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The High-Temperature Phase of 1,2,4,5-Tetrafluoro-3,6-diiodobenzene and the Phase Transition

By S. L. Chaplot,* G. J. McIntyre,† A. Mierzejewski‡ and G. S. Pawley

Department of Physics, University of Edinburgh, The King's Buildings, Mayfield Road, Edinburgh EH9 3JZ, Scotland

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Abstract

The crystal structure of the high-temperature phase (II) of the title compound, $C_6F_4I_2$, has been determined by single-crystal X-ray diffraction. The crystal was grown in a thin capillary tube and then supercooled to room temperature. The space group $P2_1/c$ is the same as in the lower-temperature phase (I). The unit cell is a = 8·026 (4), b = 6·069 (4), c = 9·239 (4) Å and β = 100·27 (5)°, which has 2·4% more volume than that of phase (I). The structure was solved and refined using a constrained-refinement technique, where an R factor of 5·4% was reached on refinement with 813 structure factors. No significant molecular distortion from the free molecular geometry of *mmm*, and no appreciable internal vibrations of the molecule could be detected. The low-temperature phase is characterized by an increase in the intermolecular distances involving the iodine atoms, and the phase transition involves relative movement in which one molecule moves 3·7 Å in its plane with very little reorientation.

Introduction

The structure of 1,2,4,5-tetrafluoro-3,6-diiodobenzene undergoes a solid-state phase transition on warming at 358 K, melting at 380 K (Pawley, Mackenzie & Dietrich, 1977). These temperatures were found by differential thermal analysis on a polycrystalline sample of about 10 mg. When this same sample was cooled from the melt, no transition was observable down to 150 K. However, when a larger sample obtained from the melt was ground in a mortar at room temperature, it gave a diffraction pattern for the lower-temperature phase, phase (I).

The present work is an analysis of the structure in the higher-temperature phase, phase (II), followed by a comparison of the two structures.

Experimental

It was decided that the crystal, when grown in the upper phase, should not be handled in any way before making measurements, in the hope that these measurements could be made at room temperature. The sample crystal was therefore grown in phase (II) inside a thin glass capillary tube. The sample tube was mounted on an arm which was slowly moved through a small loop of heating wire in which the heating current was adjusted just to melt a very small length of sample in the tube. After a few trials of 'zone refinement' a long crystal of sufficient quality was obtained, as judged with a polarizing microscope.

The first attempts were made using a capillary of diameter 0·3 mm, but that crystal shattered on cooling to room temperature. This could have been either due to the transition or due to excessively rapid cooling; tests on larger crystals have not yet been made. A later crystal grown in a tube of diameter 0·1 mm remained single at room temperature during the two weeks of the X-ray diffraction study.

The Bragg intensities were measured on an Enraf–Nonius CAD-4 four-circle X-ray diffractometer in the ω–2θ mode. Mo $K\alpha$ radiation was used with a graphite (002) monochromator. The primitive unit-cell dimensions were refined from measurements on 15 independent Bragg reflections and found to be monoclinic (see *Abstract*). Nearly 4000 reflections were then measured over a period of eight days. The measurements of individual intensities were so timed that they all had nearly the same estimated relative error from counting

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* On leave from Nuclear Physics Division, Bhabha Atomic Research Centre, Bombay 400085, India (now returned).

† Present address: Institute of Chemistry, University of Uppsala, Box 531 S751 21, Sweden.

‡ On leave from Department of Organic and Physical Chemistry, Technical University, Wrocław, Poland (now returned).

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statistics. A control reflection was also measured at nearly regular intervals of about 100 min. No significant time variation in the intensity of the control reflection was found.

Structure determination and results

The primitive unit-cell volume of 443 Å^3 suggested that the cell should contain two molecules. From the systematic absences of the reflections $0k0$, k odd and $h0l$, l odd, the space group was deduced to be $P2_1/c$, with molecules on centres of symmetry. This is the same as in phase (I), where, however, the primitive cell dimensions are quite different. The symmetry-equivalent reflections were found to be very different in intensity since many reflections suffered appreciable absorption due to the long cylindrical shape of the crystal and the presence of iodine in the molecule. It was decided that only the most intense reflections from each set of equivalent reflections be selected for further analysis, thus rejecting those with high absorption. A total of 813 structure amplitudes was thus obtained. These values have been deposited,* but no errors have been included because it was found in refinement that unit weights did not give a significantly different result as compared with results using weights derived from counting statistics.

To solve the structure a simple model was built using the assumed geometry of the molecule with *mmm* symmetry as shown in Fig. 1. The molecule is oriented in the crystal, the orientation matrix being determined by three Euler angles (φ, θ, ψ) as defined by Goldstein (1959) and used by Pawley (1972). A constrained refinement was then attempted on a few low-angle Bragg reflections with only the Euler angles and the scale factor as variables. After several unsuccessful attempts with refinement using the 11 lowest-order reflections, one with the 28 lowest orders converged to an R factor of 16%.

From this point refinement with the whole data set converged rapidly. A one-parameter extinction correction was now included, following Zachariasen (1967) in which the calculated structure factor is multiplied by a factor equal to $[(1 + x^2)^{\frac{1}{2}} - x]^{\frac{1}{2}}$, where $x = c(F_l^{\text{obs}})^2 \times \operatorname{cosec}2\theta_{\text{Bragg}}$, c being the extinction parameter. In all the refinements, the atomic scattering factors given in *International Tables for X-ray Crystallography* (1968) were used.

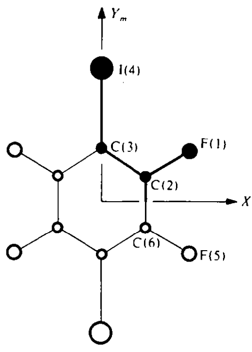

Fig. 1. The molecule of $C_6F_4I_2$, in the molecular coordinate system X_m, Y_m ($Z_m = 0$). Full *mmm* symmetry is assumed, the heavy part of the diagram indicating the molecular asymmetric unit.

Table 1. *Results of the constrained refinement of* $C_6F_4I_2$, *phase* (II)

Crystal coordinates are in Å, with $X \parallel x$, $Y \parallel y$ and $Z \parallel z^*$.

Euler angles (°) and matrix **B**

φ	24·8 (2)
θ	−33·4 (1)
ψ	22·9 (2)

$$\mathbf{B} = \begin{pmatrix} 0{\cdot}7004 & 0{\cdot}6810 & -0{\cdot}2138 \\ 0{\cdot}6754 & 0{\cdot}5354 & -0{\cdot}5072 \\ -0{\cdot}2309 & 0{\cdot}4996 & 0{\cdot}8349 \end{pmatrix}$$

Positional coordinates (Å)

	X_m	Y_m
F(1)	2·357 (4)	1·337 (4)
C(2)	1·175 (6)	0·682 (6)
C(3)	0	1·397 (9)
I(4)	0	3·472 (1)

Mean-square translational tensor

$$\mathbf{T}\ (10^{-3}\ \text{Å}^2) = \begin{pmatrix} 12\ (1) & 4\ (1) & 3\ (1) \\ & 28\ (2) & 1\ (2) \\ \text{sym.} & & 24\ (3) \end{pmatrix}$$

Mean-square librational tensor

$$\mathbf{L}\ (\text{deg}^2) = \begin{pmatrix} 29\ (2) & 7\ (1) & 8\ (1) \\ & 14\ (2) & 4\ (1) \\ \text{sym.} & & 13\ (1) \end{pmatrix}$$

Extinction parameter: $c = 1{\cdot}4\ (1) \times 10^{-6}$
Scale factor: 2·757 (23)

Crystal coordinates (Å) from X_m, Y_m above

	X_o	Y_o	Z_o
F(1)	2·561	−0·876	0·124
C(2)	1·288	−0·429	0·069
C(3)	0·951	0·748	0·698
I(4)	2·364	1·859	1·734
F(5)	0·740	−2·308	−1·212
C(6)	0·359	−1·159	−0·612

Bond lengths (Å) corrected for libration ($\sigma = 0{\cdot}009$ Å)

C(2)–C(3)	1·384	C(2)–F(1)	1·360
C(2)–C(6)	1·372	C(3)–I(4)	2·089

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36233 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The constrained refinement included symmetry constraints on the molecule, allowing the shape of the molecule to vary but restricting its symmetry to *mmm*. Such a constraint involves six parameters to define the molecule, and the best set of values found for these is given in Table 1. The atomic positions are presented in the orthogonal ångström system (X,Y,Z), as used in the constrained refinement, with $X \parallel x$, $Y \parallel y$ and $Z \parallel z^*$. Anisotropic temperature parameters were also included in the refinement, these being constrained to obey the rigid-body model for molecular motion. Thus 36 thermal parameters are determined by the 12 independent components of the rigid-body translational and librational tensors **T** and **L**. The best values for **T** and **L** are given in Table 1. No contribution from internal-mode motion was included at this stage.

This refinement achieved a conventional R factor of 5·4%, where $R(\%) = 100 \sum_i |F_i^{\rm calc} - F_i^{\rm obs}|/\sum_i|F_i^{\rm obs}|$. This was considered to be a very satisfactory result, in view of the difficulties encountered in getting accurate data, but, nevertheless, a fully unconstrained refinement was performed in order to test the validity of the constraints.

Unconstrained refinement gave an R factor of 5·3%, and the significance of this improvement was tested following Hamilton (1965). For this the ratio $R_{w(c/u)} = R_w(\text{constrained})/R_w(\text{unconstrained})$ is calculated, where the residual is given by $R_w^2 = \sum_i w_i(F_i^{\rm calc} - F_i^{\rm obs})^2/\sum_i w_i(F_i^{\rm obs})^2$, whereupon the constrained refinement is considered significantly inferior if $R_{w(c/u)}$ exceeds the value of

$$S_{(c/u)} = \left[1 + \frac{N-n}{M-N} F_{(n-n,\,M-N)}\right]^{1/2}$$

at a chosen level of the F distribution, $F_{(N-n,\,M-N)}$. We use a 99% confidence level here. M is the number of observations used in the refinement, and n and N are, respectively, the number of parameters in the constrained and in the unconstrained refinement.

Table 2 shows that the constrained refinement is not significantly poorer than the unconstrained one; thus no significant distortions from the *mmm* symmetry are detected, nor are any significant internal vibrations in the molecule. We therefore report in Table 1 only the result of the constrained refinement which is statistically more acceptable since it is based on much fewer parameters. Included in Table 1 are bond lengths corrected for the librational or riding-motion effect. The **T** and **L** tensors are expressed in the orthogonal crystal coordinate system, defined to have X_o, Y_o and Z_o along the crystallographic **a**, **b** and **c*** directions. The transformation matrix **B** is given in Table 1, where the coordinates of an atom in the molecular Cartesian system X_m are related to the orthogonal coordinates X_o by $X_o = \mathbf{B}\,X_m$.

Table 2. *Residuals for the constrained and the unconstrained refinement, all using* M = 813 *structure factors*

Atomic positions	Thermal parameters	Number of variables	R (%)	R_w	$R_{w(c/u)}$	$S_{(c/u)}$
mmm	**T, L**	23	5·4	0·060	1·03	1·04
Unconstrained		56	5·3	0·058		

The transition

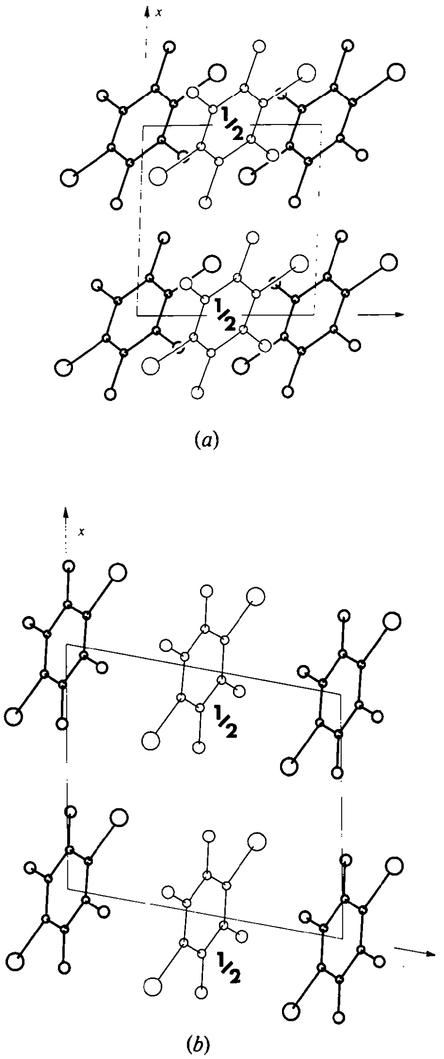
An unusual aspect of the transition in $C_6F_4I_2$ is that there is no change in the crystal symmetry. The structure in phase (I) has the space group $P2_1/a$ with unit cell (Pawley, Mackenzie & Dietrich, 1977) a = 6·268 (3), b = 11·639 (5), c = 5·929 (2) Å, β = 92·70 (3)°. As this unit cell was measured at room temperature it is valid to compare its volume, 432·1 Å^3, with the volume of the phase (II) cell, 442·8 Å^3, showing a contraction of 2·4% on undergoing the phase change. A survey of the shortest intermolecular distances is presented in Table 3 for both phases. In phase (I), the stable phase of low temperatures, it is seen that the distances involving the iodine atoms are all *increased*, and this may well be of great importance for the transition.

At first sight there would seem to be no relationship between the two unit cells as the axes have quite different values, except that the phase (II) unique axis is approximately equal to either of the phase (I) non-unique axes. However, a detailed comparison of the actual structures suggests that there may be a fundamental relationship between them. To make this comparison clearer we redefine the unit cell of phase (I) by taking the monoclinic angle as 87·30°, whereupon the new positive z axis is in the direction of the old negative z axis.

Fig. 2 shows the two structures projected down the positive y axes, and, although the cells are quite different, the projected shape of the molecules is very similar indeed. The similarities between the projections down the x axes and the z^* axes are equally striking, showing that the molecules only differ in orientation by small angles; these comparisons are made in Fig. 3.

Table 3. *Minimum intermolecular distances* (Å, $\sigma \sim$ 0·01 Å)

	C–C	C–F	C–I	F–F	F–I	I–I
Phase (I)	3·98	3·09	3·82	2·82	3·69	4·12
Phase (II)	4·40	3·19	3·81	3·40	3·53	4·06



(a)

(b)

Fig. 2. The structures of $C_6F_4I_2$ projected down the unique y axes: (a) phase (I), (b) phase (II). The molecules in light outline are positioned with their centres at a height $y = b/2$.

The relationship is further emphasised by Fig. 4. In this diagram the outlines of half of each of the projected unit cells of Fig. 2 are superimposed, the outlines being halved in the z directions, the directions of the glide planes. Superimposition is made in such a way that the upper left molecules of Fig. 2(a,b) coincide as closely as possible. These molecules are omitted from the diagram, as are all others, except those related to the initially superimposed pair by the respective screw axes. In this construction the two molecules drawn in Fig. 4 are almost coplanar. If the phase (II) molecule is moved by the translation vector $\mathbf{t} = (1\cdot8, 2\cdot8, -1\cdot7)$ Å – expressed in phase (II) orthogonal coordinates – it moves $3\cdot7$ Å in its molecular plane and almost coincides with the phase (I) molecule.

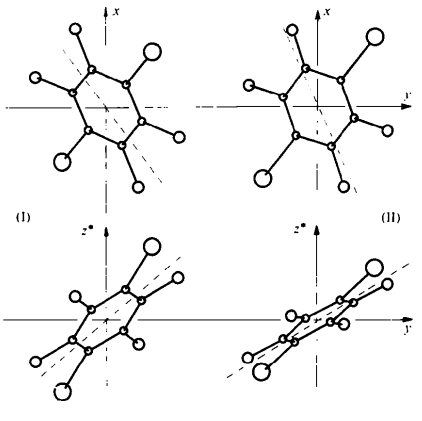


Fig. 3. Projections of the molecules down the z^* and x axes – top and bottom respectively. Projections on the left are for phase (I), on the right for phase (II). The dashed line indicates where the molecule coincides with the plane of projection in each case.

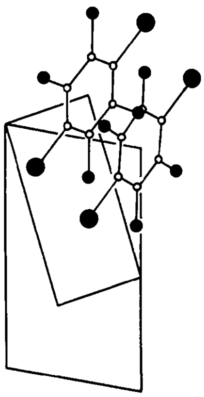


Fig. 4. The half cells of Fig. 2 ($a \times \frac{1}{2}c$) superimposed causing the top left molecules to coincide. Only the top middle molecules from Fig. 2 are reproduced, and they are nearly coplanar.

The aim of this study is thus achieved as a clear relationship is established between the two phases of $C_6F_4I_2$. In either structure we may expect to find a translational mode of vibration with eigenvector $\mathbf{t}$ associated with the transition. It would indeed be interesting to find this behaviour using the technique of coherent inelastic neutron scattering, but it may well be hard to detect as the transition is so clearly of the first order.

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Structure of Mercury(II) Hydrogenphosphate

BY ERICH DUBLER, LUCAS BECK, LOTHAR LINOWSKY AND GEOFFREY B. JAMESON

Anorganisch-chemisches Institut der Universität Zürich, Winterthurerstrasse 190, 8057 *Zürich, Switzerland*

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Abstract. Synthetic $HgHPO_4$, M_r = 296·6, triclinic, $P\bar{1}$, a = 6·288 (2), b = 7·309 (2), c = 7·276 (2) Å, α = 79·37 (2), β = 85·27 (2), γ = 82·85 (2)°, V = 325·5 Å^3, Z = 4, D_x = 6·06 Mg m^{-3}, μ(Mo $K\alpha$) = 47·65 mm^{-1}. The structure was solved by Patterson methods and refined to R = 0·041 and R_w = 0·042 for 1983 reflections having $I > 3\sigma(I)$ in the range 0·40 < $(\sin\theta)/\lambda$ < 0·81 Å^{-1}. The phosphate tetrahedra are linked in infinite chains by very strong hydrogen bonding. Each phosphate group participates in two hydrogen bonds. Two hydrogen bonds with O···O distances of 2·454 (12) and 2·518 (14) Å involve O atoms which are centrosymmetrically related, whereas the third hydrogen bond with an O···O distance of 2·495 (12) Å includes no centre of symmetry. The two independent Hg atoms have 2 + 4 and 2 + 5 coordination polyhedra. The pairs of short Hg—O bonds are approximately *trans* and average 2·07 Å.

Introduction. No definite synthesis or characterization of $HgHPO_4$ has been described in the literature so far. The compound precipitating under experimental conditions given by Klement & Haselbeck (1964) and identified as $HgHPO_4$ is claimed to be a mixture of $Hg_3(PO_4)_2$ and $Hg_2(H_2PO_4)_2$ (Nilsson, 1975). The analogous lead compounds, $PbHPO_4$ and its deuterated isomorph $PbDPO_4$, have recently been shown to be ferroelectric (Negran, Glass, Brickenkamp, Rosenstein, Osterheld & Susott, 1974). The ferroelectric transition mechanism in $PbHPO_4$ and related compounds appears to involve ordering of H atoms in strong O—H···O bonds. Since $HgHPO_4$ may show ferroelectric properties similar to $PbHPO_4$ and with a view to establishing its hydrogen-bonding system we have grown single crystals of $HgHPO_4$ and determined its crystal structure.

Colourless crystals were obtained from a solution of 10 g $Hg_3(PO_4)_2$ in 100 g 99% H_3PO_4 at 353 K. Chemical analysis and thermogravimetric measurements of the weight loss due to the liberation of water at about 413 K are in agreement with the composition $HgHPO_4$. The crystal selected for data collection was a parallelepiped with bounding planes (100), (001) and (010) and 0·18 × 0·16 × 0·14 mm in size. It was mounted such that the spindle axis was approximately parallel to **a***. A total of 4247 reflections in the range 0·0492 < $(\sin\theta)/\lambda$ < 0·8087 Å^{-1} were measured by the θ–2θ scan technique at 295 K on a Picker FACS-I diffractometer with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·7107 Å) at a take-off angle of 1·9°. A basic scan range of 1·8° (with allowance for α_1, α_2 dispersion) was used. A scan speed of 2·0° min^{-1} in 2θ with background measurements of 10 s at each end of the scan range was initially employed. For $(\sin\theta)/\lambda$ > 0·618 Å^{-1} the scan speed was 1·0° min^{-1} and background measurements were 20 s. Crystal orientation and unit-cell dimensions were determined by least-squares refinement of the setting angles of 12 automatically centred reflections in the range 0·483 < $(\sin\theta)/\lambda$ < 0·590 Å^{-1}. The intensities of three regularly monitored reflections showed no significant variation during data collection. After correction for absorption

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