Short Communications

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Neutron powder diffraction analysis and constrained refinement of perfluorodiphenyl.

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It is shown that with the small amount of data available in the neutron powder diffraction method, it is possible, by means of reasonable constraints, to refine a molecular structure involving a large number of atoms. The method has been used to refine the crystal structure of perfluorodiphenyl. Although the asymmetric unit contains 11 atoms, only three parameters are used to govern their positions, namely the central bond length, the orientation of the two rings about this bond, and the orientation of the whole molecule about the crystallographic c axis. The refinement procedure proved to be quite stable and a good fit to the observations was obtained. This procedure is clearly of value in the study of phase transitions in molecular crystals.

Introduction

The neutron powder profile method for the refinement of crystal structures has received a great deal of attention in recent years. A computer program (Rietveld, 1968) has been used extensively for the accurate determination of the positions of a small number of the atoms in the unit cell as in the case of hydrogen atoms in hydrogen-bonded ferroelectrics (Hewat, 1973). The method is here applied to a molecular crystal in which all the atomic positions are to be varied. By using a number of constraint functions the number of degrees of freedom in the problem is reduced to three. The method of Lagrange undetermined multipliers, which is incorporated in Rietveld's program, is used to apply the constraints, though for such a highly constrained problem the method of strict constraints is more appropriate (Pawley, 1972).

The molecule of perfluorodiphenyl, $C_{12}F_{10}$, consists of two fluorine-substituted phenyl rings connected by a single C–C bond, Fig. 1. The two ring systems are not coplanar, and the interplanar angle φ has been the subject of some discussion (Almenningen, Hartmann & Seip, 1968). It is important in the consideration of the dynamics of the crystal, as shown by the interpretation of the Raman spectrum (Arthur & Mackenzie, in preparation). The determination of φ and the length of the central bond were the principal structural aims of the present work.

The crystal structure was reported briefly by Neronova (1968). The space group is *Fdd*2 and the eight molecules in the unit cell are positioned on the diad axes along the *c* axis at the special positions (0,0,0), $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ *etc.*, Fig. 2. The long molecular axis lies in the *ab* plane at an angle $\psi_x = 38°$ to the *a* axis. Neronova gives an angle of 60° as the rotation of the phenyl rings, and this we deduce to be the angle with respect to the *ab* plane; this is not clear from her paper, but is consistent with our final result.

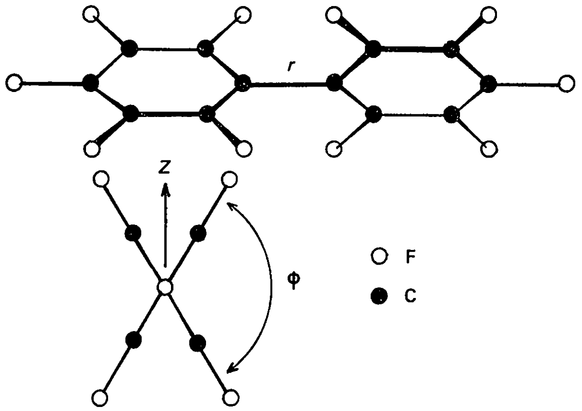

Fig. 1. The molecule of perfluorodiphenyl and the definition of *r* and φ. The ring C–C bonds are 1·37 Å and the C–F bonds are 1·38 Å, being the values used by Neronova (1968).

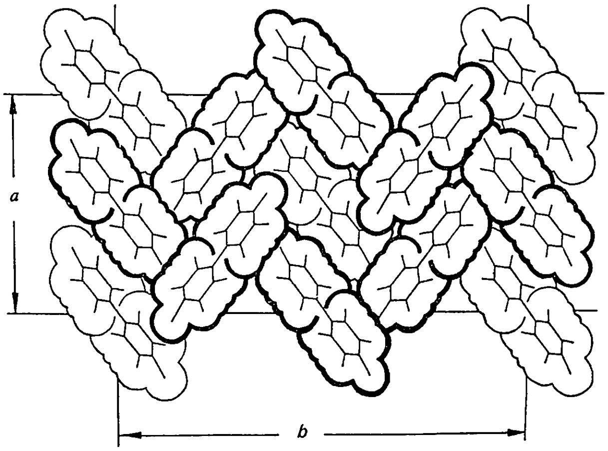

Fig. 2. The crystal structure of perfluorodiphenyl, after Neronova (1968).

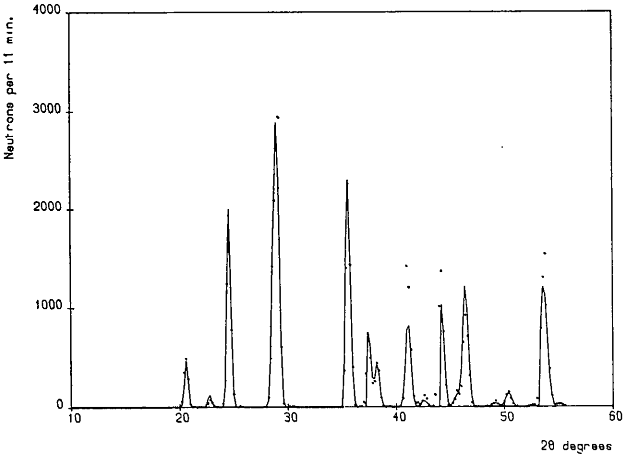

Fig. 3. The observed powder profile with background subtracted (dots) and the best calculated fit (continuous line) for perfluorodiphenyl.

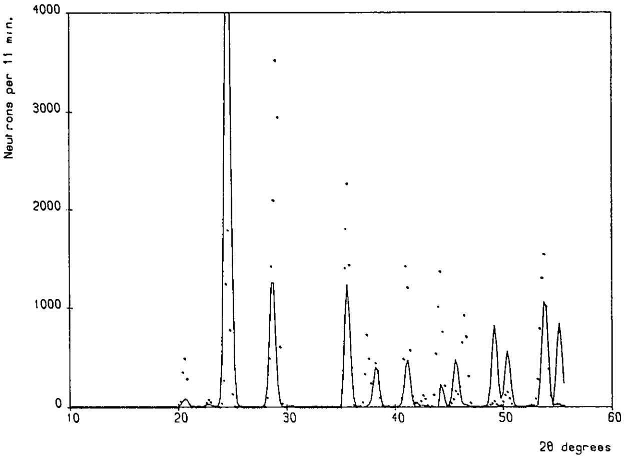

Fig. 4. Comparison of experiment (dots) and calculation (continuous line) for the case where $\varphi = 60°$. Refinement to the best value of φ (Fig. 3) was rapid and stable.

Experiment and analysis

The neutron powder diffraction pattern was measured using the triple-axis spectrometer TAS-4 at Risø, Denmark, with the analyser removed. Neutrons of wavelength 2·374 Å were used and the diffraction data recorded at intervals of 0·2° of 2θ between 10° and 90°, counting for 11 min at each point in the scan. The sample was wrapped in aluminum foil to make a cylinder, and only one aluminum powder line was detectable. The measurements were made at room temperature.

The least-squares structure refinement involved 11 independent atomic positions, giving 33 positional parameters. The facility of the Rietveld computer program for linear and quadratic constraints allowed the variations in these coordinates to be governed by three parameters only. These parameters were the central bond length, r, the angle φ between the two phenyl rings measured so that $\frac{1}{2}\varphi$ is the angle with the ab plane, and the angle ψ_x. The interatomic bond lengths used were those reported by Neronova; the phenyl rings were assumed to have a regular hexagonal shape. The initial parameter values were $r = 1{\cdot}41$ Å, $\varphi = 60°$, $\psi_x = 38°$. These were allowed to vary, along with the three orthorhombic cell parameters and an overall temperature parameter, and the refinement was stable at all times. When a minimum was reached the parameters had the following values: $r = 1{\cdot}62\,(6)$ Å, $\varphi = 120{\cdot}7\,(5)°$, $\psi_x = 37{\cdot}8\,(5)°$, $a = 13{\cdot}48\,(1)$, $b = 26{\cdot}52\,(1)$, $c = 6{\cdot}29\,(1)$ Å. Overall temperature factor $B = 6{\cdot}1\,(9)$ Å^2.

The observed and calculated profiles are shown in Fig. 3, where the background counts have been subtracted. Fig. 4 shows a similar comparison where the calculated profile is that corresponding to the initial values of r, ψ_x and φ. The angle φ was in error by about 60° initially, and it is clear that the calculated fit with the final value of φ gives much the better agreement with experiment. The fit becomes poorer at higher scattering angles where there is considerable overlapping of the diffraction peaks, but this is to be expected as the parameters varied correspond to low atomic resolution. Any molecular distortion which might be present cannot be detected with this procedure, and it is planned to continue the investigation of the structure of this material using single-crystal four-circle diffractometer measurements and strict constrained refinement methods. Such an analysis will enable us to examine the thermal motion in the structure, as very little reliance can be put on the temperature factor obtained in the present low-resolution work.

Conclusion

It has been shown that the method of powder profile refinement can be used to obtain low-resolution information about the structure of molecular crystals. With the correct choice of constraints the large number of degrees of freedom of the system can be considerably reduced so that large scale features of the structure, such as molecular orientation, may be investigated. Such large-scale features are of dominant importance in the phase transitions of molecular crystals, and hence this method will have considerable value in such studies.

For the molecule of perfluorodiphenyl it is shown that the angle φ between the two ring systems is 120·7° with an error of perhaps $\frac{1}{2}$°. The bond between the two rings is 1·62 Å, but as this is highly correlated to structural features which were held fixed, no good estimate of an error is possible. The error given above of 0·06 Å should be interpreted as the error between the centres of the two rings.

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