XRPD:
Challenging organic disordered structures

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Content

1. Iso-butyl-lithium

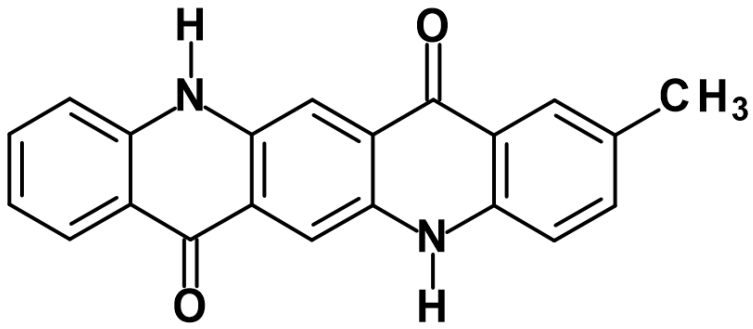
   Ordered phase and rotator phase

2. NaOEt

   Disordered structure with unclear space group

3. Monomethyl-quinacridone

   Head-to-tail disorder



^{i}BuLi
iso-Butyl-lithium

Crystal structure determined by
X-ray powder diffraction

Alexander Bodach, Lothar Fink, Martin U. Schmidt*:
Crystal structures of ordered and plastic-crystalline phases of iso-butyllithium by X-ray powder diffraction,
Chem. Commun., ***2018****, 54, 10734-10737.*

Preparation and measurement

^{i}BuLi: highly sensitive to air and moisture
All procedures under N_2 or Ar

^{i}BuLi obtained as solution in hexane

2x recrystallised

Evaporated

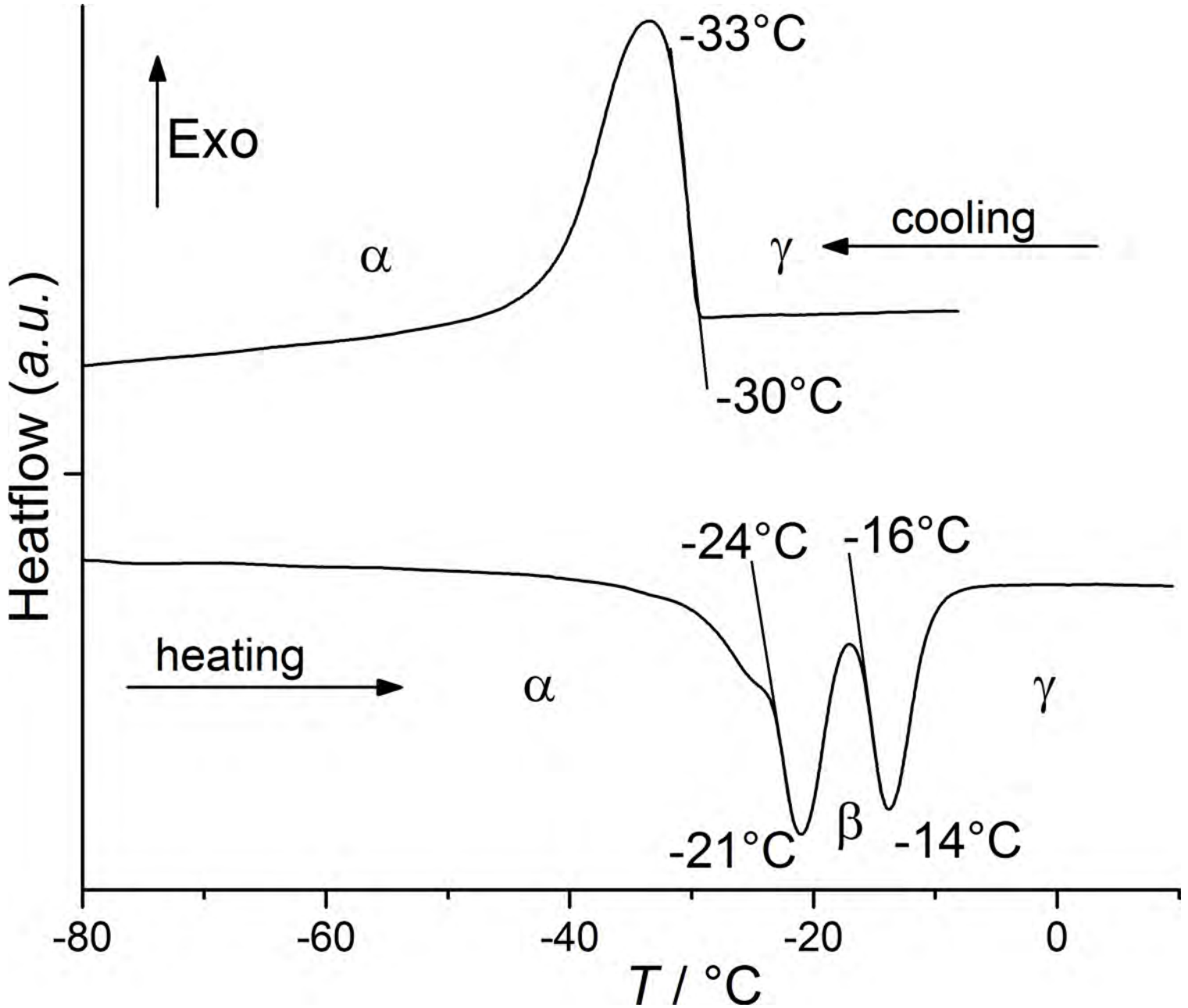
Filled in capillary and sealed

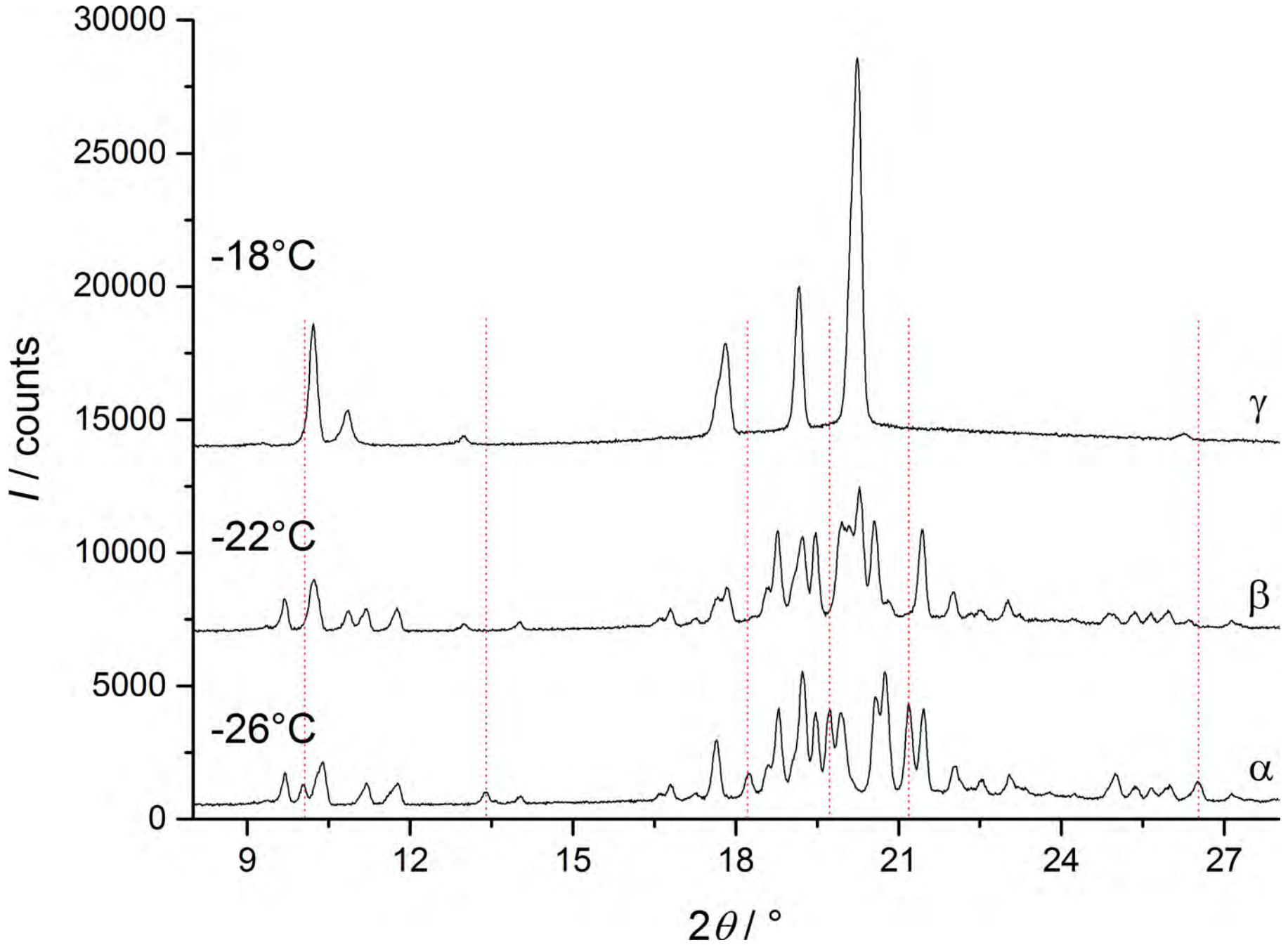
Measured in sealed capillary

STOE Stadi-P diffractometer, Cu-Kα_1 radiation

Temperature control by Oxford Cryostream

DSC


Exo
-33°C
α
γ
cooling
-30°C
Heatflow (a.u.)
-24°C
-16°C
heating
α
γ
β
-21°C
-14°C
-80
-60
-40
-20
0
T / °C


30000
25000
20000
15000
10000
5000
0
I / counts
-18°C
-22°C
-26°C
γ
β
α
9
12
15
18
21
24
27
2θ / °

Structure determination of the low-temperature phase (α)

Indexing: triclinic

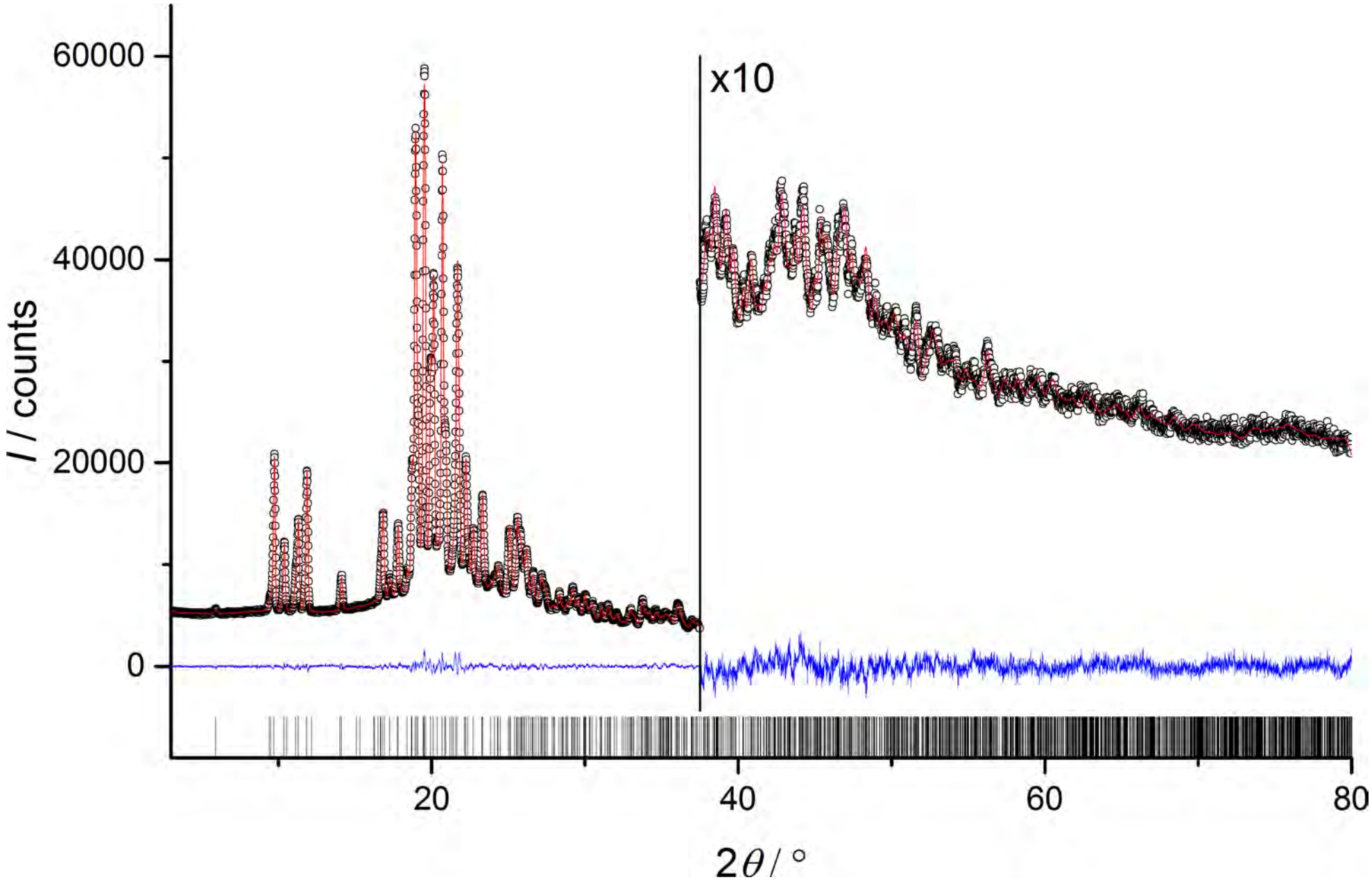
Space group P 1 or P $\bar{1}$?

From unit cell volume: Z = 12
=> 3 tetramers or 2 hexamers?

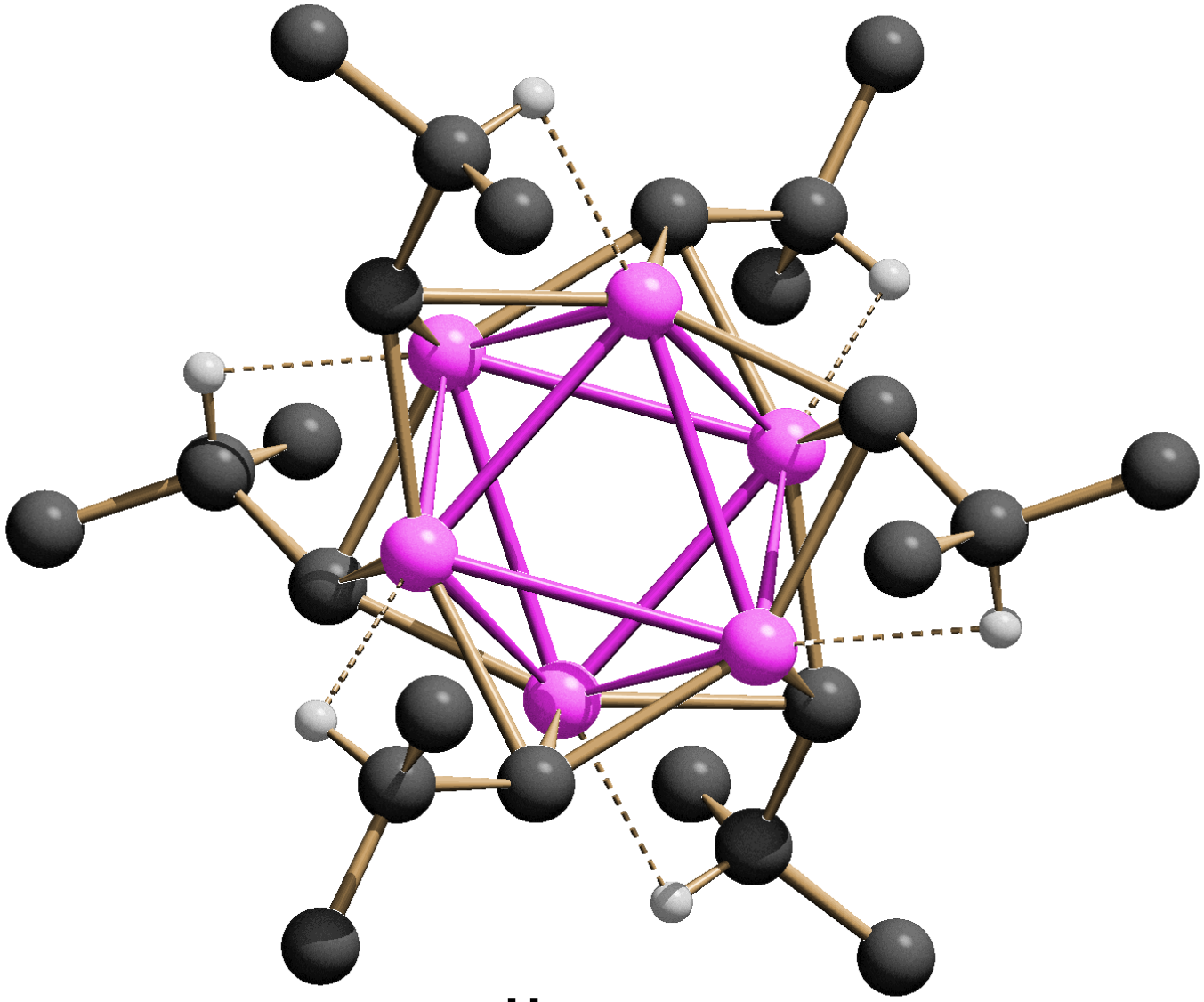
Structure solution by direct-space methods with DASH
- with tetramers in P 1 and P $\bar{1}$
- with hexamers in P 1 and P $\bar{1}$

Final solution:
Space group P $\bar{1}$ with two symmetrically independent hexamers, both on inversion centres

Low-temperature phase (α-phase)



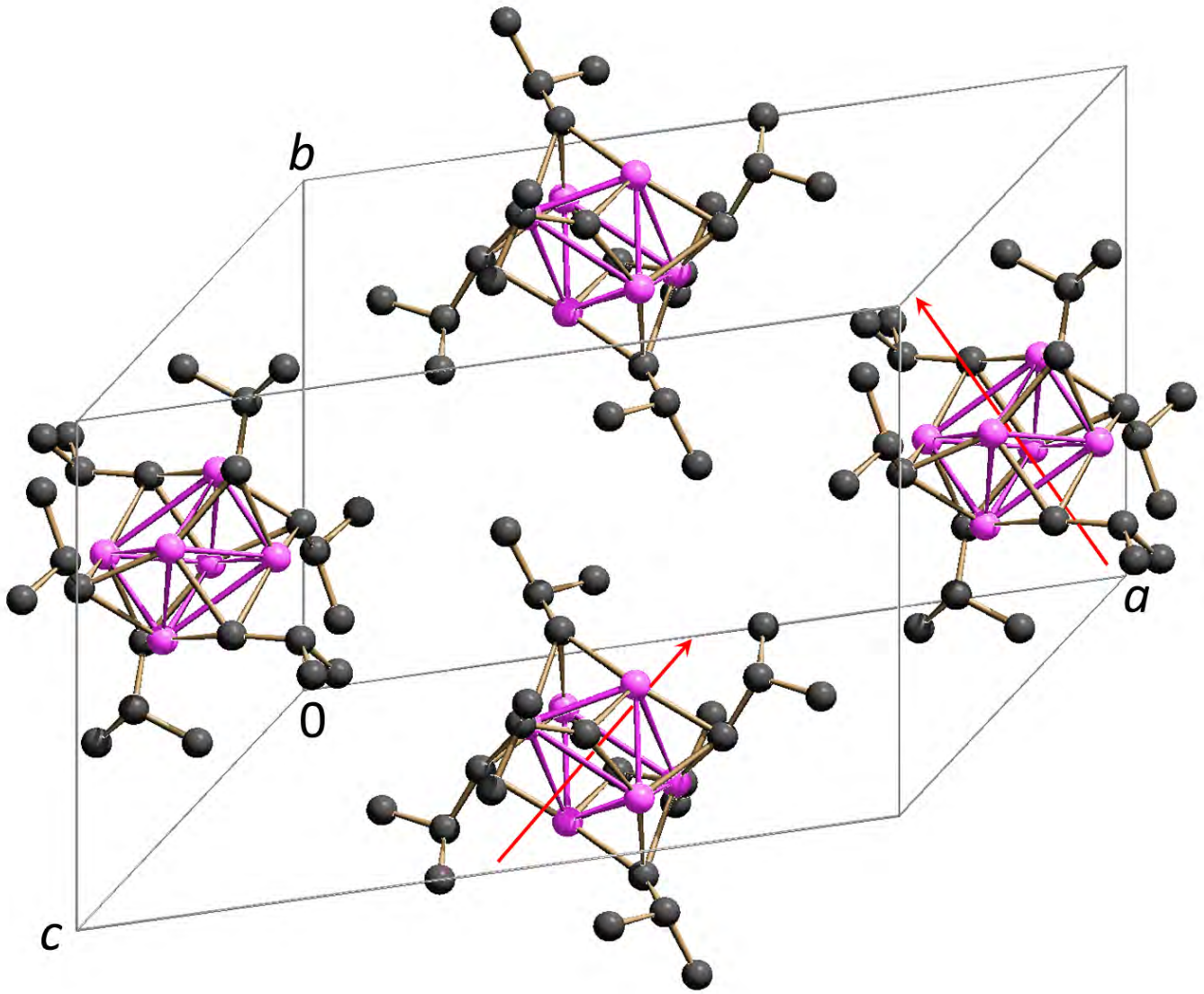
Low-temperature phase (α-phase)



Hexamer

SCHAKAL

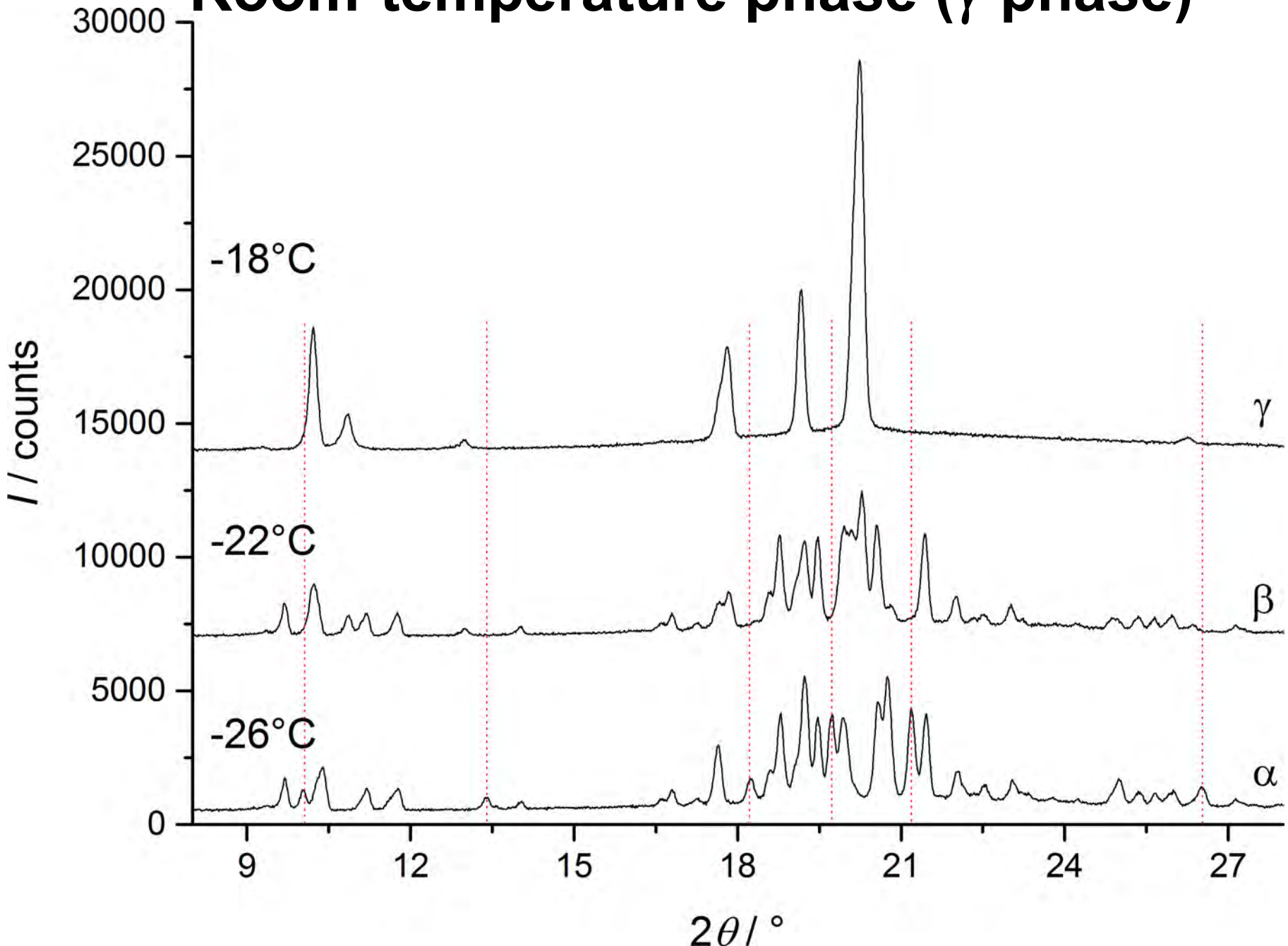
Low-temperature phase (α-phase)



$P\bar{1}$, $Z = 2$

Two symmetricylly independent hexamers, both on inversion centres

Room-temperature phase (γ-phase)



Rotator phase

Structure not determined

Room-temperature phase (γ-phase)

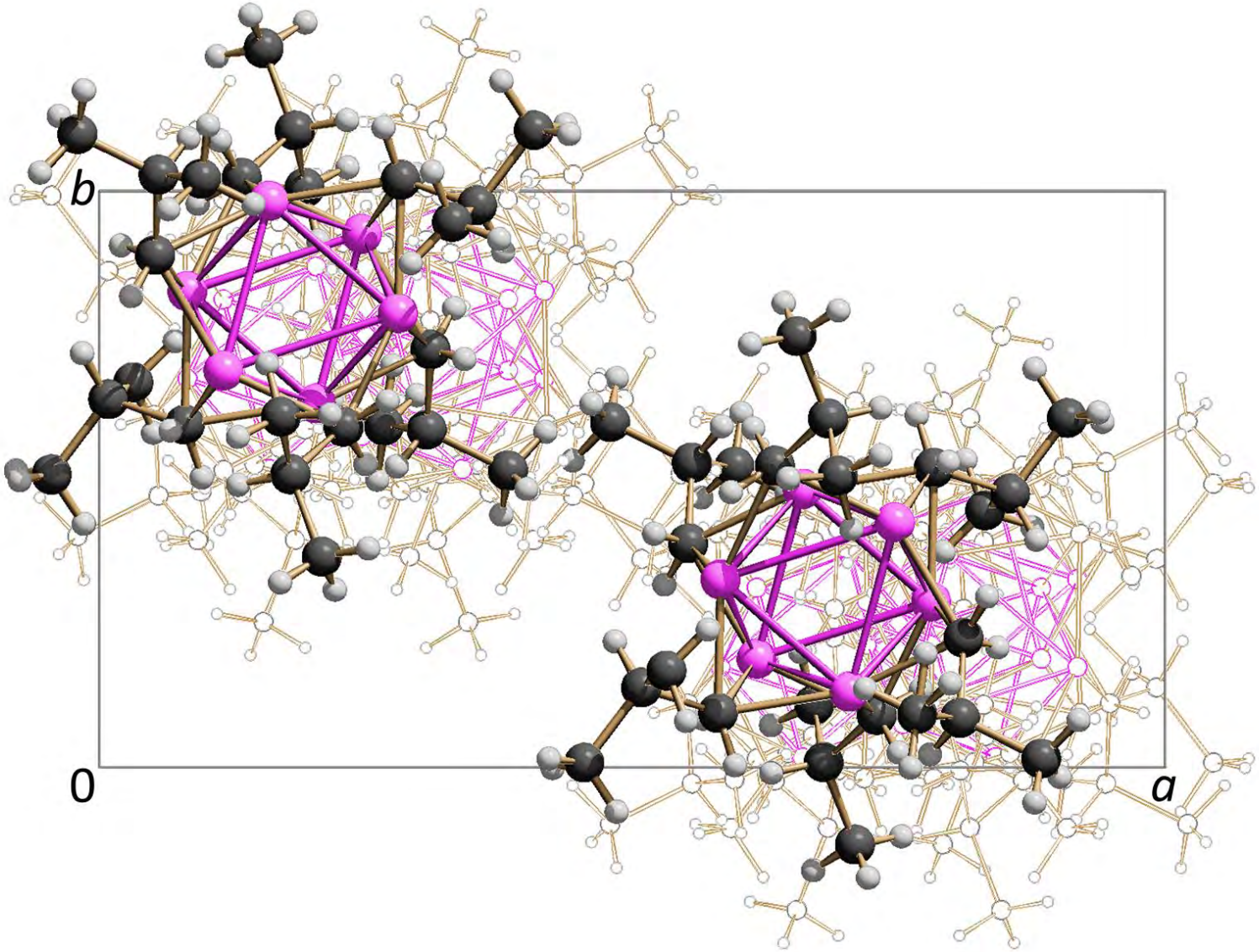
Indexing: orthorhombic, Z' = 2

Space group unclear

Rotator phase (Plastic phase)!

Structure filnally solved in Pnnn
Molecules 4-fold disordered

Room-temperature phase (γ-phase)



Rotator phase (Plastic phase)

Hexamers rotate in the solid state (Dynamic disorder)

NaOEt

First Synthesis: Liebig (1837)

180 years later:

Crystal structure determined by X-ray powder diffraction (2019)

Na + EtOH $\rightarrow$ NaOEt in EtOH (Solution)

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Vacuum $\rightarrow$ Solid

Na + EtOH $\rightarrow$ NaOEt in EtOH (Solution)

Vacuum $\rightarrow$ Solid

Ar $\rightarrow$ liquid

Na + EtOH $\rightarrow$ NaOEt in EtOH (Solution)

Vacuum $\rightarrow$ Solid

Ar $\rightarrow$ liquid

Vacuum $\rightarrow$ Solid

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Vacuum $\rightarrow$ Solid

Ar $\rightarrow$ liquid

Vacuum $\rightarrow$ Solid

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Na + EtOH $\rightarrow$ NaOEt in EtOH (Solution)

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Ar $\rightarrow$ liquid

Vacuum $\rightarrow$ Solid

Ar $\rightarrow$ Liquid

Vacuum $\rightarrow$ Solid

Na + EtOH $\rightarrow$ NaOEt in EtOH (Solution)

Vacuum $\rightarrow$ Solid

Ar $\rightarrow$ liquid

Vacuum $\rightarrow$ Solid

Ar $\rightarrow$ Liquid

Vacuum $\rightarrow$ Solid

Ar $\rightarrow$ Solid

Na + EtOH $\rightarrow$ NaOEt in EtOH (Solution)

Vacuum $\rightarrow$ Solid

Ar $\rightarrow$ liquid

Vacuum $\rightarrow$ Solid

Ar $\rightarrow$ Liquid

Vacuum $\rightarrow$ Solid

Ar $\rightarrow$ Solid

Mixture of 3-4 phases. Mainly NaOEt * 2 EtOH

Na + EtOH → NaOEt in EtOH (Solution)

Vacuum → Solid

Ar → liquid

Vacuum → Solid

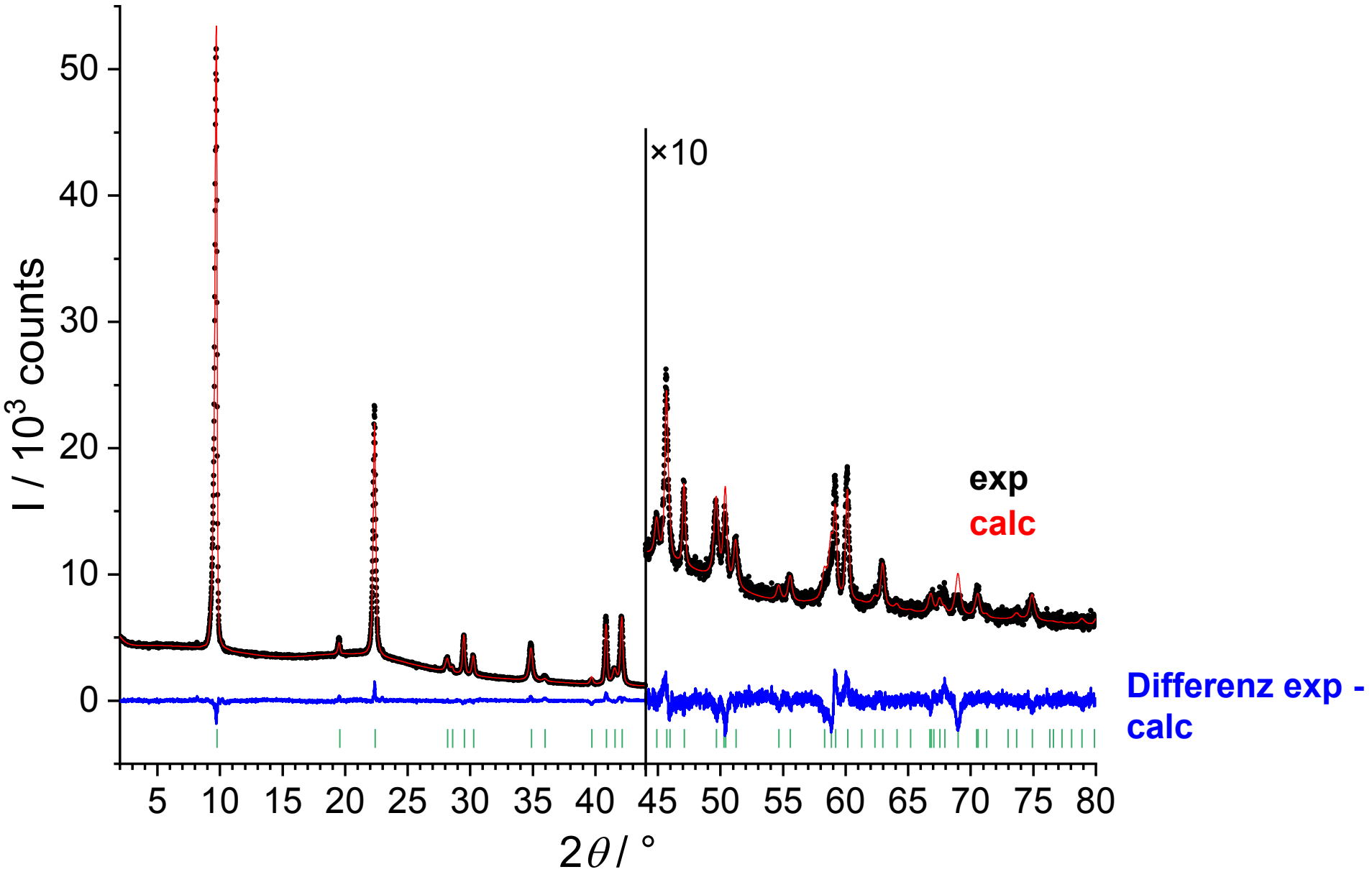
Ar → Liquid

Vacuum → Solid

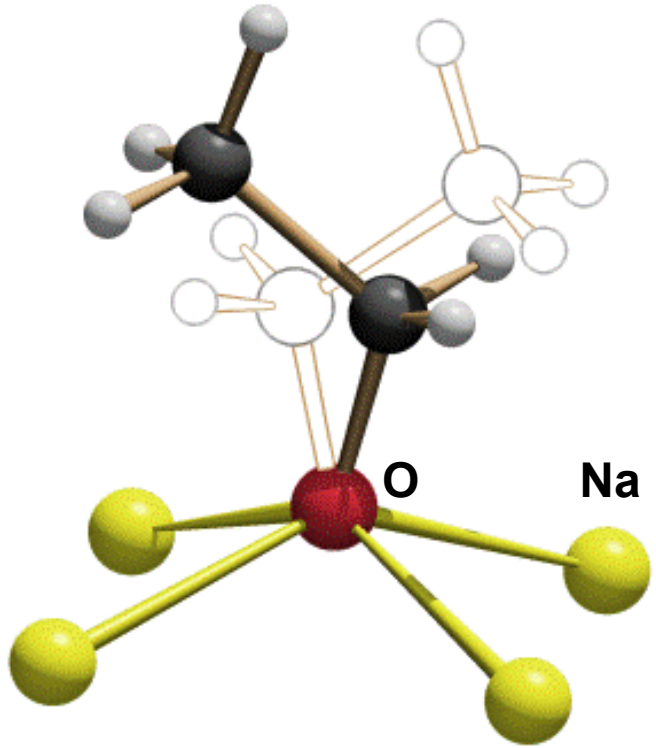
Ar → Solid

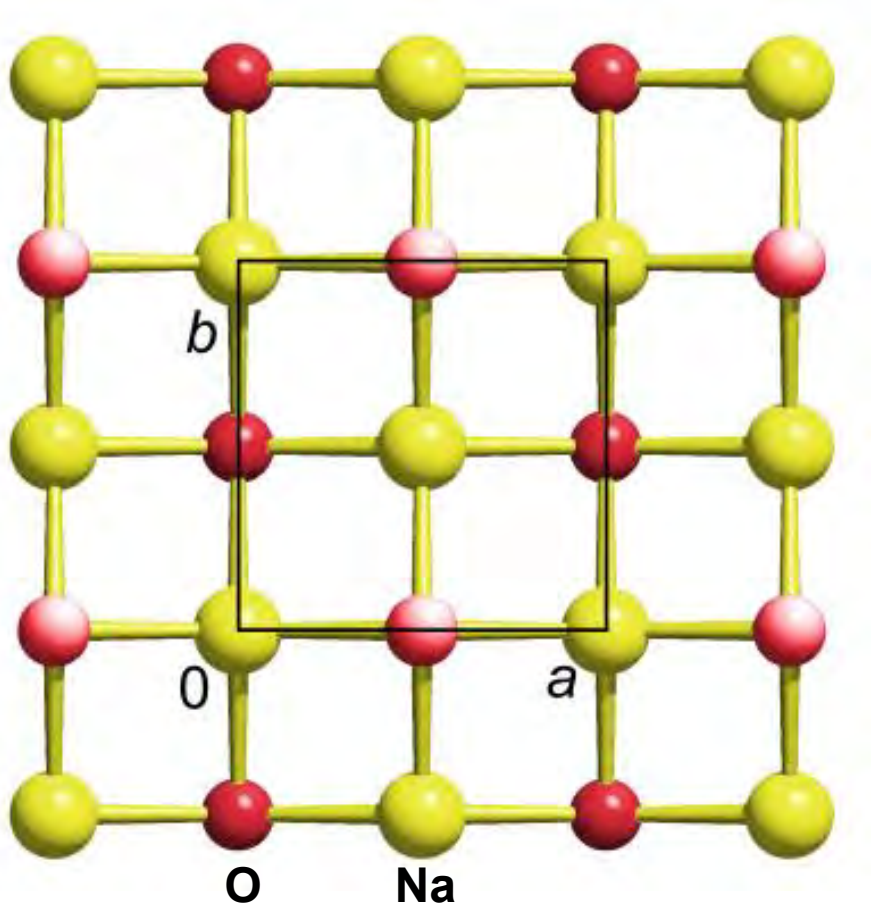
Mixture of 3-4 phases. Mainly NaOEt * 2 EtOH

Vacuum, 50°C, several hours → NaOEt (pure)

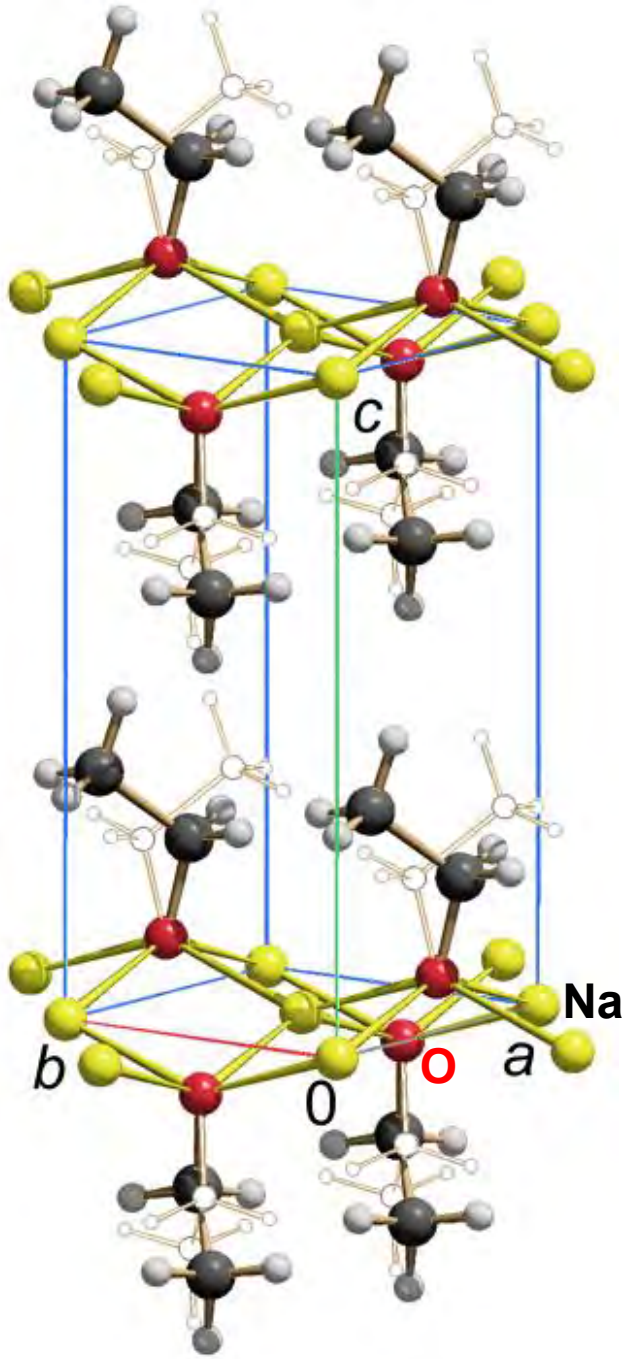


NaOEt: Rietveld refinement

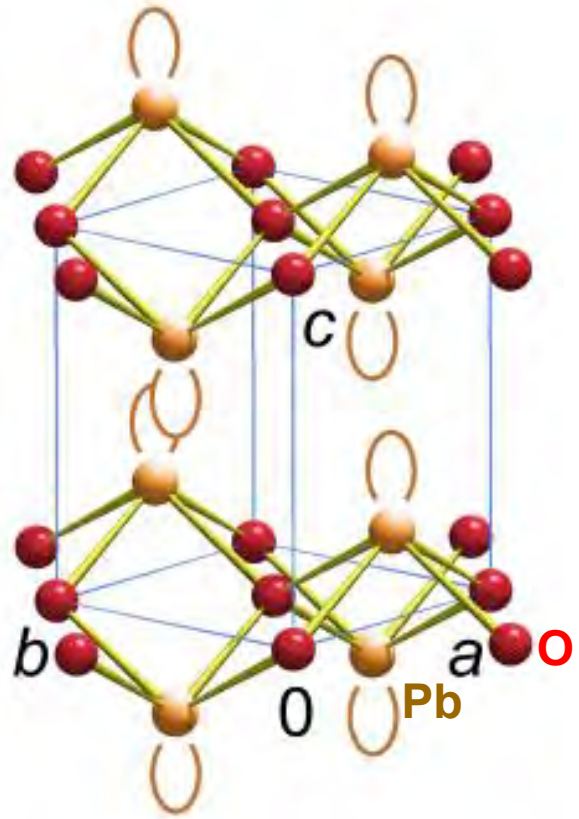




NaOEt



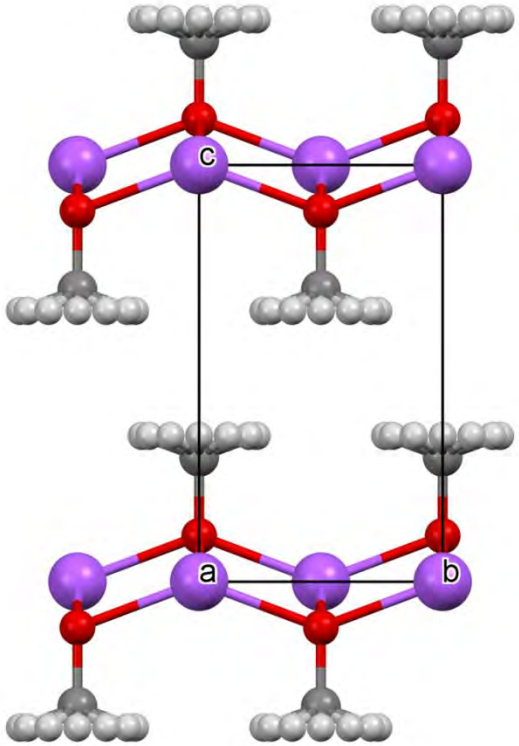
NaOEt



PbO

Na	O	Et
O	Pb	LP

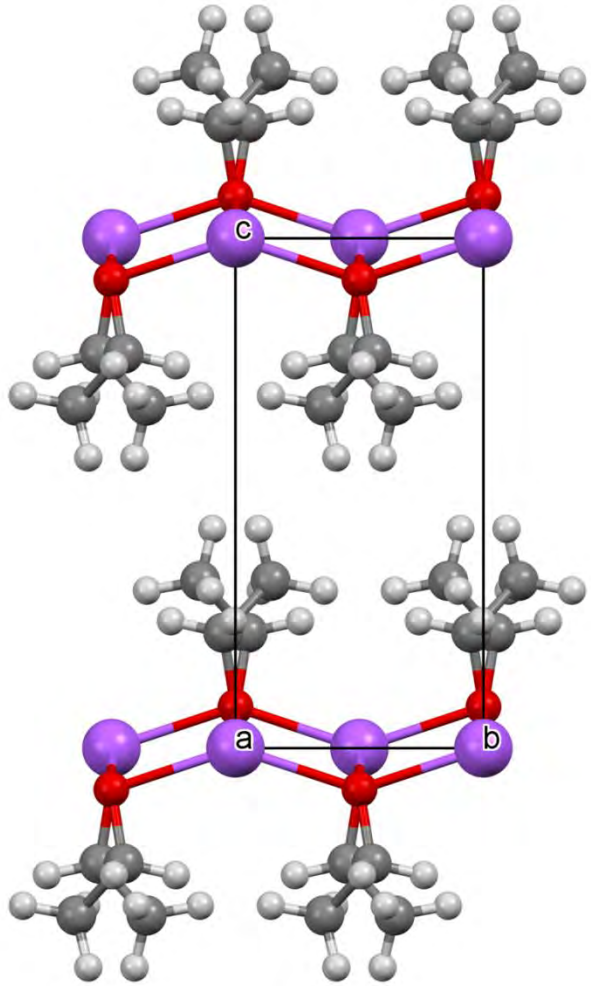
NaOEt has
Anti-PbO structure.



(*a*)

NaOMe

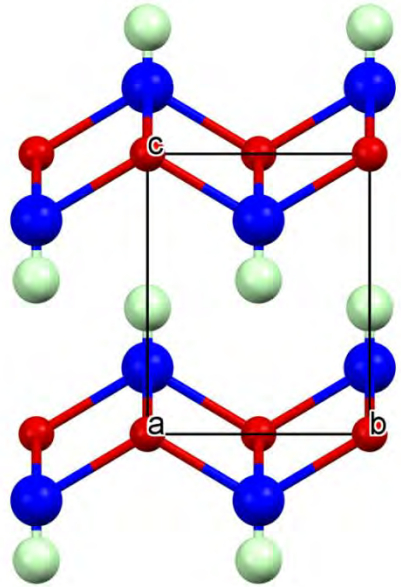
$P4/nmm$



(*b*)

NaOEt

$P\bar{4}2_1m$

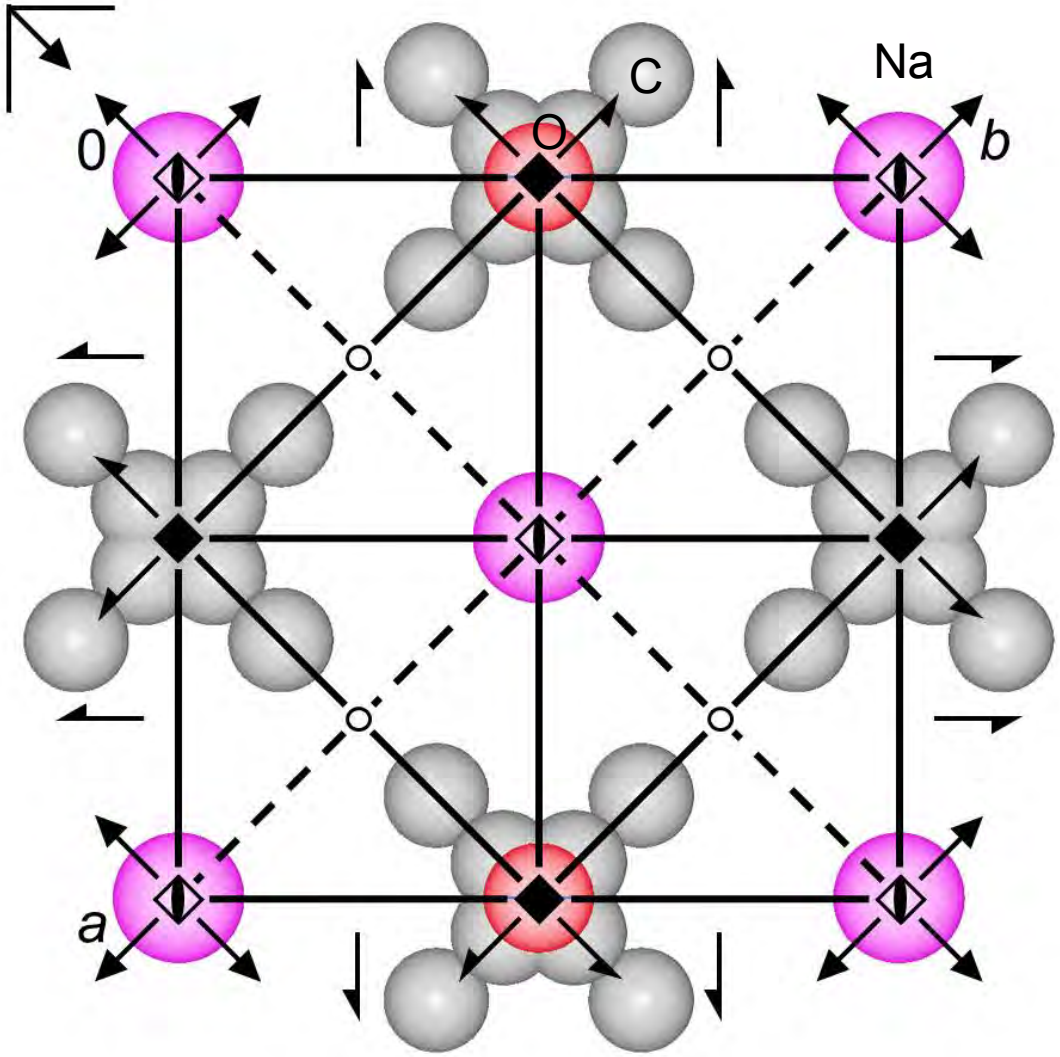


(*c*)

PbO

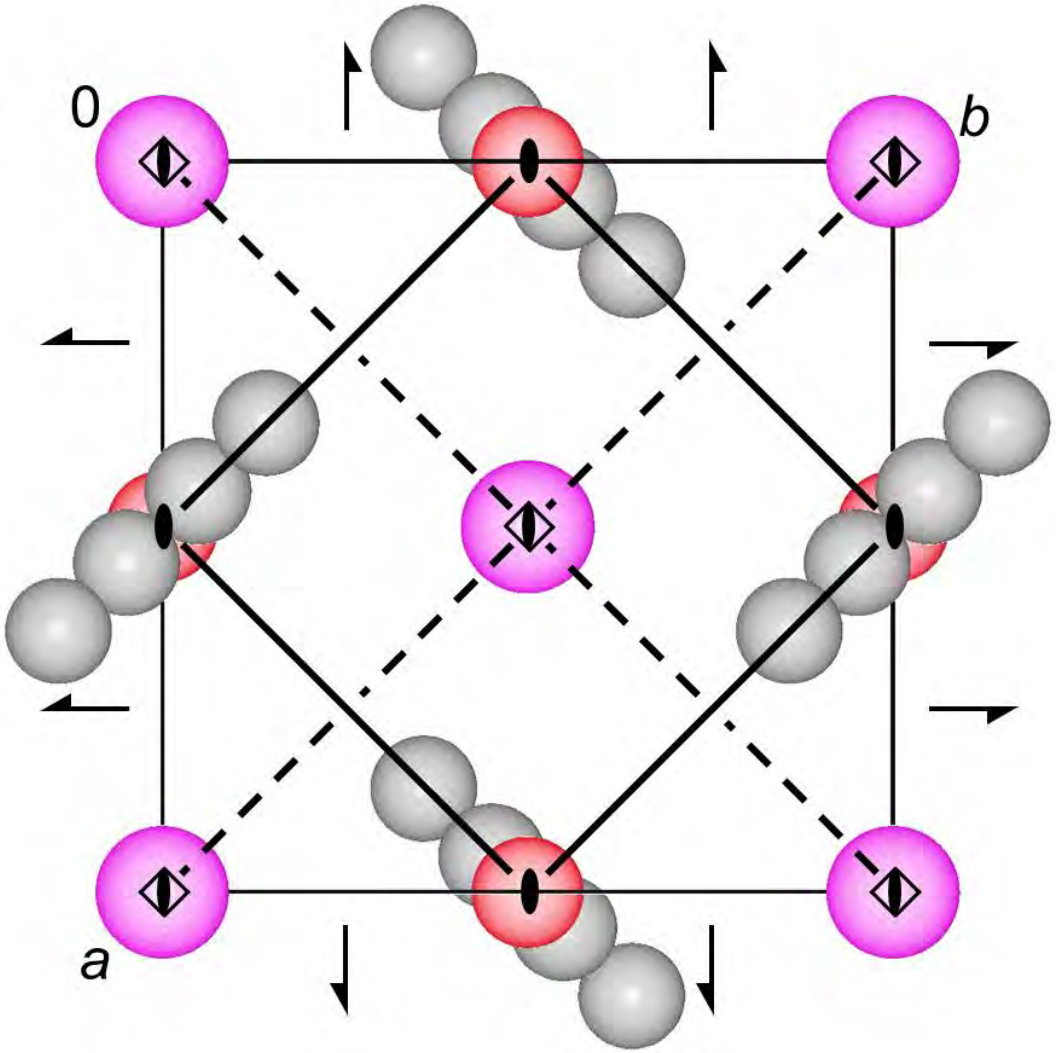
$P4/nmm$

NaOEt: Space group and disorder



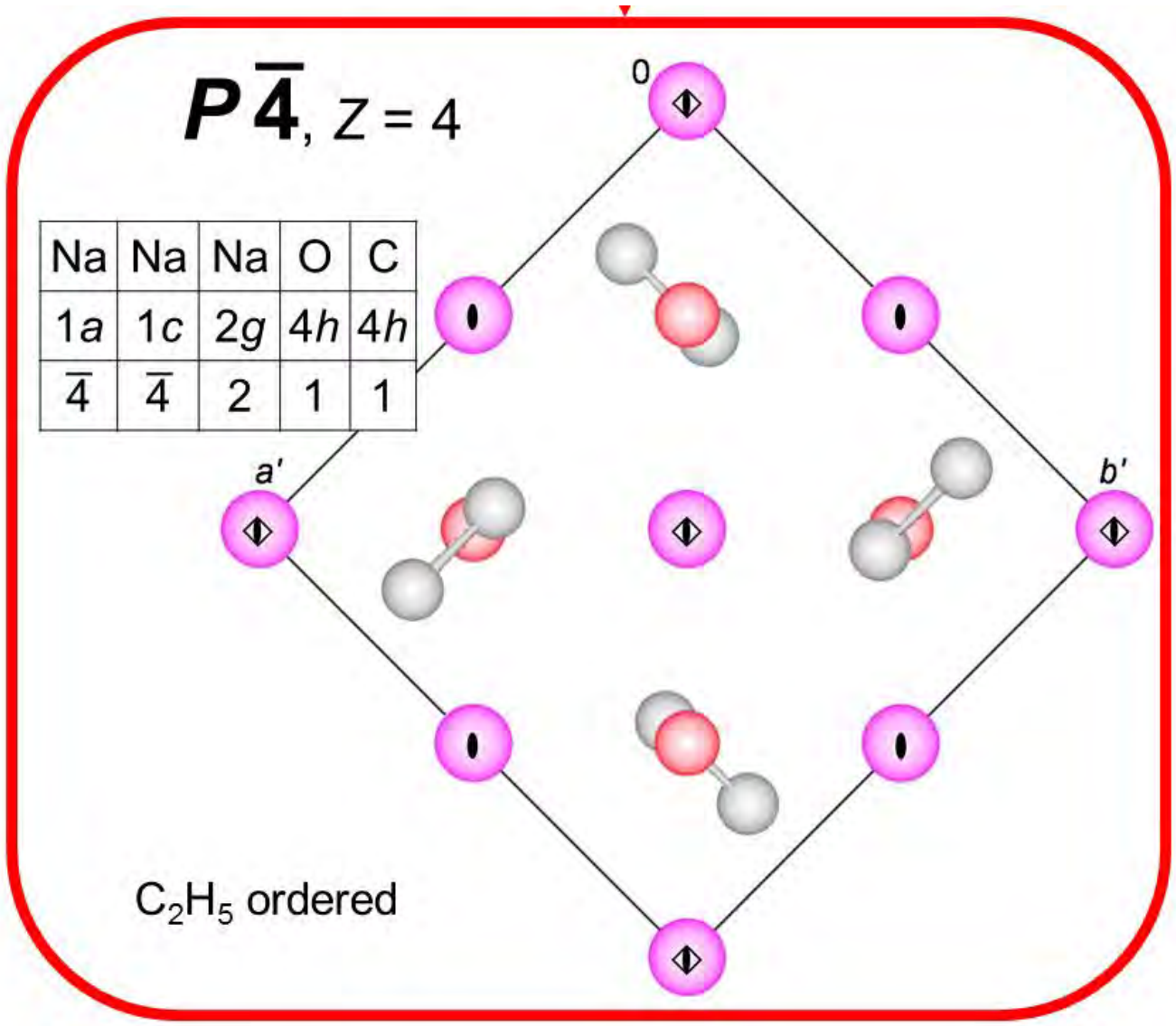
***P* 4/*nmm*, *Z* = 2**

4-fold disorder

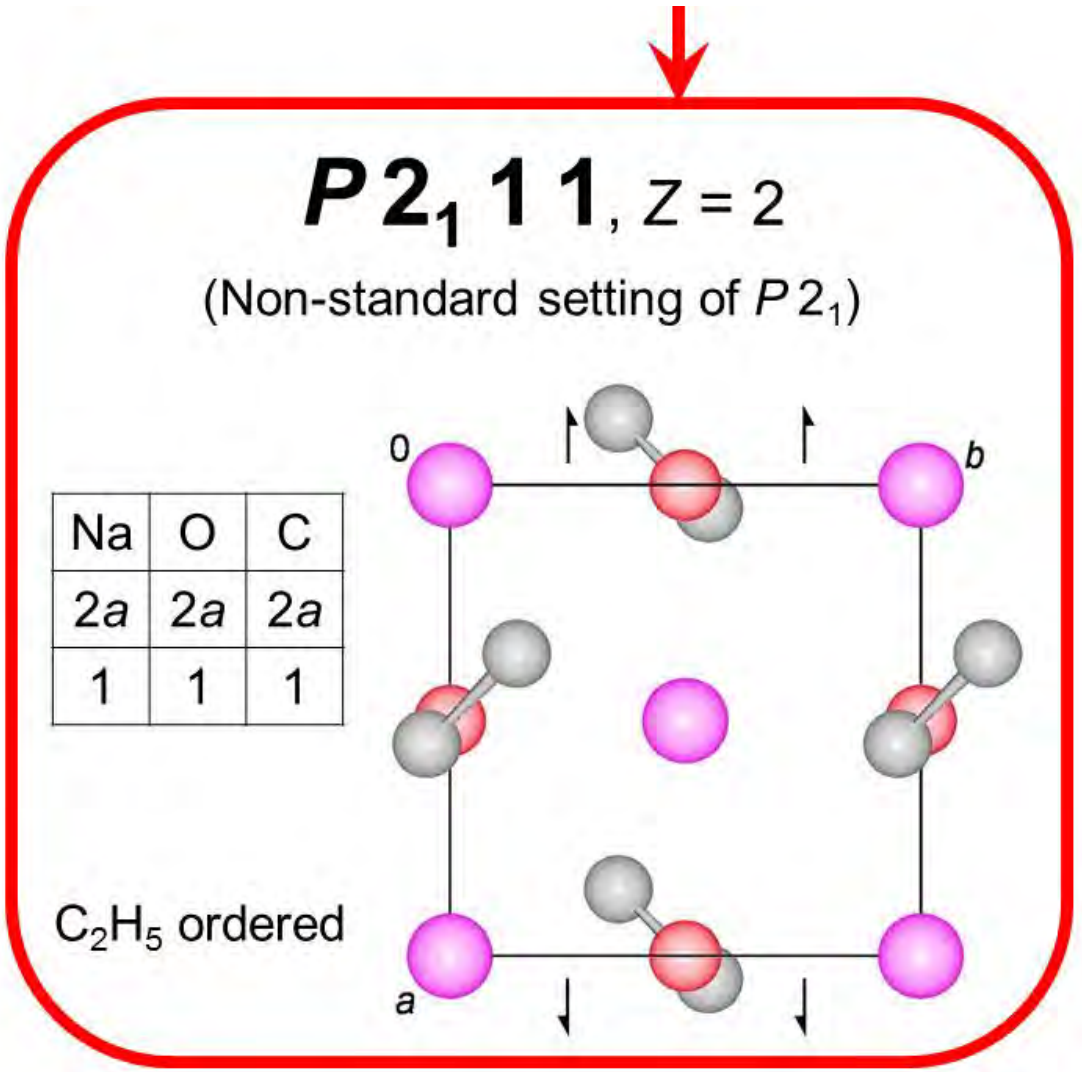


***P* $\bar{4}$ 2_1 *m*, *Z* = 2**

2-fold disorder

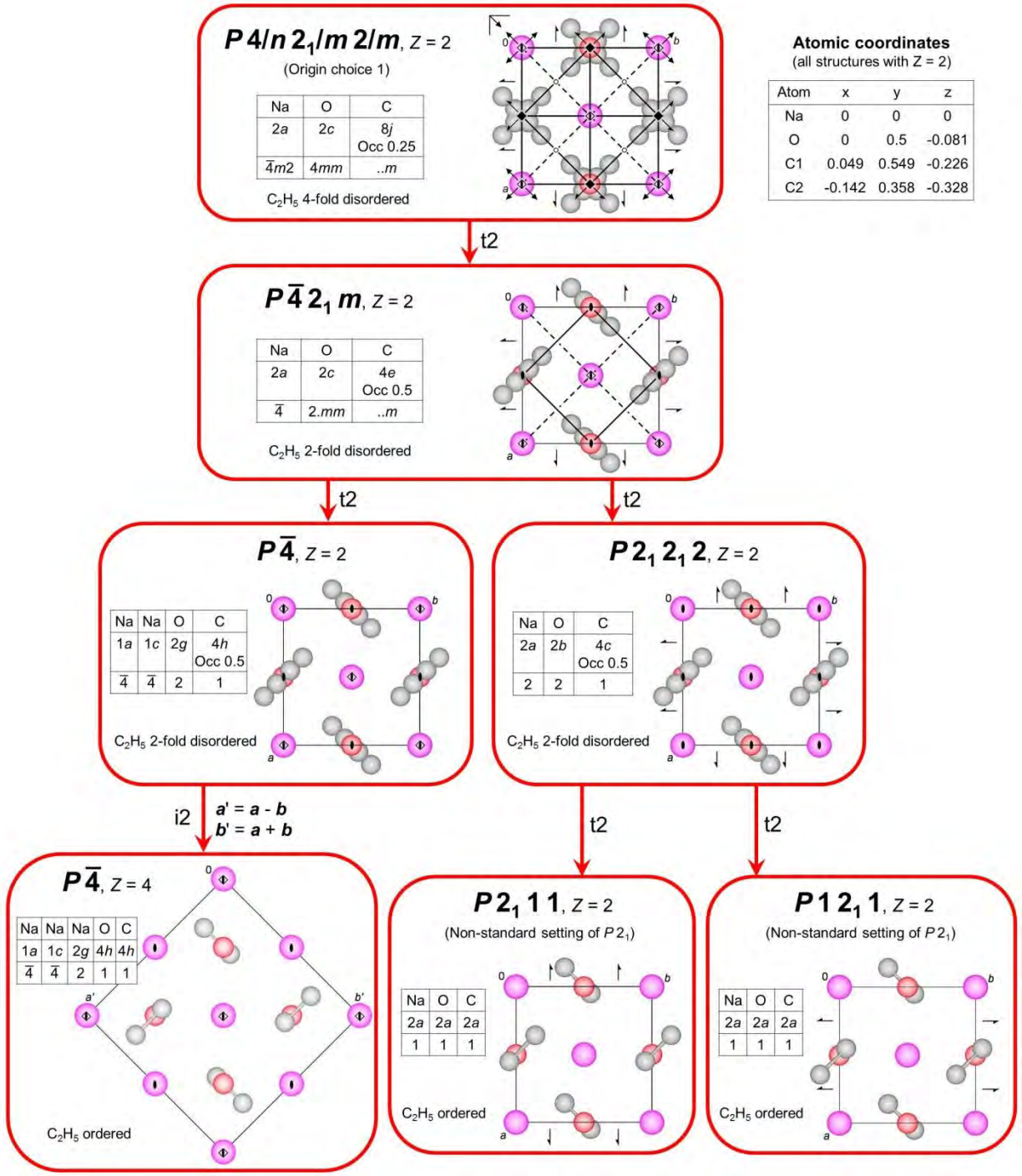


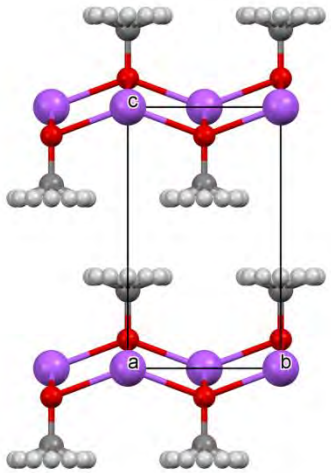
ordered



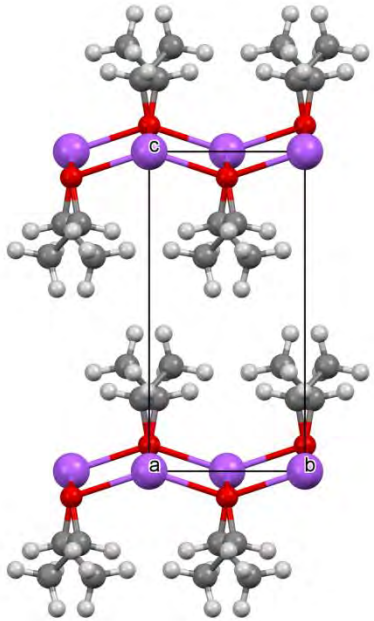
ordered

Bärnighausen tree

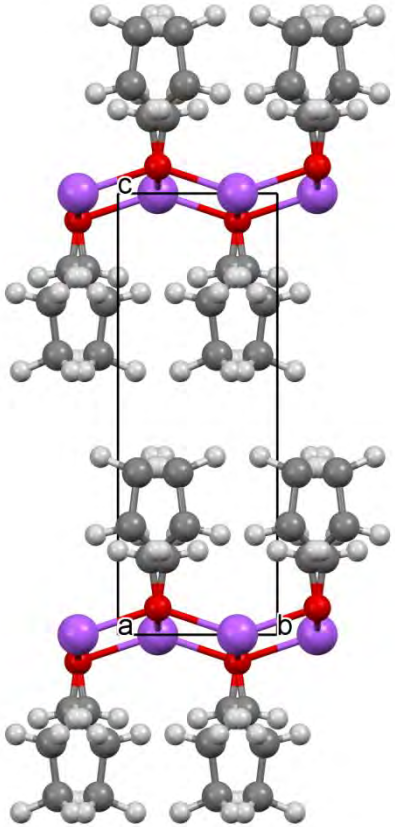




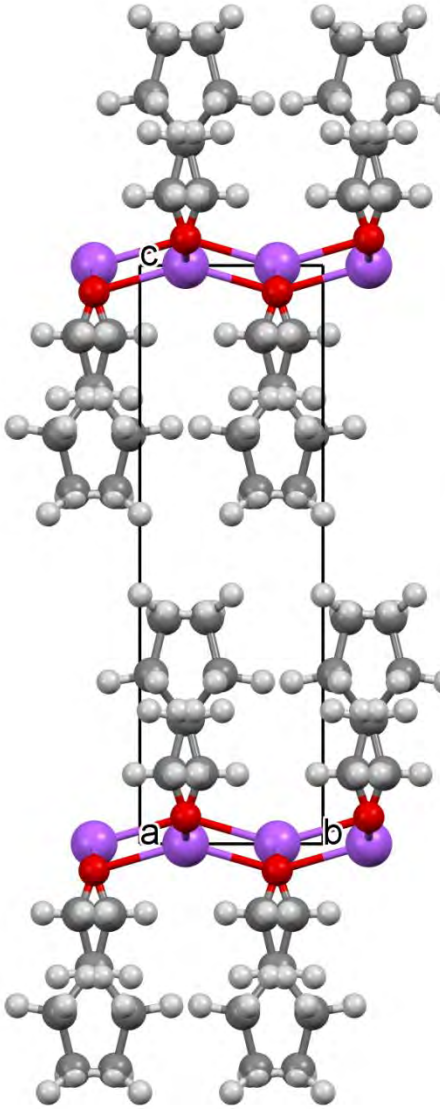
NaOMe



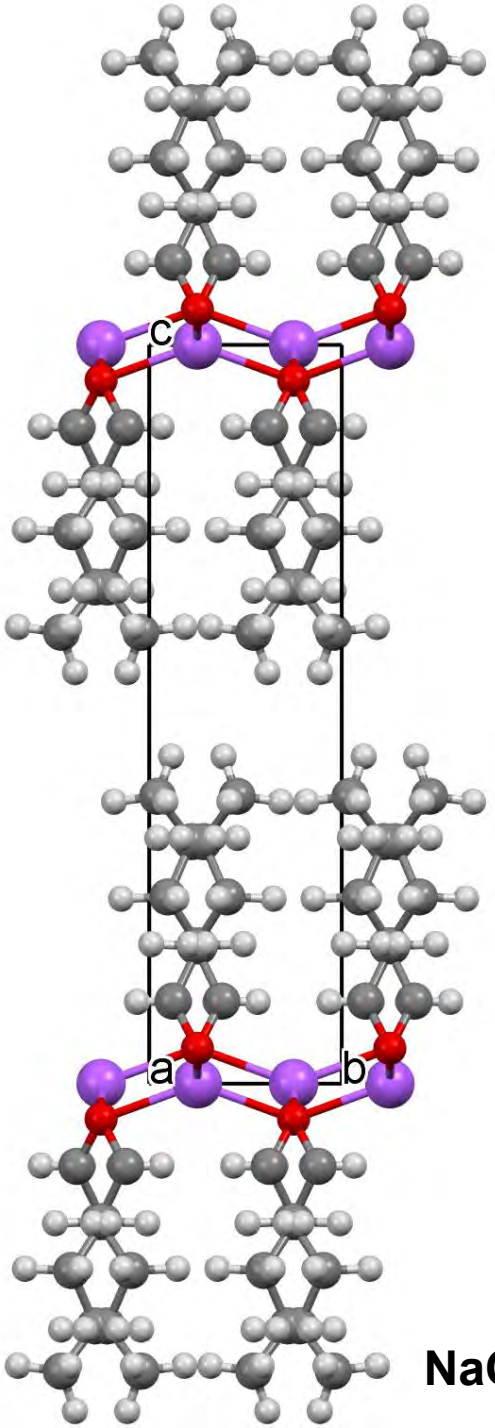
NaOEt



NaOPr



NaOBu



NaOAm

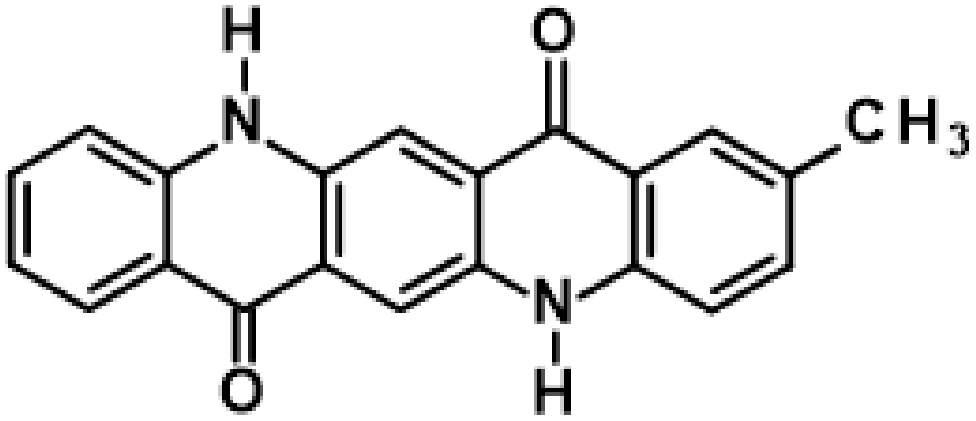
Published as:

1) Maurice Beske, Lukas Tapmeyer, Martin U. Schmidt:
"Crystal structure of sodium ethoxide (C_2H_5ONa), unravelled after a 180 years"
Chem. Commun., **2020**, 56, 3520-3523

2) Maurice Beske, Stephanie Cronje, Martin U. Schmidt*, Lukas Tapmeyer:
"Disordered sodium alkoxides from powder data: crystal structures of sodium ethoxide, propoxide, butoxide and pentoxide, and some of their solvates"
Acta Cryst., **2021**, B77, 1-15.

Orientional disorder in monomethyl-quinacridone investigated by Rietveld refinement, pair-distribution function analysis and lattice-energy minimisations

Monomethyl-quinacridone



Magenta pigment for paints

Pigment Red 192

Hardly soluble in all solvents.
No single crystals

Powder diffraction:
- **STOE STADI-P**
- **Capillary**
- **Transmission geometry**
- **Cu-Kα_1 radiation**

Structure determination from powder data

- Indexing
- Structure solution by real-space methods with DASH
- "Rietveld" refinement with TOPAS
  Restrains on bond lengths, bond angles and planarity

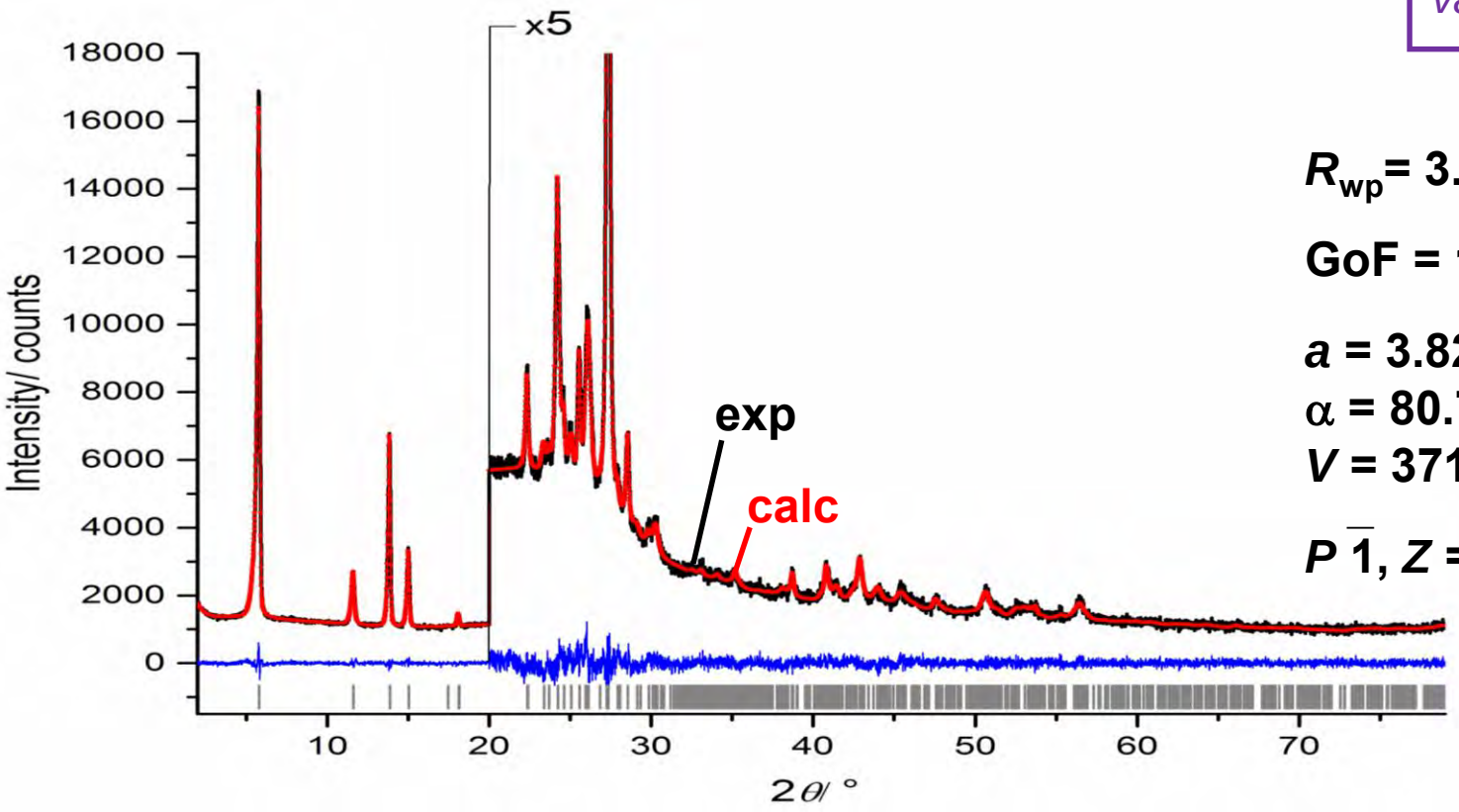
Comment on the name "Rietveld method":

- Idea of Loopstra, 1963

- Programmed by Rietveld, 1966

⇒ Correct name: "Loopstra method"

[Loopstra & Rietveld, Acta Cryst B25, 787 (1969); van Laar & Schenk, Acta Cryst A74, 88 (2018)]



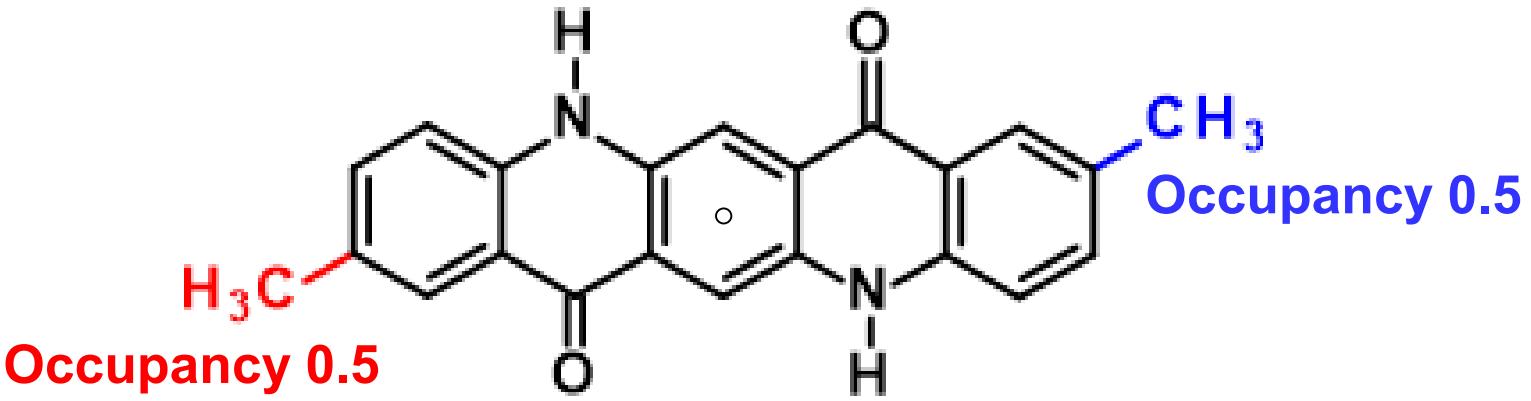
R_{wp}= 3.888

GoF = 1.065

a = 3.82627 (2), *b* = 6.87845 (4), *c* = 16.800 (19) Å,
α = 80.77 (10), β = 64.38 (8), γ = 68.14 (5)°,
V = 371.44 Å^3

P $\bar{1}$, *Z* = 1, *Z* ' = 0.5

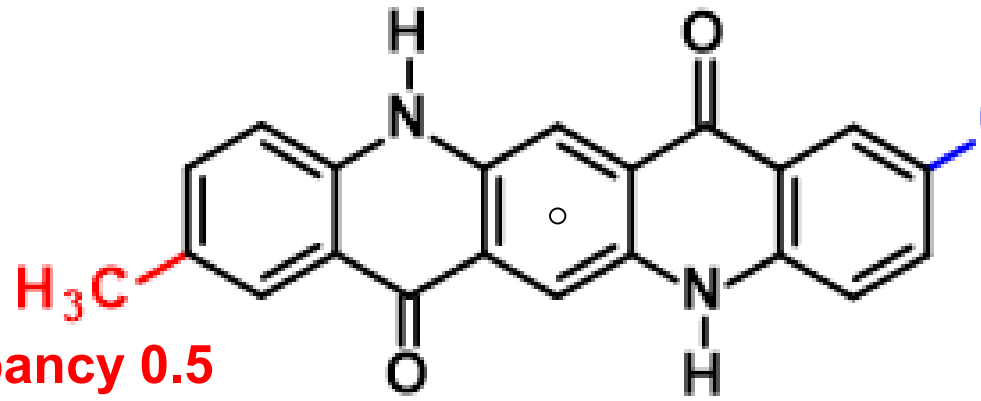
Average structure



P 1, *Z* = $\bar{1}$, *Z*' = 0.5

Molecule on inversion centre

Average structure

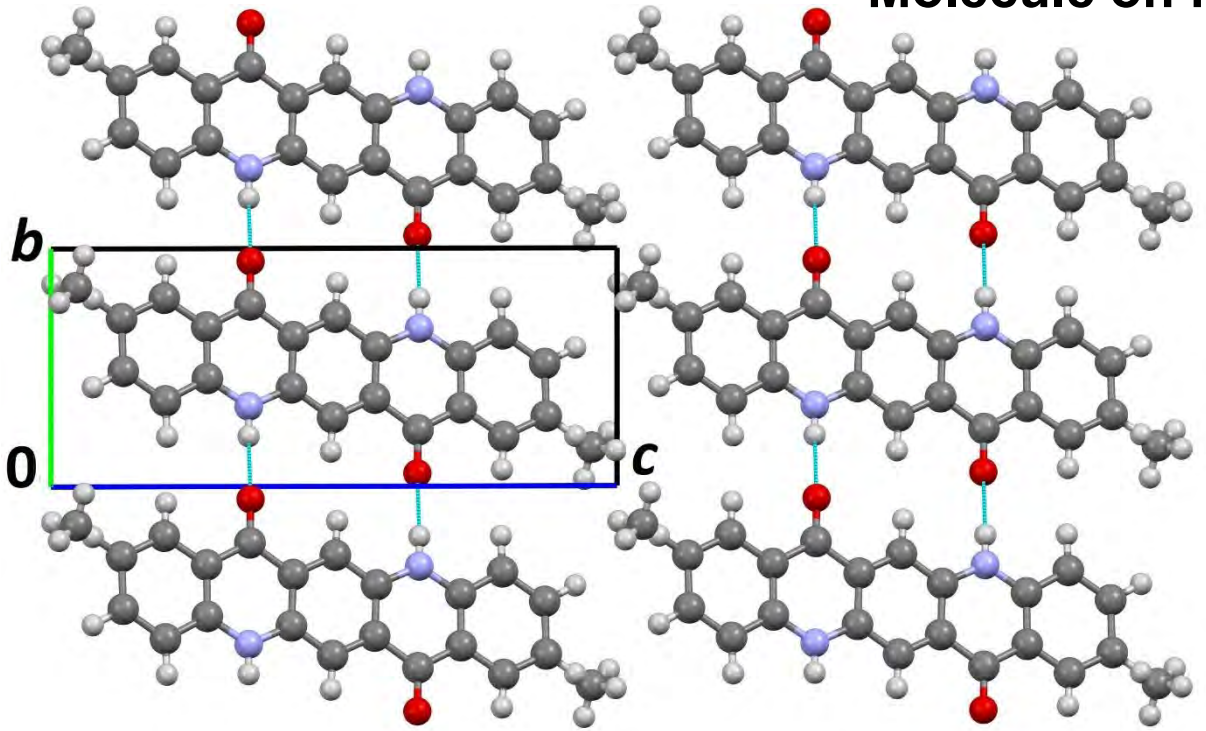


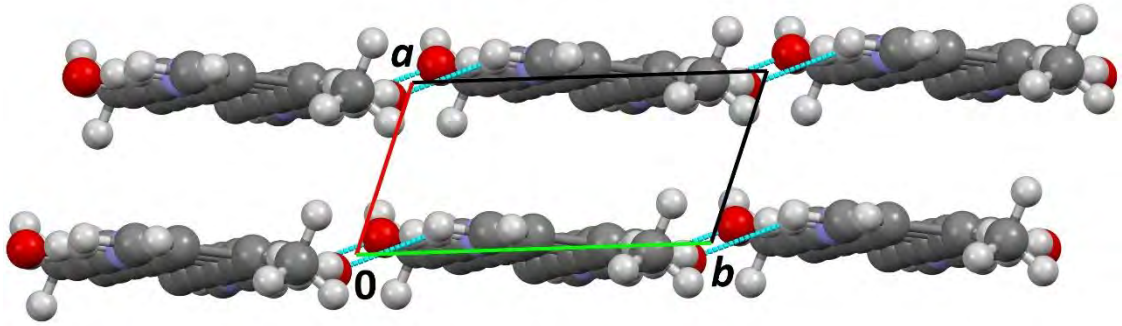
Occupancy 0.5

Occupancy 0.5

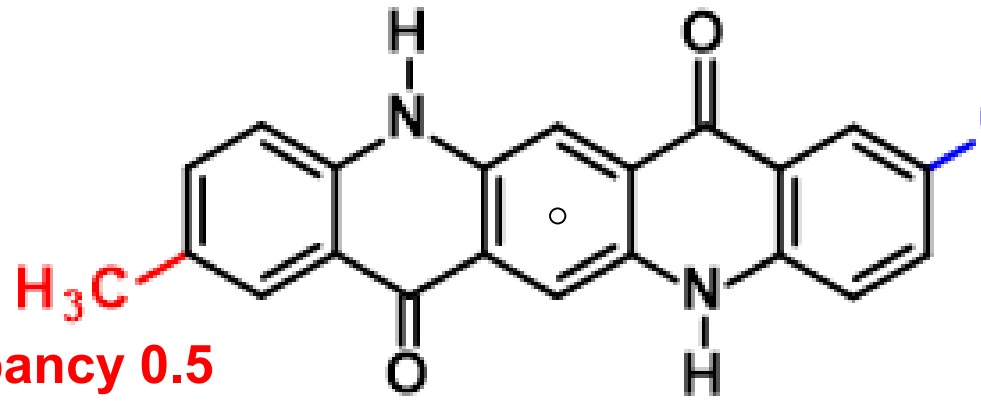
$P\,1, Z = \bar{1}, Z' = 0.5$

Molecule on inversion centre





Average structure

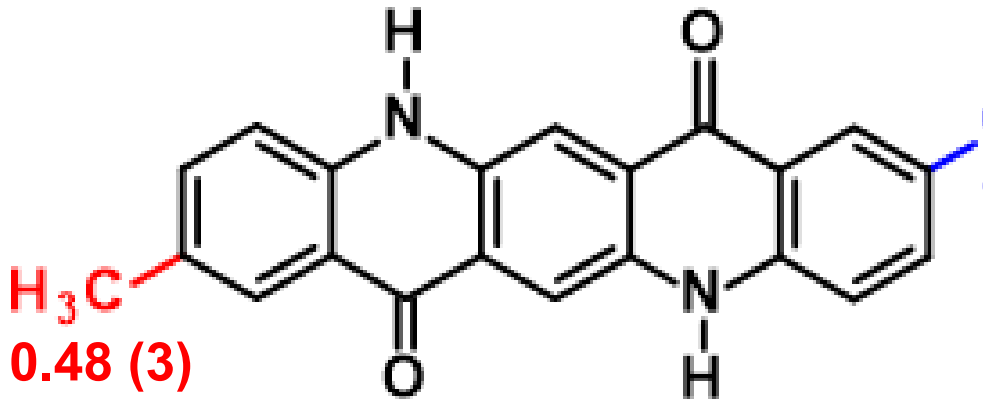


Occupancy 0.5

Occupancy 0.5

$P\bar{1}$, $Z = 1$, $Z' = 0.5$

Molecule on inversion centre

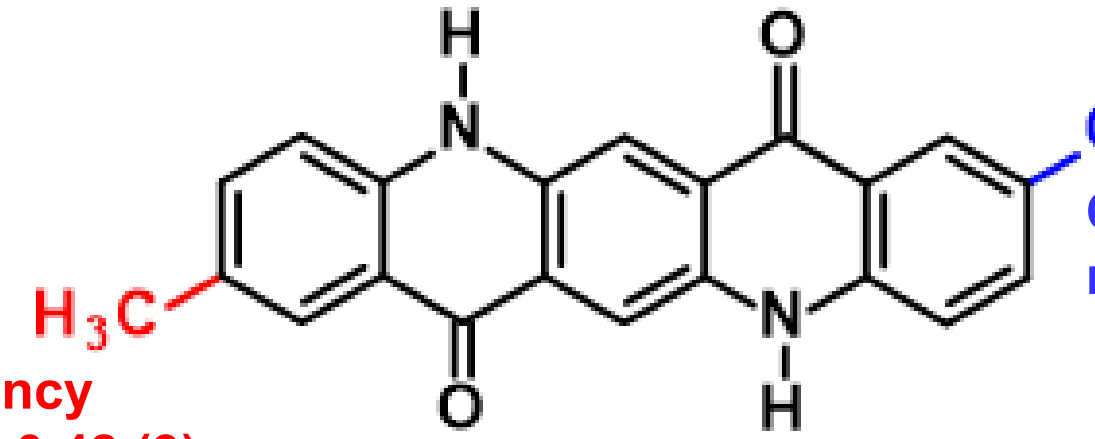


Occupancy refined: 0.48 (3)

Occupancy refined: 0.52 (3)

$P\,1$, $Z = 1$

Refinement of occupancies

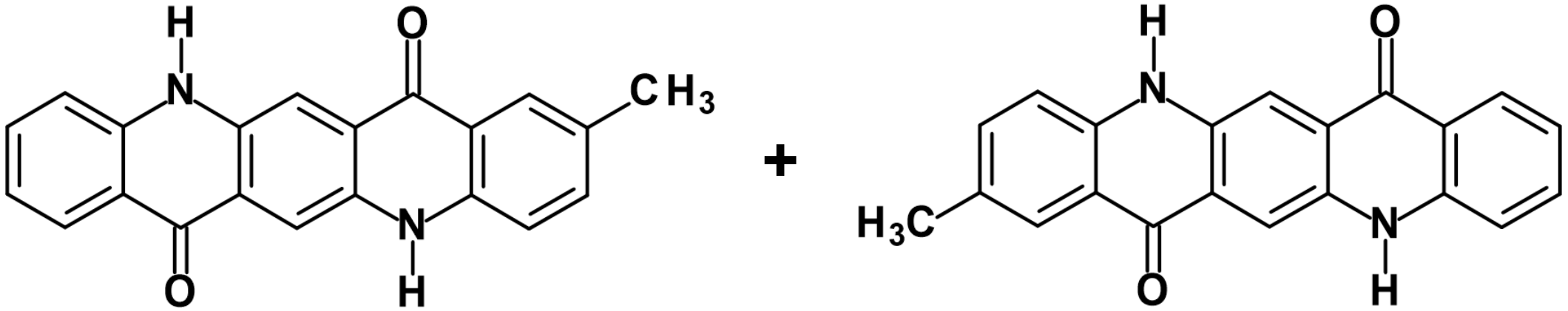


Occupancy refined: 0.52 (3)

Occupancy refined: 0.48 (3)

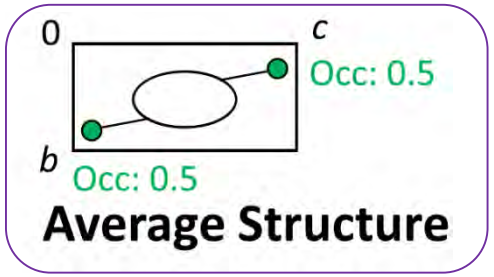
P 1, *Z* = 1

Head-to-tail disorder

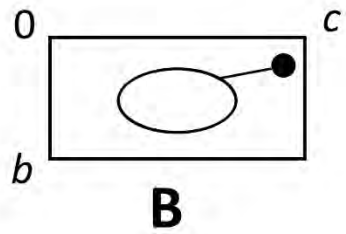


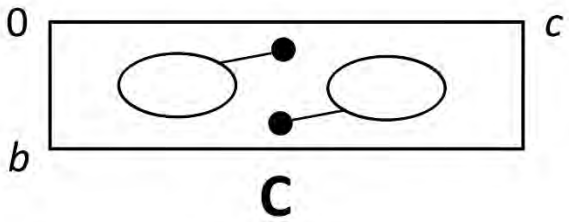
Local ordering?

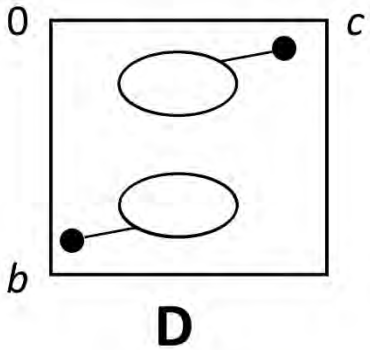
- No superstructure reflections visible
- No diffuse scattering visible (Powder data!)

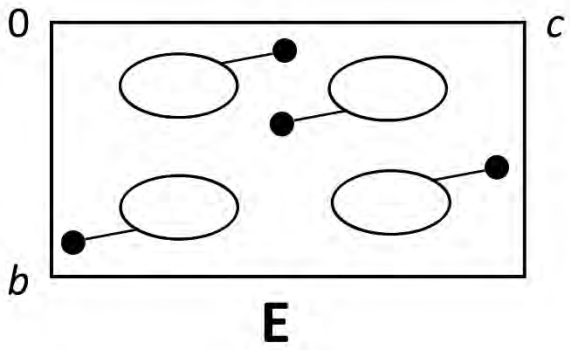


Construction of ordered models

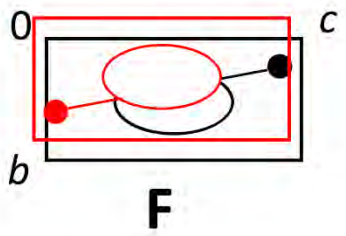


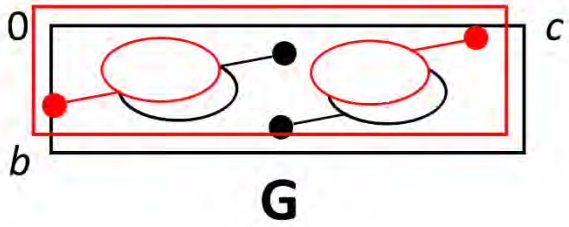


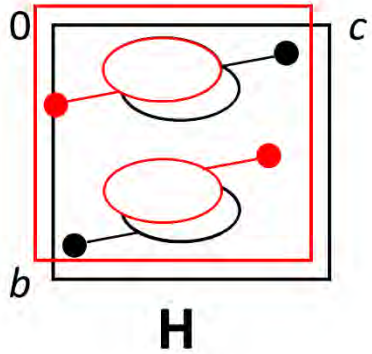


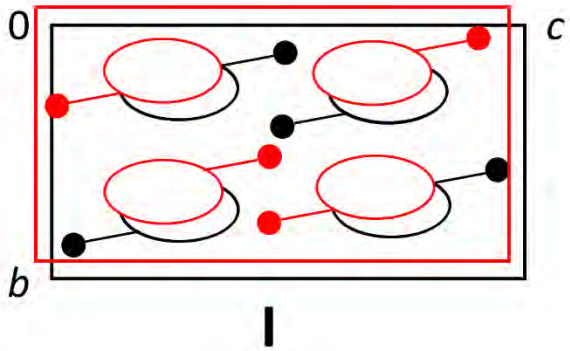


x = 0.5
x = 0



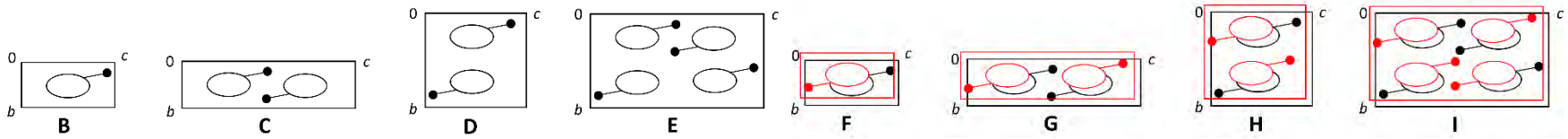




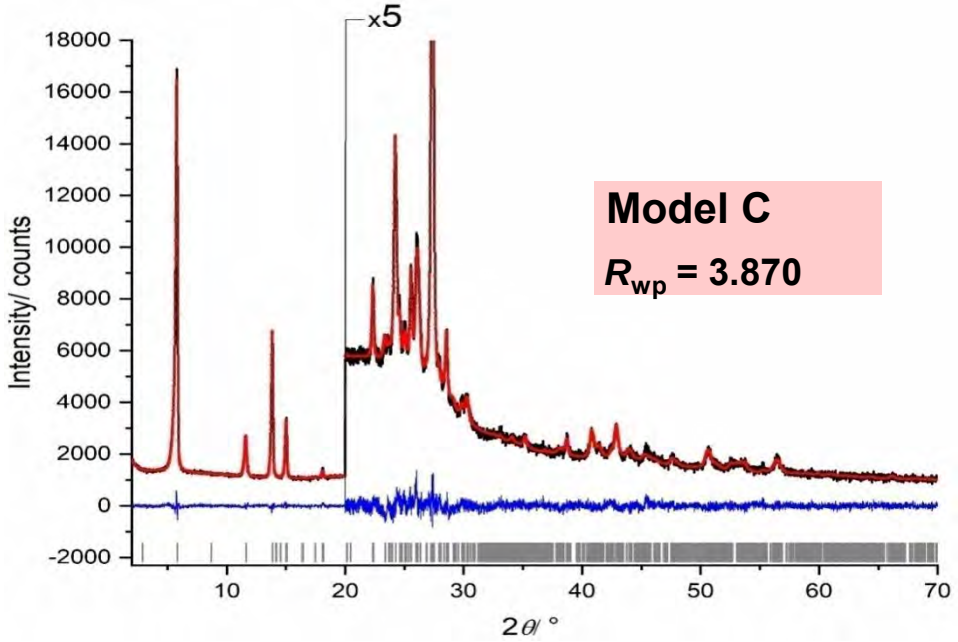


- Rietveld refinements
- Refinement to the Pair-Distribution Function (PDF)
- Lattice-energy minimisations

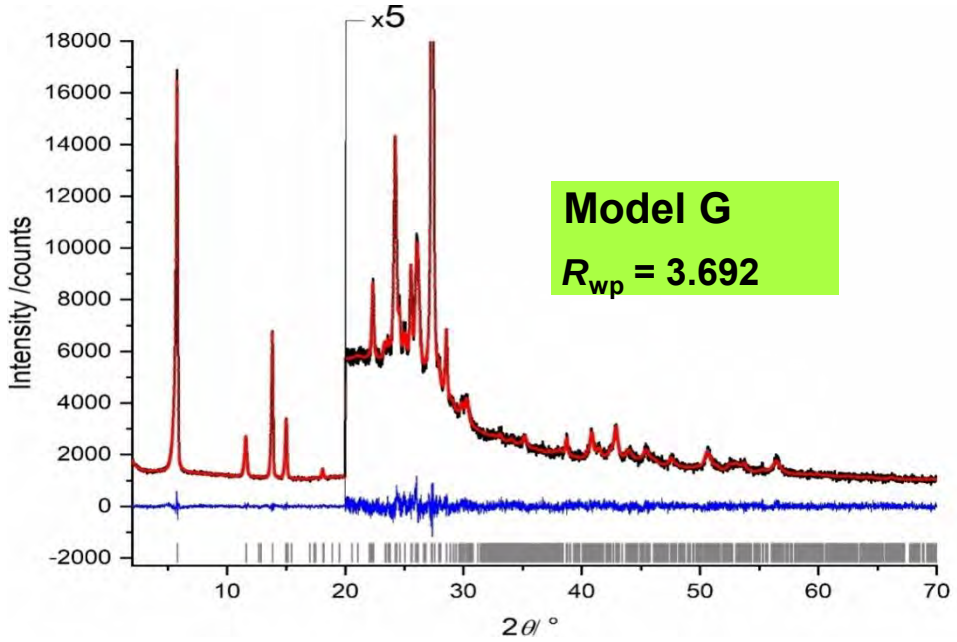
Rietveld refinements



Structural model	Average structure	B	C	D	E	F	G	H	I
Space group	$P\bar{1}$	$P1$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	1	1	2	2	2	2	2	2	2
R_{wp} / %	3.888	3.713	3.870	3.783	3.706	3.799	3.692	3.843	3.757
χ^2	1.065	1.020	1.063	1.039	1.018	1.044	1.014	1.056	1.032



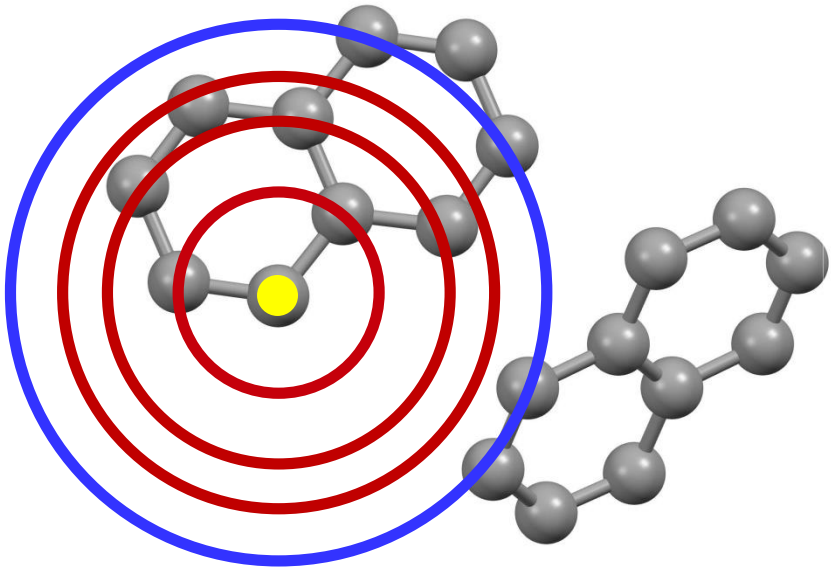
Model C
R_{wp} = 3.870

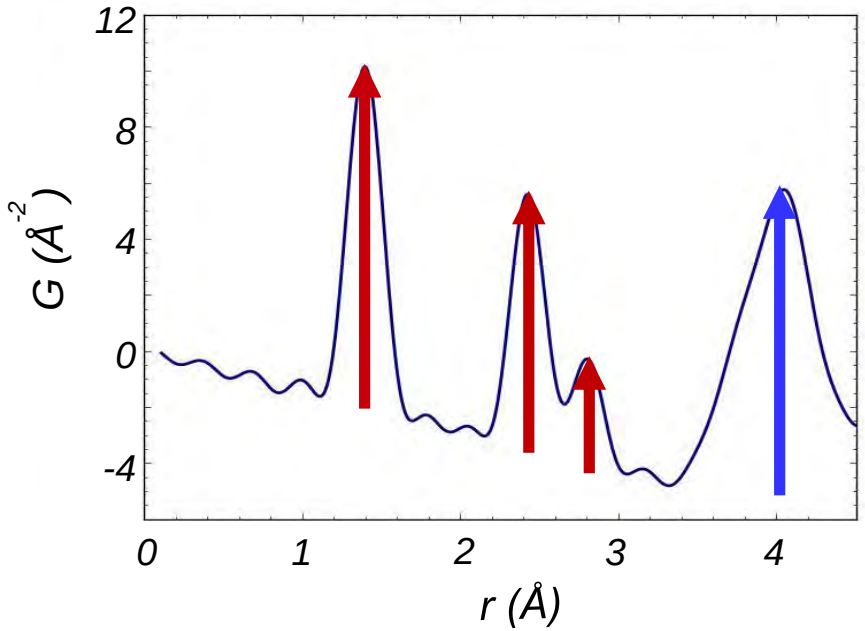


Model G
R_{wp} = 3.692

No unique ordering

The Pair-Distribution Function (PDF)





PDF: Probability to find two atoms separated by a distance *r*

- weighted with the scattering power

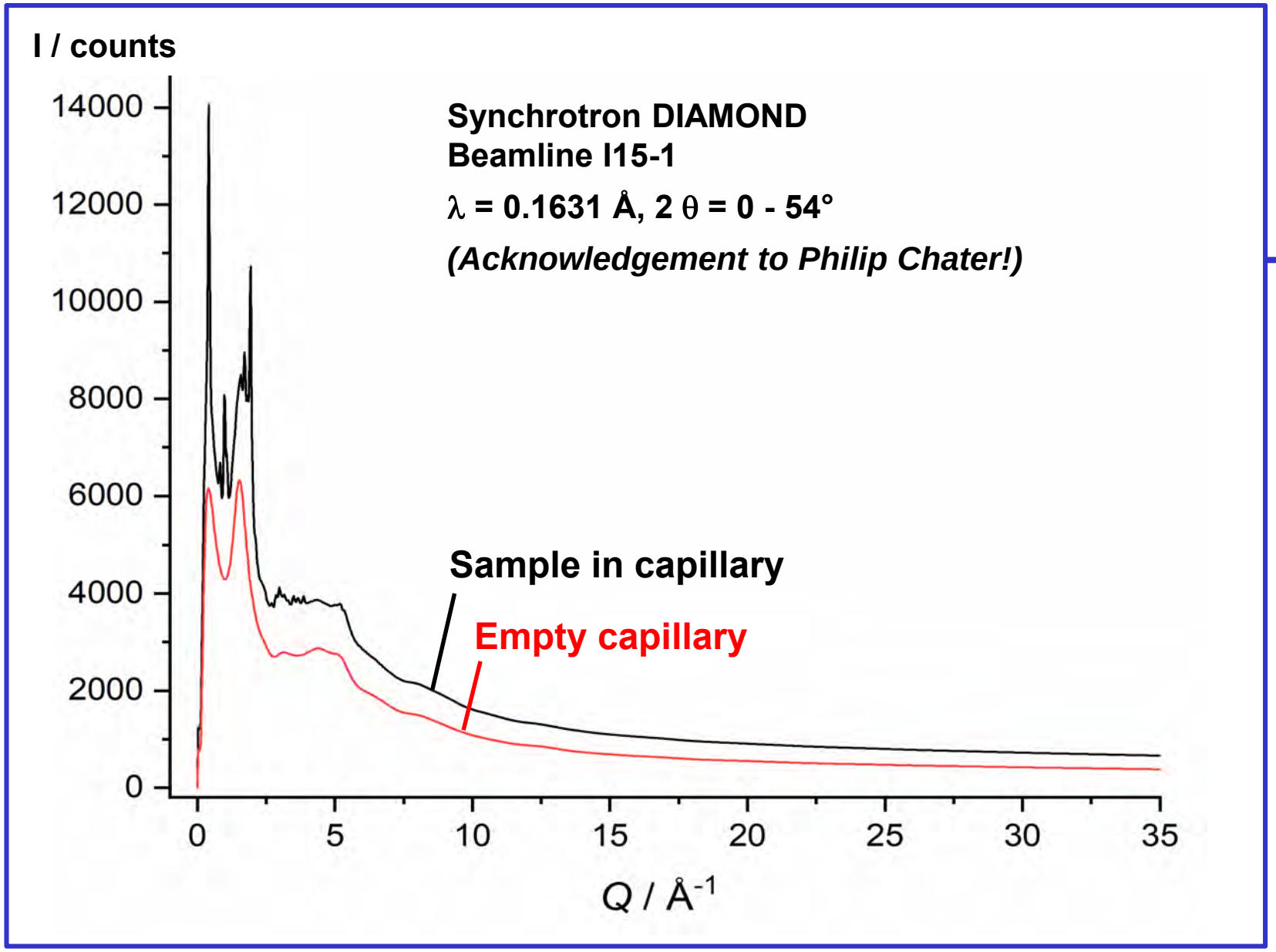
- summed over all atoms

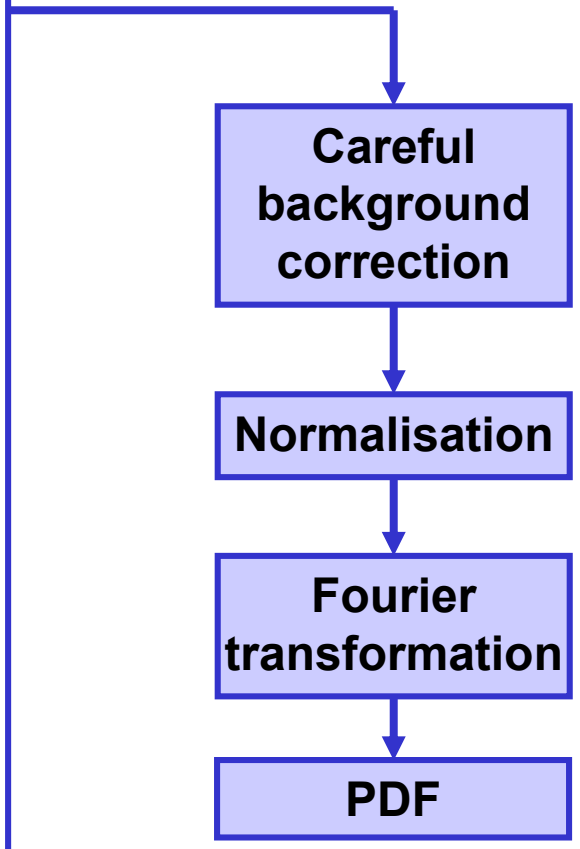
- normalised to a homogeneous atom density

- Fourier transform of the Intensities of a powder pattern (total scattering)

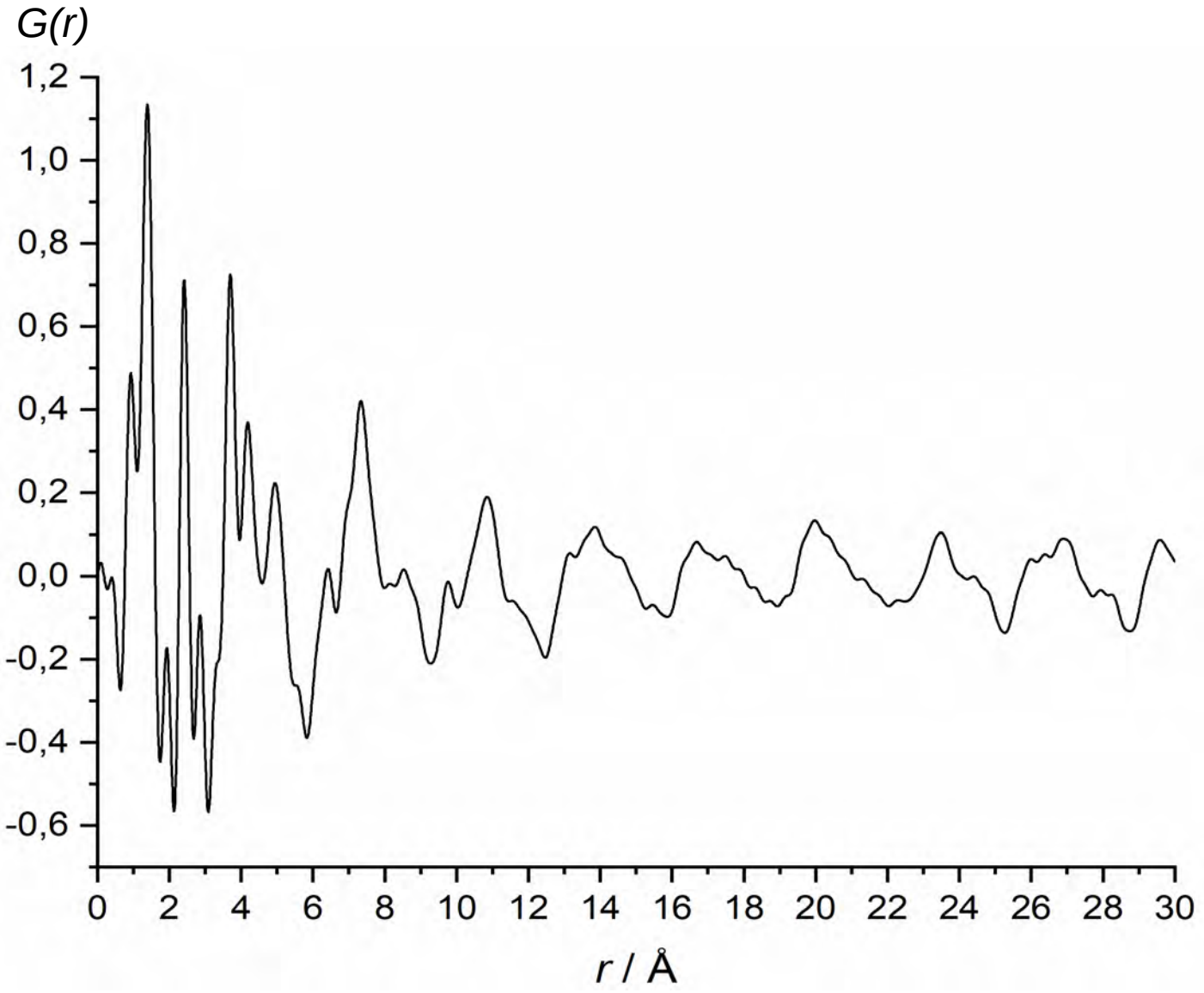
$$G(r) = 4\pi r[\rho(r) - \rho_0] = \frac{2}{\pi}\int_{\min}^{\max} Q[S(Q) - 1]\sin(Qr)\,\mathrm{d}Q$$

The Pair-Distribution Function (PDF)



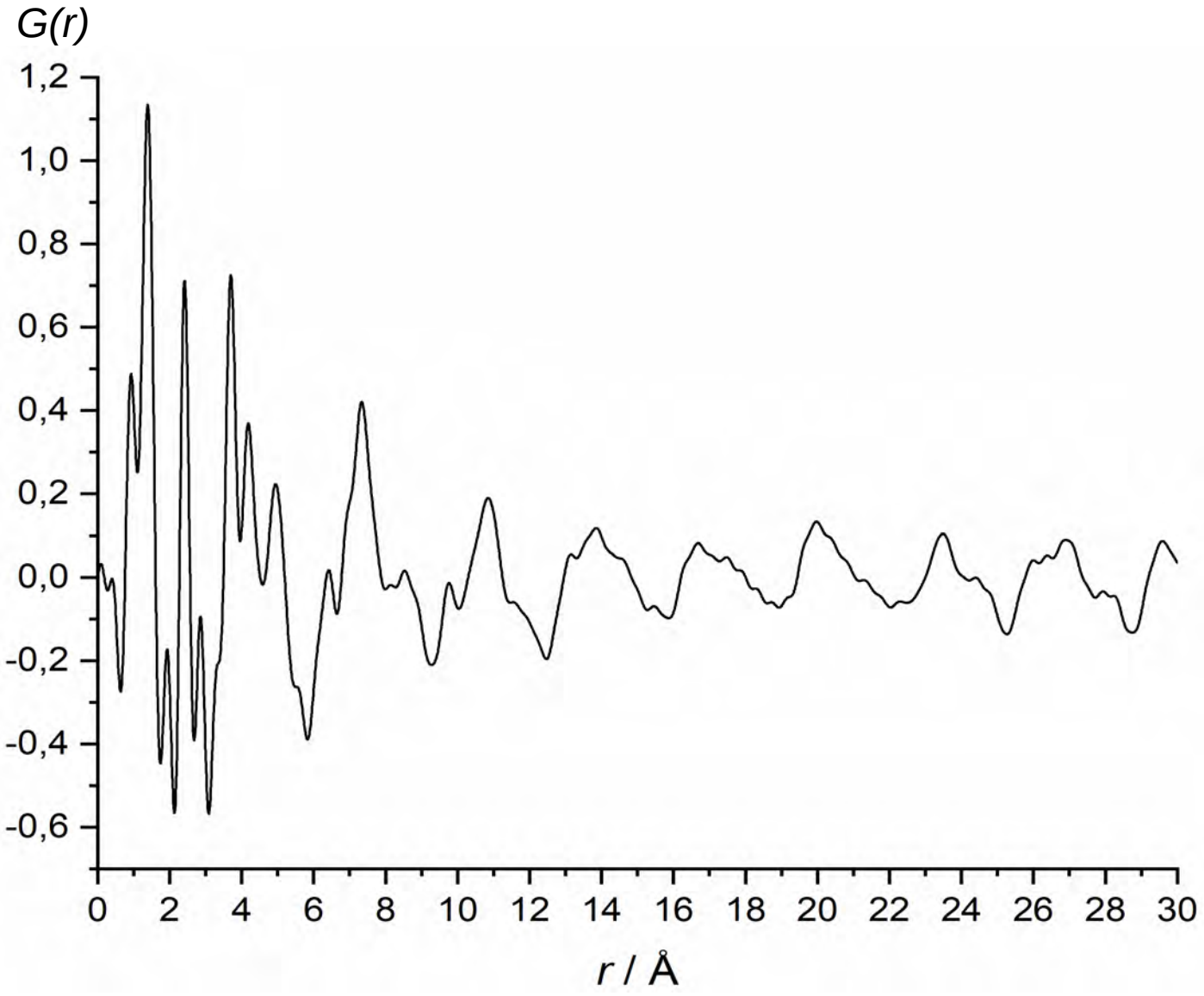


Structure refinement by fit to the PDF



Experimental PDF

Structure refinement by fit to the PDF



Experimental PDF

Input: Structural models B - I

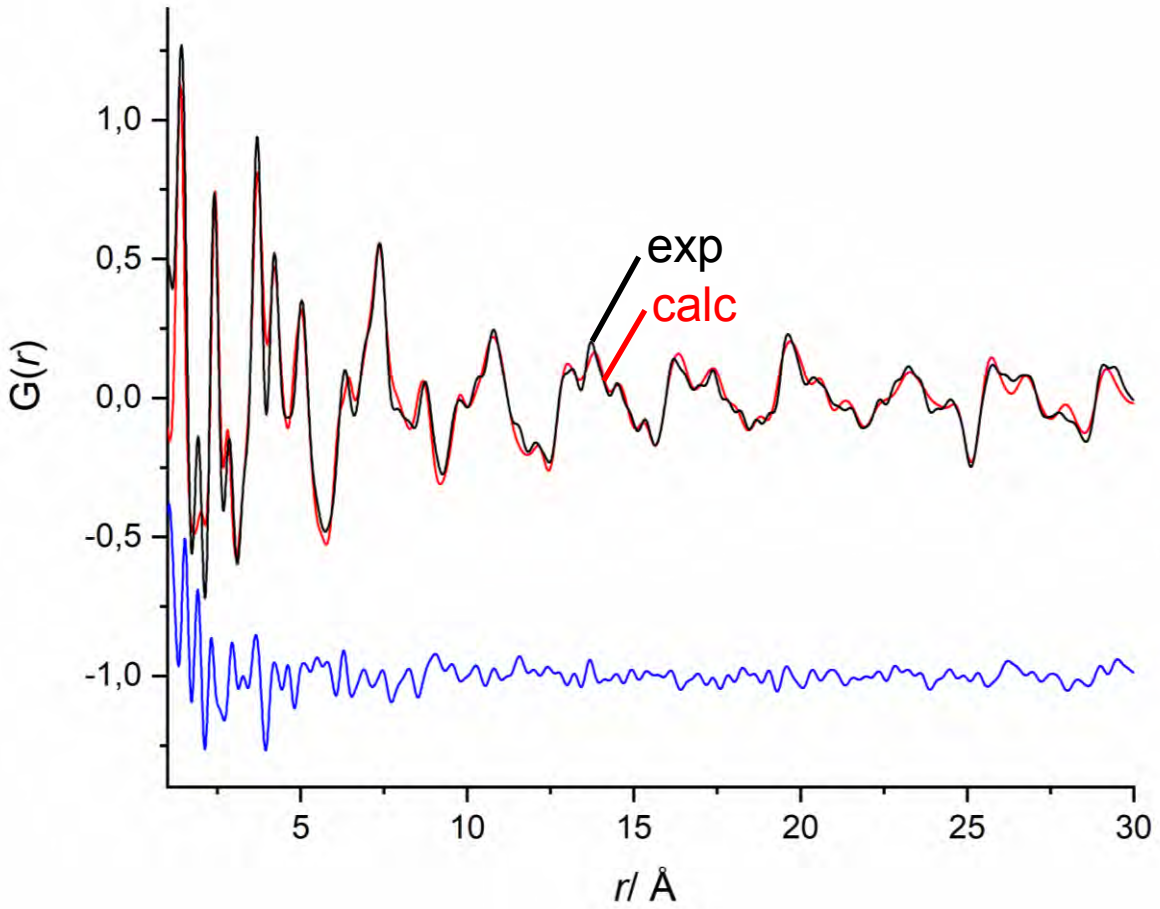
Refinement of:

- **Lattice parameters**
- **Atomic coordinates** (Molecules rigid)
- **Scale factor**
- **Peak widths** (described by B_{intra} and B_{inter})
  [N. Rademacher et al., *J. Appl. Cryst.* 45, 482-488 (2012).
  D. Prill et al., *J. Appl. Cryst.* 48, 171-178 (2015).
  D. Prill et al., *Acta Cryst.* A72, 62-72 (2016).]
- **Dampening of PDF at higher *r***

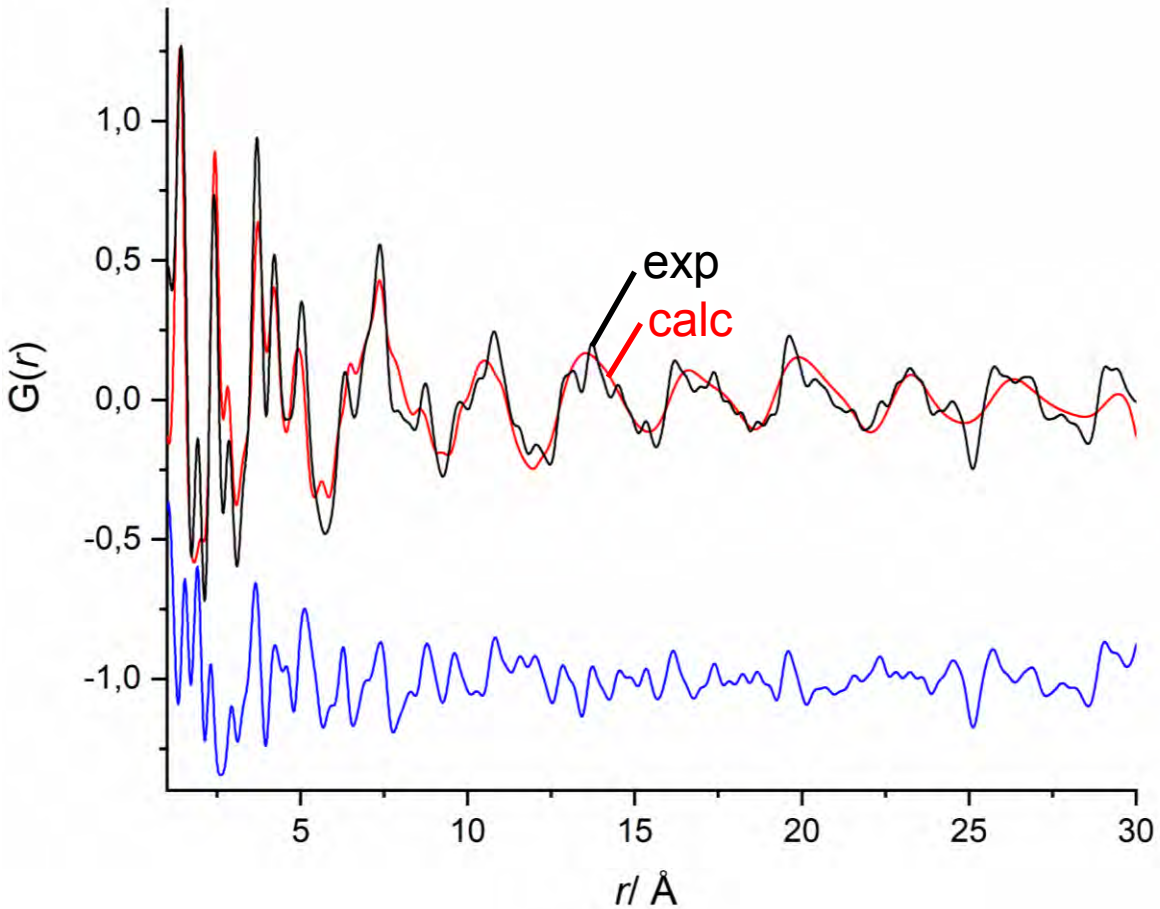
Programs:

- **PDFgetX3** (calculation of the PDF curve)
- **TOPAS-6** (for structure fit to the PDF)
  [Acknowledgement to Alan Coelho!]
  Calculation time: 20-30 min per structure

Structure refinement by fit to the PDF

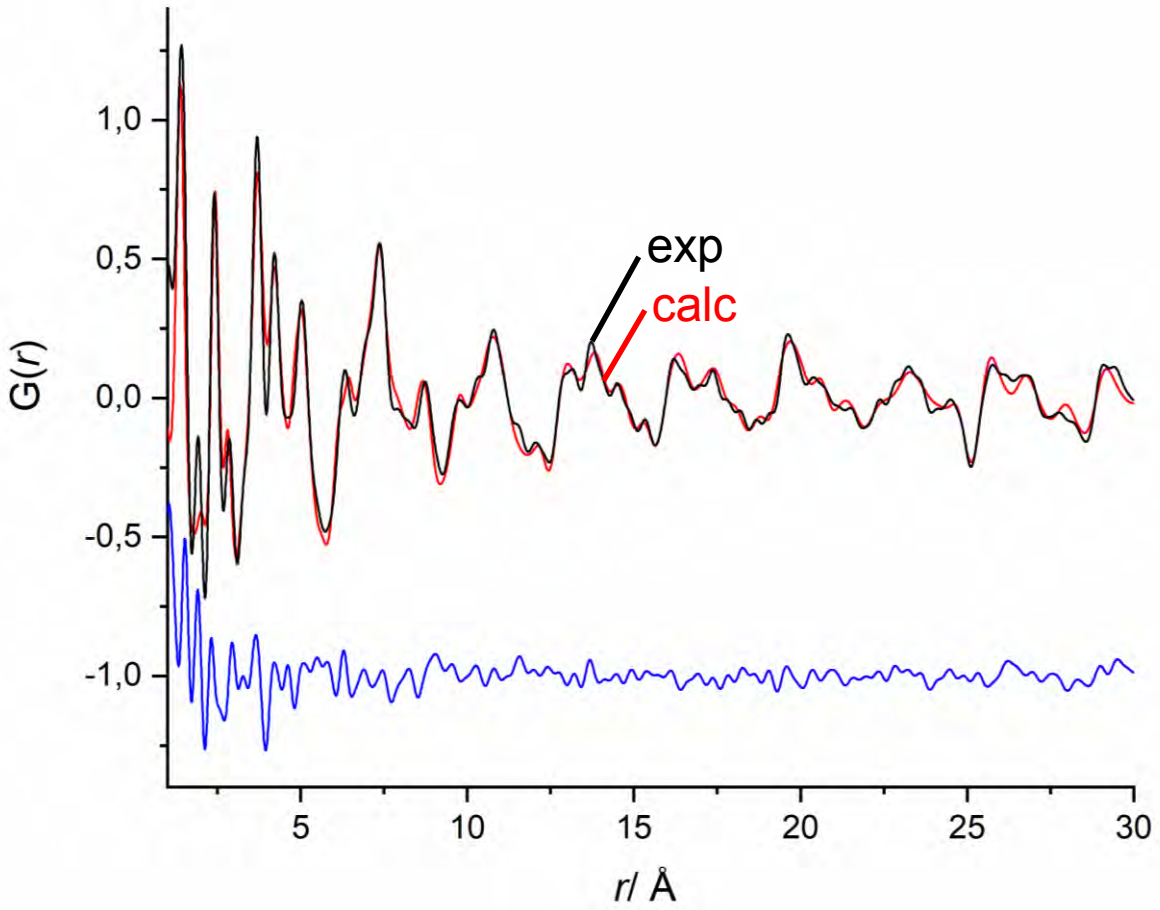


Model E
(best fit to the PDF, R_{wp}^{PDF} = 0.341)

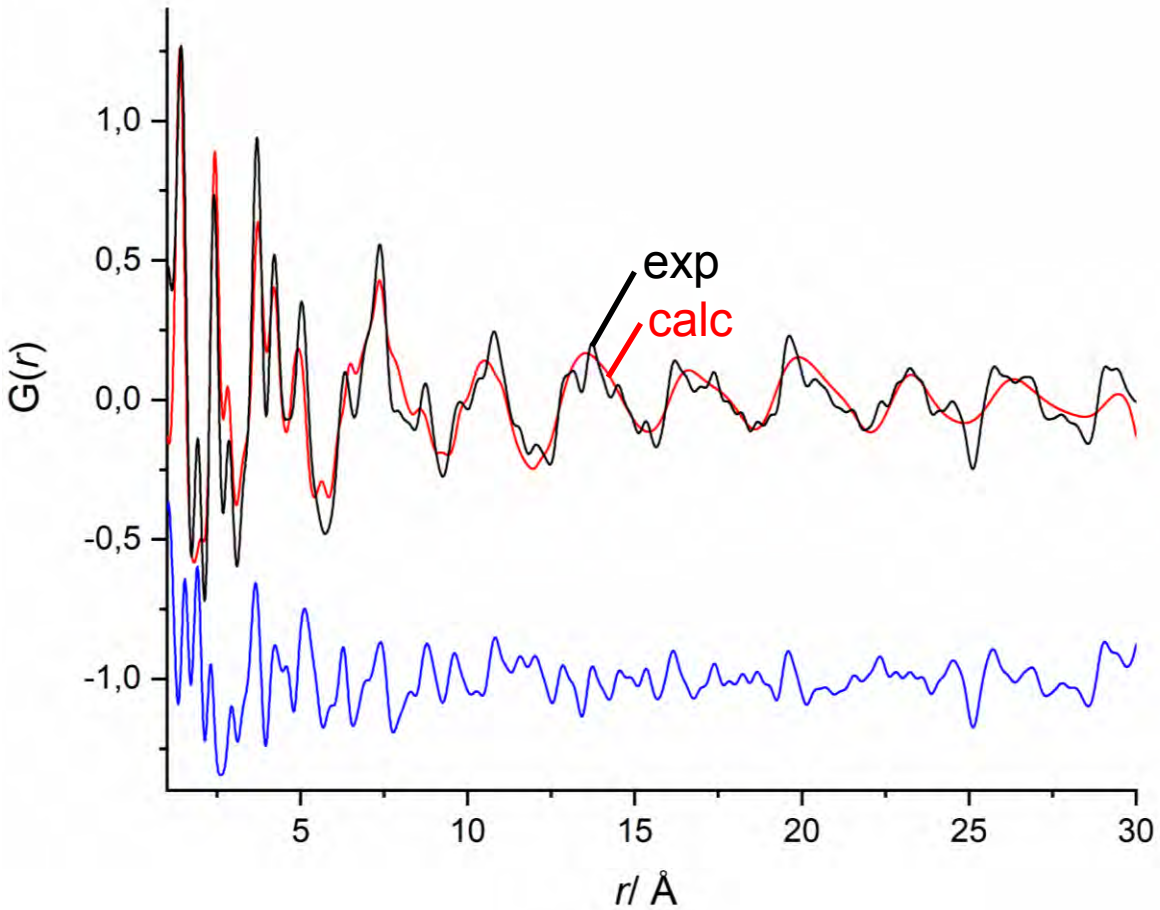


Model I
(worst fit to the PDF, R_{wp}^{PDF} = 0.469)

Structure refinement by fit to the PDF



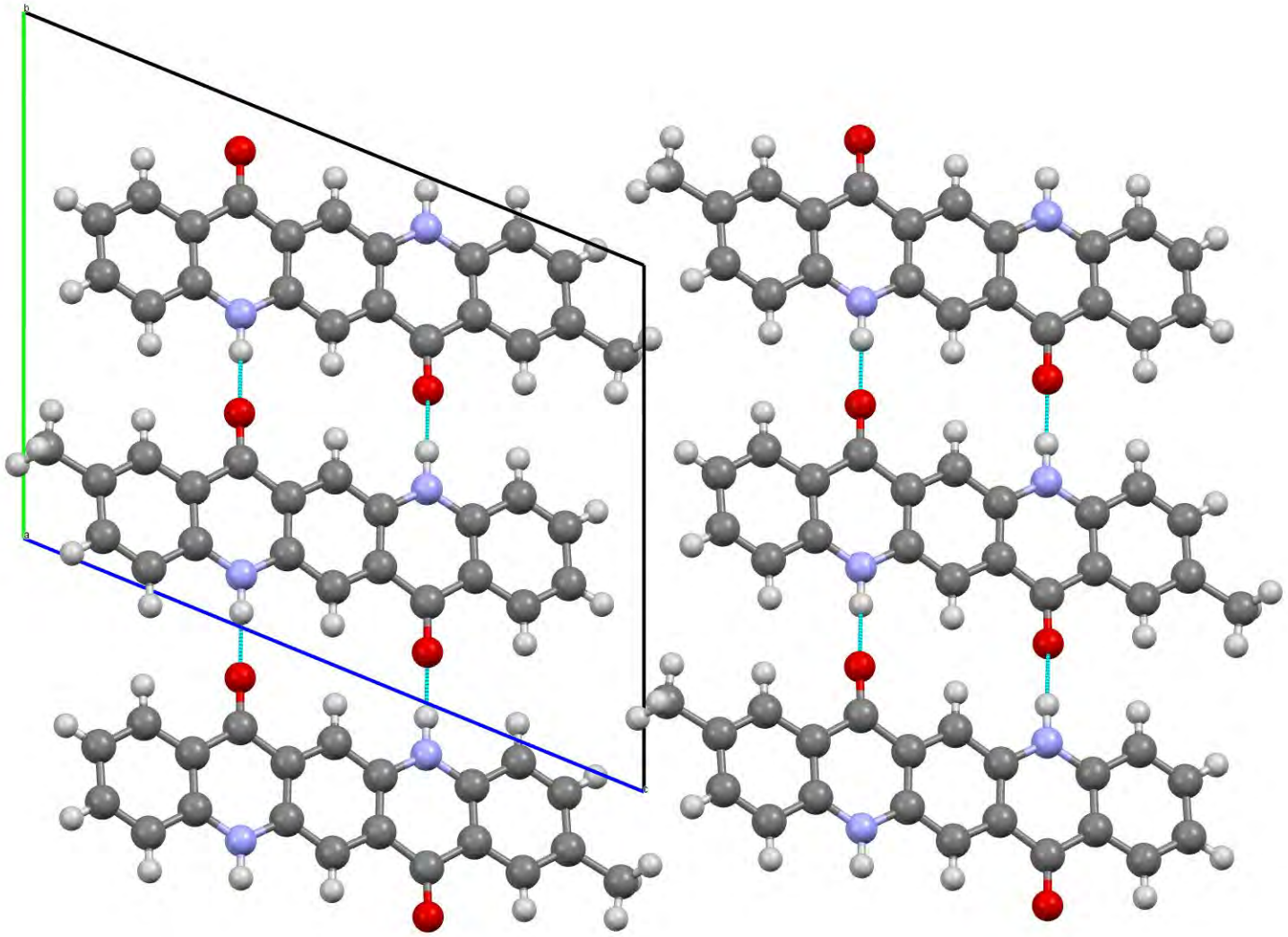
Model E
(best fit to the PDF, R_{wp}^{PDF} = 0.341)



Model I
(worst fit to the PDF, R_{wp}^{PDF} = 0.469)

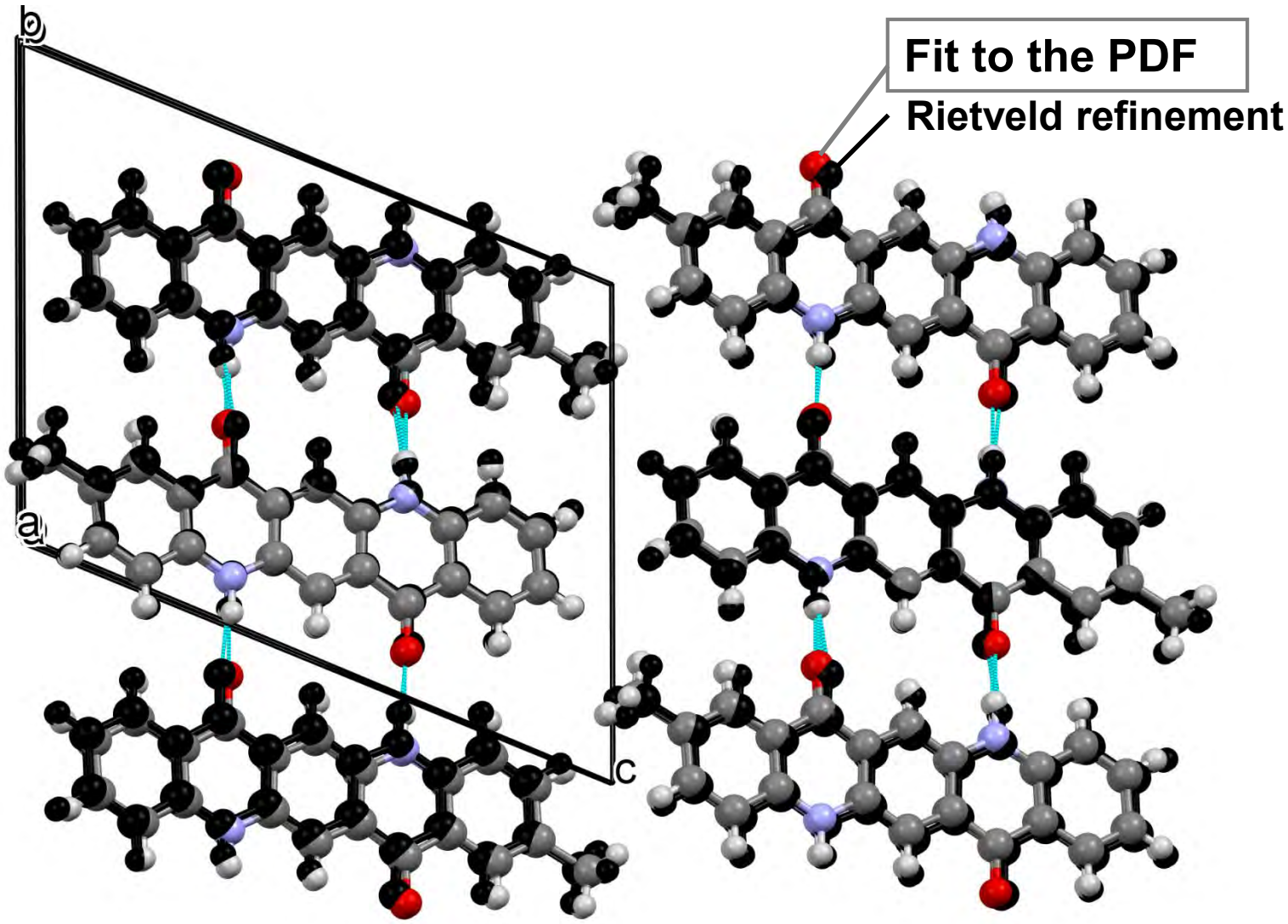
Refinement of organic structures to PDF data:
- sensitive to small structural deviations

Structure refinement by fit to the PDF



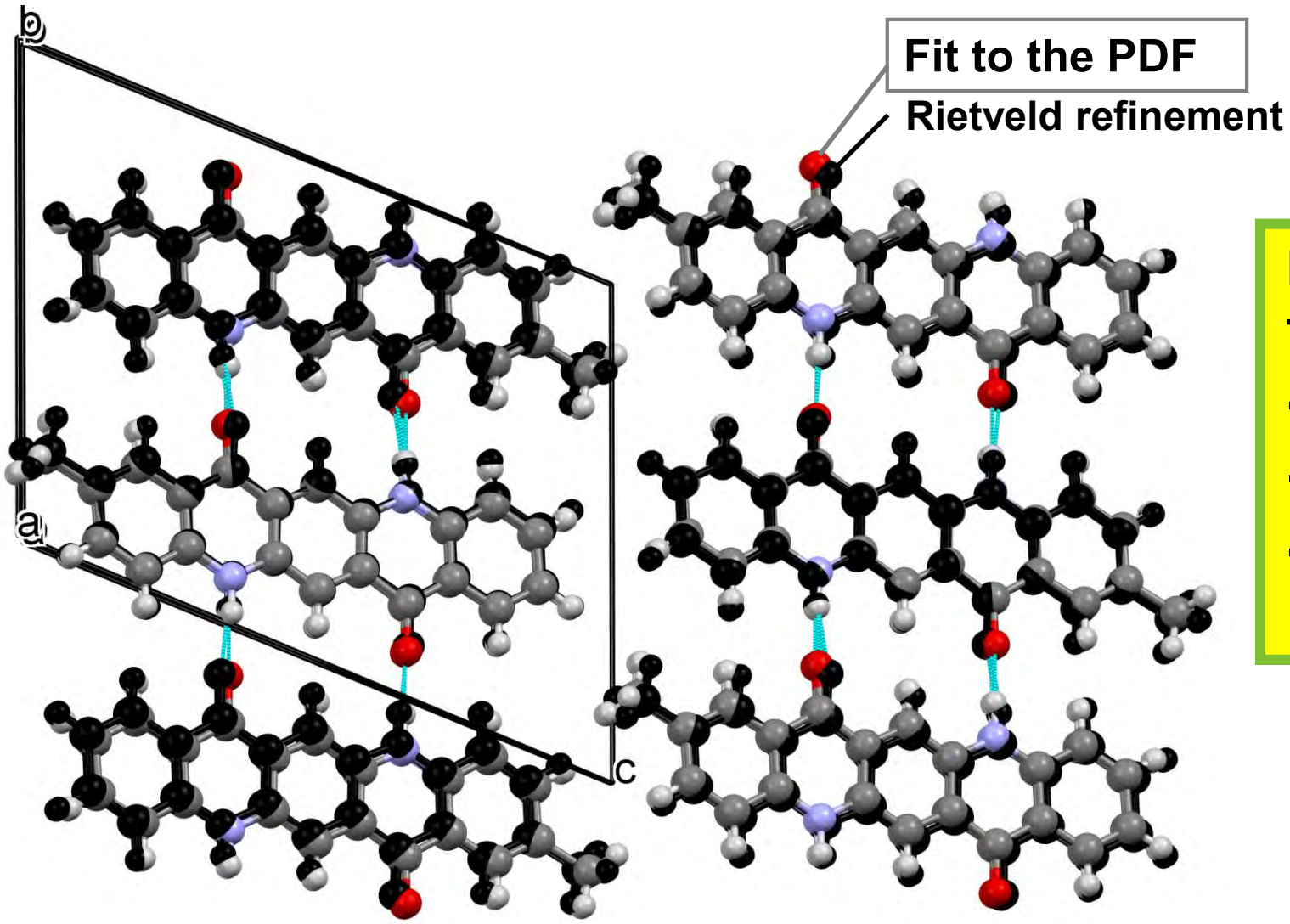
Model E (best fit to the PDF)

Structure refinement by fit to the PDF



Model E (best fit to the PDF)

Structure refinement by fit to the PDF

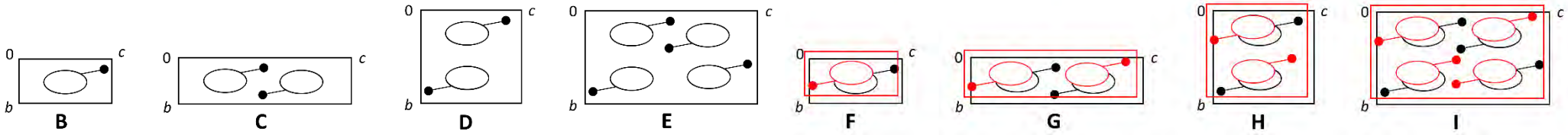


Model E (best fit to the PDF)

Refinement of organic structures to PDF data:

- feasible
- reliable
- sensitive to small structural deviations

Structure refinement by fit to the PDF



Structural model	B	C	D	E	F	G	H	I
R_{wp}^{PDF}	0.364	0.345	0.377	0.341	0.450	0.450	0.354	0.469

Different local structures possible

Lattice energy minimisations

Input:

- Models B - I

Method:

- Dreiding force field

- Charges: HF/6-31G + ESP**

Refinement of:

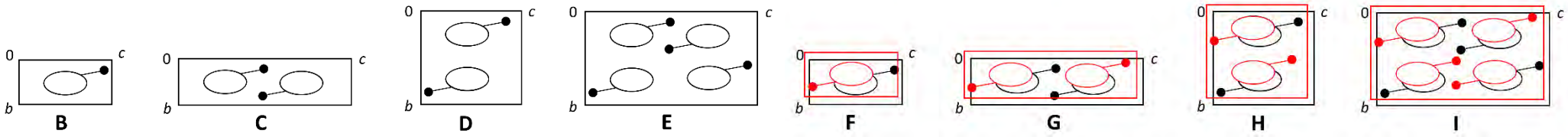
- Lattice parameters

- All atomic coordinates (flexible molecules)

Program for lattice-energy minimisations:

- Materials Studio

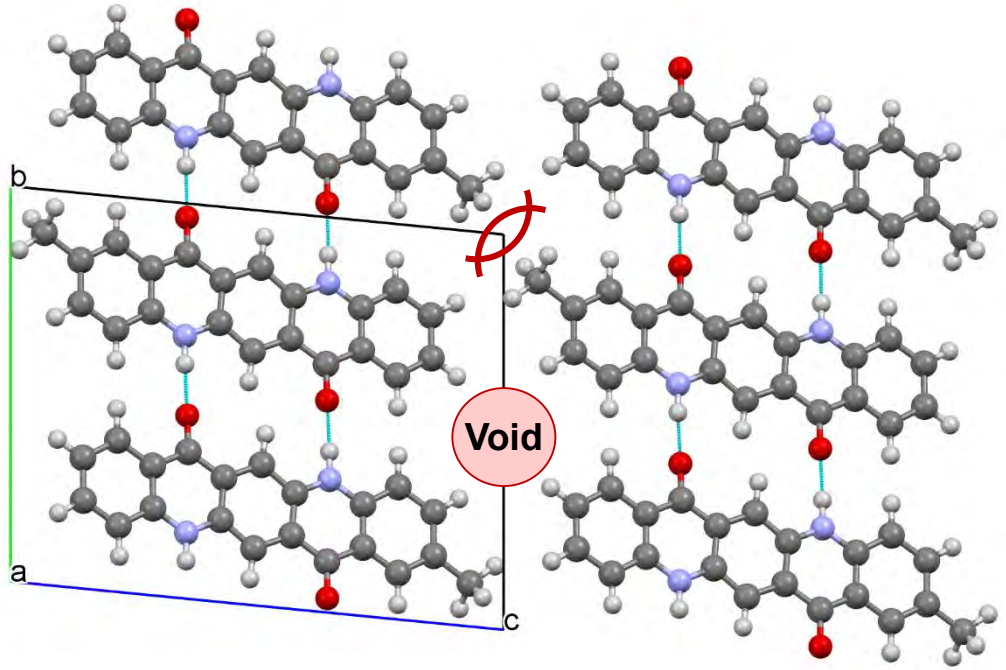
Lattice energy minimisations



Structural model	B	C	D	E	F	G	H	I
E_{rel} / *kJ/mol*	1.84	0.5	6.48	0.63	0.04	1.76	4.89	0
V_{mol}	369.2	369.7	384.1	369.1	366.7	370.7	377.2	366.4

Different local structures possible

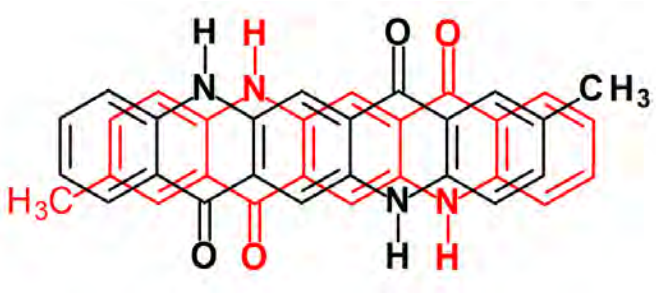
Unfavorable local structure (Models D + H):



Local structure

Superposition of molecules:

or

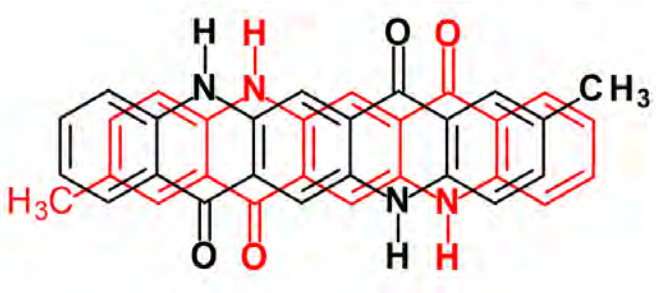


?

Local structure

Superposition of molecules:

or



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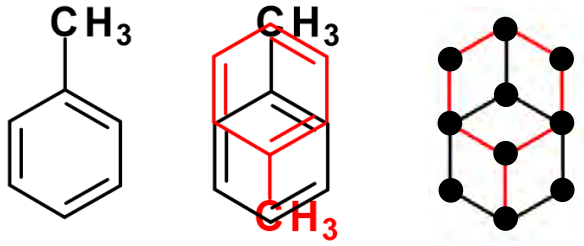
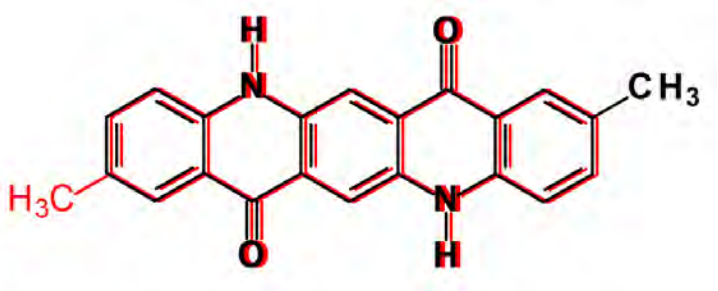
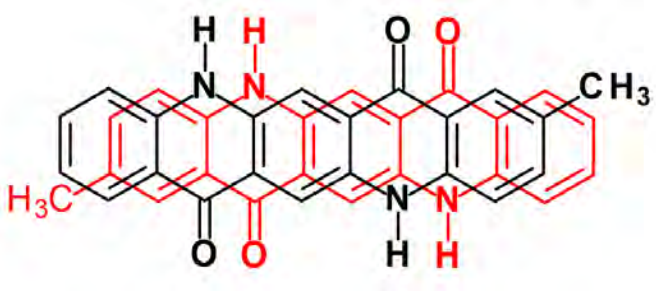


Local structure

Superposition of molecules:



or



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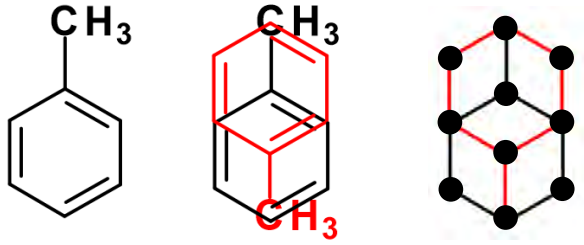
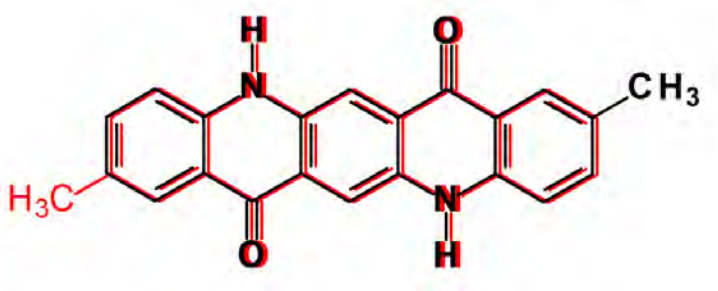


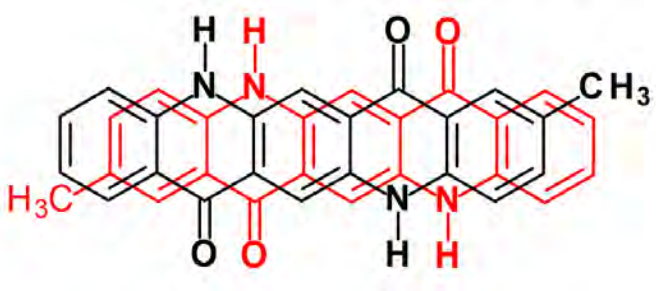
(Idea + Photo:
Peter Müller)

Local structure

Superposition of molecules:



or



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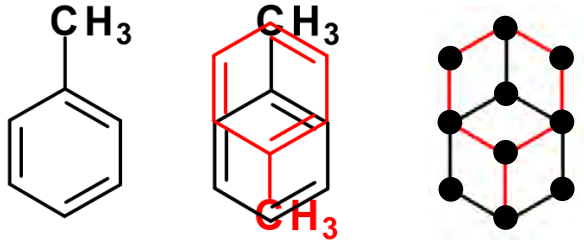


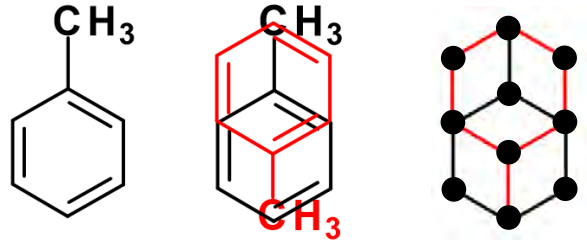
(Idea + Photo:
Peter Müller)

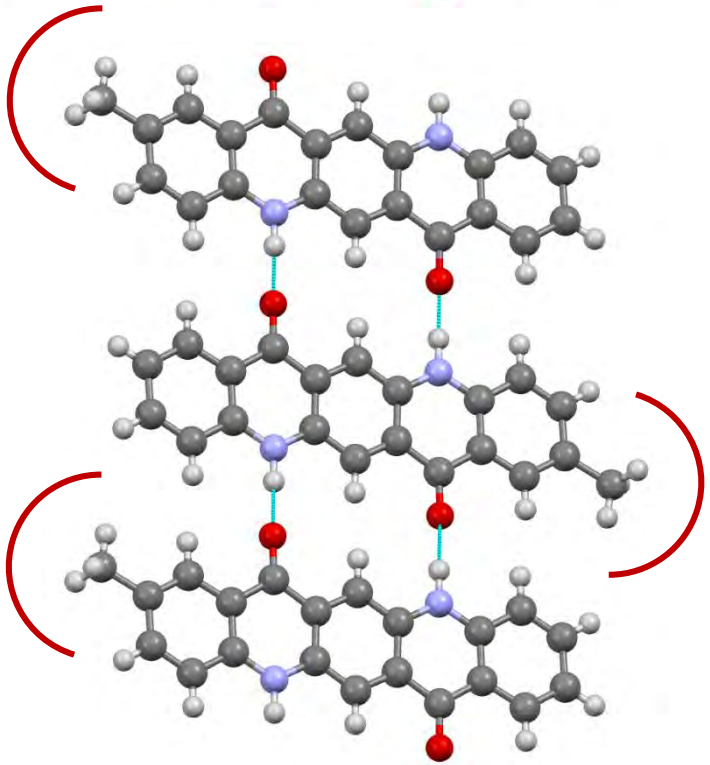
Local structure

Superposition of molecules:

or

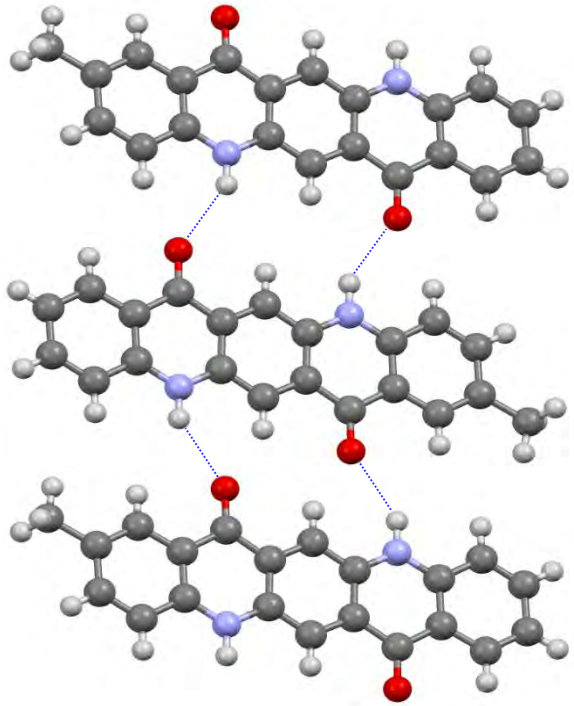
?





Good H-bonds

Sterically demanding



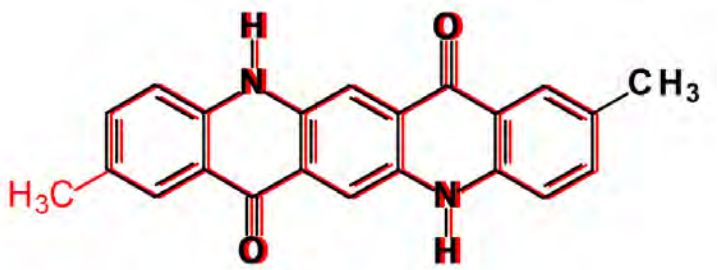
Worse H-bonds

Better space filling

(Idea + Photo:
Peter Müller)

Local structure

Superposition of molecules:



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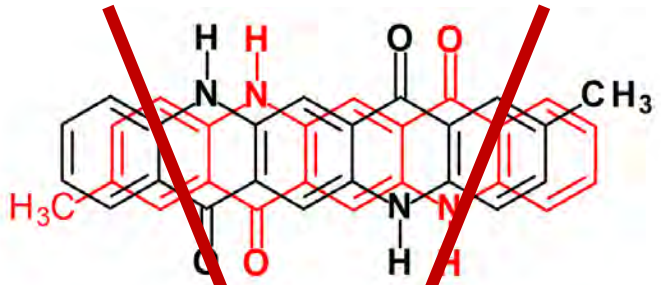

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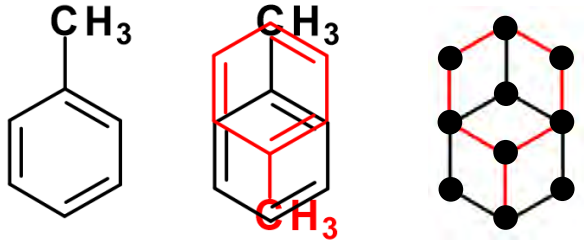
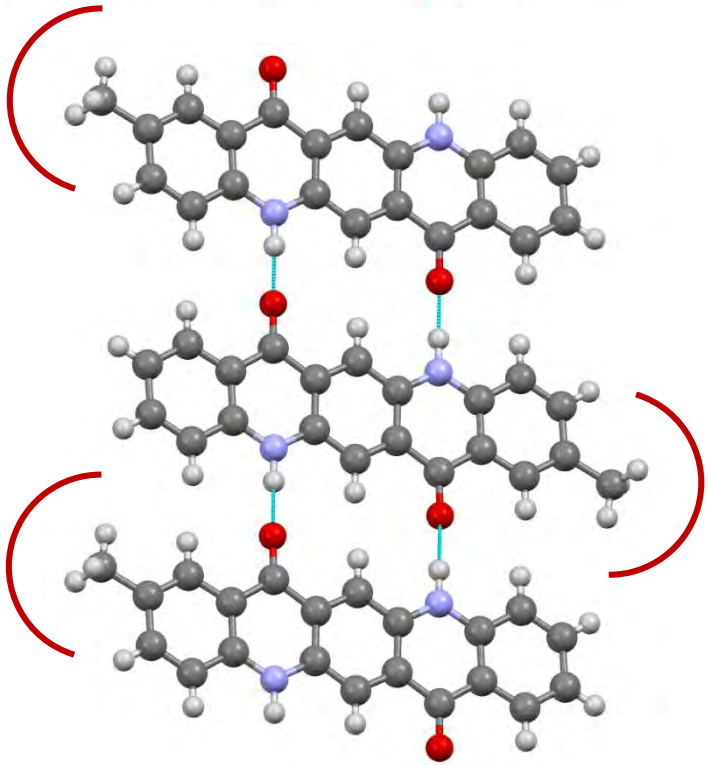
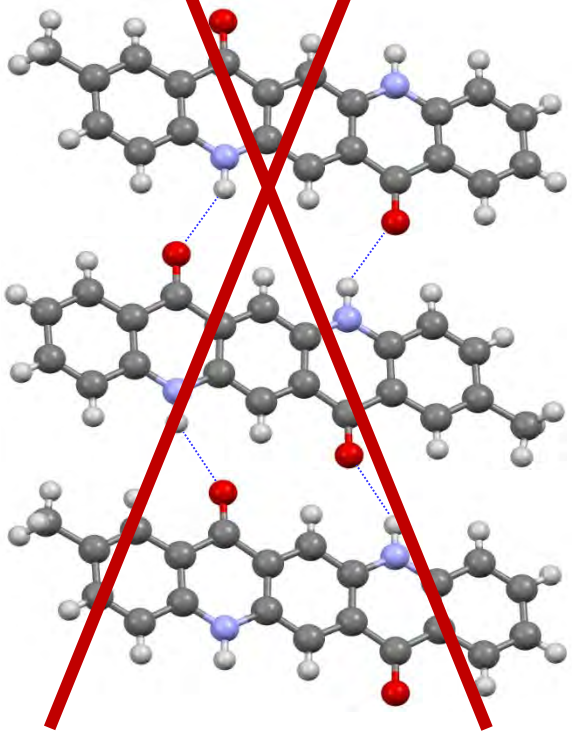




Good H-bonds

Sterically demanding



Worse H-bonds

Better space filling

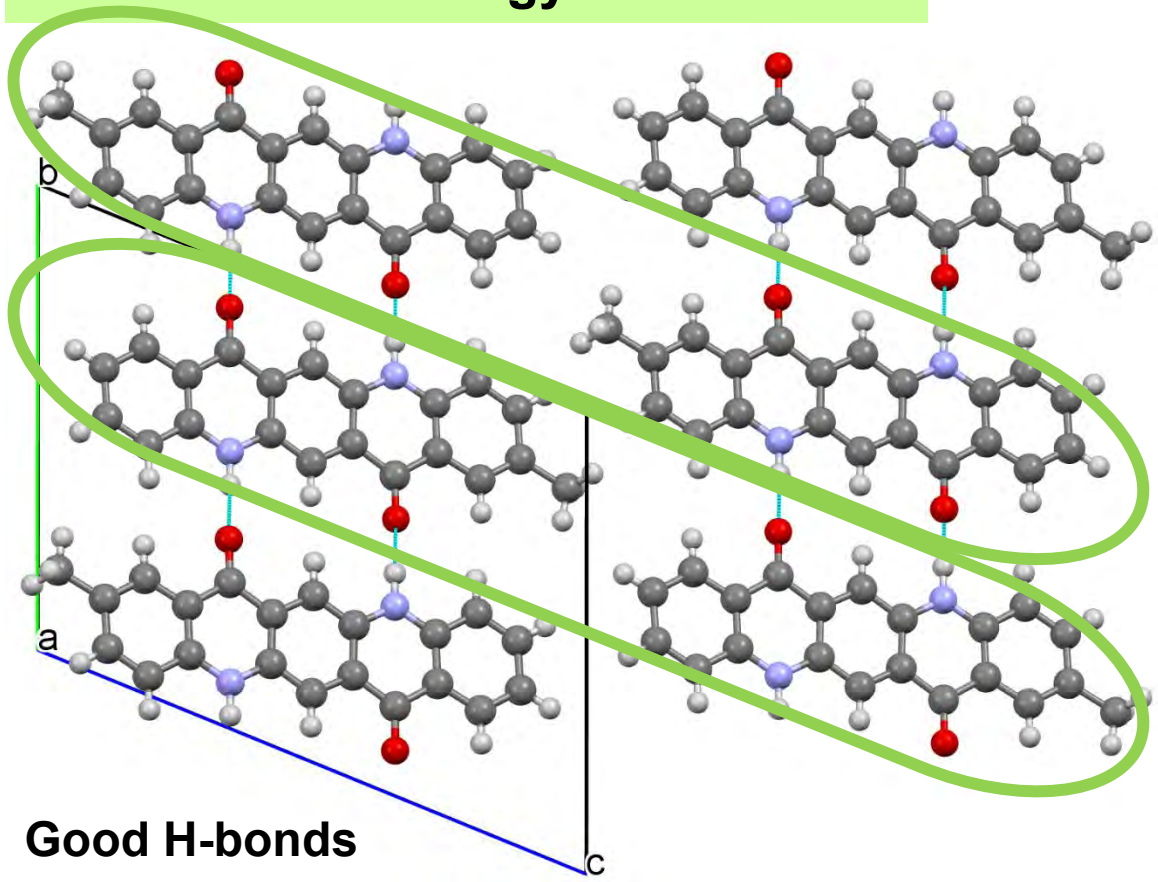
(Idea + Photo:
Peter Müller)

Never observed

Local structure

Typical local structure: Model E

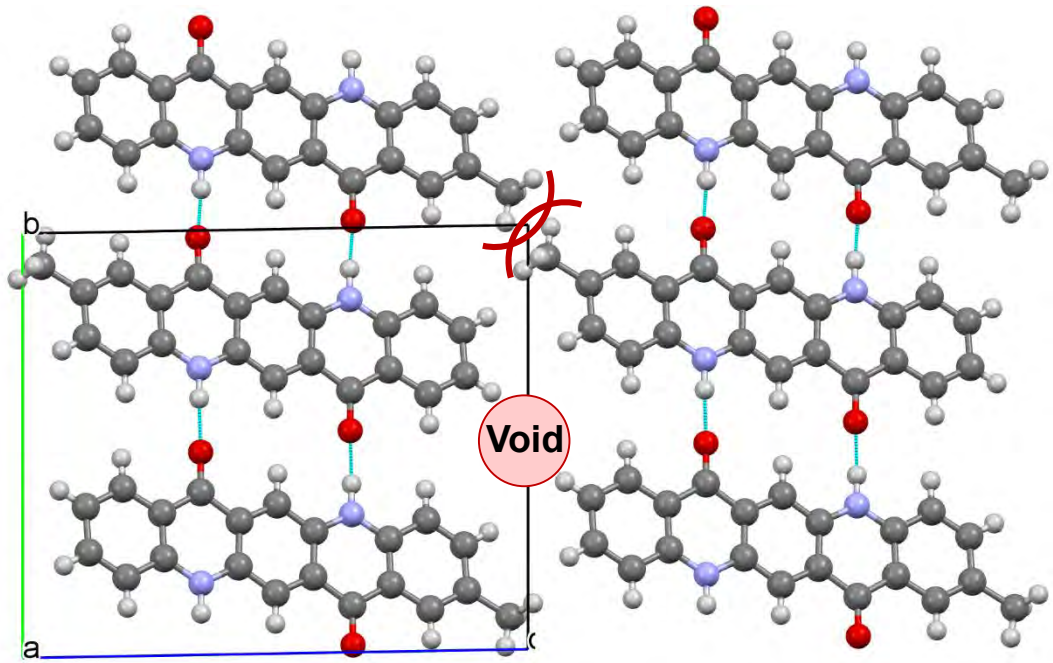
- **Good Rietveld fit**
- **Best PDF fit**
- **Good lattice energy**



Good H-bonds

Good space filling due to local ordering

Unfavorable local structure:



Local ordering

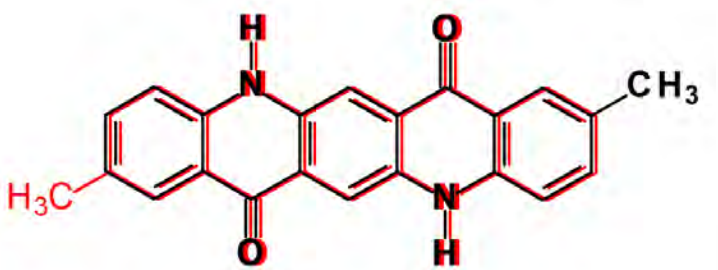
of neighbouring molecules

in this direction

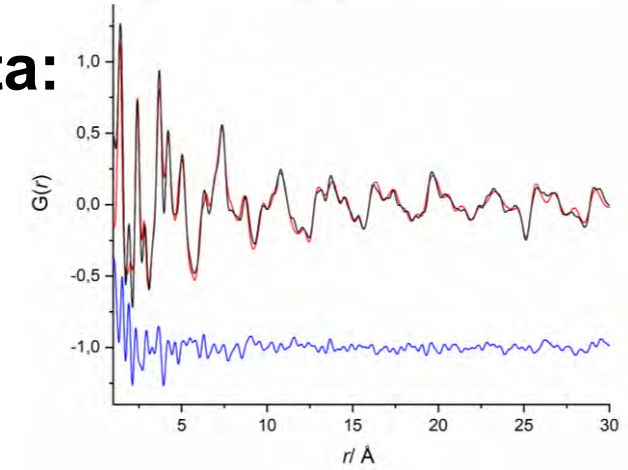
No superstructure reflections

Conclusion

1. **Statistical head-to-tail disorder with local ordering of molecules in 1 direction**



2. **Refinement of organic crystal structures to PDF data:**
   - **feasible**
   - **reliable**
   - **sensitive to small structural deviations**



Acknowledgements:

- Carina Schlesinger
- Dragica Prill