



Fundamental Study of a Strategy for Solving Disordered Crystal Structures from PXRD Data by Direct-Space Techniques

Gin Keat Lim ^{§†} & Kenneth D. M. Harris [§]

[§] School of Chemistry, Cardiff University
Park Place, Cardiff, CF10 3AT, Wales

[†] Current Address: School of Chemical Sciences,
Universiti Sains Malaysia
11800 Minden, Penang, Malaysia

Contents



- Background
- Strategy for Solving Disordered Crystal Structures Involving Three Molecular Orientations
- Strategy for Solving Disordered Crystal Structures Involving Two Molecular Orientations
- Concluding Remarks

Background



- Phenomenon of structural disorder in materials* has become an increasingly popular field of investigation for researchers studying the relation between thermodynamic stability and structural properties of crystals.
- A literature study reveals that about 20%[€] of the crystal structures exhibit disorder. Virtually all disordered crystal structures have been solved from single-crystal X-ray diffraction data rather than PXRD data. [€](136534 entries out of a total of 658047 entries) in the Cambridge Structural Database [CSD version 5.34 (February 2013) with updates May 2013]
- Importantly, the direct-space strategy for structure solution from PXRD data implicitly assumes an ordered model, and therefore it is prone to failure if the crystal structure is actually disordered.

* 1. D. Braga and F. Grepioni, *Chem. Soc. Rev.*, 2000, **29**, 229. 2. L. Leibler, *Macromolecules*, 1980, **13**, 1602.
 3. B. M. Kariuki, C. L. Bauer, K. D. M. Harris and S. J. Teat, *Angew. Chem. Int. Ed.*, 2000, **39**, 4485.
 4. R. C. B. Copley, S. A. Barnett, P. G. Karamertzanis, K. D. M. Harris, B. M. Kariuki, M. Xu, E. A. Nickels, R. W. Lancaster and S. L. Price, *Cryst. Growth Des.*, 2008, **8**, 3474.
 5. Y. Funasako, T. Mochida and K. Yoza, *J. Organomet. Chem.*, 2012, **698**, 49-52.

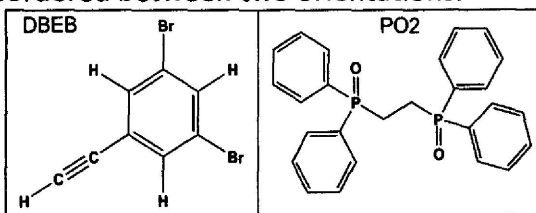
Background



- Especially, when the independent evidence for disorder structure can often be obtained from solid-state NMR[#].

[#]S. Meejoo, B.M. Kariuki, S.J. Kitchin, E.Y. Cheung, D. Albesa-Jove, K.D.M. Harris, *Helv. Chim. Acta*, 2003, **86**, 1467-1477

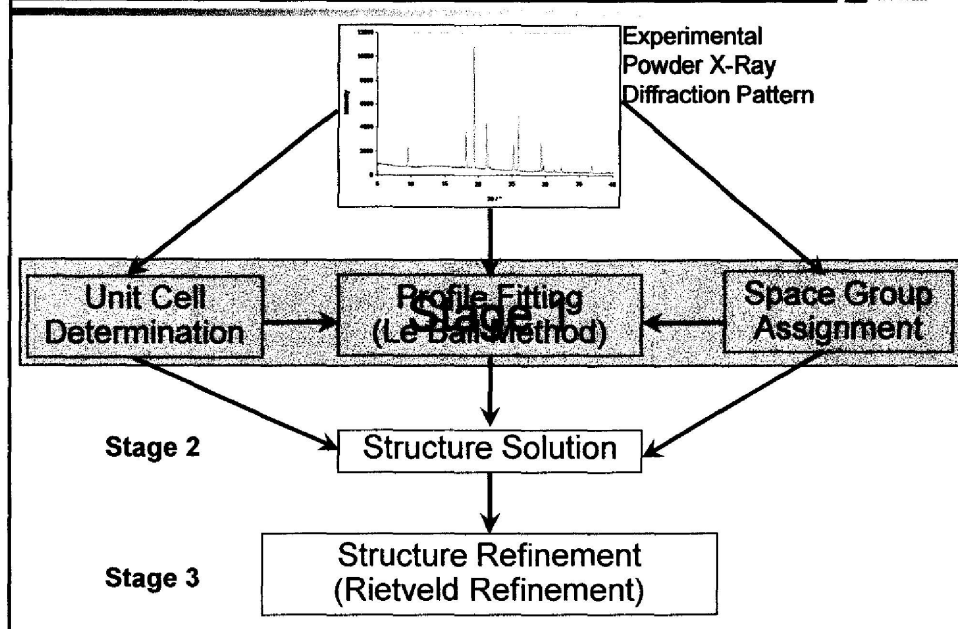
- For this reason, we are exploring a strategy for implementing the direct-space strategy in cases of disordered structures
- Two examples : **DBEB**^{*} and **PO2**[§], were determined previously from single-crystal X-ray diffraction.
- Both crystal structures exhibit orientational disorder, with the **DBEB** molecule disordered between three orientations and the **PO2** molecule disordered between two orientations.



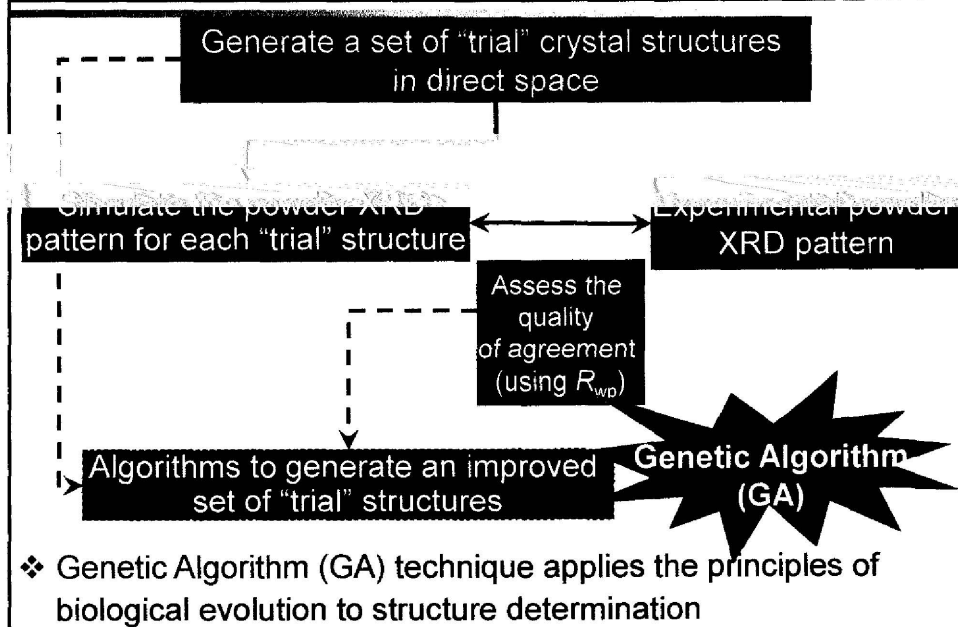
^{*}J. M. A. Robinson, B. M. Kariuki, K. D. M. Harris and D. Philp, *J. Chem. Soc., Perkin Trans. 2*, 1998, 2459.

[§]P. Calceagno, B. M. Kariuki, S. J. Kitchin, J. M. A. Robinson, D. Philp and K. D. M. Harris, *Chem. Eur. J.*, 2000, **6**, 2338.

Crystal Structure Determination from PXRD



Structure Solution of Direct-Space Strategy



Structure Solution of Direct-Space Strategy



How Are The "Trial" Crystal Structures Generated?

Known Information About Molecular Geometries

- ✓ Standard Bond Lengths
- ✓ Standard Bond Angles
- ✓ Standard Geometries of Well-Defined Structural Units (e.g. aromatic rings)

Structural Variables

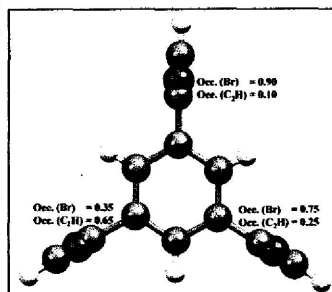
- ? Position of Molecule in Unit Cell: x, y, z
- ? Orientation of Molecule Relative to Unit Cell: θ, ϕ, ψ
- ? Molecular Conformation (Unknown Torsion Angles): $\tau_1, \tau_2, \tau_3, \dots$

Three Molecular Orientations



- 1,3-dibromo-5-ethynylbenzene, **DBEB**, the molecule shows orientational disorder among three orientations, representing disorder of the bromine (Br) and ethynyl (C_2H) substituents among three sites corresponding to the 1, 3 and 5 positions on the benzene ring.

- ❖ The carbon atoms of the benzene ring are completely ordered, and
- ❖ The three different orientations are related by 120° rotation about an axis perpendicular to the plane of the molecule and passing through the centre of the benzene ring.



- The relative occupancies of the three orientations are 0.65, 0.25 and 0.10.

Three Molecular Orientations



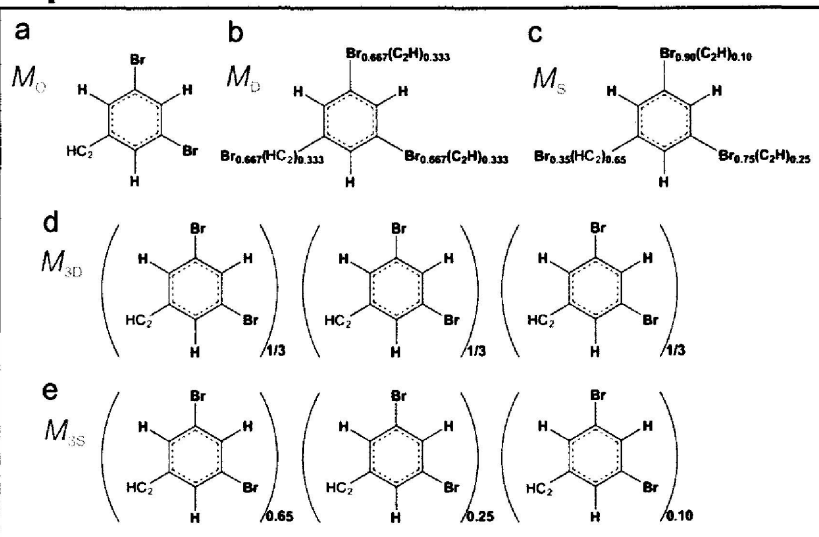
Methodology

- Three PXRD patterns were generated:
 - the PXRD pattern of a hypothetical ordered structure with only one orientation of the **DBEB** molecule and with occupancy of 1 (D_0)
 - the PXRD pattern of a hypothetical disordered structure with equal occupancy for the three orientations of the **DBEB** molecule (D_D)
 - the PXRD pattern of the actual disordered crystal structure (D_S).

Three Molecular Orientations



Input Models



Three Molecular Orientations



- In each molecular fragment, the rigid **DBEB** molecule was defined by three positional variables and three orientational variables.
- single-fragment model: 6 structural variables
- three-fragment model: 18 structural variables
- GA structure solution calculations:
 - a total of 10 independent calculations were carried out for each of the input models [i.e. (a) – (e)] above
 - a population size of 100 trial structures
 - evolve for 100 generations
 - with 80 offspring and 20 mutations created per generation

Three Molecular Orientations



RESULTS AND DISCUSSION

Data	Model	Lowest R_{wp} (%)	Success Rate	Status
D_0	M_0	0.00050	10/10	1
	M_D	81.39	0/10	3
	M_S	43.25	10/10	2
	M_{3D}	0.0010	10/10	1
	M_{3S}	0.00054	5/10	1
D_1	M_0	71.82	10/10	1
	M_S	0.00053	10/10	1
	M_D	40.35	10/10	2
	M_{3D}	0.98	10/10	2
	M_{3S}	15.47	0/10	3

Three Molecular Orientations

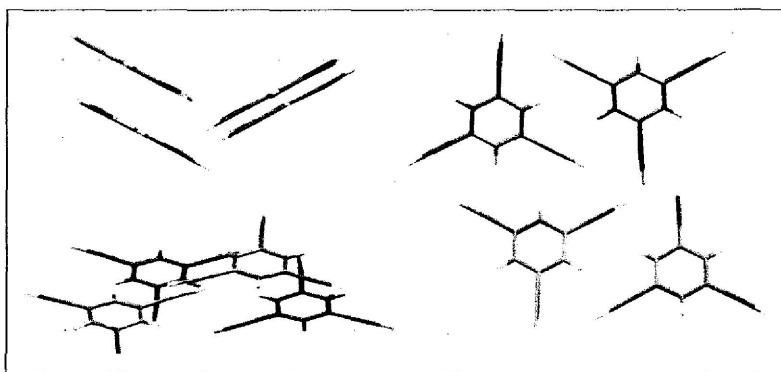


- Status 1 category: were all able to find the correct structure solution
- E.g. D_S-M_S , D_S-M_{3S} , D_O-M_O , D_O-M_{3D} , D_O-M_{3S} , D_D-M_D , and D_D-M_{3D} calculations
- The models that gave successful structure solutions were either represented by the correct occupancy of a single-fragment models, or represented by the multi-fragment models that are able to build the correct occupancy ratio of the substituents in each site
- A very high quality of agreement of the calculated and experimental PXRD data (reflected by a value of $R_{wp} < 1.00\%$)

Three Molecular Orientations



- E.g. M_{3D} input model for the D_D data, a perfectly correct structure solution may be constructed by all three molecules sitting on top of each other and with the occupancy of the three substituents represented correctly.

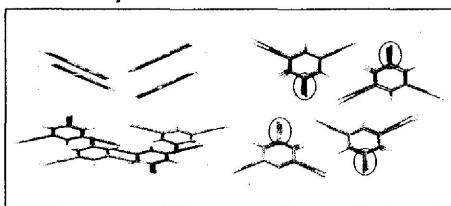


Three Molecular Orientations



- In the category **2** positioning the benzene ring and the substituents at the correct positions in the unit cell, but they are incapable to representing the correct occupancies of the substituents at each site
 - i.e. D_S-M_O , D_S-M_D , D_O-M_S , D_D-M_O , D_D-M_S and D_S-M_{3D}
 - except D_S-M_{3D} , all of these calculations involved were from single-fragment models
 - Reasonable fit, found the global minimum on the R_{wp} hypersurface for these models, but the value of R_{wp} at the global minimum is only moderately low

E.g. D_S-M_{3D}
calculations

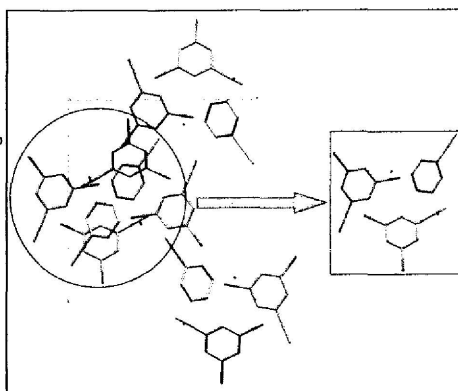


Three Molecular Orientations

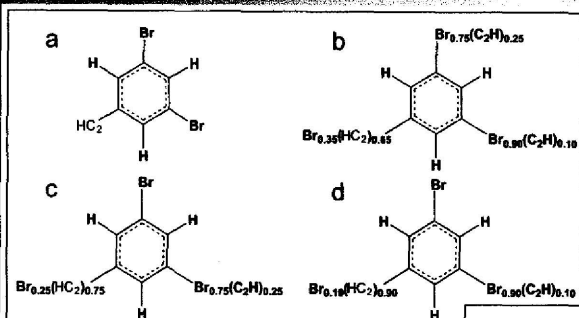


- In the status **3** category, i.e. D_O-M_D and D_D-M_{3S} .
 - The trial structures with lowest R_{wp} in these GA calculations correspond to wrong crystal structures
 - These cases are considered as failed structure solution calculations

E.g. D_D-M_{3S} The structure with lowest R_{wp} (16.87 %) in this case corresponds to an incorrect structure.

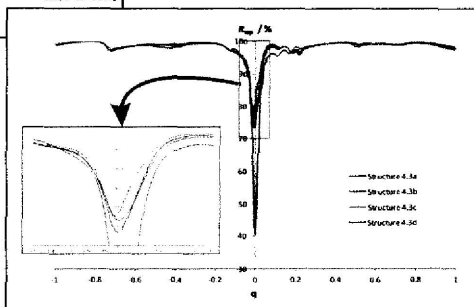


Three Molecular Orientations

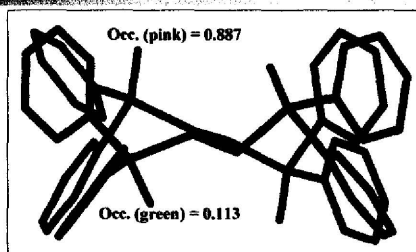


Four possible structures that could be achieved by model M_{3S} , but which do not give rise to low values of R_{wp} for the D_D data because the occupancies deviate significantly from those in the structure used to calculate the PXRD data.

The cross-section calculations of the R_{wp} hypersurface of the four [(a) - (d) above] "reasonable" structures for D_D - M_{3S} shown (in each case the "reasonable" structure corresponds to $q = 0$).



Two Molecular Orientations



- The crystal structure of **PO2** was determined previously from single-crystal X-ray diffraction.
- The **PO2** molecule is disordered between two orientations related approximately by 180° rotation about the long axis of the molecule (approximately the crystallographic c -axis) with the proportions of 88.7 % (in pink) : 11.3 % (in green).
- **Methodology:** Three PXRD patterns were generated from structures representing different degrees of disorder of **PO2**

Two Molecular Orientations



- A total of six input models were used in the direct-space GA structure solution calculations, representing different occupancy proportions of the two molecular fragments.

Model	Occupancy (%)	
	Major	Minor
M_{10}	100	-
M_9	90	10
M_8	80	20
M_7	70	30
M_6	60	40
M_5	50	50

- Clearly, model M_9 has occupancies of the fragments that are the closest to those observed in the actual crystal structure (88.7 % and 11.3 %)

Two Molecular Orientations



Results and Discussions

- The results from the structure solution calculations can be divided into two categories, denoted **A** and **B**.
 - The calculations in **A** were successful to establish the correct position and orientation of each molecule in the unit cell.
 - On the other hand, calculations in category **B** were successful only to locate one molecular fragment correctly in the unit cell.
- Hence, structure solutions in category **A** would be suitable starting models for a successful Rietveld refinement.

Two Molecular Orientations

RESULTS
AND
DISCUSSION

Data	Models	Lowest R_{wp} (%)	Classification (out of 10)	
			A	B
D_s	M_{10}	6.95	0	10
	M_9	0.72	8	2
	M_8	4.14	5	5
	M_7	7.45	3	7
	M_6	8.72	0	10
	M_5	10.40	0	10

Two Molecular Orientations



Data	Models	Lowest R_{wp} (%)	Classification of the Structure Solutions (out of 10)	
			A	B
D_s	M_7	7.45	3	7

- Overall, one important observation from these results is that only the model M_7 (two-fragment model with occupancies 70 % and 30 % obtained successful structure solution for calculations carried out for each of the different sets of PXRD data (D_o , D_s , D_d).

CONCLUDING REMARKS



- A multi-fragment modelling strategy has been introduced as a new strategy for implementing GA structure solution for a with suspected disorder structure.
- Clearly, with the application of this strategy, we can overcome a limitation of the standard approach (i.e. using a single fragment representation of each molecule in the asymmetric unit with full occupancy, representing an ordered model) which is not guaranteed to achieve successful structure solution in the case of disordered structures.
- Specifically, in the case of disordered structure involving two orientations, the two-fragment model with relative occupancies 70 : 30 is clearly a robust model that can achieve successful structure solution across the full range of disordered structures from 100 : 0 occupancies to 50 : 50 occupancies.

ACKNOWLEDGEMENTS



Prof. Kenneth D. M. Harris

Colleagues in Lab



Cardiff University

Government of Malaysia



University of Science Malaysia





THE END



THANKS FOR YOUR ATTENTION

Presented by
Keat | School of Chemical Sciences, USM, Malaysia