0·000 Å respectively. The plane equation for the formic acid moiety is $-0{\cdot}0007X - 0{\cdot}9528Y - 0{\cdot}3037Z = 0{\cdot}0532$. The angle between the two planes is 85·4°.

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The Structure of Octafluoronaphthalene at High Pressures Investigated by Neutron Powder Diffraction

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The structure of the molecular crystal octafluoronaphthalene at high pressures has been studied by neutron powder diffraction. Evidence was found at about 0·8 kbar for a structural phase transition similar to that which occurs at 266·5 K at atmospheric pressure. The structures at atmospheric pressure and at 2 and 4 kbar have been refined using the powder-profile-refinement program *EDINP*. There is evidence for a further structural change between 4 and 6 kbar, but there are insufficient data for a detailed analysis of this change.

Introduction

Neutron powder diffraction is well suited to the study of the variation of crystal structure with temperature and pressure where conventional single-crystal measurements are either difficult or impossible. Essential to the analysis of the diffraction data has been the development of the total-profile-refinement method (Rietveld, 1969). Recent work on this method has shown that the structures of relatively complicated molecular crystals can be refined successfully (Mackenzie, Pawley & Dietrich, 1975; Pawley, Mackenzie & Dietrich, 1977). Since in such crystals there is generally a large amount of thermal motion which leads to a rapid fall-off in intensity with scattering angle the diffraction data are often limited to a small number of low-order peaks in the pattern. In such cases there is insufficient structural information in the data to justify refinement of the atomic positions as independent parameters. Instead the atomic positions are constrained so that the molecular shape is preserved and the molecular orientational and positional coordinates are allowed to be variable parameters. The profile-refinement program *EDINP* (Pawley *et al.*, 1977) was developed specifically for the purpose of introducing such constraints in the refinement process following the methods outlined by Pawley (1972).

The method is now applied to structural studies of octafluoronaphthalene, $C_{10}F_8$, at high pressures. This molecular crystal has been the subject of recent structural and dynamical studies at atmospheric pressure (Pawley & Dietrich, 1975; Mackenzie, Arthur & Pawley, 1977), which were concerned with the structural phase transition occurring at 266·5 K on cooling and at 281 K on heating. The structure of the low-temperature phase was solved by profile refinement and was shown to belong to the same space group as the room-temperature phase, monoclinic $P2_1/c$, but with four molecules in the unit cell instead of two. It was reasonable to expect that a similar transition might occur at high pressure and for this reason the present study was initiated.

Experimental

The measurements were carried out using a triple-axis spectrometer at the DR3 reactor, Risø, and the pressure cell shown in Fig. 1, enabling conventional variable-2θ scans at sample pressures up to about 8 kbar (Buras, Kofoed, Lebech & Bäckström, 1977). The powdered sample without any container was placed directly in the 16 mm cylindrical bore of the high-pressure cell. The amount of material in the beam was about 10 cm^3. The scans were done using the triple-axis spectrometer in the elastic mode, with a fixed neutron wavelength of 2·38 Å monochromated and analysed by pyrolytic graphite (002) with an oriented pyrolytic-graphite filter to remove $\lambda/2$ neutrons. The scan range was $2\theta = 7$ to 55° measured in intervals of 0·1° and counting was for about 6 min per point.*

In order to check whether the preferred orientation of crystallites affects the diffraction patterns a comparison was made between diffraction patterns taken

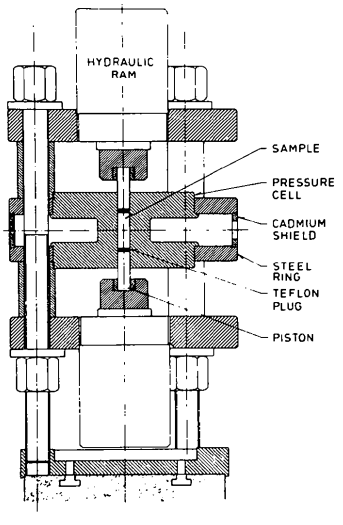

Fig. 1. High-pressure apparatus. The pressure cell is made of a high-tensile-strength aluminium alloy.

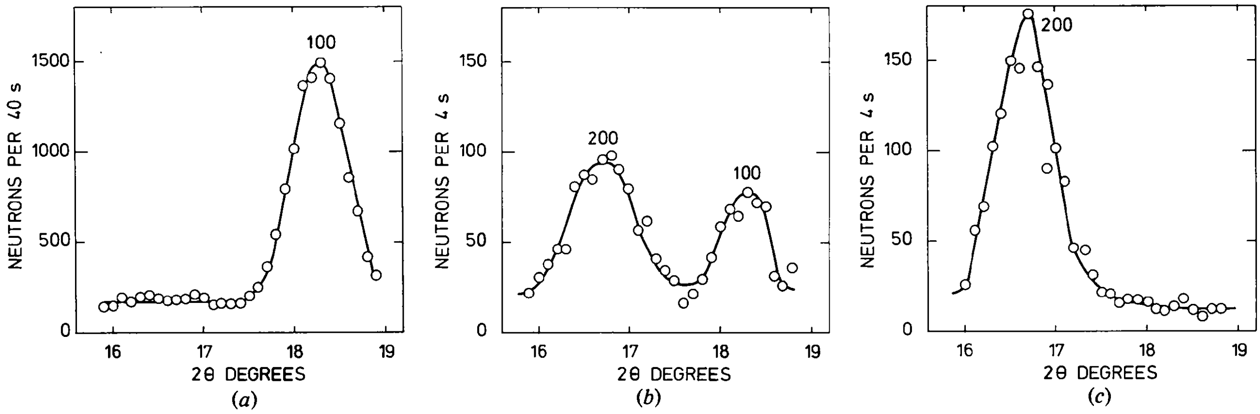

Fig. 2. Measured neutron intensities showing (*a*) the 100 peak of phase I at 0·7 kbar, (*c*) the 200 peak of phase II at 0·9 kbar; (*b*) shows the peaks of both phases simultaneously at 0·8 kbar.

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* It should be noted that the first diffraction peak from the aluminium cell is seen at $2\theta \simeq 61{\cdot}35°$ and is thus outside the measured range.

before applying pressure and after releasing it. No significant differences were found, either in the patterns themselves or in the refined structure parameters. Some of the reflections were also recorded at different positions of the cell (obtained by rotation of the sample table) and no significant differences were found, either in the reflections themselves or in the background. Thus we conclude that neither preferred orientation nor inhomogeneity of the cell affects in a significant way the neutron patterns and the results of the refinement.

The phase transition

It was found that the transition occurs at a pressure of about 1 kbar and that the high-pressure patterns at 2 and 4 kbar were very similar to that measured at low temperature (~100 K) (Mackenzie *et al.*, 1977) and that the diffraction peaks could be indexed accordingly. In order to study the transition more precisely pressure scans were done at pressures of 0·7, 0·8 and 0·9 kbar over a small region of scattering angle which included the 100 reflection of the atmospheric-pressure room-temperature phase (phase I) and the 200 reflection of the low-temperature or high-pressure phase (phase II). The results of these scans are shown in Fig. 2 and a plot of the peak intensities of the respective reflections against pressure is shown in Fig. 3. It can be seen that the transition occurs at about 0·8 kbar, the uncertainty in sample pressure being about 0·1 kbar. Some time dependence of the intensity of the peaks was found around the transition on going from phase I to phase II, but the intensities reached stable values after a few minutes. This contrasts with the observed time dependence in the Raman spectrum which took about 2 h to stabilize after cooling through the transition (Mackenzie *et al.*, 1977). It is expected that a hysteresis effect similar to that found with cooling and heating (Pawley & Dietrich, 1975) occurs with increasing and decreasing pressure. However, because of frictional effects in the cell it was impossible to measure the pressure with any reliability while it was being released.

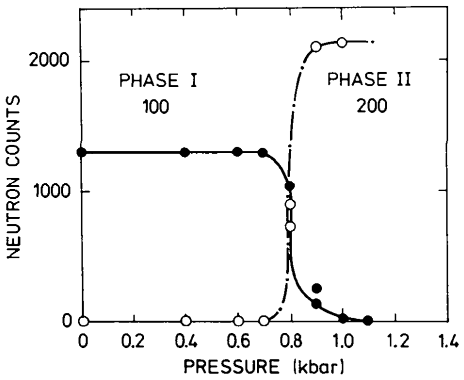

Fig. 3. Measured peak intensities ($\lambda = 2{\cdot}38$ Å) of the phase I 100 peak and the phase II 200 peak as a function of increasing pressure.

Structure refinement

The neutron powder diffraction patterns were analysed using the structure-refinement program *EDINP* (Pawley *et al.*, 1977). The background intensity was first subtracted from the data by linear interpolation between scan points where the amount of background was estimated by graphical methods. While it is recognized that this is unsatisfactory in cases where accurate thermal parameters are required it has been found that reasonably reliable positional parameters can be obtained.

The positions of the atoms within the molecule were constrained throughout the refinements to the values listed in Table 1, as used in the low-temperature refinement (Mackenzie *et al.*, 1977). The orientation of the molecule in the crystal is determined by the rotation matrix **R** (φ,θ,ψ) where the three Euler angles φ,θ,ψ are as defined by Goldstein (1959) and used extensively by Pawley (1972). In the atmospheric-pressure (phase I) structure there is only one independent molecule centred at the origin so that only three Euler angles are required.

In phase II there are two independent molecules, one at the origin and one at $(\frac{1}{2},0,0)$, requiring a total of six Euler angles. In all cases the molecules lie on centres of inversion symmetry. The peak-shape parameters (u,v,w) are as defined by Rietveld (1969) and give the full width at half maximum, H, of the diffraction peaks as a function of the Bragg angle thus: $H^2 = u \tan^2 \theta + v \tan \theta + w$.

The final values of all the variable parameters are listed in Table 2. The R factor is defined by $R = (100 \sum |y^{\text{obs}} - y^{\text{calc}}|/\sum y^{\text{obs}})\%$, where y^{obs} and y^{calc} are the observed and calculated profile intensities respectively and the summation is over all points in the scan.

Table 1. *Planar coordinates of atoms in Å for the asymmetric part of a molecule before rotation to the crystalline orientation*

The remaining coordinates are generated by application of the molecular symmetry *mmm*.

	x	y	z
C	1·242	1·400	0·000
C	2·422	0·707	0·000
C	0·000	0·705	0·000
F	3·630	1·400	0·000
F	1·225	2·800	0·000

In assessing the quality of the refinements it is helpful to compare the R factors obtained with those from previous examples of the method which used the similar constraints:

$C_{10}F_8$ (low temperature) (Mackenzie *et al.*, 1977)	$R = 20\%$
p-$Br_2C_6F_4$ (Pawley *et al.*, 1977)	$R = 10\%$
p-$I_2C_6F_4$ (Pawley *et al.*, 1977)	$R = 14\%$
$C_{12}F_{10}$ (Mackenzie, 1976)	$R = 19\%$.

The results of $R \sim 12\%$ for the 2 kbar and 4 kbar refinements compare favourably while the result of $R = 15\%$ for atmospheric pressure is somewhat poorer. The latter result is probably due to the very large thermal motion caused by the proximity of the phase transition. It may be noted that the single-crystal structure refinement of phase I (Pawley & Dietrich, 1975) gave the rather poor result $R = 38\%$ (conventional R factor) with similar parameters.

Although the numerical value of the R factor gives an indication of the quality of the fit it is essential in this type of work to compare the observed and calculated profiles directly. Small discrepancies between the measured and fitted intensities at particular points in the scan can point to deficiencies in the structural model used. Such comparison is most easily done by visual inspection of computer-drawn plots. Figs. 4 and 5 show the observed and calculated profiles for the atmospheric-pressure and 2 kbar scans respectively. The major discrepancies in the atmospheric-pressure fit occur at 2θ values of 34·5, 41·5, 44 and 49°. These weak peaks, although badly fitted, do correspond to Bragg reflections allowed by the space group $P2_1/c$ so

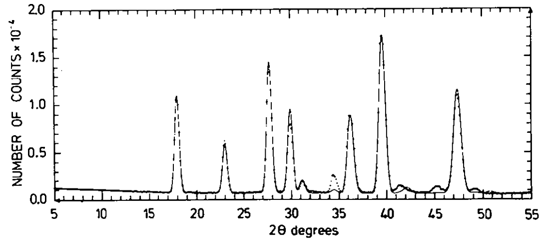

Fig. 4. Measured (points) and fitted (solid line) diffraction patterns including background at atmospheric pressure ($\lambda = 2 \cdot 38$ Å).

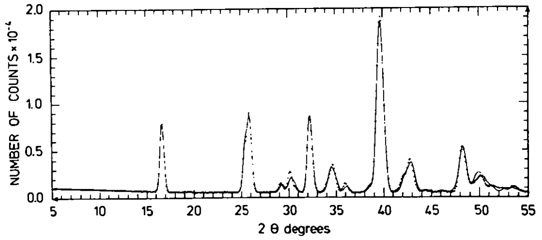

Fig. 5. As Fig. 4 but at 2 kbar.

Table 2. *The final values of the parameters for the structure refinements*

All measurements were at room temperature.

	Atmospheric pressure	2 kbar	4 kbar	6 kbar	7 kbar
Scale factor	6·95 (12)	1·54 (3)	1·58 (3)	1·80 (6)	1·84 (8)
Counter zero-width point (°)	0·32 (1)	0·41 (1)	0·43 (1)	0·33 (2)	0·31 (3)
Half-width parameters, $(°)^2$					
u	5·6 (9)	2·7 (8)	2·2 (8)	1·4 (14)	1·7 (22)
v	−1·5 (5)	−0·2 (5)	0·1 (5)	−0·2 (8)	−0·7 (13)
w	0·40 (7)	0·19 (6)	0·16 (6)	0·35 (12)	0·51 (19)
Unit-cell parameters					
a (Å)	7·550 (6)	17·042 (13)	16·884 (13)	16·874 (22)	16·866 (31)
b (Å)	4·960 (2)	4·612 (2)	4·573 (2)	4·570 (3)	4·564 (4)
c (Å)	11·865 (6)	11·129 (5)	11·057 (4)	11·066 (7)	11·053 (10)
β (°)	96·67 (3)	110·79 (2)	110·72 (2)	110·55 (5)	110·54 (6)
Isotropic temperature factor $B = 8\pi^2\langle u^2\rangle$, where $\langle u^2\rangle$ is the mean-square atomic displacement measured in $Å^2$	17·4 (4)	11·1 (5)	9·5 (5)	7·6 (8)	8·1 (12)
Euler angles for molecules 1 and 2 in radians					
φ_1	2·103 (4)	2·555 (8)	2·520 (8)	2·438 (14)	2·430 (20)
θ_1	0·842 (2)	0·966 (6)	0·968 (5)	0·987 (8)	0·992 (11)
ψ_1	3·669 (2)	−2·649 (4)	−2·640 (4)	−2·622 (7)	−2·619 (10)
φ_2		3·073 (7)	3·061 (7)	3·080 (11)	3·080 (15)
θ_2		0·754 (6)	0·750 (6)	0·731 (9)	0·721 (12)
ψ_2		−3·034 (4)	−3·032 (4)	−3·039 (6)	−3·038 (8)
R factor (%)	14·6	12·4	11·6	19·6	23·1

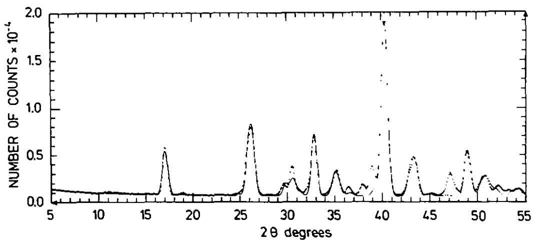

Fig. 6. As Fig. 4 but at 7 kbar.

there is no reason to suspect an error in the choice of crystal symmetry. As mentioned above, the poor fit is most likely to be due to the thermal motion, in particular the inability of the overall isotropic temperature factor to describe the large anisotropic molecular motion. There is clearly insufficient data for a more realistic treatment of the thermal motion which would require a much greater number of variable parameters.

It is difficult to place any reliance on the absolute values of the refined isotropic temperature factors which are consistently rather large. This is probably due to the small range of sin θ/λ used and the uncertainty in choosing the level of background at high 2θ values where the peaks overlap considerably. It is well known that the temperature factors are highly correlated with the background level. The Euler angles which define the molecular orientation are not strongly correlated with the temperature factors and should therefore be more reliable.

The results of the refinements confirm that the structure of octafluoronaphthalene at 2 kbar and 4 kbar is similar to that at low temperature, namely phase II.

A second phase transition

Scans made at 6 and 7 kbar revealed a second phase transition between 4 and 6 kbar. Although the patterns measured at 6 and 7 kbar were different from those obtained at 2 and 4 kbar we tried to fit them using the phase II structure, and R factors of ~20% and ~23%, respectively, were obtained. Observed and calculated profiles for the new phase (phase III) at 7 kbar are shown in Fig. 6. The unfitted peaks at 2θ values of 18, 38, 39 and 47° cannot be indexed using the unit cell of phase II. Apart from these features the pattern is reasonably well fitted. A possible explanation of this is a distortion of the structure leading to a doubling of the unit cell along either the **b** or the **c** direction. Such a distortion would cause weak Bragg reflections to appear in the regions where we see new peaks.

We noticed that the new peak at 39° increases in intensity as the pressure is increased indicating that the distortion develops. The nature of this structural distortion could be ascertained by introducing the appropriate degrees of freedom in the refinement process, as was done in the refinement of the low-temperature phase II (Mackenzie *et al.*, 1977). In the present case, however, this would lead to a very large number of least-squares parameters because of the loss of symmetry between molecules in the unit cell. The amount of data available from the powder diffraction scans does not permit the use of a greatly increased number of parameters. While it would be possible to measure more diffraction data at high values of $(\sin\theta)/\lambda$ such data is difficult to analyse because of the large number of overlapping peaks and the influence of thermal motion. We have therefore made no attempt to refine the phase III structure at present. However, for the sake of completeness the results of the fit of phase III using the phase II structure are included in Table 2.

Conclusions

It has been shown that octafluoronaphthalene undergoes, at room temperature and 0·8 ± 0·1 kbar, a structural phase transition. Using the profile-refinement program with constraints it was found that the high-pressure structure up to about 4 kbar is similar to phase II present at atmospheric pressure below 266·5 K.

There is evidence of a further structural change to a new phase III at room temperature and pressures between 4 and 6 kbar, possibly involving a distortion of the structure which increases with pressure. The results of fitting in this case are limited by the low symmetry of phase III, which would require more parameters than the data permit.

Encouraged by the good quality of neutron patterns obtained at pressures up to 7 kbar and by results obtained using the profile-refinement program with constraints we have recently measured neutron diffraction patterns of pyrene, $C_{16}D_{10}$, at high pressures and found a transition at about 6 kbar. This work is in progress and at this stage it is difficult to say whether it is the same transition as reported for $C_{16}H_{10}$ by Zallen, Griffiths, Slade, Hayek & Brafman (1976), who used Raman spectroscopy and found transitions at 300 K and 4 kbar, and at 110 K and 1 bar.

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The Crystal Structures of Some Oligomeric Conjugated Dithienylalkapolyenes

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Crystals of *trans*-1,4-di(2-thienyl)-1,3-butadiene, $C_{12}H_{10}S_2$, monoclinic, space group $P2_1$, and *trans*-1,6-di(2-thienyl)-1,3,5-hexatriene, $C_{14}H_{12}S_2$, triclinic, space group $P\bar{1}$, have the lattice parameters: $a = 11{\cdot}683$ (6), $b = 7{\cdot}559$ (4), $c = 6{\cdot}333$ (3) Å, $\beta = 104{\cdot}52$ (2)°; and $a = 9{\cdot}736$ (2), $b = 10{\cdot}312$ (4), $c = 6{\cdot}338$ (3) Å, $\alpha = 92{\cdot}40$ (2), $\beta = 96{\cdot}27$ (2), $\gamma = 100{\cdot}11$ (2)°. The number of formulae per unit cell is two in both cases. The structures were determined by direct methods and refined by the full-matrix least-squares method using three-dimensional X-ray data. In both cases the final residual R was 0·039. Bond lengths and angles in the thiophene rings are compared with those in unsubstituted thiophene. The crystal structures are two-layered and controlled by intermolecular electrostatic attraction between protons and delocalized π electrons.

Introduction

The crystal structures of two oligomeric conjugated dithienylalkapolyenes, *trans*-1,4-di(2-thienyl)-1,3-butadiene (A) and *trans*-1,6-di(2-thienyl)-1,3,5-hexatriene (B), are reported here; that of *trans*-1,2-di(2-thienyl)ethylene has already been published (Ruban & Zobel, 1975). Besides the general crystallographic interest which these structures have (they can be compared to those of stilbene and related compounds) there is special interest in them since they have semiconducting properties and, because of their chemical simplicity, may serve for basic investigations in the field of organic semiconductors. Both compounds were synthesized by Bohn (1975). Crystals are transparent and colorless (A) or yellow (B).

Experimental

Platelet-shaped crystals were grown by solvent evaporation from methanol solutions (A) or by sublimation at a temperature of 185 °C under N_2 gas (B). The space groups determined from Weissenberg photographs were $P2_1$ for A and $P1$ or $P\bar{1}$ for B. Densities were measured by the neutral buoyancy method. Additional crystal data are given in Table 1. Crystal A was elongated in the [010], crystal B in the [100] direction. The crystal volumes were 0·016 (A) and 0·0024 mm³ (B), and the platelet thicknesses 0·07 (A) and 0·02 mm (B).

The intensity data were collected at room temperature with Cu $K\alpha$ radiation on an automatic four-circle single-crystal X-ray diffractometer, applying the

Table 1. *Crystal data not given elsewhere*

	A	B
Formula	$C_{12}H_{10}S_2$	$C_{14}H_{12}S_2$
M_r	218·4	244·38
Unit-cell volume, V	541·4 (8) Å³	621·5 (7) Å³
Number of formula units per asymmetric volume	1	2/2
Density calculated [measured], ρ	1·340 (2) [1·3] g cm⁻³	1·306 (2) [1·3] g cm⁻³
Number of electrons per unit cell, $F(000)$	228	256
Linear absorption coefficient for Cu $K\alpha$ radiation, μ	38·2 cm⁻¹	34·65 cm⁻¹