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Neutron Powder Diffraction and Constrained Refinement. The Structures of *p*-Dibromo- and *p*-Diiodotetrafluorobenzene

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The first use of a new program, *EDINP*, is reported. This program allows the constrained refinement of molecules in a crystal structure with neutron diffraction powder data. The structures of *p*-C₆F₄Br₂ and *p*-C₆F₄I₂ are determined by packing considerations and then refined with *EDINP*. Refinement is stable and rapid, and the data are sufficiently accurate to allow the choice of the correct minimum in the presence of a number of false minima. A fuller report on *EDINP* is planned.

Introduction

The purpose of this study is to investigate the potential of the neutron powder diffraction method as applied to molecular crystals. The structures most commonly found in molecular systems tend to be of low symmetry, predominantly monoclinic, and with fairly large unit cells. This gives rise to a large number of powder diffraction peaks, even at low angles, which overlap each other considerably. Thermal motion causes a more rapid fall-off in intensity with scattering angle than is observed with harder crystals. In consequence, studies of such systems must rely considerably on the restricted range of low-order peaks in the diffraction pattern.

It is well known that in single-crystal structure refinements it is impossible to vary more parameters than there are observations. The problem – how many structure parameters can be varied with a given powder scan? – is not yet solved, and the solution may have to be based on experience. However, it will always be true to say that success is more likely if the number of variable parameters is sensibly reduced, and in the case of molecular systems, where the number of atoms may be very large, such a reduction can be made by the use

of constraints (Pawley, 1972*a*). This imposes a restriction on the type of problem that can be tackled, as the refinement of a completely unknown structure with a large number of atoms is (at present at least) out of the question.

Phase transitions, brought about by changing pressure or temperature, are common in molecular systems, and the study of such systems can give information about the intermolecular forces. In most phase transitions no chemical reaction takes place, and therefore it can be assumed that no change other than a steric rearrangement has taken place in the molecule. In constraining a molecule so that it retains its integrity this fact can be used to advantage.

The structures chosen for study are very similar to *p*-dichlorobenzene which shows an interesting phase transition [Housty & Clastre (1957); Reynolds, Kjems & White (1972)]. They are *p*-dibromo- and *p*-diiodotetrafluorobenzene, and DTA shows the latter to have a phase change at approximately 85°C. Their melting points are approximately 80 and 107°C respectively. Only the room-temperature phases have been thoroughly studied, and powder diffraction scans of both samples were measured at 150 and 300 K on the TAS II spectrometer at AEK Risø. Neutrons of

wavelength 2.36 Å were monochromatized by pyrolytic graphite, with a graphite filter to remove $\lambda/2$. The diffracted beam was analyzed, again by a graphite crystal, and each point in the scan was counted in about 90 s.

The high-temperature phase of $p\text{-C}_6\text{F}_4\text{I}_2$ gave a poor diffraction pattern in the later experiment on the PANDA diffractometer at UKAEA, Harwell, and this scan was confused by scattering from the furnace. However we could say from these scans that our observations with DTA were confirmed. These observations were that the substance transforms to the high-temperature phase and then remains in that phase even after cooling to liquid-nitrogen temperatures. This prompts us to plan future experiments on this phase but at lower temperatures where a furnace is not required.

Structure determination

One of the great advantages of the powder technique is that it can be used to study samples for which single crystals are not available. In the present case single crystals appropriate for X-ray work were available, and we fell to the temptation of measuring the unit cells from single-crystal photographs. To do this from the powder scans alone is a difficult task, but as there was no overlapping in the four lowest orders in either case this would have been feasible in principle for these monoclinic crystals. The symmetry of the cells was also deduced from the photographs to be $P2_1/c$; this stage has to be guesswork when working solely with the powder diffraction scans.

The two materials were clearly isostructural, and to solve the structure a three-dimensional model was constructed with cardboard molecules which were adjusted to give the most favourable packing. This structure was then fed into the first part of our lattice-dynamics program (Pawley, 1972*b*), which found a potential minimum after a slight readjustment in molecular orientation. This structure was used as the starting point for both refinements.

Structure refinement

Both structures were refined entirely by least-squares techniques using the program *EDINP*. This program is based on *ORFLS* (Busing, Martin & Levy, 1962) in the orthogonalized version (Pawley, 1972*a*). Strict constraints are easily applied and were used throughout refinement. The molecule remains planar at all times. The coordinates of the atoms within this plane are x^{planar} and their final values are listed in Table 1. The *mmm* symmetry of the molecule was retained in the refinement by transformation of the atoms in this table. The centre of the molecule was placed on a centre of symmetry, and its orientation was determined by the rotation matrix $R(\varphi, \theta, \psi)$ where the three Euler angles φ, θ, ψ were allowed to vary. The definition

used for the Euler angles follows Goldstein (1959) and is used extensively by Pawley (1972*a*). Thus the positions of the atoms in the orthogonal unit cell are given by $R(\varphi, \theta, \psi)x^{\text{planar}}$; these and the final Euler angles are listed in Table 2. The orthogonal cell has axes which coincide with the monoclinic axes except for the z axis which is parallel to c^* .

Table 1. *The final coordinates of the atoms in the two molecules (in Å), before the rotation to the crystalline orientation*

The atoms not listed are generated from these by application of the molecular symmetry *mmm*.

	x^{planar}	y^{planar}	z^{planar}
Both structures			
C	1.209	0.702	0.000
C	0.000	1.400	0.000
$p\text{-C}_6\text{F}_4\text{Br}_2$			
F	2.402 (14)	1.352 (12)	0.000
Br	0.000	3.208 (14)	0.000
$p\text{-C}_6\text{F}_4\text{I}_2$			
F	2.446 (26)	1.484 (22)	0.000
I	0.000	3.399 (31)	0.000

Table 2. *The final coordinates of the atoms in the two structures (in Å) with respect to the orthogonal cell*

The axes x and y are parallel to the monoclinic axes, while z is along c^* . The orientations of the molecules are determined by the Euler angles (φ, θ, ψ) [-0.124 (4), 0.757 (1), 2.446 (2)] for $p\text{-C}_6\text{F}_4\text{Br}_2$ and [-0.161 (8), 0.805 (3), 2.489 (4)] for $p\text{-C}_6\text{F}_4\text{I}_2$ (in radians).

	x	y	z	x	y	z
C	-0.461	-1.185	-0.581	-0.481	-1.142	-0.647
C	0.780	-0.664	-0.954	0.764	-0.616	-0.999
C	-1.242	-0.520	0.376	-1.247	-0.525	0.354
F	-0.938	-2.335	-1.125	-0.959	-2.391	-1.386
F	-2.445	-1.053	0.718	-2.614	-1.056	0.779
Br or I	1.787	-1.521	-2.187	1.836	-1.480	-2.401

Table 3. *Final values for the parameters not already given for the two experiments, with the R , background count (not refined) and temperature*

The full width at half height of a peak is given by $(u \tan^2 \theta + v \tan \theta + w)^{1/2}$, thus $w^{1/2}$ is an indication of the resolution of the experiment.

	$p\text{-C}_6\text{F}_4\text{Br}_2$	$p\text{-C}_6\text{F}_4\text{I}_2$
Unit-cell parameters (Å, °)		
a	6.089 (1)	6.268 (3)
b	11.414 (2)	11.639 (5)
c	5.403 (1)	5.929 (2)
β	93.11 (1)	92.70 (3)
Scale factor (arbitrary)	1.71 (2)	1.55 (4)
2θ zero correction (°)	-0.028 (5)	-0.010 (10)
Peak shape parameters (°) ²		
u	1.26 (22)	3.70 (78)
v	-0.48 (15)	-0.98 (49)
w	0.296 (25)	0.377 (74)
R (%)	9.6	14.0
Background count subtracted	60	150
Overall temperature factor, B	2.42 (22)	5.66 (49)
Temperature of measurement, K	150	300

The parameters varied in the refinement were: one overall scale factor, one overall temperature factor, three Euler angles, one parameter for the CBr (or CI) bond, two for the CF bond, four for the unit cell, one for the zero angle of the scan, and three for the peak shape (Rietveld, 1969). The six position parameters should be compared with the 18 required for an unconstrained refinement. The final parameters not already quoted above and the final R values are given in Table 3, R is defined as $R = 100 \left[\frac{\sum_{\text{obs}} |y^{\text{obs}} - y^{\text{calc}}|}{\sum_{\text{obs}} y^{\text{obs}}} \right] \%$. This differs from the R quoted in most papers to date as the summation is over all the observed points, including the background region. Thus R will be increased if there is a peak with no corresponding calculated peak, *i.e.* the R value reflects the reliability of the whole scan.

Two regions of each scan were masked out because there was a considerable contribution to the scattering from the aluminium holder assembly. Unit weights gave better refinement stability than statistical weights, and were used throughout.

The monoclinic angle of about 92.5° presented a problem because the preliminary calculations were not sufficiently accurate to determine whether the angle was 92.5 or 87.5° . The choice can be stated in a different way: if the angle is chosen to be 92.5° then the other possibility is obtained by altering ψ by π . Smooth refinement of β through the 90° position or of ψ by π proved impossible as this corresponds to a reindexing of the reflexions. The value of R in such a refinement would have to go through a large intermediate value in going from the false to the true minimum. However this choice was very easy to make after trying the separate refinements.

A strange result occurred at the end of the refinement – the CBr and the CI bond lengths both shortened until they equalled the CF bond lengths. As this is chemically unsatisfactory there had to be an error in the result. The scattering lengths used in the refinement were C = 0.665, F = 0.565, Br = 0.679, I = 0.528, so it is clear that an error in assigning scattering lengths would not be immediately apparent as in the X-ray case. The bromine (or iodine) atoms could be positioned at any of the three independent positions around the benzene ring without greatly affecting the result. The different molecular orientations to choose between corresponded to differences of $\pi/3$ in φ . Refinements of the three possibilities soon showed that our previous result was in a false minimum, and in the true minimum the bond lengths became chemically reasonable, namely CF = 1.36 (2); CBr = 1.81 (1); CF = 1.46 (4); and CI = 2.00 (3) Å.

The true minimum and the two false minima are shown for $p\text{-C}_6\text{F}_4\text{Br}_2$ in Fig. 1. R was calculated at intermediate points allowing the scale factor, θ and ψ to vary, keeping φ fixed. This shows the size of the barrier to reaching the true minimum from the false. It is interesting to note that although it would be impossible for φ to refine through one of these barriers,

the true minimum could be smoothly reached if all three substituent atoms were allowed to move independently, each with a variable scattering length.

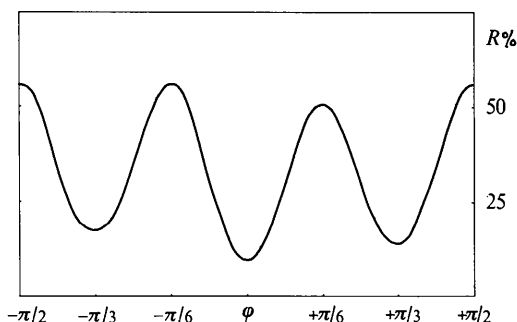


Fig. 1. The variation of R with φ , showing the true minimum in the centre and the two false minima $\pi/3$ on either side. Intermediate R values were calculated varying the scale factor, θ and ψ , holding φ constant.

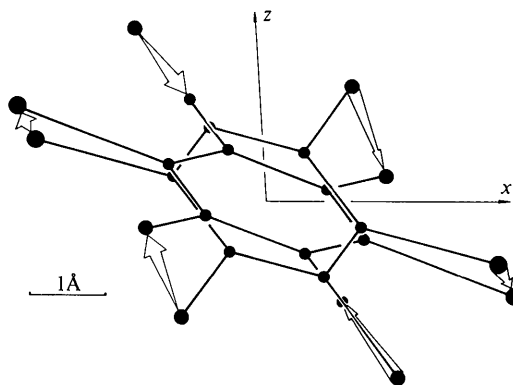


Fig. 2. The position of the $p\text{-C}_6\text{F}_4\text{I}_2$ molecule before the first refinement cycle and its position in the false minimum. The view is down y .

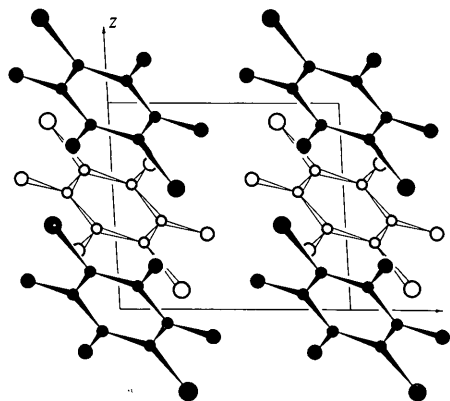


Fig. 3. Projection on the (010) plane of the structure of $\text{C}_6\text{F}_4\text{Br}_2$. The largest circles are the bromine atoms. The structure of $\text{C}_6\text{F}_4\text{I}_2$ differs imperceptibly from that of $\text{C}_6\text{F}_4\text{Br}_2$.

Fig. 2 shows the position of the $p\text{-C}_6\text{F}_4\text{I}_2$ molecule before the first refinement and the shift into the false minimum. Clearly some of the atomic movements exceed 1 Å; this would not be possible without the application of constraint.

Fig. 3 shows the projection on the (010) plane of the structure of $p\text{-C}_6\text{F}_4\text{Br}_2$. The structure of $p\text{-C}_6\text{F}_4\text{I}_2$ differs imperceptibly from this, making a separate

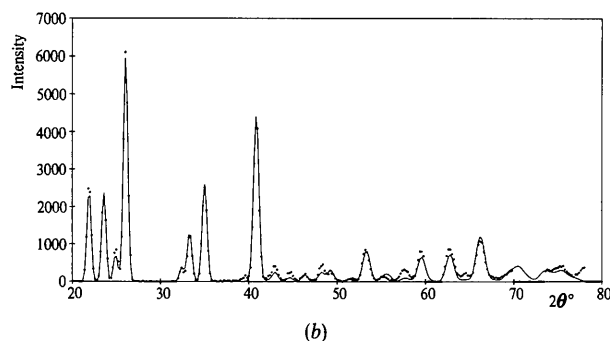
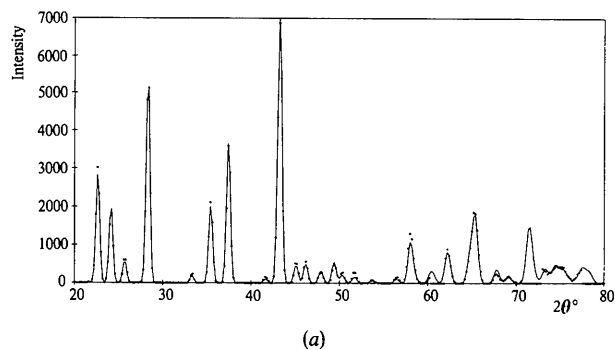


Fig. 4. The observed and calculated scans for (a) $p\text{-C}_6\text{F}_4\text{Br}_2$ and (b) $p\text{-C}_6\text{F}_4\text{I}_2$ with the background removed. The zeros in the observed scans just above $2\theta = 60$ and 70° are the parts of the scans removed because of the presence of (111) and (200) Al scattering. The scan ends just before $2\theta = 80^\circ$.

diagram pointless. Fig. 4(a) and (b) shows the fit between observed and calculated scans for $p\text{-C}_6\text{F}_4\text{Br}_2$ and $p\text{-C}_6\text{F}_4\text{I}_2$ respectively.

Conclusion

The method of strict constraints (Pawley, 1972a) has been successfully used to determine the structures of $p\text{-C}_6\text{F}_4\text{Br}_2$ and $p\text{-C}_6\text{F}_4\text{I}_2$, and the data were sufficiently accurate to give a clear indication of the correct minimum in the presence of two false minima. The strict constraint procedure is much more adaptable than the constraint through Lagrange undetermined multipliers used previously (Mackenzie, Pawley & Dietrich, 1975). A fuller report on the program is planned when more experience of its use has been gained.

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