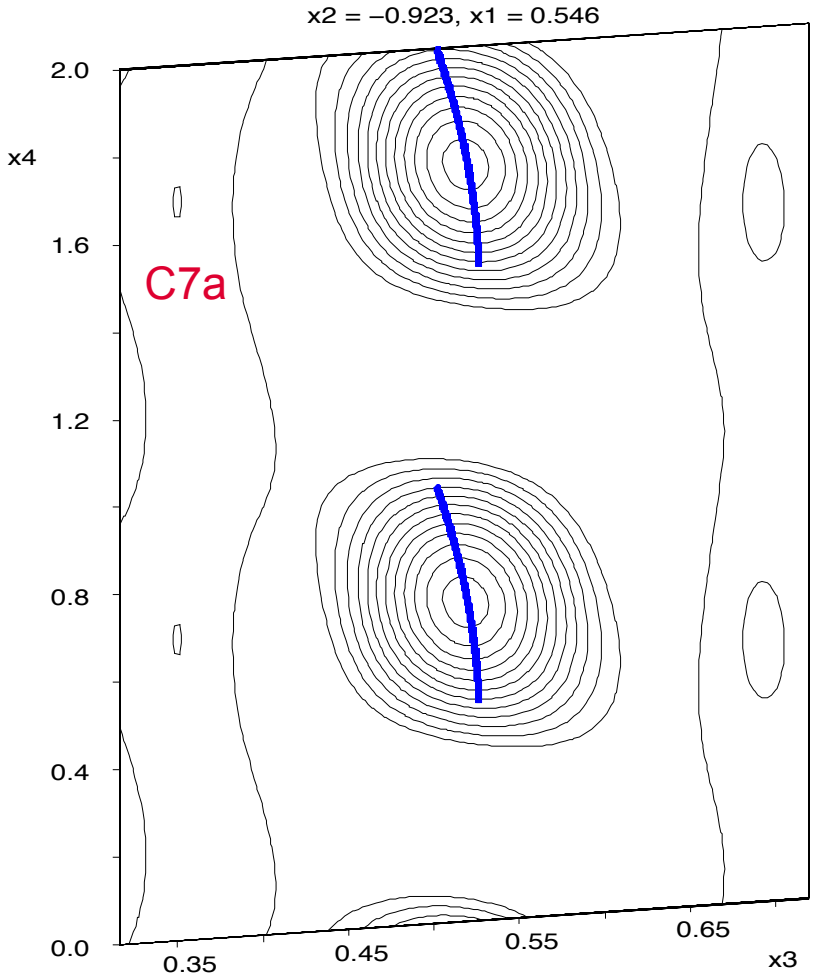


BNBA (9). Sequence of different molecular conformations depending on the variable *t*.

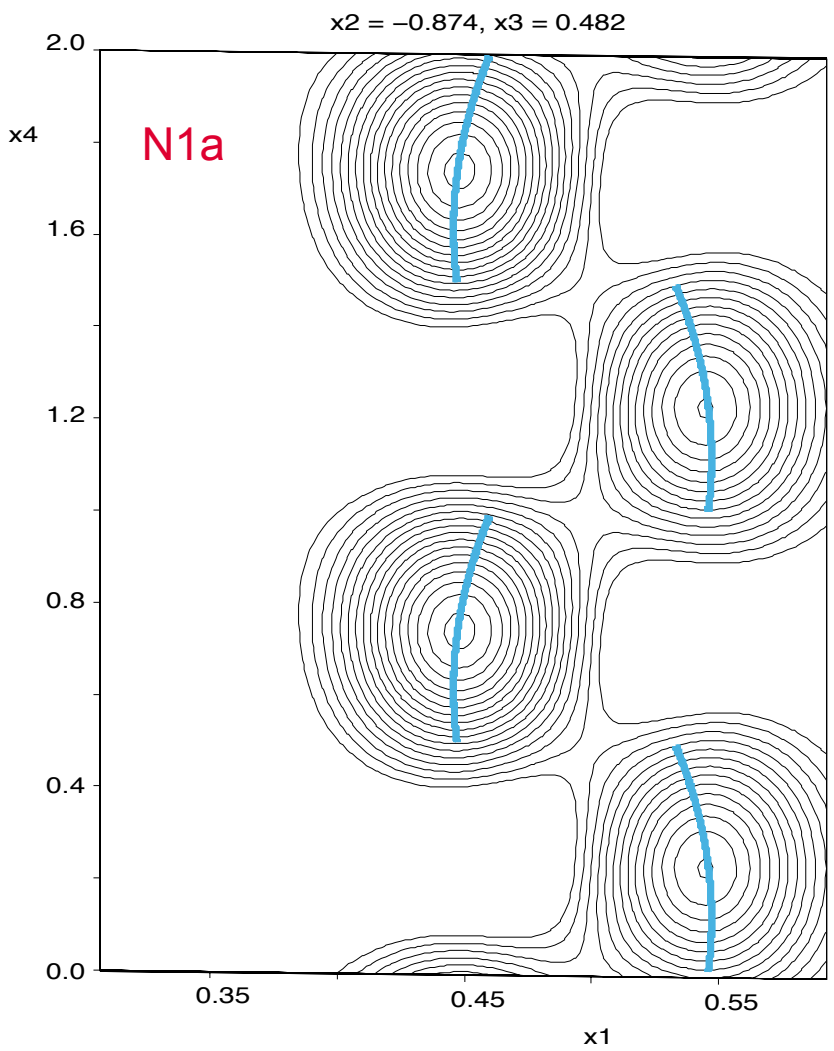


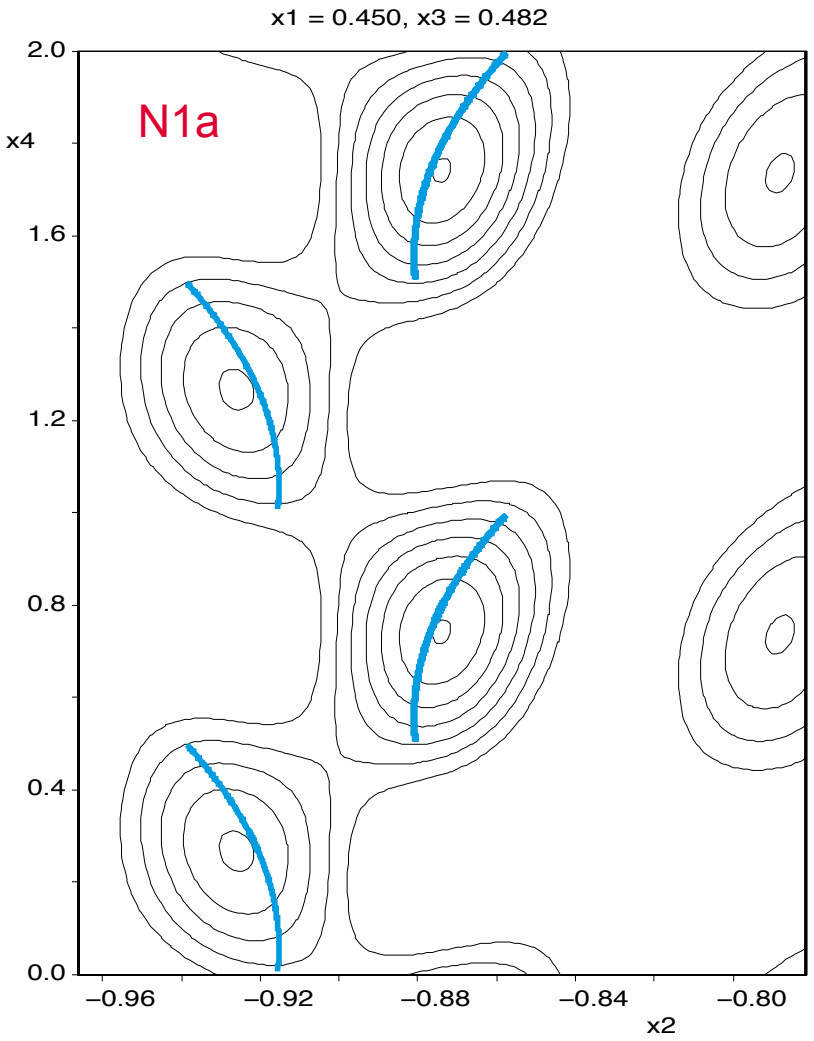
BNBA (10). The displacement of the N atom is better represented by a combination of Crenel and modulation functions





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

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- Quininium R mandelate (QuiRMa)
- HMT Resorcinol

Organic compounds with large Z' treated as commensurately modulated structures

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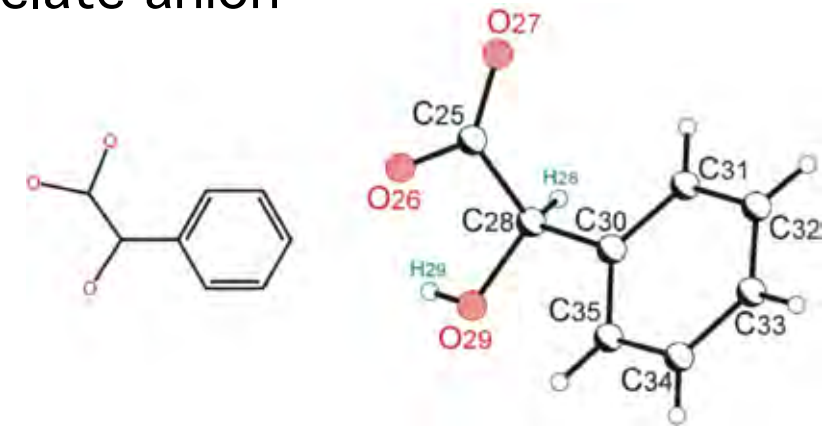
Quininium (R)-mandelate (QuiRMa)

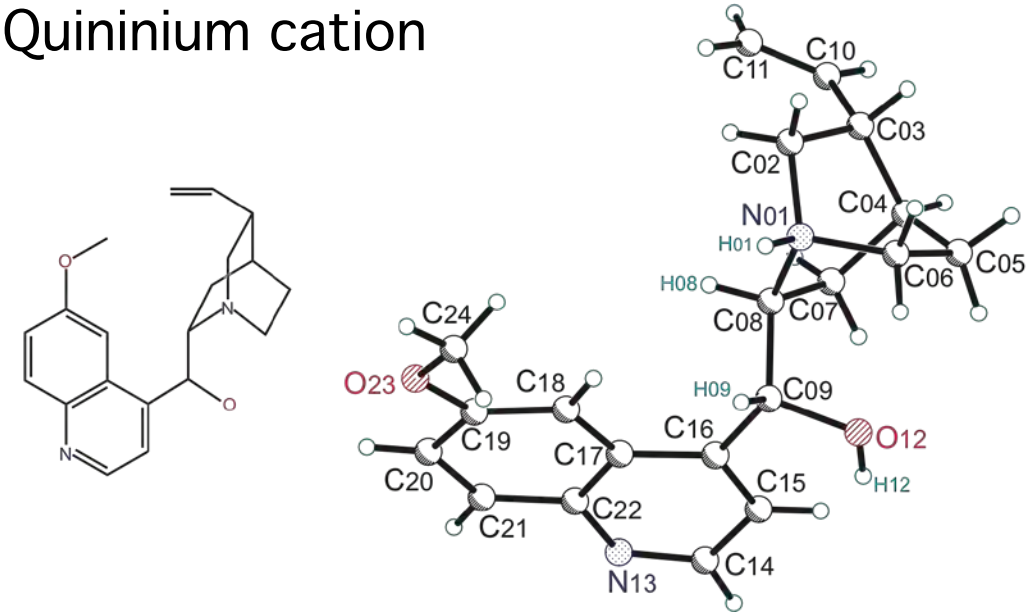
Chemical formula	$C_{20}H_{25}N_2O_2^+ C_8H_7O_3^-$
superspace group	Monoclinic, $P2_1(\alpha 0 \gamma)$
a, b, c (Å)	6.614, 18.552, 10.377
β(°)	107.47
Modulation wavevector	0.3329, 0, -0.2713
No. of measured, independent and observed reflections (> 2σ)	204'354, 40'498, 12'714
No. of independent and observed fifth-order satellites (> 2σ)	6936, 287

Schönleber et *al.* Acta B (2004)

Mandelate anion

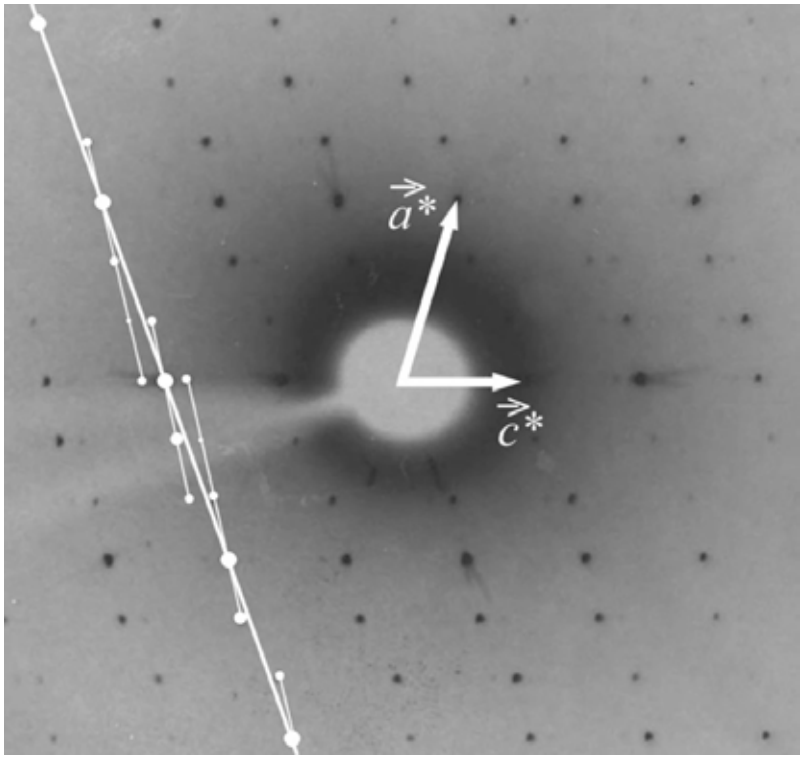


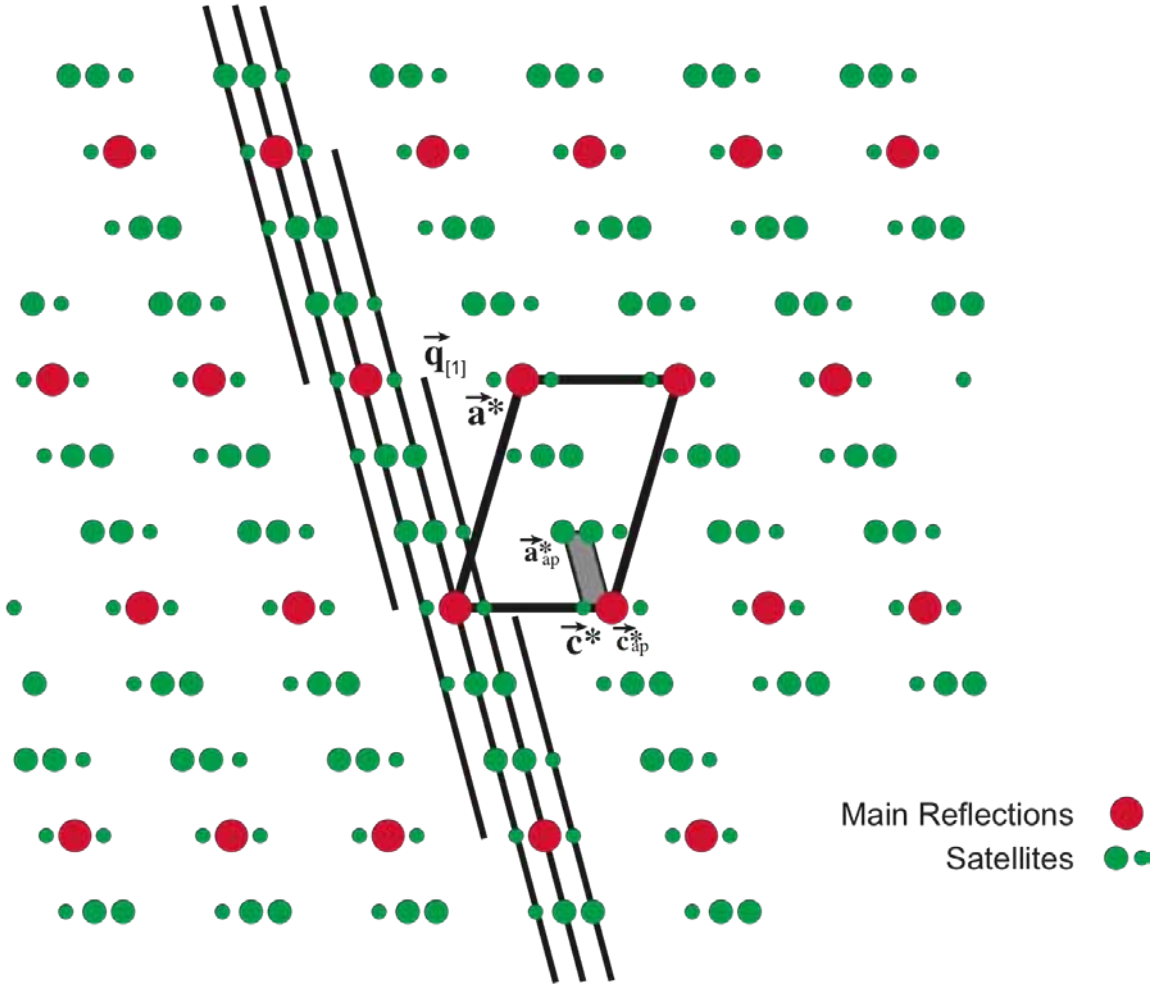
Quininium cation



QuiRMa. The reciprocal space.

h1l precession layer





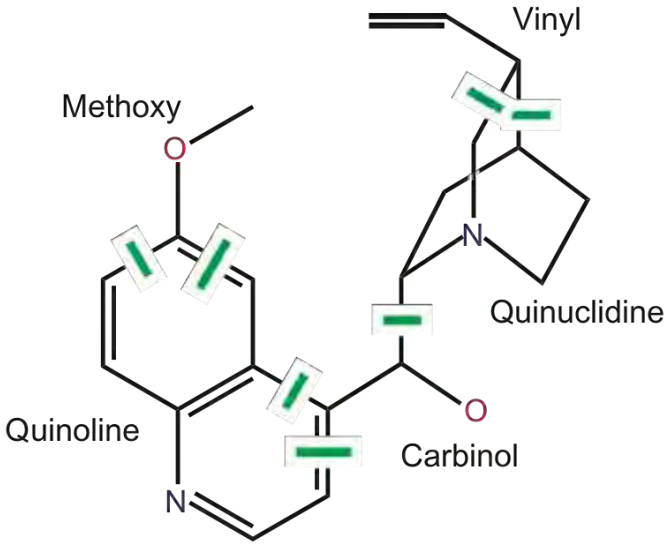
QuiRMa. Resolution and refinement.

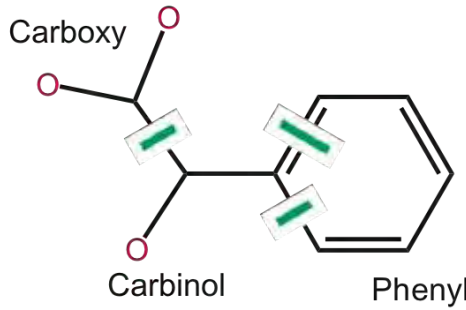
Structure solution

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

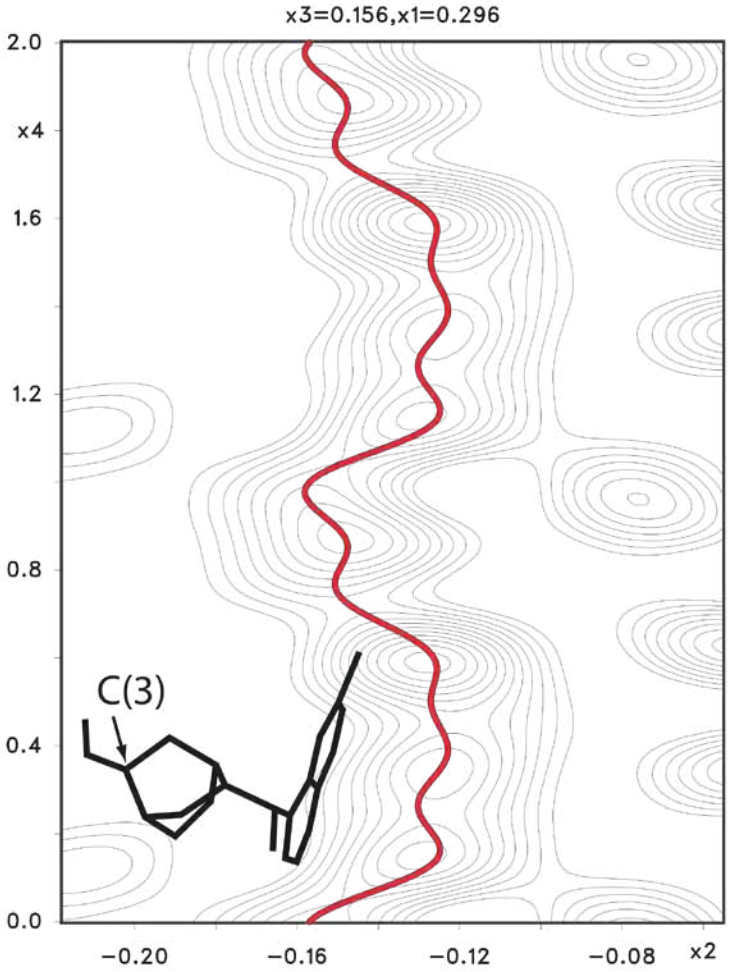
Structure refinement

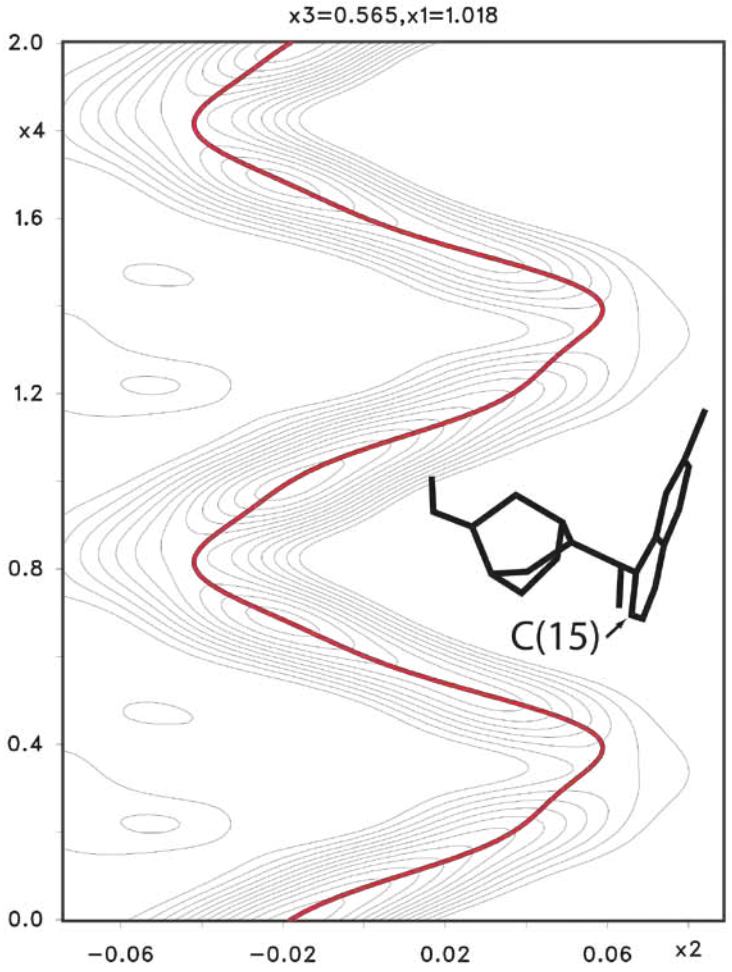
- Introduction of rigid entities
- Four harmonic terms for displ. modul.



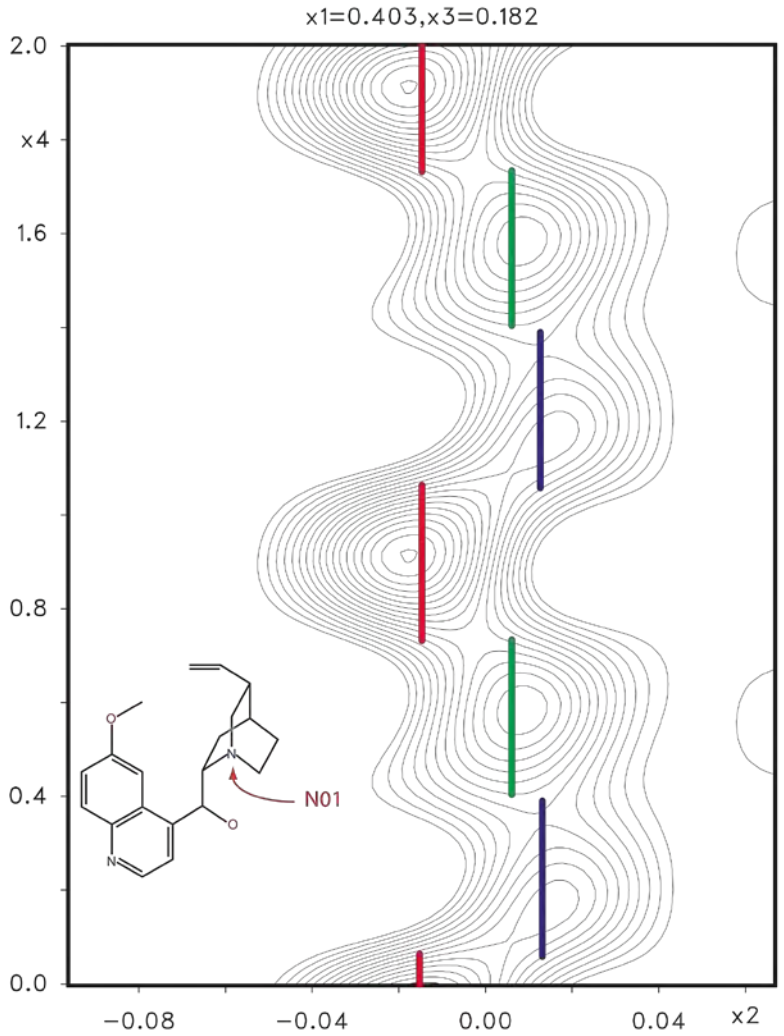


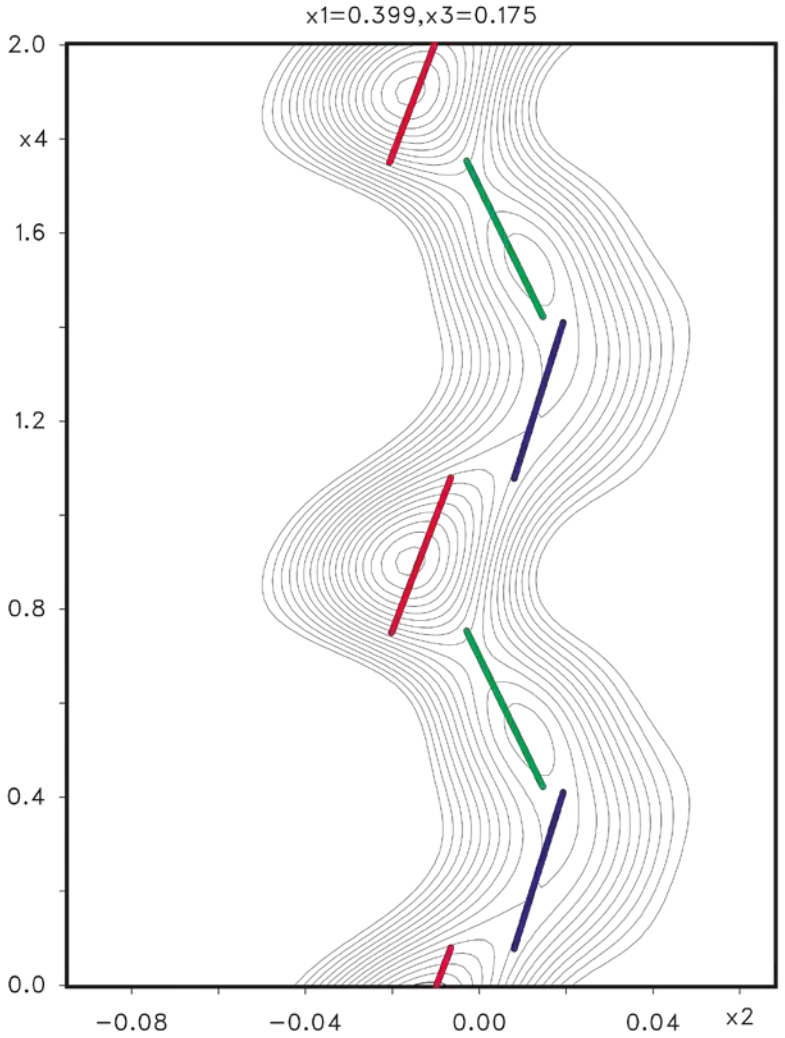
QuiRMa. Refinement results.



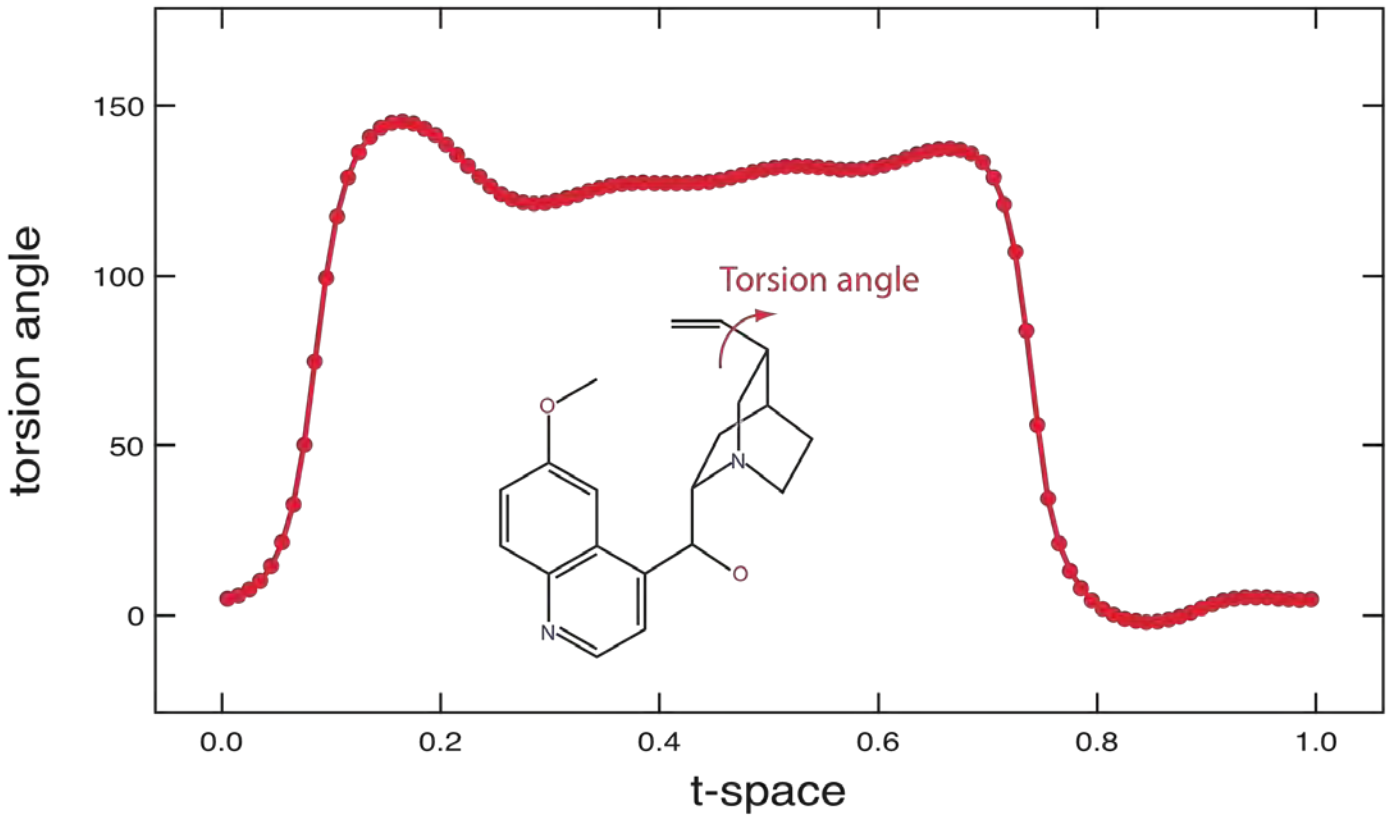


QuiRMa. Crenel and sawtooth functions refinements.

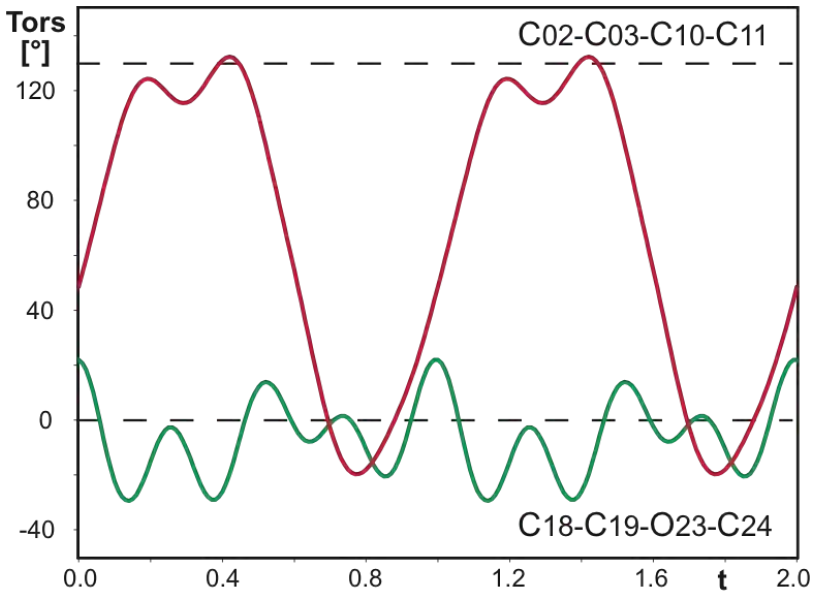


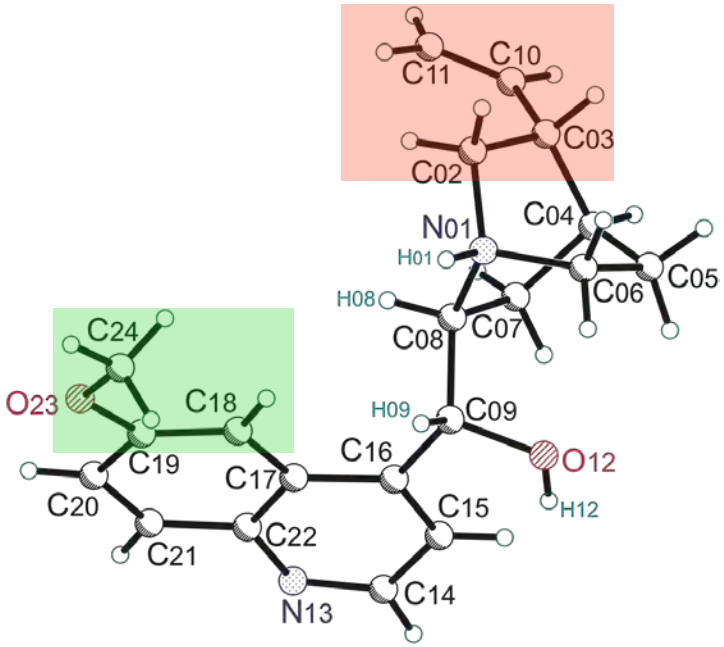


QuiRMa. Torsion angle of the vinyl group.

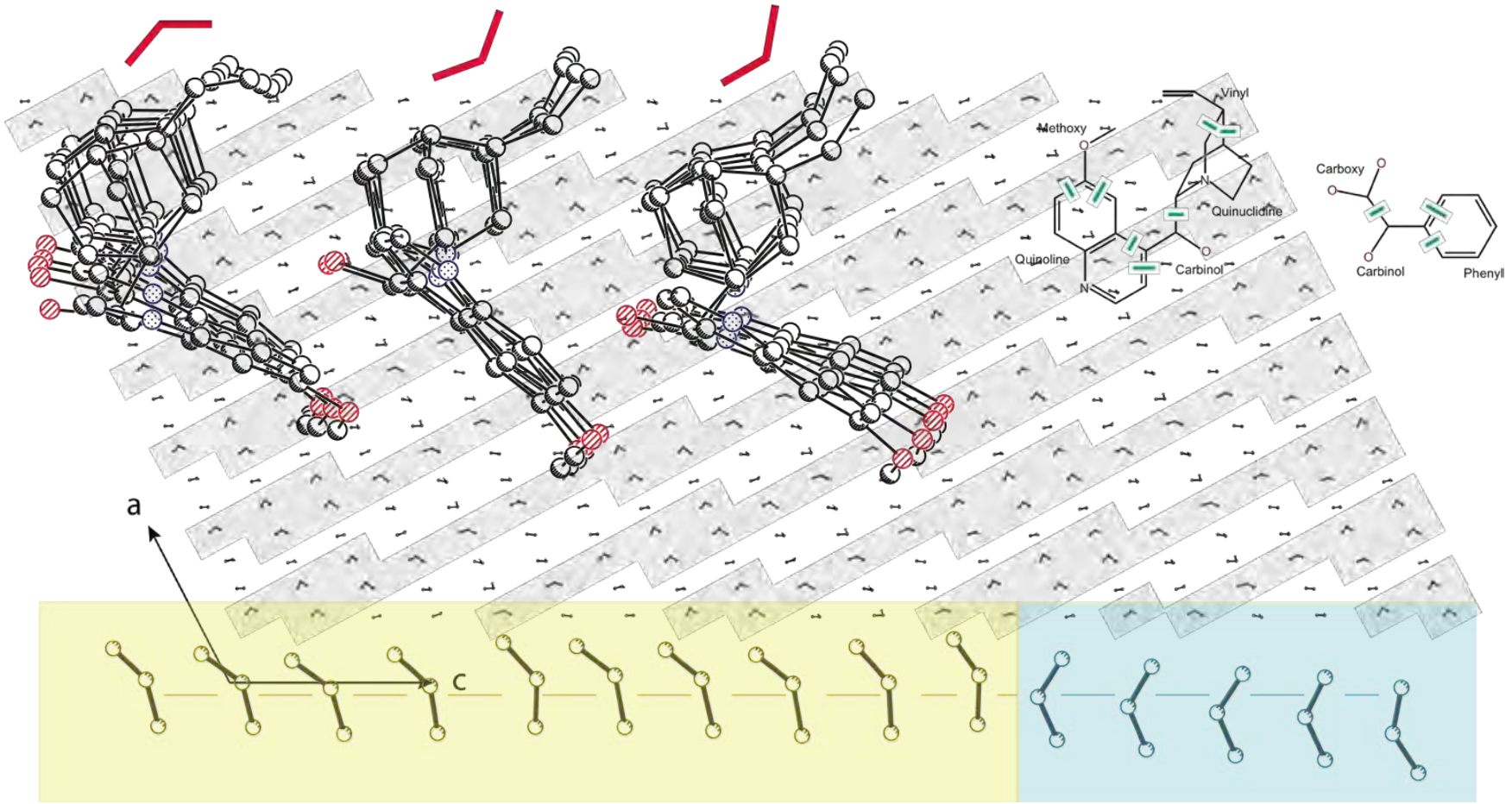


QuiRMa. The vinyl group.

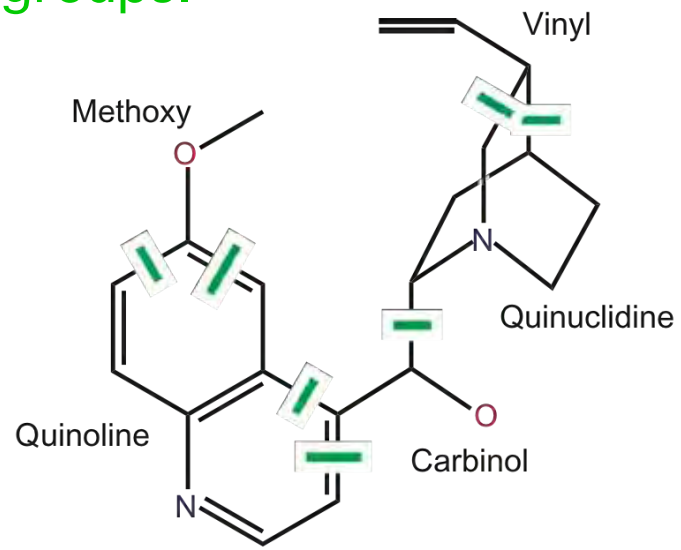


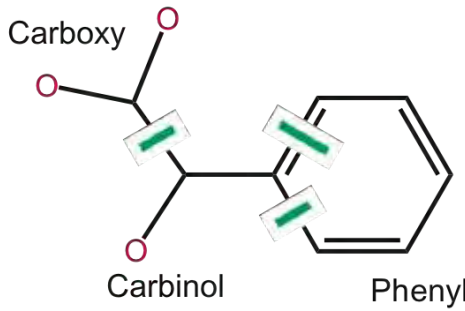


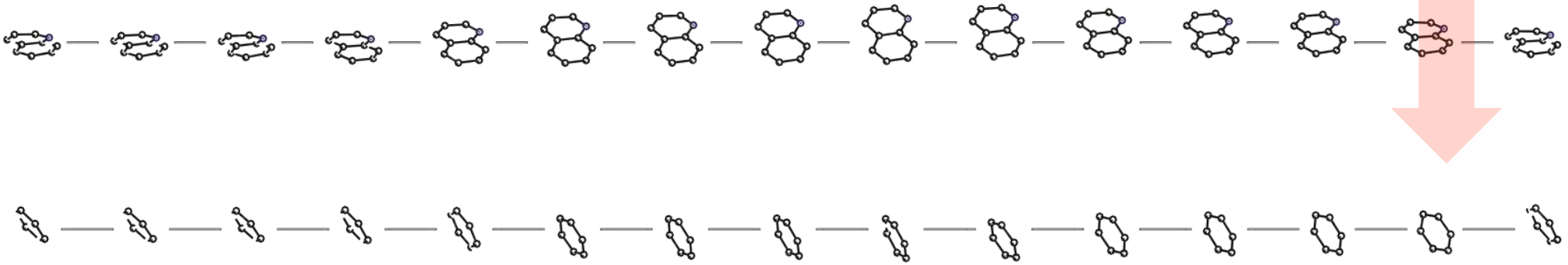
QuiRMa. The vinyl group.



QuiRMa. Others functional groups.

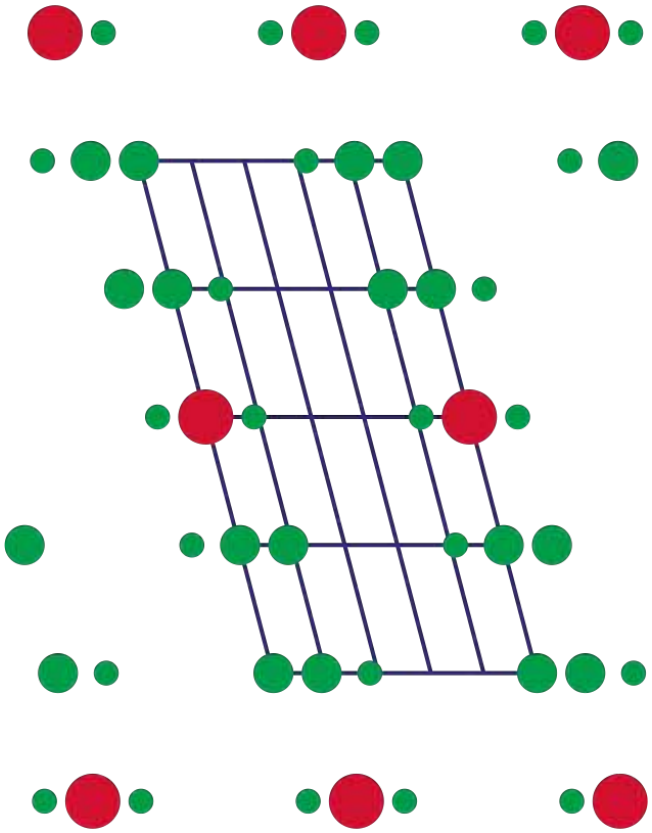




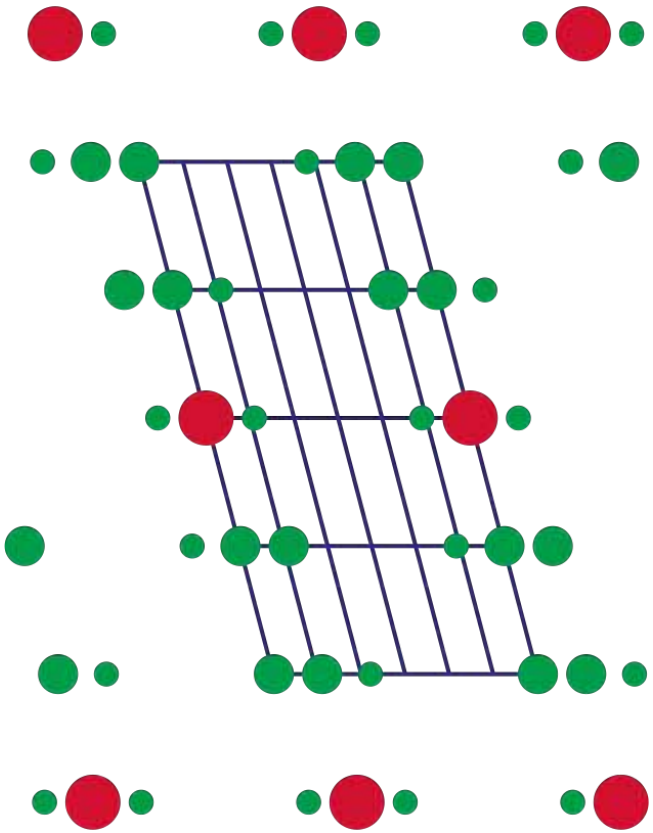


QuiRMa. What about a commensurate approximation?

3x5 approximation ?



3x6 approximation ?



QuiRMa. 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.

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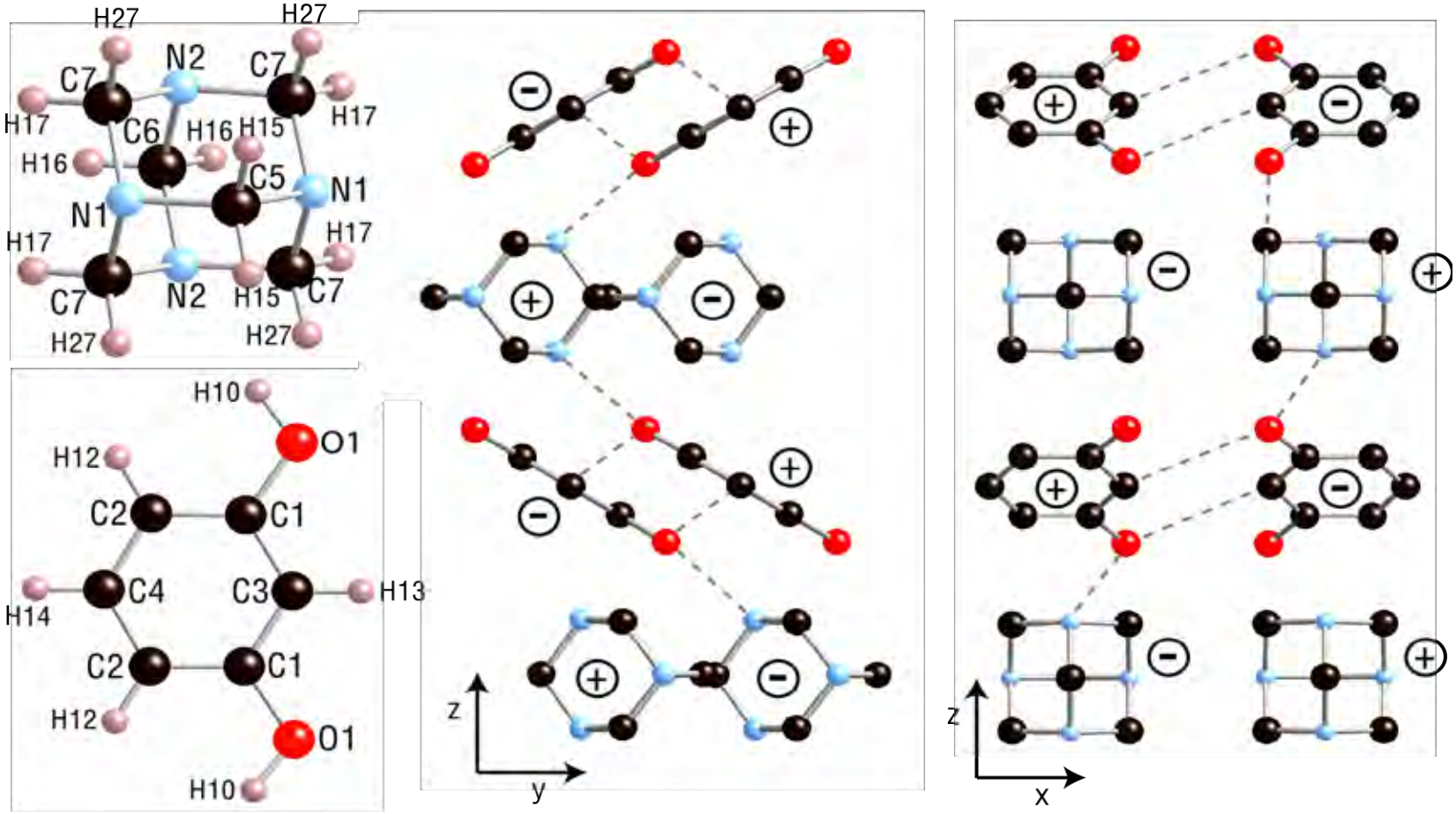
Hexamine resorcinol, an organic incommensurate structure



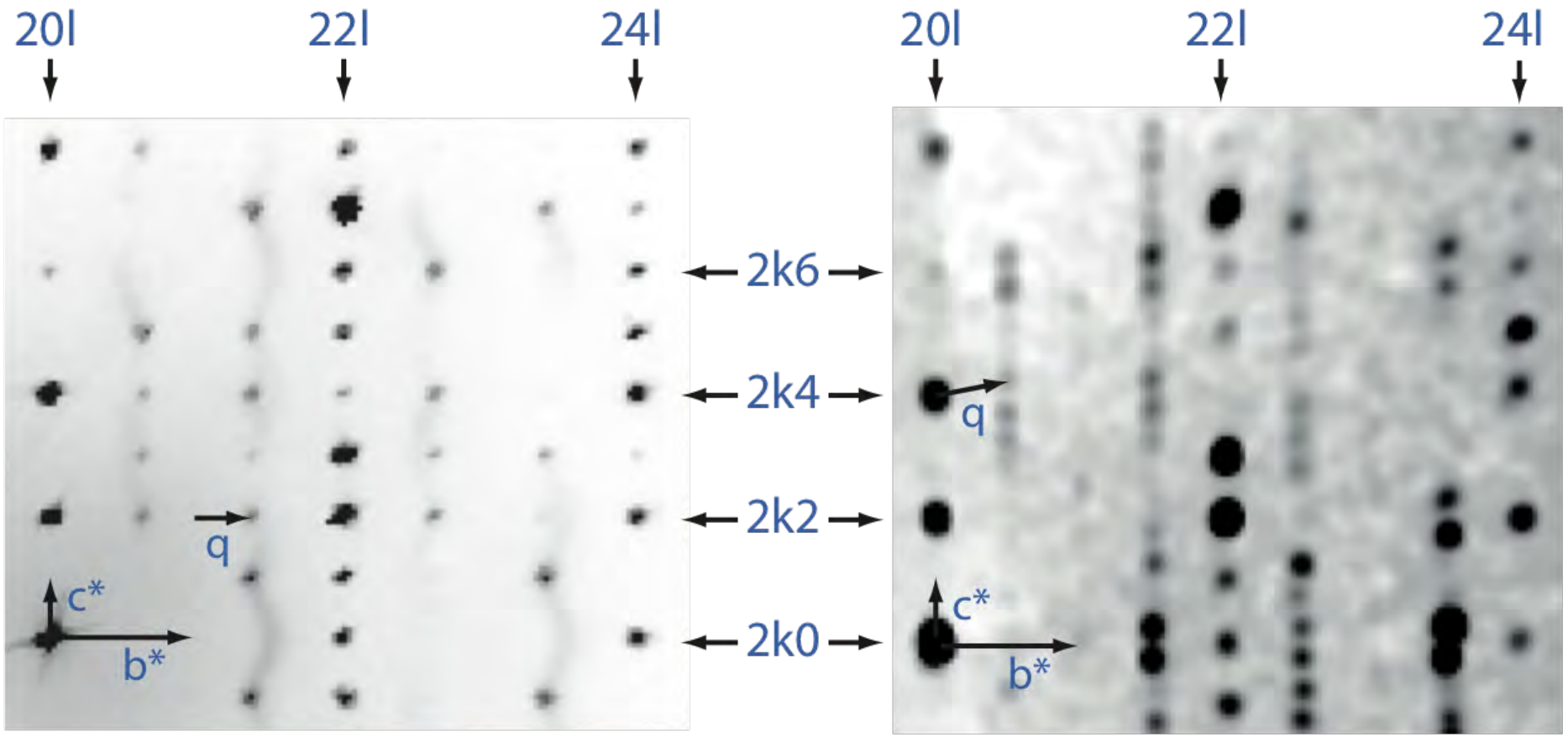
hexamine resorcinol

projection along x

projection along y

Rodriguez *et al.* Acta B (2006)

The diffraction patterns



Room temperature

Low temperature

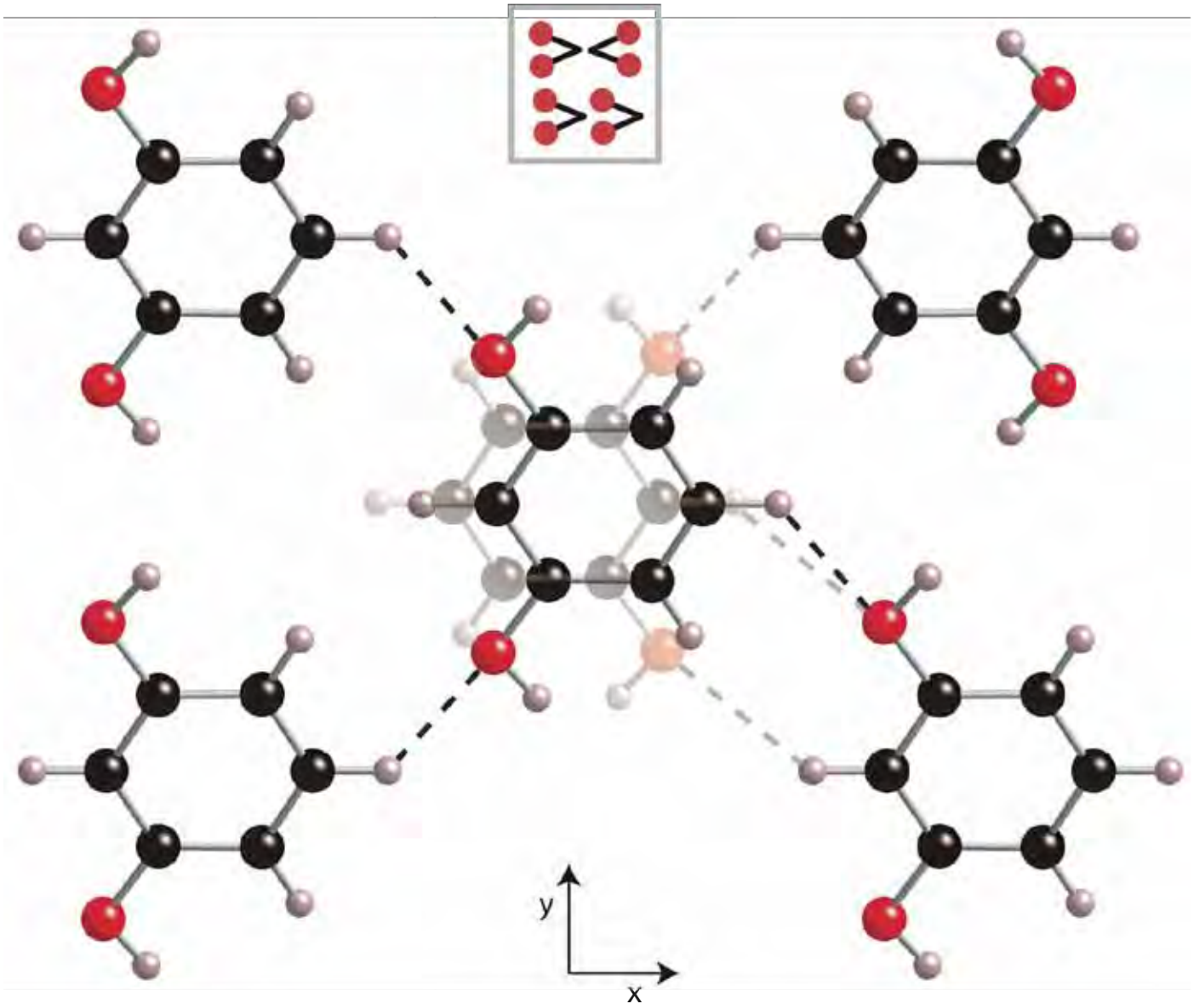
q = (0, 0.376, 0) → 268K → **q** = (0½¼)

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.

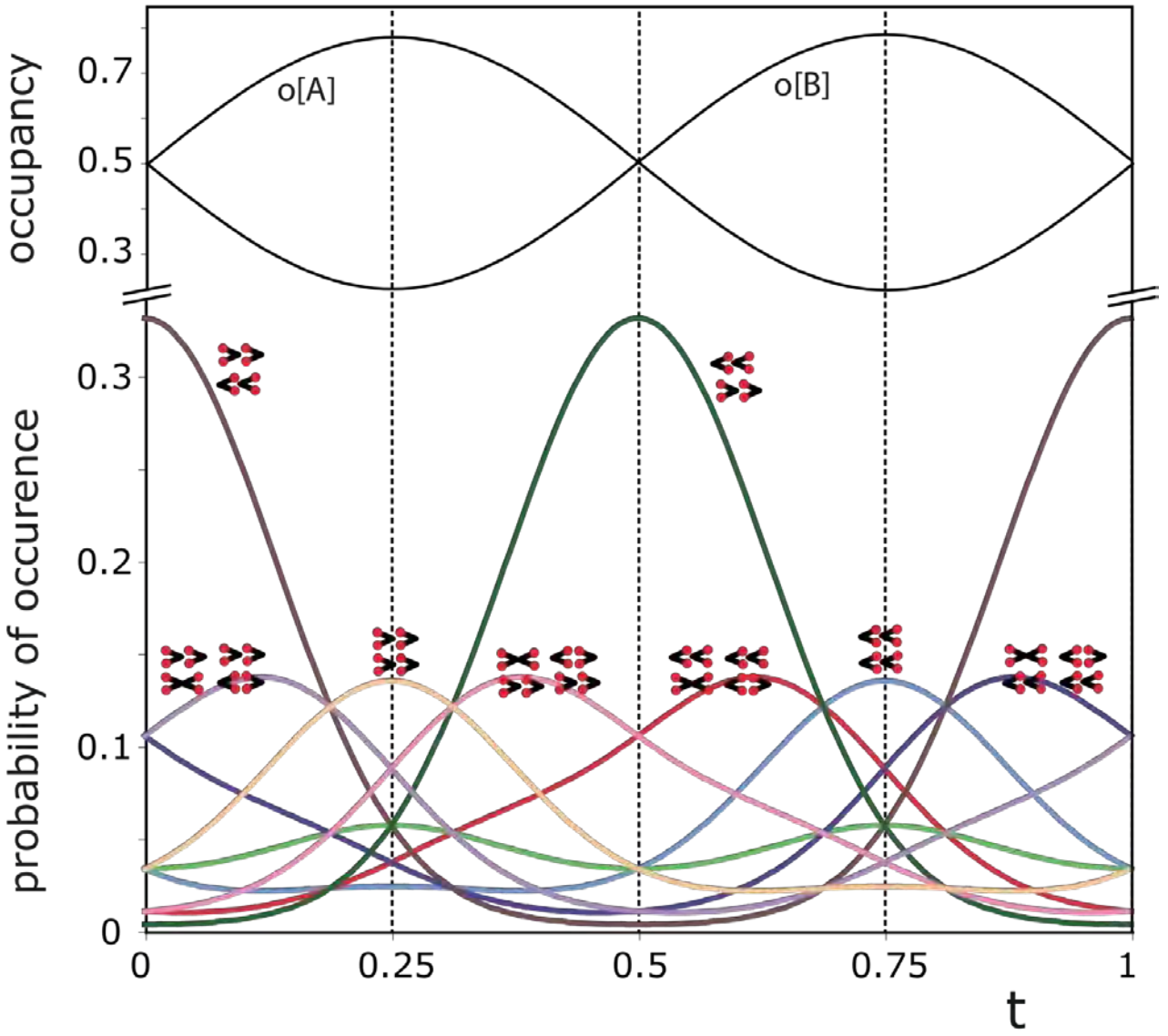
The pictogram is used to characterise each possible H-bond environment.



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.

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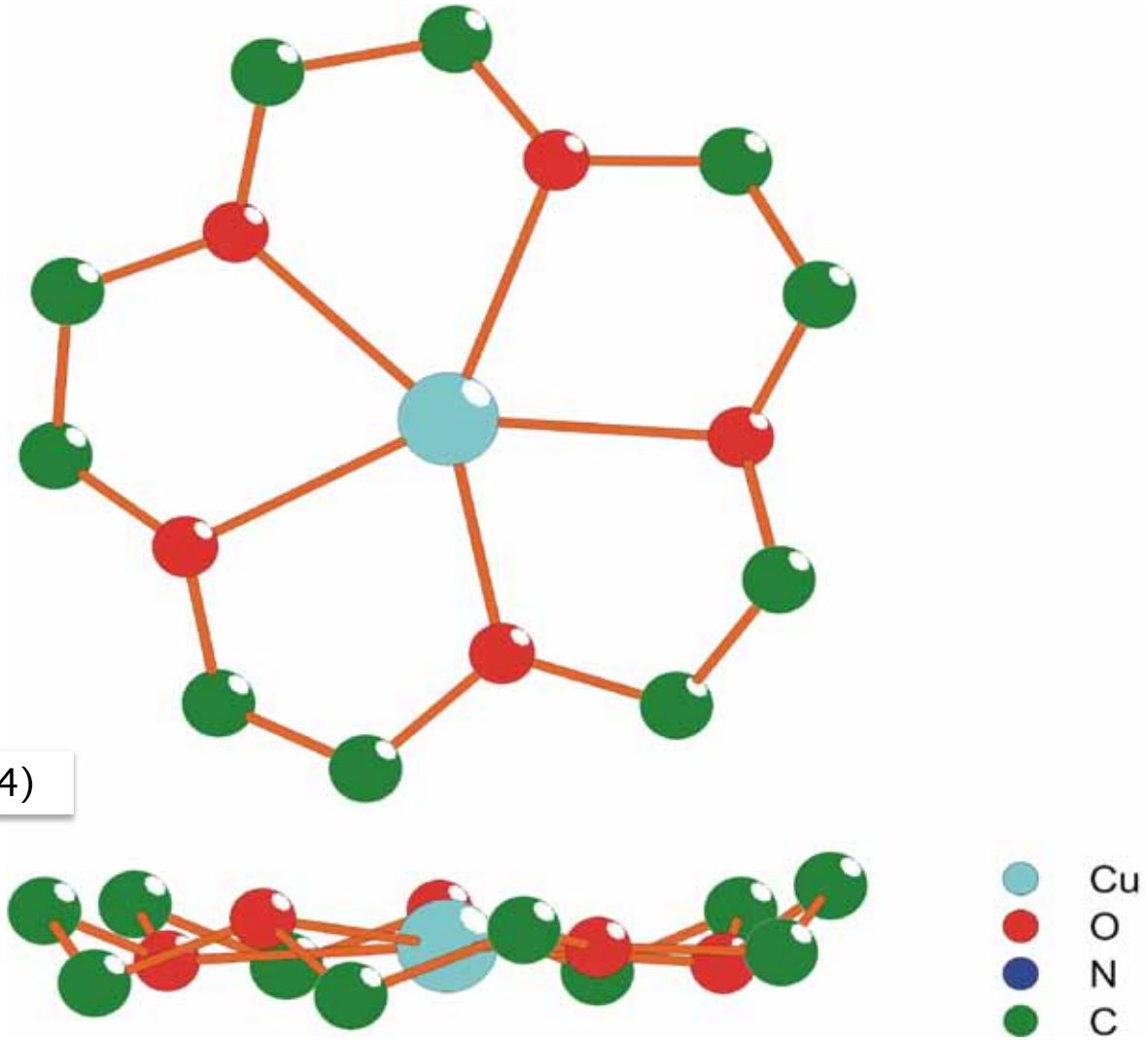
Crown ether

$[Cu(H_2O)_2(C_{10}H_{20}O_5)](NO_3)_2$

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

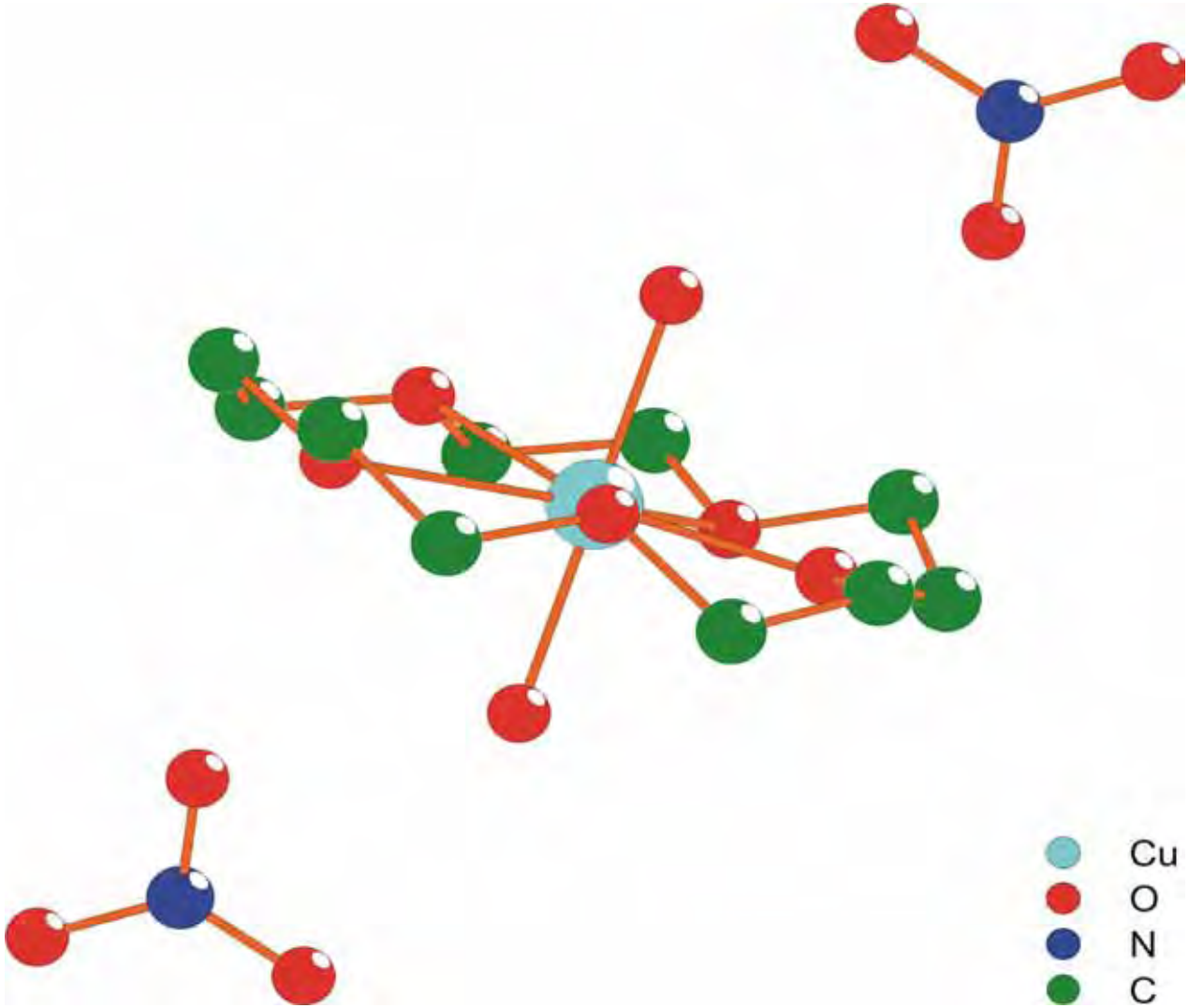


Schönleber *et al.*, Ferroelectrics, 2004)

Crown ether

$[Cu(H_2O)_2(C_{10}H_{20}O_5)](NO_3)_2$

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



Crown ether

	[1]	[2a]	[2b]	[3]
Z, Z'	2, 1/2	20, 10	20, 10	2, 1
space group	$P2_1/c$	Pc	Pn	$Pc(\alpha 0 \gamma)s$
a (Å)	7.375(3)	14.758(5)	14.7668(9)	7.3820(8)
b (Å)	13.981(4)	13.978(4)	13.9749(7)	13.9705(13)
c (Å)	8.657(3)	43.914(13)	43.3500(30)	8.6690(10)
β (°)	97.35(3)	102.19(3)	97.369(5)	97.371(7)
q	-	-	-	(0.5, 0, -0.4)

[1] Rogers & Song (1995)
[2a] Dejehet *et al.* (1987)
[2b] Pc → Pn
[3] Schönleber *et al.* (2004)

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 $[Cu(H_2O)_2(15\text{-crown-5})](NO_3)_2$ (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.

(...)

(1) Dejehet, F., Debuyst, R., Wei, Y. Y., Declercq, J.-P. & Tinant, B. (1987). J. Chim. Phys. Phys.-Chim. Biol., 84, 975-979.
(2) Rogers, R. D. & Song, Y. (1995). J. Coord. Chem., 34, 149-157.

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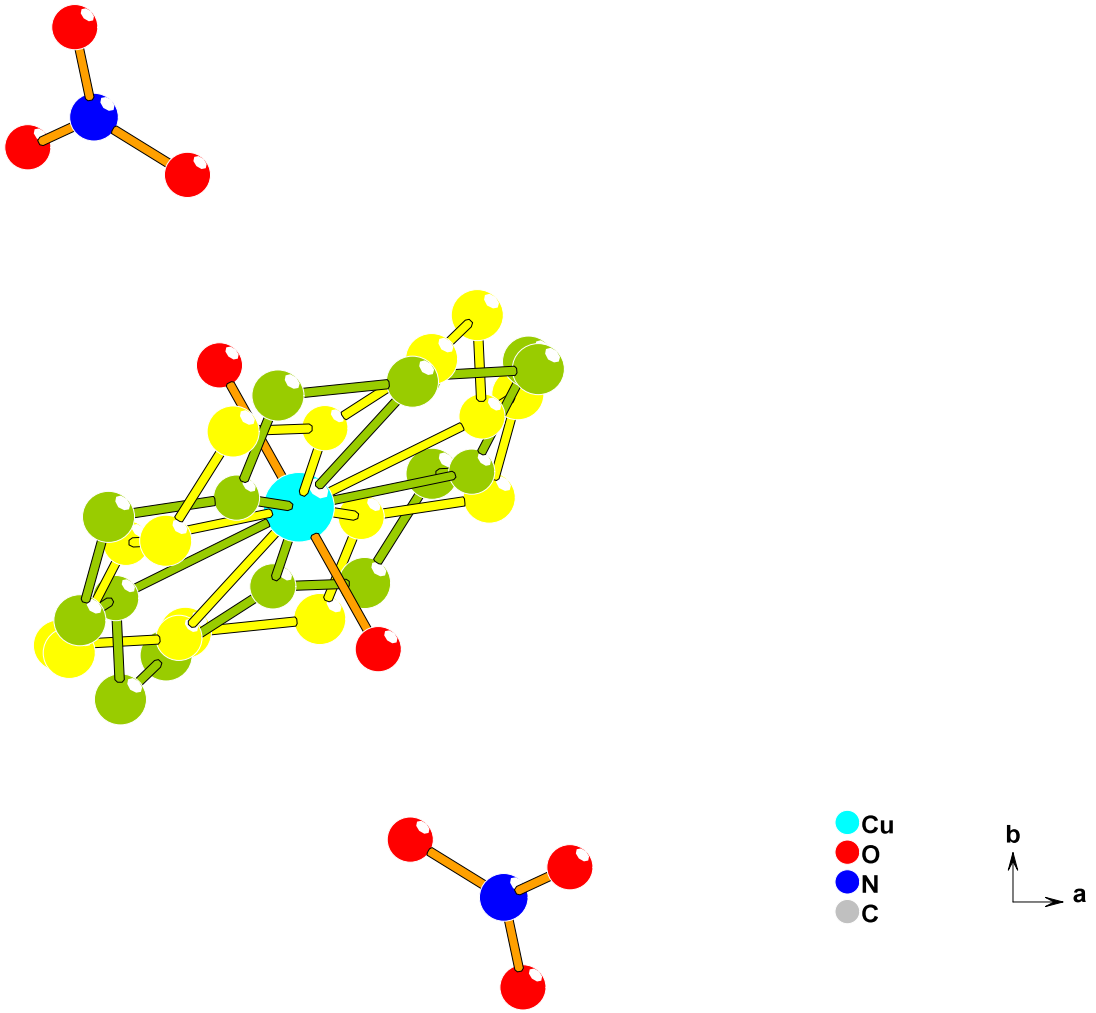
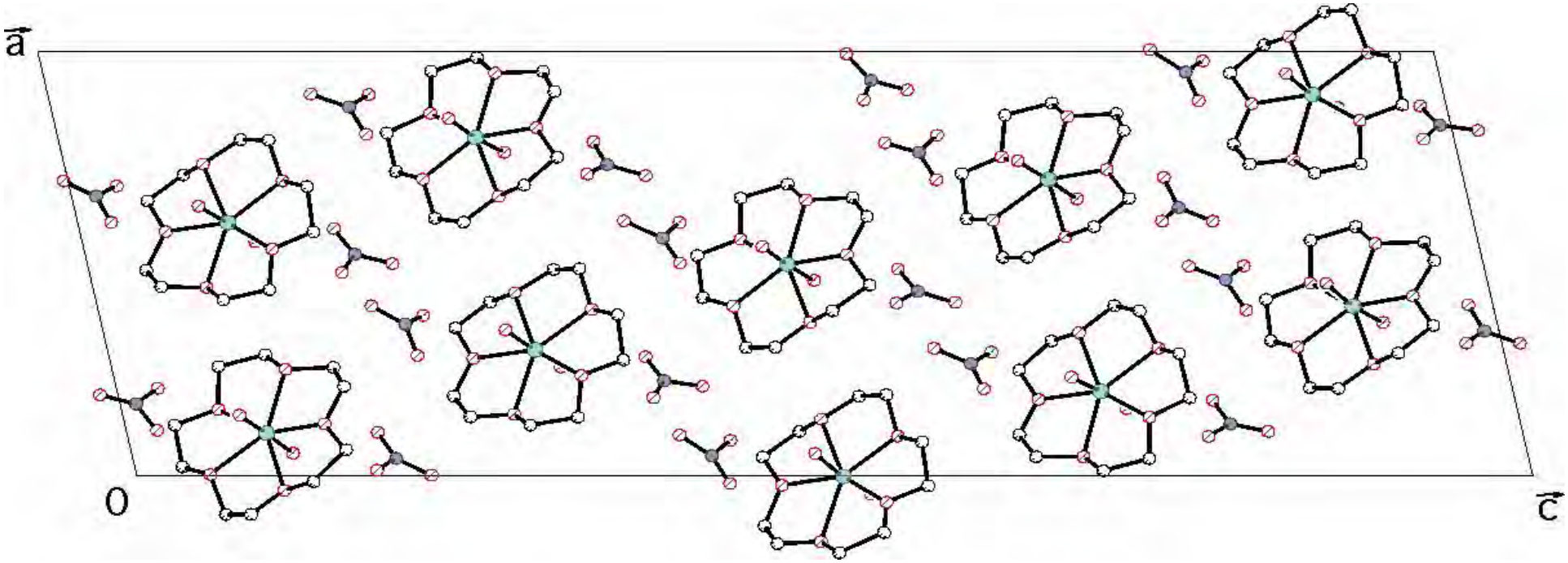
(...) A partially disordered Z'=5 structure in $P2_1/n$ seems reasonable, but preliminary results suggest that the noncentrosymmetric *Pn* description is preferable. Phase transitions from disordered to ordered structures are usually associated with a decrease in molar volume, but this one is not. Careful 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.

(1) Dejehet, F., Debuyst, R., Wei, Y. Y., Declercq, J.-P. & Tinant, B. (1987). J. Chim. Phys. Phys.-Chim. Biol., 84, 975-979.
(2) Rogers, R. D. & Song, Y. (1995). J. Coord. Chem., 34, 149-157.

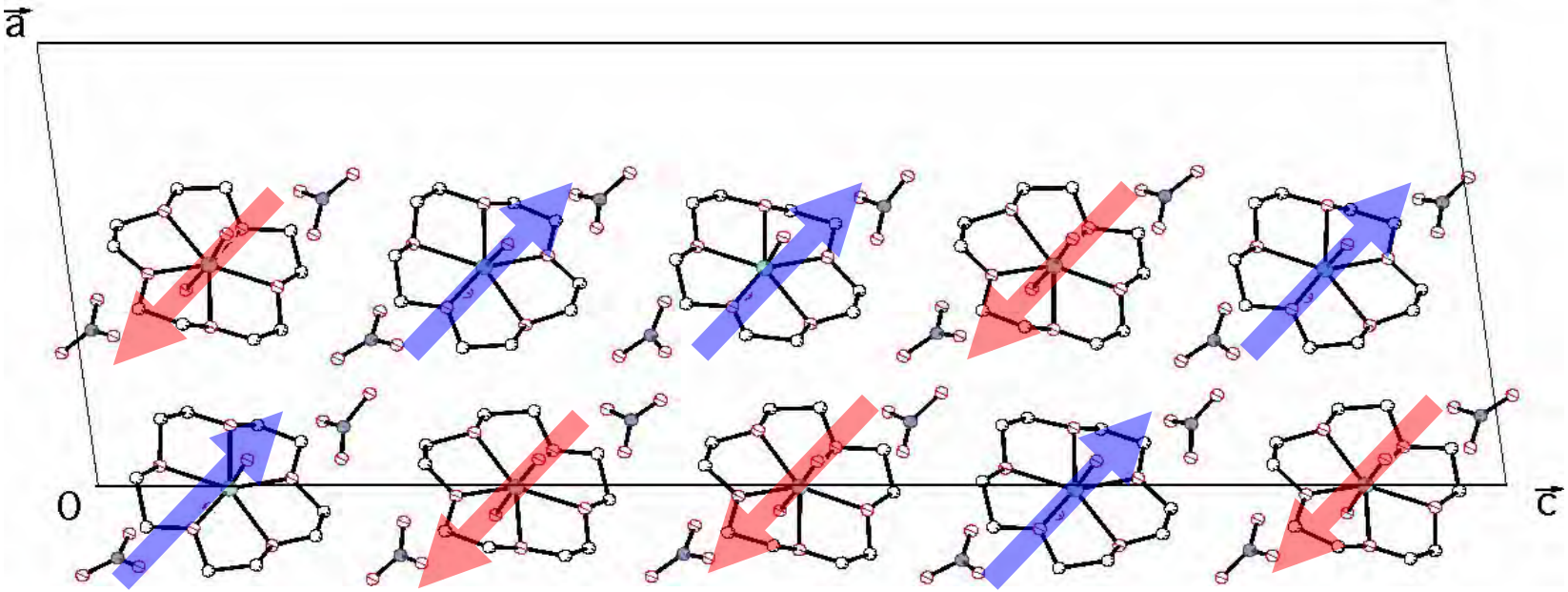
The structure with Z’ = 1/2

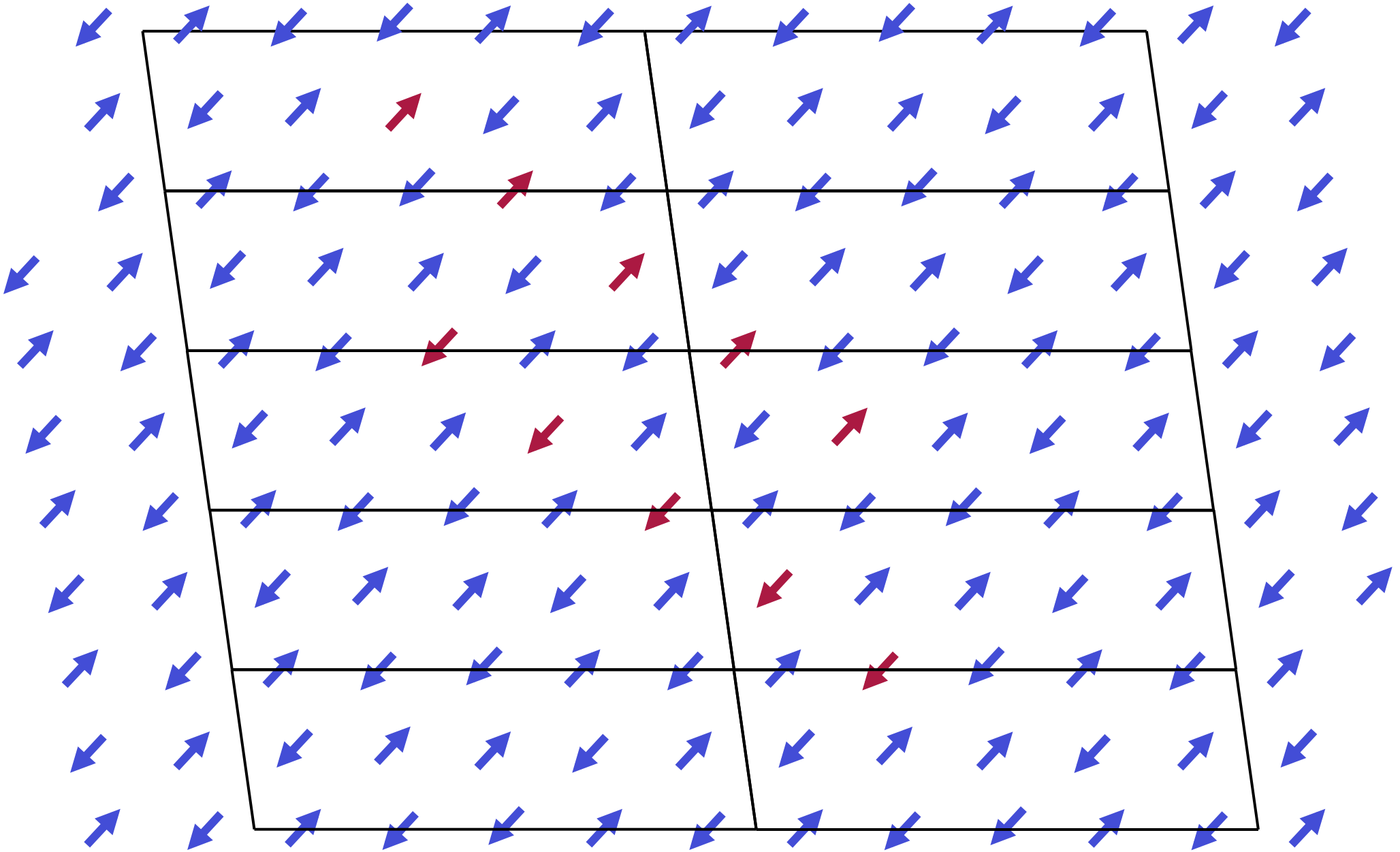


The structure with Z' = 10 (SG: *Pc*)



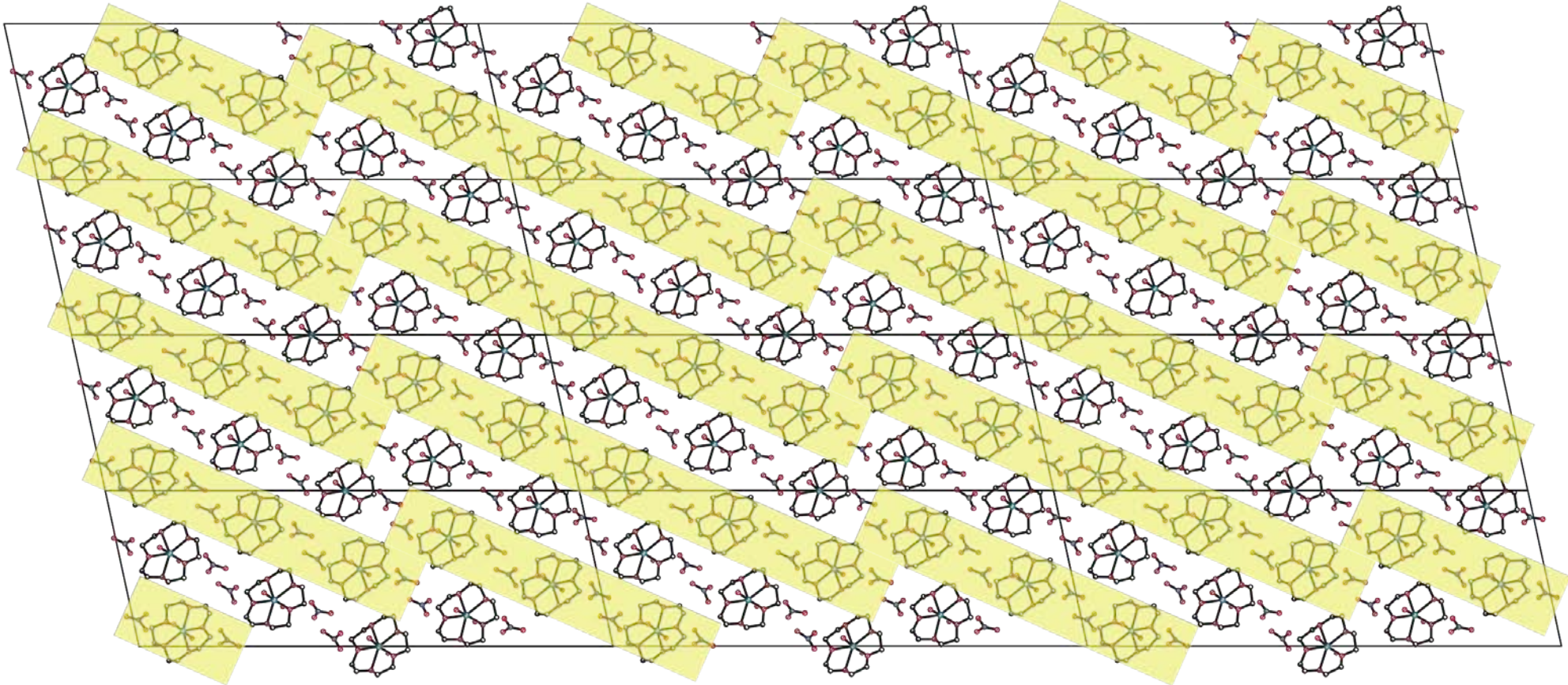
Crown ether

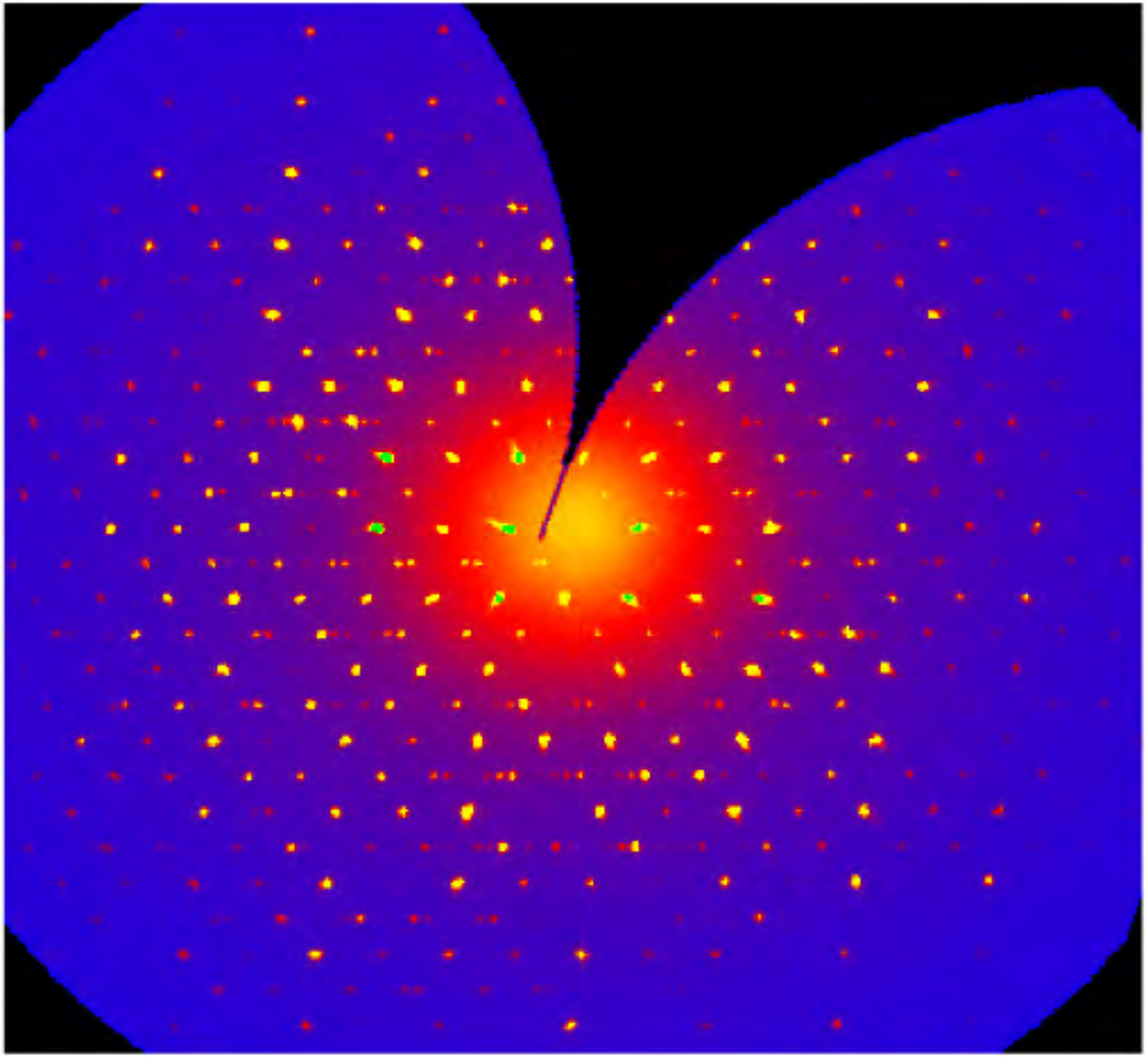




The motif

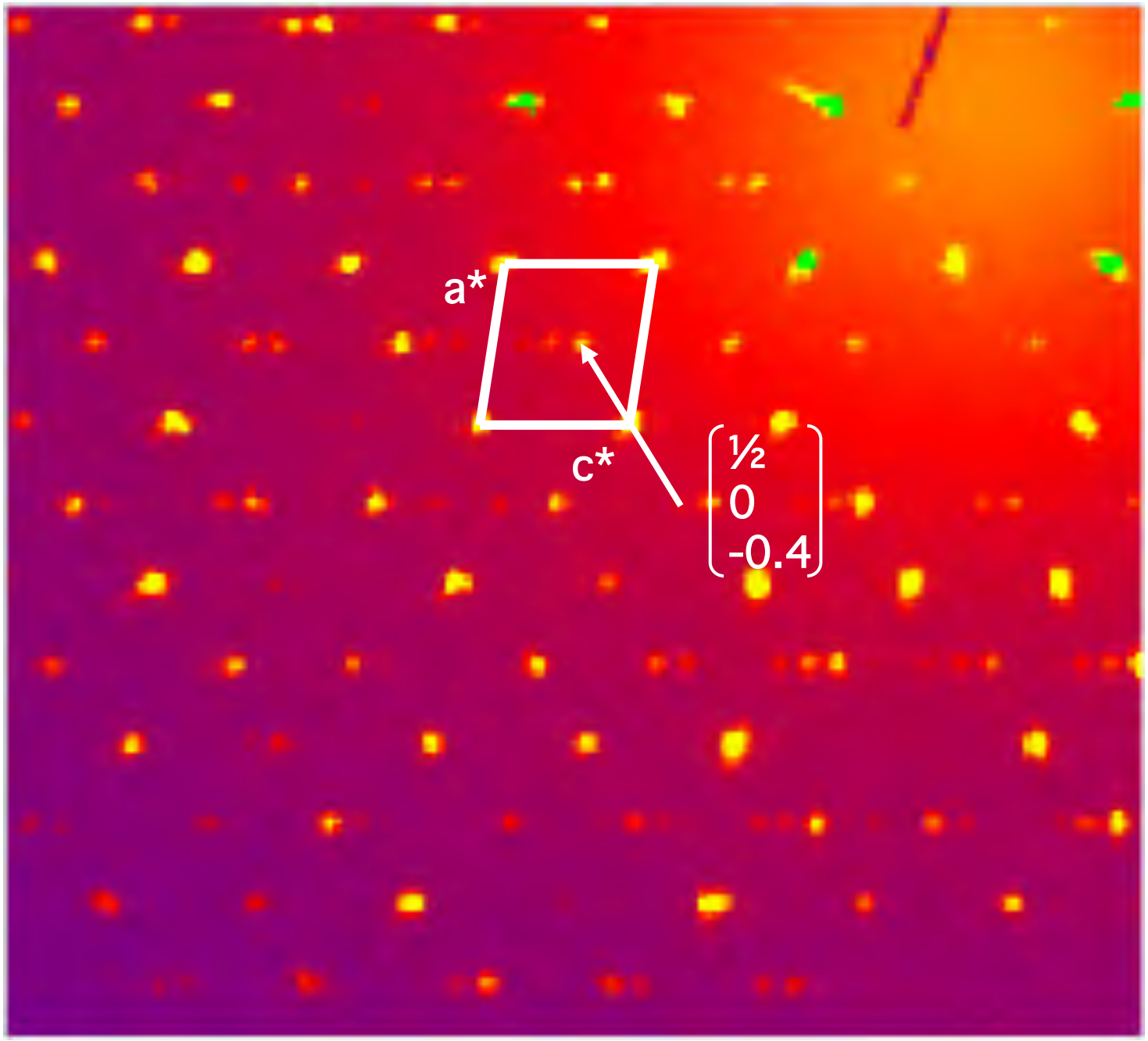
A sequence of 10 successive molecules, 5 in one orientation and 5 in the other can be defined as the motif, *i.e.* the distinct repeat unit.



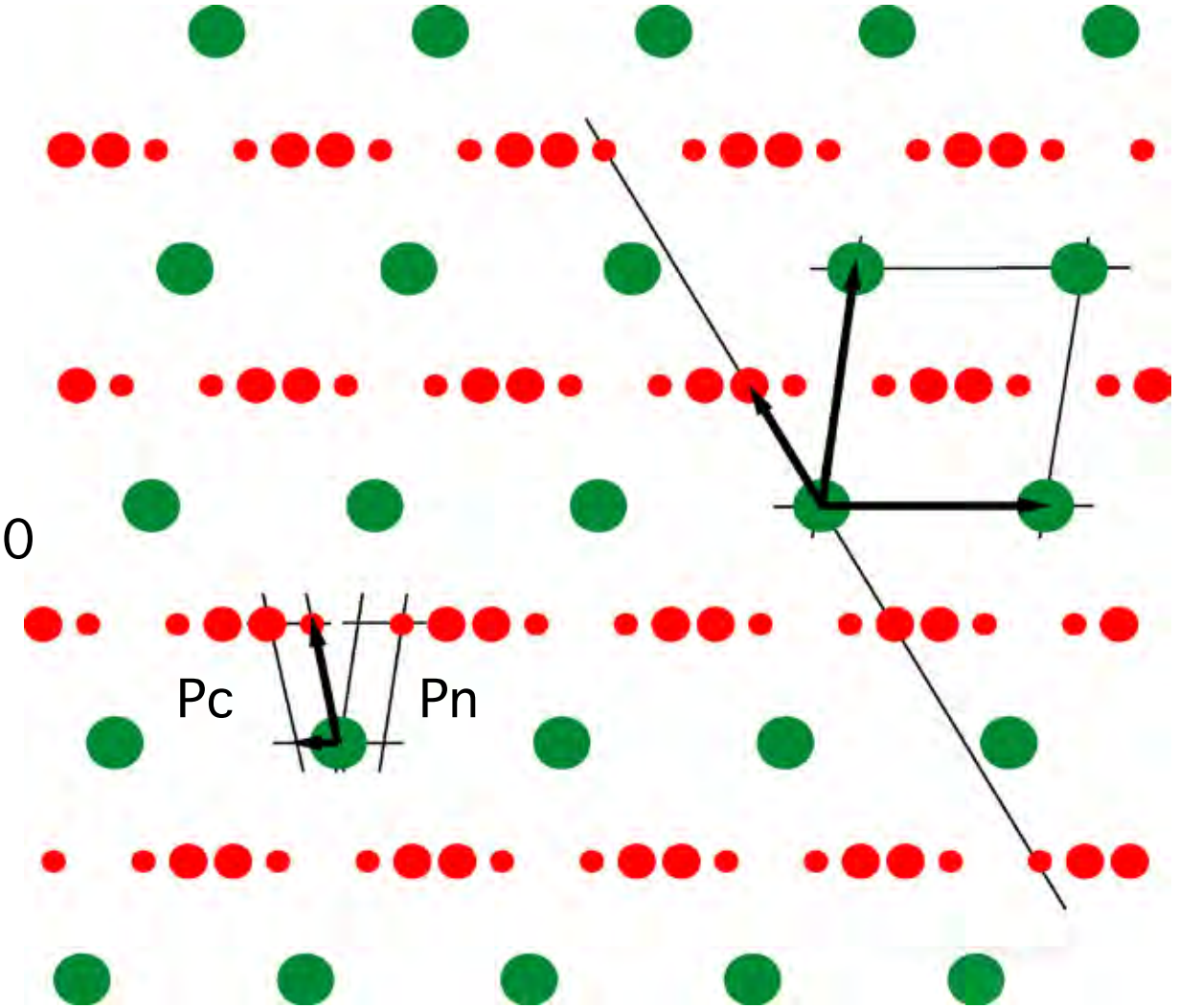


h1l

h1l zoom



Reciprocal Space



Superspace groups

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

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

} 3D supercell symmetry: Pn

Superspace structure in *Pc*(α0γ)*s*

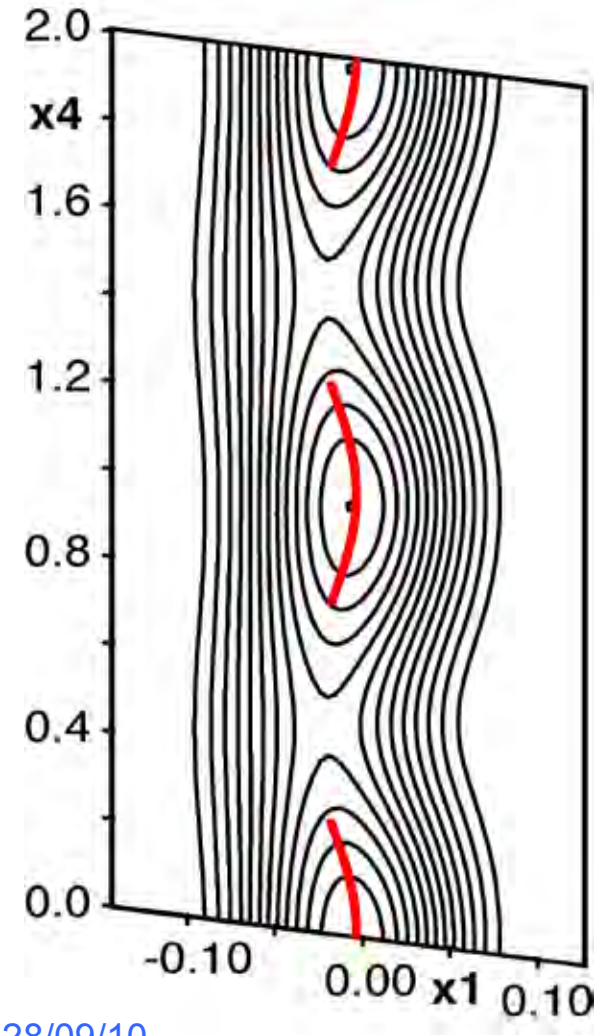
- The starting model (fractional coordinates) is derived from the molecules of the Z' = 10 superstructure with one formula unit for each orientation

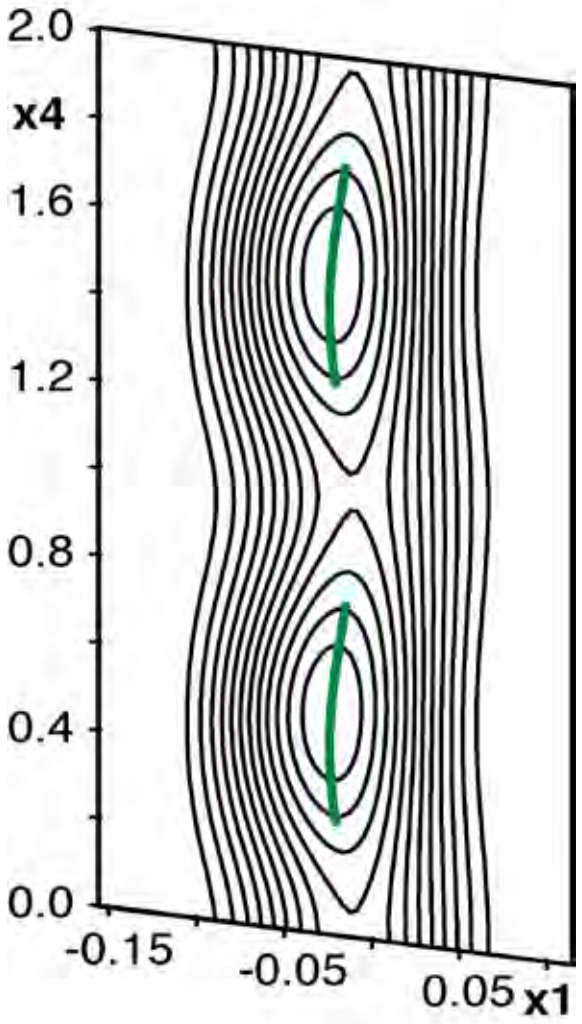
- For each of the orientations the width of the crenels is set to Δx_4 = 1/2

- Main and 1st order satellite reflections are used in the refinement.

Superspace structure in *Pc*(α0γ)*s*

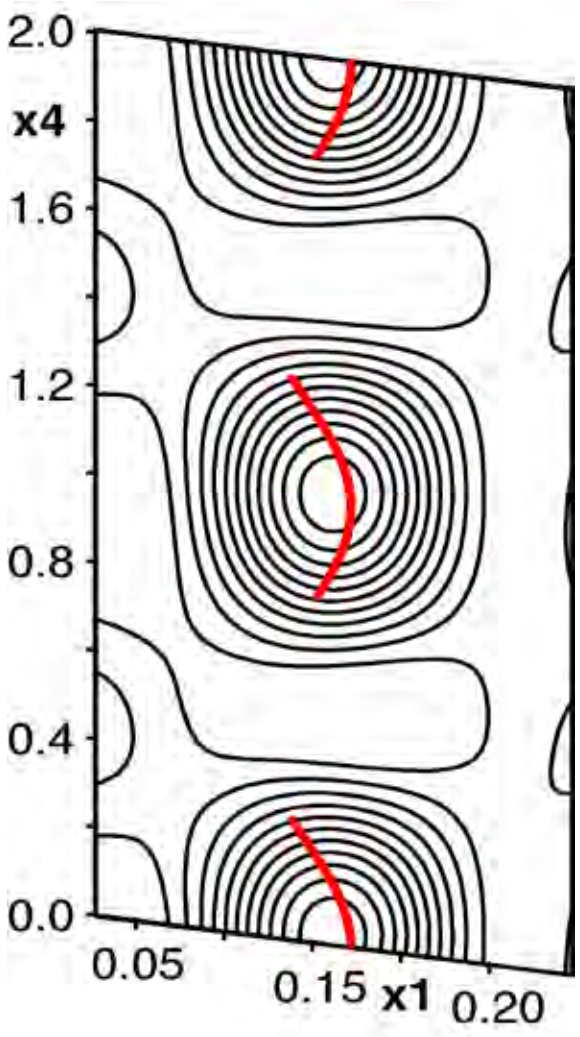
- Fourier maps of corresponding Cu atoms in the x_1-x_4 plane

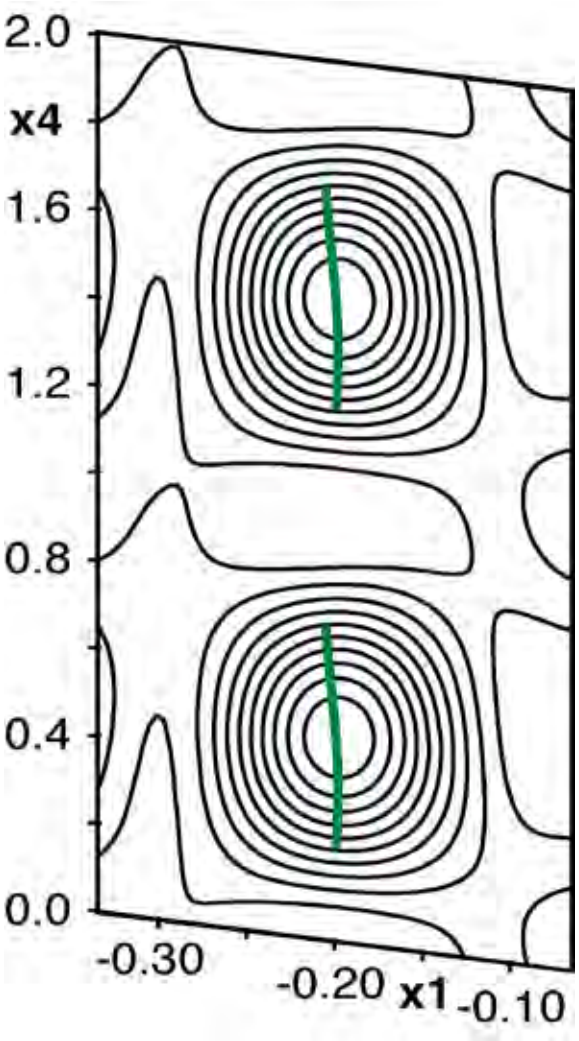




Superspace structure in *Pc*(α0γ)*s*

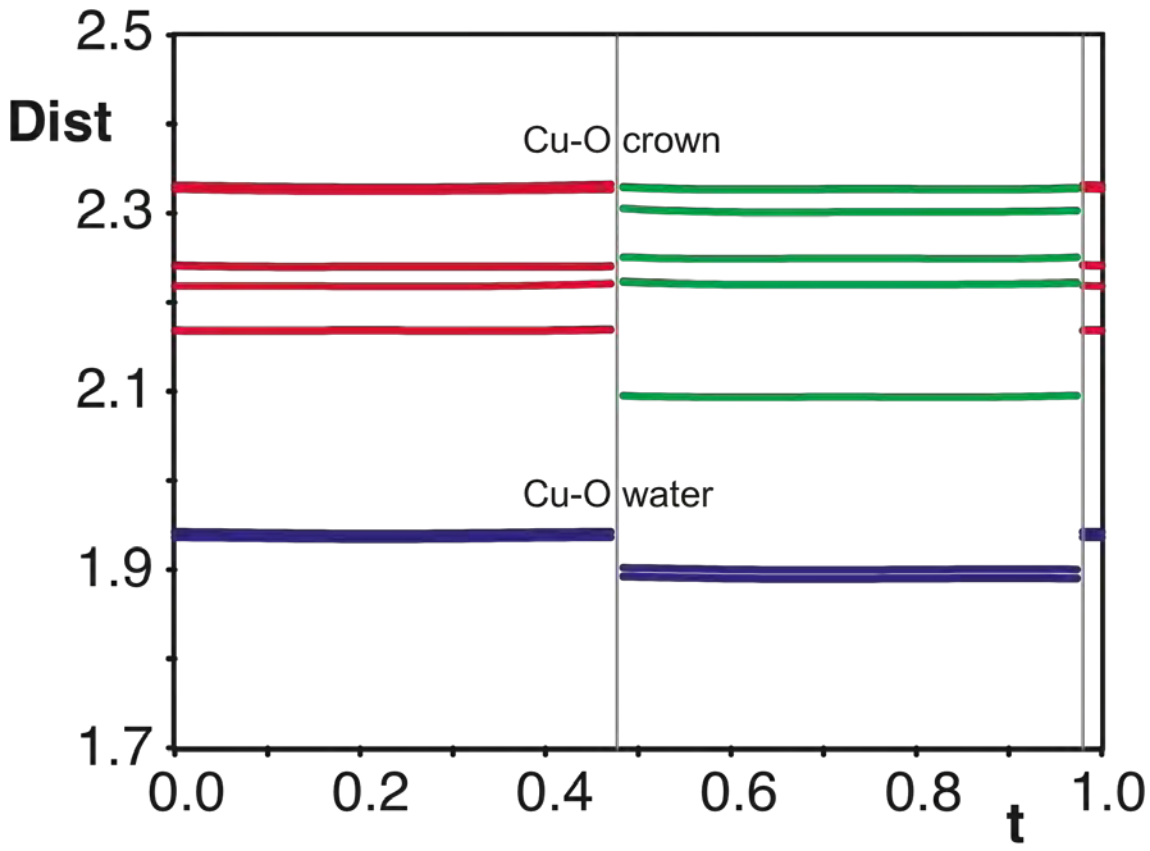
- Fourier maps of corresponding O atoms in the x_1-x_4 plane





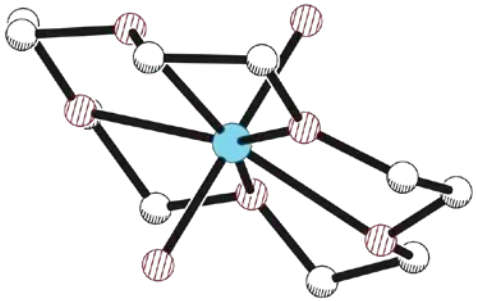
Superspace structure in *Pc*(α0γ)*s*

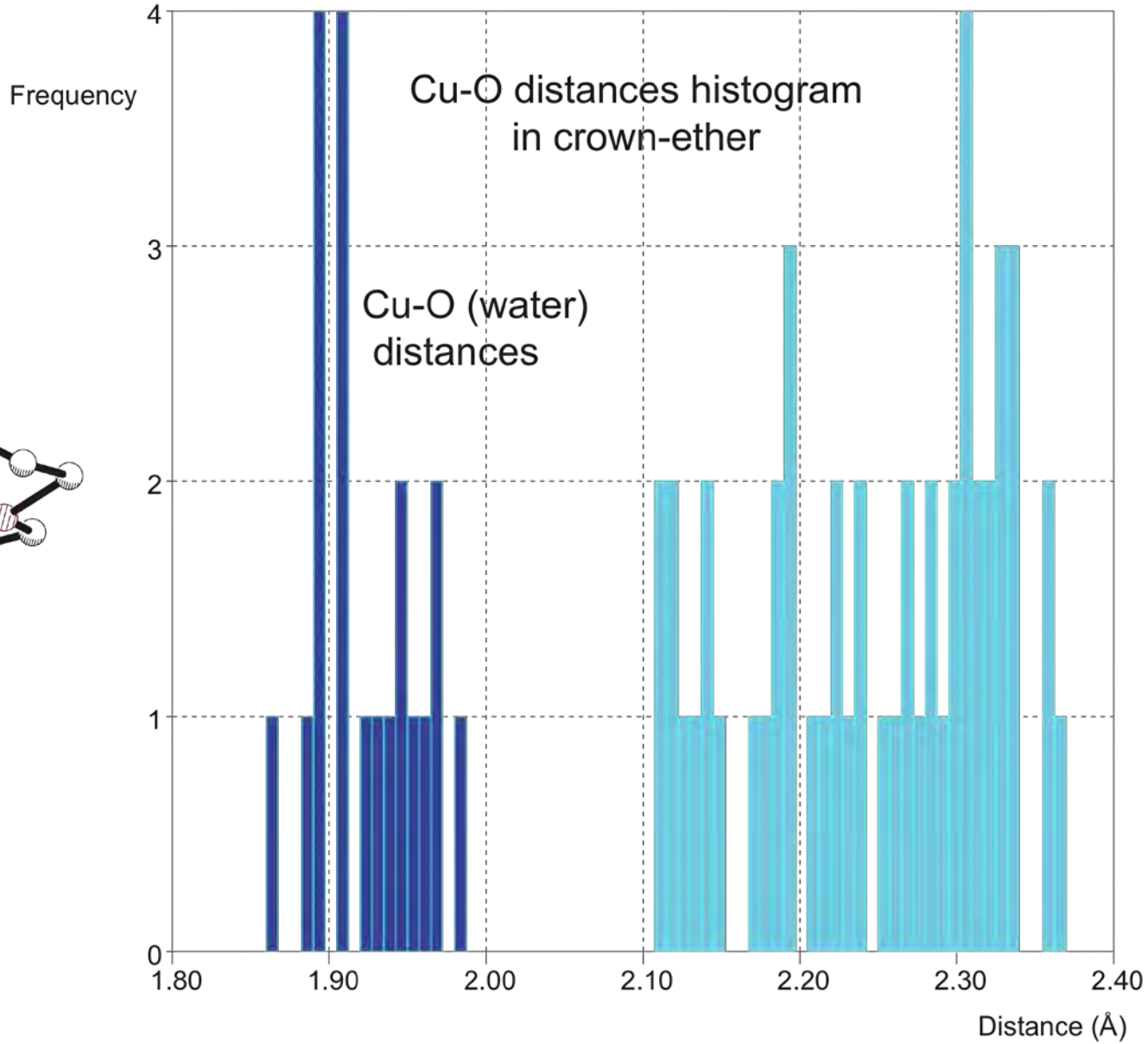
- Cu – O distances in the crown-ether (5) and with water (2)



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.