

## An X-ray Single-Crystal Study of the Molecular System $C_6F_6 \cdot C_6D_6$

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### Abstract

An X-ray diffraction study of the molecular complex system hexafluorobenzene–deuterobenzene at 279 K is reported. The structure has been determined for the first time as rhombohedral, space group  $R\bar{3}m$  or  $R3m$ , and of unit-cell dimensions  $a = 7.310(19) \text{ \AA}$  and  $\alpha = 109.67(43)^\circ$ , giving a unit-cell volume of  $299(5) \text{ \AA}^3$ .  $R = 0.098$  for 150 independent reflections. There is one molecule of each species within the unit cell and they are alternately arranged in infinite stacks along the unique [111] crystallographic direction, the molecular planes being perpendicular to this direction. Both constrained and unconstrained refinements have been done and the results of both are presented. The constraints consisted of rigidly fixing the bond lengths and geometry of the molecules such that the resulting molecular hexad symmetry axis was coincident with the unique axis of the structure. The unconstrained model relaxes the fixed bond lengths but the hexad symmetry is retained. The possibility of pairing of the molecules along the unique direction is considered for this phase, and crystallographic evidence is given for at least two other solid-state phases of this system.

### Introduction

Considerable interest was generated by the report by Patrick & Prosser (1960) of the existence of several molecular complexes between hexafluorobenzene (HFB) and various aromatic hydrocarbons. A great variety of studies of these complex systems using different experimental techniques has been performed and a brief account of that work is given here.

Thermodynamic measurements (Duncan & Swinton, 1966; Duncan, Sheridan & Swinton, 1966) were made in order to establish the phase diagrams, amongst other properties, of several complexes involving HFB, including HFB–benzene. Gilson & McDowell (1966) have made nuclear magnetic resonance (NMR) measurements on the HFB–benzene system, and reported line

width and second-moment transitions at about 90 K on cooling. They conclude that these transitions are probably caused by reorientations about the sixfold axis of the molecules. Spectroscopic measurements by Beaumont & David (1967) and dipole measurements by Bauer, Knobler, Horsma & Perez (1970) of complexes containing HFB do not show any evidence of charge transfer between the different species of molecules as was first assumed by Patrick & Prosser (1960). This led to the X-ray diffraction studies of Dahl (1971, 1972, 1973), performed to gain information concerning the intermolecular forces present in the two complexes HFB–mesitylene and HFB–hexamethylbenzene. Dahl concludes that the possibility of forces stronger than the van der Waals type should not be ignored in these systems.

The differential scanning calorimetry measurements done by Brennan, Brown & Swinton (1974) on the HFB–benzene system demonstrated a thermal anomaly at 249 K on warming and at 246 K on cooling. However, the work done by Gilson & McDowell (1966) showed no unusual NMR behaviour at  $\sim 250$  K.

More recently, Potenza & Mastropaolo (1975) have determined the crystal structure of the closely related complex system naphthalene–octafluoronaphthalene. The molecules were found to be arranged in infinite stacks, alternating in the two species but unpaired, and where the differing species are laterally displaced, relative to each other, by about  $1.4 \text{ \AA}$ .

Further calorimetric and NMR experiments on the HFB–benzene- $d_6$  system have been done by Ripmeester, Wright, Fyfe & Boyd (1978) and they observed a number of transition phenomena on warming at temperatures of 199, 247.5 and 272 K. They also propose that the HFB molecule is rotationally disordered to some extent in the temperature range 100 to 300 K in accord with the observations of Gilson & McDowell (1966). The transition at 247.5 K is in agreement with the calorimetric work of Brennan *et al.* (1974). Recently the Raman light-scattering technique was used in order to probe the temperature dependence of the dynamics of the HFB–benzene system (Mackenzie, Overell & Pawley, 1979). Polycrystalline samples, both protonated and deuterated, were studied in this

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work in the temperature range 4.2 to 300 K, and a structural phase transition was reported at  $\sim 170$  K on cooling and  $\sim 200$  K on warming. This will be related to the thermal anomaly reported by Ripmeester *et al.* (1978). Since the crystal structure was unknown at any temperature, this prompted the present X-ray diffraction study of a small single crystal of the 1:1 molar complex HFB–benzene- $d_6$  at just below room temperature. Previously, Small (1979) had reported a very weak X-ray diffraction pattern for this system at room temperature.

### Experimental

Constituent chemicals were obtained from the Imperial Smelting Co. ( $C_6F_6$ , stated purity 99.95 at.%) and Fluka Chemicals ( $C_6D_6$ , stated purity 99.6 at.%) and were used without further purification. The mixture used was equimolar in the two constituents to  $\sim 0.3\%$ .

A sample was prepared by sealing some of the frozen, polycrystalline, mixture in a Lindemann capillary tube of diameter 0.5 mm and approximate length 4 mm. To avoid any combustion, and hence contamination from the combustion products that would result by sealing the ends of the tube by melting the glass, the sample tube was sealed with epoxy glue, and then attached directly to the goniometer head. This goniometer arrangement was then mounted on an Enraf–Nonius CAD-4 four-circle diffractometer.

The zone refining technique was used to grow the crystal on the diffractometer, using a fine wire as the heater. Since the materials used were impure before mixing, this crystal growing technique would aid in the partial purification of the mixture. The result of this process was a single crystal  $\sim 2$  mm in length, and nitrogen-gas cooling apparatus was used to maintain the crystal at a temperature of about 280 K, well below its melting point of about 297 K. Great care had to be taken when growing the crystal to ensure that the temperature of the cold nitrogen stream was above 272 K, where the constituent chemicals tended to supercool and then separate and solidify below their natural individual freezing points of about 279 K.

The crystal gave a distinct diffraction pattern and it was also observed that considerable diffuse scattering was present underneath the Bragg reflections, but this has not been measured and analysed. It is probable that this diffuse scattering is related to the dynamical disorder reported by Ripmeester *et al.* (1978).

The data were collected using a CAD-4 diffractometer operating with filtered Cu  $K\alpha$  radiation of wavelength  $\lambda = 1.5405 \text{ \AA}$ . 1487 reflections were measured in concentric shells out to  $(\sin \theta)/\lambda = 0.532 \text{ \AA}^{-1}$  in reciprocal space (corresponding to a maximum scattering angle of  $2\theta = 110^\circ$ ). The average sample temperature throughout the experiment was 279 (1) K.

The beam width was 0.4 mm at the sample, this value being taken from the collimator specifications. The shape of the crystal relative to the incident beam is not the optimum spherical shape that would normally be chosen, had the choice been available. This problem was partially overcome in the analysis by applying a rudimentary volume correction to the measured integrated intensities, the form of which will be given later.

### Results and analysis

The raw data consisted of 1487 integrated intensities grouped over 150 symmetry-independent reflections, both the reflection and its Friedel pair having been measured. The variation of the integrated intensities of the three control reflections as a function of time throughout the experiment was less than 4% from the corresponding mean integrated intensities, showing that the experimental conditions were satisfactorily stable. The linear absorption coefficient was calculated as  $14.14 \text{ cm}^{-1}$ , but no corrections were applied to account for any possible variation in the diffracted intensity caused by the absorption process. This was justified in terms of the asymmetrical crystal shape relative to the incident and diffracted beams. The process of extinction becomes important only when crystals of very high perfection are used, and therefore in the present study this process is ignored. Hereon we use the word intensity to imply integrated intensity.\*

From an initial analysis of the reflection intensities it was deduced that the only possible space groups were  $R\bar{3}m$  and  $R3m$  (*International Tables for X-ray Crystallography*, 1952). Reflections were grouped according to this symmetry, and within these groups there were about 30 reflections with spuriously high intensity. Each was investigated for double Bragg scattering, and all were found to be possible combinations of the nine strongest reflections and so were discarded. The intensities were then averaged within each group, giving a mean variation within each group of 5.5%. It is not possible to perform a reliable test for centrosymmetry (Wilson, 1949) using the final 150 independent reflections to distinguish between the two possible rhombohedral space groups as any possible  $R3m$  structure would result from a small distortion of an  $R\bar{3}m$  structure and concomitant intensity changes would be of second order.

The correction to be applied that accounts approximately for the volume variation of the crystal in the

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36755 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

incident beam is of the form  $I = I_0 \operatorname{cosec} \delta$ , where  $I_0$  and  $I$  are the measured and corrected intensities respectively. The angle  $\delta$  is that between the incident-beam direction and the axis of the cylindrical tube in which the crystal is contained. With knowledge of the four orientation angles the angle  $\delta$  was calculated for each individual reflection. It is convenient at this point to introduce an overall consistency factor in order to test whether or not the above correction makes an improvement on the data. This quantity will be defined as

$$R_{\text{overall}} = \frac{\sum_j \left( \sum_i |\bar{I}_j - I_{ij}| \right)}{\sum_j \left( \sum_i I_{ij} \right)},$$

where the sum over  $i$  is for a proposed individual symmetry group of reflections of intensities  $I_{ij}$  and mean intensity  $\bar{I}_j$ , and the sum over  $j$  runs over the 150 symmetry-independent groups.  $R_{\text{overall}}$  had the value 0.12 for the raw data and 0.085 for the volume-corrected intensities. This indicates a considerable overall improvement in the data, and therefore the corrected intensities were used in the refinements.

The molecular planes are necessarily aligned perpendicular to the unique axis of the structure but there are four possible relative orientations of the two species of molecule about this axis. In the possible structure in space group  $R\bar{3}m$  we choose to set the benzene molecule at the origin and the HFB at the body-centre position. The four distinct possibilities arise since an atom must lie either on a mirror plane or midway between a pair of such planes. In order to distinguish easily between various structural models in the text that follows, abbreviations are introduced where  $D$  indicates the carbon–deuterium pair in the benzene molecule and  $F$  the carbon–fluorine pair in the HFB molecule. The abbreviations used are:

- DOM only  $D$  on mirror planes
- FOM only  $F$  on mirror planes
- AOM all atoms on mirror planes
- NOM no atoms on mirror planes.

For atoms that lie on a symmetry plane in this structure there is a possibility of ‘puckering’ of the molecules as there is no crystalline hexad axis. This distortion was not finally included in the calculations but the structural models that would allow this molecular distortion, along with the relations between the fractional coordinates and the anisotropic temperature parameters, are indicated in Table 1. Also given in Table 1 for each model is an indication of the possibility of one of the molecules being displaced from its centre of symmetry, thereby reducing the space-group symmetry from  $R\bar{3}m$  to  $R3m$ .

The constraints that are used fix the molecular geometry to be planar, and to have a hexad symmetry

Table 1. *Molecular distortions and translations allowed by the various structural models cited in the text within the space groups considered in the absence of constrained hexad symmetry of the molecules*

Also given are the relationships of the fractional coordinates and anisotropic temperature parameters for atoms on (1) and midway between (2) symmetry planes.

Space group	Model	Puckering allowed in absence of hexad axis	Translation along unique axis						
$R\bar{3}m$	DOM	C–D only	Not allowed						
	FOM	C–F only							
	AOM	C–D, C–F							
	NOM	None							
$R3m$	DOM	C–D only	Allowed for all models						
	FOM	C–F only							
	AOM	C–D, C–F							
	NOM	None							
	$x_f$	$y_f$	$z_f$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{23}$	$\beta_{31}$	$\beta_{12}$
(1)	$x$	$x$	$-2x$	$A$	$A$	$C$	$D$	$D$	$E$
(2)	$x$	$-x$	$z$	$A$	$A$	$C$	$D$	$-D$	$E$

axis that is parallel to the unique axis of the structure. Hence the puckering of the molecules mentioned above is not allowed in this regime of constraints. The bond lengths are also fixed and their values are C–C = 1.38 Å following Cox, Cruickshank & Smith (1958), C–F = 1.34 Å following Boden, Davis, Stam & Wesselink (1973) and C–D = 1.08 Å. The unconstrained models retain the hexad molecular symmetry but relax the fixed bond lengths, with the exception of the C–D bond, and the initial values for these bonds in the unconstrained refinements are taken from those of the constrained results.

The refinement program is based on the familiar *ORFLS* program (Busing, Martin & Levy, 1962) but differs in that it has the facility of adding constraints in the orthogonal coordinate system (Pawley, 1972). The structure refinements were started using an overall scale factor and an overall isotropic temperature parameter, with extra isotropic thermal motion allowed for the fluorine atoms. Both the constrained and unconstrained calculations were done, where the number of parameters in these initial refinements was three and six respectively. The results are given in Tables 2 and 3, rows I. The first two columns of these tables give the model abbreviation and the  $R$  factor

$$R = \frac{\sum_j w_j |I_j^{\text{calc}} - I_j^{\text{obs}}|}{\sum_j I_j^{\text{obs}}}$$

where the  $j$  labels the intensity of the  $j$ th observed ( $I_j^{\text{obs}}$ ) and calculated ( $I_j^{\text{calc}}$ ) symmetry-independent reflection.

The weight associated with the  $j$ th reflection is  $w_j$ , and unit weights were used throughout, accentuating the importance of the weaker reflections. The function that is minimized in all refinements is

$$R_w = \sum_j w_j (I_j^{\text{calc}} - I_j^{\text{obs}})^2$$

and the value of this is given in column 3 of Tables 2 and 3. The corresponding refined parameters are given in the other columns, along with their respective standard deviations in parentheses and, where appropriate, isotropic temperature parameters are given.

Table 2. *Salient results from the constrained refinements cited in the text*

The shifts are given in Å and the mean square displacements ( $\text{TO}_{\text{C,D}}$  for carbons and deuteriums,  $\text{TO}_{\text{F}}$  for fluorines) in Å<sup>2</sup>. Rows labelled I, II, III, IV are as follows:

- I isotropic refinements in  $R\bar{3}m$ ;  
 II isotropic refinements in  $R3m$  with the shift parameter refined;  
 III anisotropic refinements in  $R\bar{3}m$ ;  
 IV as III but using the strongest 51 reflections.

Model	$R$	$R_w$ ( $\times 10^{12}$ )	$\text{TO}_{\text{C,D}}$	$\text{TO}_{\text{F}}$	Shift	
NOM	0.174	1.40	0.19 (4)	0.27 (5)	—	I
DOM	0.182	1.36	0.18 (4)	0.28 (5)	—	
AOM	0.442	5.57	0.20 (8)	0.36 (14)	—	
FOM	0.393	5.12	0.17 (7)	0.40 (15)	—	
NOM‡	0.174	1.40	0.19 (3)	0.27 (—)	0.034 (46)	II
DOM‡	0.179	1.32	0.18 (3)	0.28 (—)	0.096 (22)	
AOM*	0.443	5.51	0.18 (7)	0.35 (—)	0.155 (32)	
FOM*	0.397	4.88	0.16 (6)	0.38 (—)	0.215 (21)	
NOM	0.184	0.684	—	—	—	III
DOM†	0.167	0.676	—	—	—	
NOM	0.160	0.628	—	—	—	IV
DOM	0.138	0.624	—	—	—	

\* These refinements had an initial shift of 0.01 Å.

† A full parameter set is given in Table 4.

‡ These refinements had an initial shift of ~1.02 Å.

The above refinements have been done for the space group  $R\bar{3}m$ , the highest symmetry consistent with the data. However, the other possibility,  $R3m$ , must also be considered. In order to reduce the symmetry we must introduce a further parameter into the refinement in the form of a shift of one of the molecules, chosen arbitrarily to be the HFB, along the unique axis of the unit cell. This corresponds to a dimerization of the molecules and we call this the shift parameter, the variation of which alters the separation of the molecules along the unique axis.

Refinements involving the shift parameter showed unacceptable correlation between this parameter and the extra thermal motion of the fluorine atoms, and therefore the latter was held fixed in these refinements. It was necessary to start refinement with a non-zero shift parameter value of arbitrary sign, and several such starting values were tried with the initial values of the other parameters the same for each refinement. Results from constrained and unconstrained refinements are given in Tables 2 and 3, rows II, but as the unconstrained refinements of models AOM and FOM were unstable their results are omitted. Results for DOM and NOM are illustrated in Fig. 1(a) and (b) respectively. Each figure shows the results of refinements with ten different fixed shift parameters and then (inset) the results of these ten refinements as the shift parameter is allowed to vary. For DOM these refinements converge to give a shift parameter of  $0.092 \pm 0.002$  Å whereas for NOM the spread of the results is inconclusive. The possible significance of this result is discussed in the next section.

We now introduce anisotropic temperature parameters,  $\beta_{ij}$ , for NOM and DOM, as defined in Table 4 (*International Tables for X-ray Crystallography*, 1974). Improvement is expected as the  $R$  factors achieved so far are considerably greater than the value 0.055, the consistency factor obtained

Table 3. *Salient results from the unconstrained refinements cited in the text*

All bonds and the shift parameter are given in Å and the mean square displacements (isotropic  $\text{TO}_{\text{C,D}}$  for the carbons and deuteriums, isotropic  $\text{TO}_{\text{F}}$  for the fluorines) are given in Å<sup>2</sup>. Rows labelled I, II, III, IV are as in Table 2.

Rows labelled I, II, III, IV are as in Table 2.

Model	$R$	$R_w$ ( $\times 10^{12}$ )	(HFB) C—C	C—C	C—F	$\text{TO}_{\text{C,D}}$	$\text{TO}_{\text{F}}$	Shift	
NOM	0.134	0.611	1.20 (4)	1.33 (3)	1.35 (3)	0.19 (3)	0.23 (3)	—	I
DOM	0.133	0.643	1.21 (3)	1.34 (3)	1.33 (3)	0.18 (3)	0.24 (4)	—	
NOM*	0.135	0.614	1.21 (5)	1.33 (4)	1.34 (4)	0.19 (2)	0.23 (—)	0.015 (22)	II
DOM*	0.133	0.643	1.21 (4)	1.34 (4)	1.32 (4)	0.18 (3)	0.23 (—)	0.015 (32)	
NOM	0.098	0.154	1.20 (3)	1.38 (3)	1.33 (3)	—	—	—	III
DOM	0.104	0.159	1.16 (3)	1.31 (4)	1.42 (3)	—	—	—	
NOM	0.080	0.137	1.19 (5)	1.39 (6)	1.31 (5)	—	—	—	IV

\* These refinements had an initial shift of ~1.02 Å.

when averaging the symmetry-related intensities. The correlation between these new parameters and the shift parameter causes ill-conditioning; therefore these refinements were restricted to the space group  $R\bar{3}m$ . Some of the  $\beta_{ij}$ 's for different atoms were found to be highly correlated and were therefore removed from the variable list. Thus, in the case of constraints, of the 13 possible parameters only 12 for DOM and NOM were

varied, whereas, in the unconstrained case, of the 16 possible parameters only 13 for NOM and 14 for DOM were varied. Where a parameter is held fixed, the tabulated standard deviation is left blank. These results are given in Tables 2 and 3 in rows III. From these tables it is seen that the constrained and unconstrained 'best fits' occur for different structural models. The value of  $R_w$  is least for constrained model DOM, whereas it is least for unconstrained model NOM. The final  $R$  factor for the constrained and unconstrained cases are 0.167 and 0.098 respectively and the final parameter set values are given for the constrained model DOM in Table 4, with standard deviations where applicable. The  $R$  factor was further reduced to 0.138 and 0.080, for the respective constrained and unconstrained refinements, by repeating the above anisotropic thermal parameter calculation but using a reduced data set consisting of the strongest 51 reflections whose intensities exceeded 4000 counts. The unconstrained-refinement  $R$  factor of 0.080 is consistent with the expected limit set by the previously calculated internal consistency factor. No further reduction of the  $R$  factor is expected and the results of these refinements are given in the final rows (IV) in Tables 2 and 3.

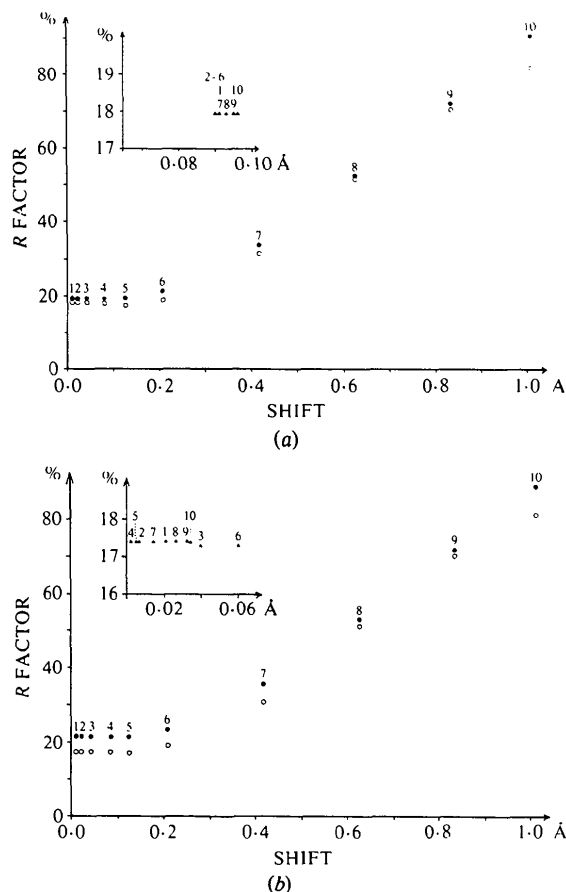


Fig. 1. Plots for constrained models (a) DOM and (b) NOM showing the variation of: (i) initial  $R$  factor against initial shift (●); (ii) final  $R$  factor against the initial shift when all parameters except the shift are refined (○). The inset shows the variation of the final  $R$  against the refined shift, when all parameters are refined (▲).  $R$  factors are given in % and shifts in Å.

## Discussion

The isotropic refinements give values of the temperature parameters that are large, especially for the C-F pair in HFB. This is in accord with the observation of Ripmeester *et al.* (1978) that the HFB molecule is to some extent dynamically disordered in the temperature range 100 to 300 K. Large-amplitude thermal motion and disorder would both give rise to diffuse scattering such as we have observed with this system. In accordance with this result the anisotropic temperature parameters show large values, with the largest ( $1.1 \text{ \AA}^2$ ) exceeding the largest found in benzene ( $0.09 \text{ \AA}^2$ ) by Cox, Cruickshank & Smith (1958).

Although an acceptable  $R$  factor is achieved with certain unconstrained refinements, in all such cases the

Table 4. Full parameter set for the anisotropic constrained refinements of the DOM model

The temperature parameters,  $\beta_{ij}$ , are defined by  $\exp[-(\beta_{ij} h_i h_j)]$ ,  $i, j = 1, 2, 3$ , using the summation convention. All coordinates and bond lengths are in orthogonal Å, temperature parameters (*i.e.* mean square displacements) in Å<sup>2</sup>.

	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{23}$	$\beta_{31}$	$\beta_{12}$
C	0.5636	0.5636	-1.1272	0.232 (95)	0.232 (95)	0.445 (153)	-0.041 (55)	-0.041 (55)	-0.025 (69)
D	1.0048	1.0048	-2.0096	0.232 (95)	0.232 (95)	0.445 (153)	-0.041 (55)	-0.041 (55)	-0.025 (69)
C	1.1149	3.0651	2.0900	1.092 (280)	1.092 (280)	0.588 (223)	-0.182 (-)	0.182 (-)	0.417 (185)
F	0.1705	4.0095	2.0900	0.487 (57)	0.487 (57)	0.211 (33)	0.018 (58)	-0.018 (58)	-0.327 (25)

C—C bond length refined to the chemically unacceptable value of 1.2 Å. Thus we must deduce that the presence of disorder, which can take many forms, is the reason for our inability to achieve a chemically and statistically acceptable result. The presence of disorder is consistent with the fact that the system under study is the highest-temperature solid phase of a rather complex system. A crystallographic proof of the existence of other solid phases is given in Fig. 2 — a collection of three neutron powder diffraction scans. The first of these is a calculated profile using the structural parameters reported here (280 K) and the other two are the observed data, as yet unsolved, taken at 250 K (warming sequence) and 5 K. We believe the structure at 250 K to be monoclinic.

In view of the problems just outlined it is impossible for us to make any firm conclusion as to whether the structure is DOM or NOM, or whether the DOM structure favours the non-centrosymmetric  $R3m$ . Our result for this last possibility however gives a clear value for a maximum possible shift parameter of about 0.2 Å and a best estimate of 0.092 (2) Å. The best estimate leads to a molecular pairing with a separation of 3.52 Å, with dimers separated by 3.71 Å. Such a pairing is more likely to be stable in the lower phases, and would be consistent with the work of Dahl (1971, 1972, 1973) where forces stronger than van der Waals have been shown to exist in some HFB complexes.

The main difference between models DOM and NOM is that in the former the molecules are eclipsed as viewed down the unique axis, whereas in the latter the molecules are staggered. Part of the rhombohedral structure DOM is shown in Fig. 3 where the nearest-neighbour interstack  $F \cdots D$  separations given have been calculated for a shift parameter of 0.1 Å. These intermolecular separations are somewhat larger than

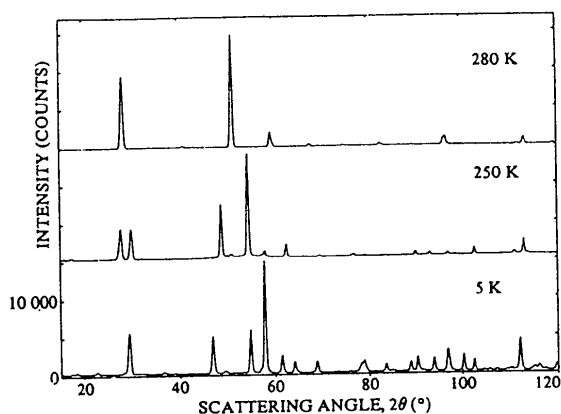


Fig. 2. Neutron powder diffraction profiles of this system at temperatures of 280 K (calculated), 250 K (observed) and 5 K (observed). The range of scattering angle is 25 to  $\sim 129^\circ$  for a wavelength of 2.98 Å.

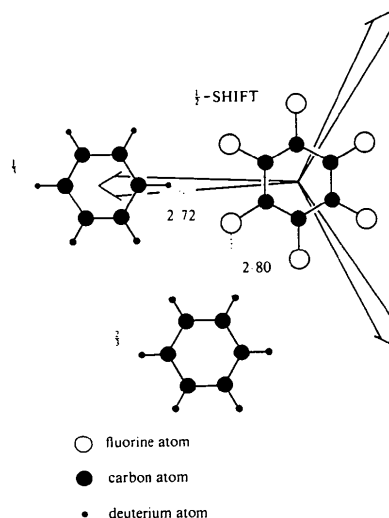


Fig. 3. Projection of part of the structure in space group  $R3m$ , along the unique axis. Heights of molecules are given in fractions of the body diagonal. The symmetry planes are vertical and coincident with the rhombohedral axes shown. Some separations are also shown (in Å).

Table 5. Intermolecular distances for models NOM and DOM with a shift of 0.10 Å

Van der Waals radii and separations are also shown. All values are in Å.

Van der Waals radii		Van der Waals separations	
C	1.55	C—F	2.90
F	1.35	F—D	2.55
D	1.20	C—D	2.75

Observed separations						
Model		Shift	C—C	C—F	F—D	C—D
NOM	Intra-stack	0	3.62	3.86	3.63	3.78
NOM	Inter-stack	0	—	—	2.69	—
DOM	Intra-stack	0	3.69	3.99	3.87	3.90
DOM	Intra-stack	0.10	3.60	3.91	3.78	3.81
DOM	Inter-stack	0	—	—	2.76	—
DOM	Inter-stack	0.10	—	—	2.72	—

those expected from van der Waals radii estimates (see Table 5), suggesting that dynamic disorder is dilating the structure. This is supported by the fact that the unit-cell volume, 299 (5) Å<sup>3</sup>, is about 13% larger than that given by the sum of two molecular volumes from the separate structures.

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## Struktur von *cis*-1,2,4,5-Tetramethyl-3,6-diphenoxy-1,2,4,5-tetraaza-3,6-diphosphacyclohexan-3,6-disulfid

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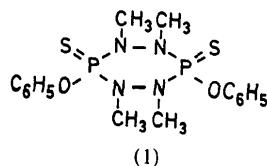
### Abstract

$C_{16}H_{22}N_4O_2P_2S_2$  is orthorhombic, *Pbca*, with  $a = 15.655$  (2),  $b = 30.984$  (2),  $c = 8.780$  (2) Å,  $V = 4253.8$  (5) Å<sup>3</sup>,  $Z = 8$ ,  $D_c = 1.338$  Mg m<sup>-3</sup>. The structure was solved by direct methods and refined to  $R = 0.047$  ( $R_w = 0.045$ ) for 2484 contributing reflections. The heterocycle has a twist conformation; the PNN angles range from 113.7 (3) to 115.1 (4)°, and the NPN angles are 99.6 (2) and 100.7 (2)°. Mean bond distances: P–N 1.655 (6), N–N 1.413 (2), P–S 1.910 (3), P–O 1.595 (1), O–C 1.410 (3) Å.

### Einleitung

Bei der Fortsetzung der Arbeiten über anorganische Phosphor-Stickstoff-Ringverbindungen (z.B.: Engelhardt & Jürgens, 1980) ist es jetzt erstmals

gelungen, 1,2,4,5-Tetramethyl-3,6-diphenoxy-1,2,4,5-tetraaza-3,6-diphosphacyclohexan-3,6-disulfid (1) in grösseren Ausbeuten herzustellen (Bünger, Merrem & Engelhardt, 1982).



Dabei kristallisierte (1) in zwei verschiedenen Kristallformen, bei denen die aufgenommenen NMR-Daten die Vermutung nahelegen, dass es sich um das *cis*- bzw. *trans*-Isomere von (1) handelt. Da sich bei Untersuchung des nichtmethylierten Analogens von (1) (Engelhardt & Hartl, 1975*a,b*, 1976) gezeigt hatte, dass das *cis*-Isomere in der für gesättigte Sechsringe un-