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Structure of 1,3,5-Trichloro-2,4,6-trifluorobenzene

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Abstract

The crystal structure of the symmetric 1,3,5-trichloro-2,4,6-trifluorobenzene, $C_6Cl_3F_3$, was determined at room temperature by single-crystal X-ray diffraction and at 4·2 K by neutron powder diffraction. The space group is $P6_3/m$ with a hexagonal primitive cell of dimensions $a = b = 8{\cdot}541$ (3) and $c = 6{\cdot}282$ (2) Å [which become $a = b = 8{\cdot}441$ (2) and $c = 6{\cdot}052$ (2) Å at 4·2 K], $V = 397$ Å^3 and $Z = 2$. The cell contains two planar molecules at $\bar{6}$ (2*d*) sites. The single-crystal *R* factor of 3·9% was reached with unconstrained refinement on 401 symmetry-independent Bragg intensities. The structure was solved using constrained refinement on the molecular orientation. Constrained refinement on the thermal parameters has indicated significant internal vibrations in the molecule. The low-temperature study showed there to be no phase transition when the powder is cooled.

Introduction

The structure determination of *sym*-$C_6Cl_3F_3$ was undertaken as part of a project to study the effect of intermolecular forces in systems comprising rigid molecules. In this paper we present the evidence for molecular distortion due to these forces, and show that the internal molecular vibrations contribute significantly to the thermal motion as evidenced through structural studies. A detailed study of the lattice vibrations is planned, for which a large single crystal has been prepared suitable for inelastic coherent neutron scattering measurements.

The similarity of the molecular shape of *sym*-$C_6Cl_3F_3$ with that of *sym*-triazine suggests that the possibility of a phase transition should not be overlooked. Preliminary measurements by Raman scattering and also measurements reported here of powder neutron diffraction at helium temperatures, however, give no indication of a transition. The structure found for *sym*-$C_6Cl_3F_3$ is different from either phase of *sym*-triazine (Smith & Rae, 1978), although there are close similarities with the upper phase of *sym*-triazine in that some of the trigonal molecular symmetry is retained in the crystal structure.

Experimental

A commercial sample of $C_6Cl_3F_3$ was first purified by zone refining. Since the solid, which melts at about 330 K, sublimes very quickly in open conditions, it was necessary to grow a crystal for the X-ray diffraction in confined conditions. The crystal was grown in a thin Lindemann-glass capillary tube of 0·5 mm diameter. The tube containing the sample was slowly moved through a small loop of heating wire in which the heating current was adjusted so as to melt a very small length of sample in the tube. When a long crystal was obtained of sufficient quality as could be judged with a polarizing microscope, material was allowed to sublime from both ends until a suitable small length of about 0·5 mm remained. The capillary tube and the heating loop were enclosed in a small transparent cover to reduce air convection currents and also to slow the sublimation process. The tube was actually mounted on a moving arm which facilitated the slow movement of the tube through the fixed heating loop. The tube containing the finished sample was sealed at both ends, but some material was left in the tube at a safe distance from the crystal. In the course of the experiment the trapped residue of material sublimed through imperfections in the seals, and in this way gave protection to the sample proper.

The measurements of Bragg intensities were made 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-cell dimensions were refined from measurements on 25 independent Bragg reflections. Then nearly 4000 reflections were measured in three zones of reciprocal space. The measurements of individual intensities were so timed that they all had about the same estimated

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relative error, a weaker reflection being measured for a longer time than a stronger one. Four different control reflections were monitored at regular intervals of 30 minutes.

The intensities of the control reflections were observed to decrease with time. This variation was due to the slow sublimation of the sample and extra material, and was analysed following the method recommended by McCandlish, Stout & Andrews (1975) and described by Lundgren & Liminga (1979). Variation occurred in two main phases, the first ending after 124 h at which time the extra material had fully sublimed. The time-dependent scale factor deduced by this method was used as a correction, but no absorption correction was applied owing to the low coefficient of absorption for the sample material and to the nearly spherical shape of the sample, it being a cylinder with its length similar to its diameter.

From the unit-cell volume it was deduced that one cell should contain two molecules and then from the systematic absence of the reflections 00*l*, *l* odd, the space group was deduced to be $P6_3/m$ with both molecules at sites of $\bar{6}$ symmetry, 2(*a*) or 2(*d*) in Wyckoff's notation. Using this information, the symmetry-equivalent reflections were averaged in intensity. It was found that the reflections contributing to an average were of nearly equal intensity, thus confirming the assignment of the space group and the site symmetry. An internal consistency check on these averages indicated a standard deviation of 3·7% for an individual intensity about its mean, giving an e.s.d. for each mean value of roughly 1·5%. This should be compared with 2·9% expected from counting statistics alone.

A final total of 407 symmetry-independent Bragg intensities were obtained from which the six strongest reflections were excluded from the refinement.* The weights used were $w_i = 1/\sigma_i^2$, where σ_i is the estimated standard error in the *i*th intensity based on counting statistics, internal symmetry consistency and the error in determining the time variation.

A one-parameter extinction correction was used, following Zachariasen (1967) in which the calculated intensity was multiplied by a factor equal to $[(1+x)^{1/2} - x]$, where $x = c(F_i^{\text{obs}})^2 \operatorname{cosec} 2\theta_{\text{Bragg}}$, c being the extinction parameter.

Structure determination and results

The space group of $P6_3/m$ and the $\bar{6}$ site symmetry for the two molecules suggested the positions of the molecules at sites 2(*a*) or 2(*d*) in Wyckoff's notation. Although packing considerations favoured 2(*d*), both were tried in constrained refinements using only 32 of the lowest-order reflections. The molecular shape as shown in Fig. 1 was assumed. Since the site symmetry of the molecule is $\bar{6}$, only the atoms labelled in the figure are in the asymmetric unit. An idealized geometry for the molecule is thus taken for the constrained refinement in which the C—F and C—Cl bonds are assumed to be arranged radially and the benzene ring is a perfect hexagon. The constrained molecule is therefore completely characterized by three parameters, namely the bond lengths r_{C} (= C—C), r_{F} (= C—F), r_{Cl} (= C—Cl), and is oriented in the crystal by a rotation through θ about the axis perpendicular to the molecular plane. This axis is the crystallographic *c* axis, and for convenience an orthogonal Å coordinate system is used throughout the refinement in which the *X* axis is parallel to **a**. The orientation shown in Fig. 1 is in fact the final refined orientation. Initially r_{C}, r_{F} and r_{Cl} were respectively taken to be 1·4, 1·3 and 1·7 Å,

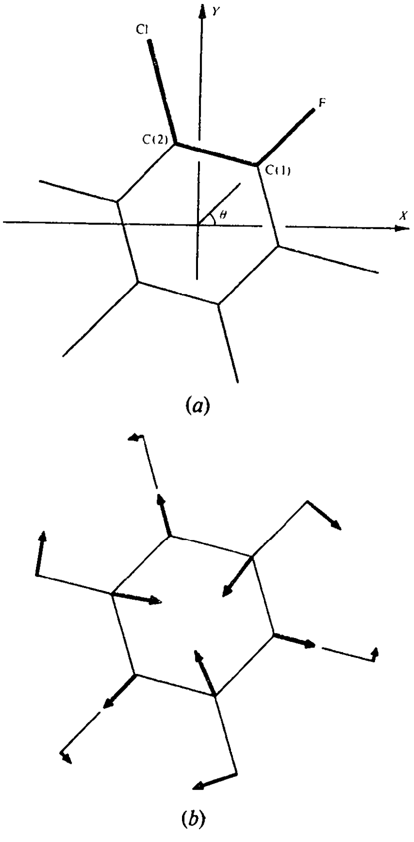

Fig. 1. (*a*) An idealized geometry for the *sym*-$C_6Cl_3F_3$ molecule as used in refinement I (see Table 1). *X* and *Y* are parallel and perpendicular to the crystallographic *a* axis, and are both perpendicular to the crystallographic *c* axis. θ is the only molecular orientational variable. The asymmetric unit is drawn with a heavy line. (*b*) The distortion of the molecule from the idealized geometry (see Table 3). The distortion vectors are magnified 50 times.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36118 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

these being typical bond lengths in the aromatic molecules (*International Tables for X-ray Crystallography*, 1969), leaving θ as the only structural variable. Fig. 2 illustrates how the R factor changed with θ in successive cycles of the constrained refinement on 32 low-order intensities when only θ and the scale factor were varied and the molecules occupied the correct sites $2(d)$. It is interesting to mention that several unsuccessful attempts using unconstrained refinement were made to solve the structure. In further constrained refinements all the four parameters $r_{\rm C}$, $r_{\rm F}$, $r_{\rm Cl}$ and θ were varied.

The constrained-refinement technique can also be used to obtain the statistical significance of the atomic positions and the thermal parameters, since various models can be tested for significant differences among themselves using standard statistical tests (Hamilton, 1965; Pawley, 1972). Table 1 shows the various refinements carried out. In this table 'atomic positions constrained' means that atomic positions were obtained from the constrained molecule described above with $r_{\rm C}$, $r_{\rm F}$, $r_{\rm Cl}$ and θ varied, and **TL** means that the atomic thermal parameters were derived from rigid-body translational and librational tensors for the molecule with no contribution from the internal modes. The residuals given in Table 1 are calculated using intensities y_i and are defined as

$$R = \sum_i |y_i^{\rm cal} - y_i^{\rm obs}| / \sum_i y_i^{\rm obs},$$

$$R_w^2 = \sum_i w_i(y_i^{\rm cal} - y_i^{\rm obs})^2 / \sum_i w_i(y_i^{\rm obs})^2.$$

In order to test the statistical significance of the constraints, the ratio $R_{w(c/u)} = R_w(\text{constrained})/R_w(\text{unconstrained})$ is compared with the value of

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

at a chosen confidence level of the F distribution, $F_{(N-n,M-N)}$. We used 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 1 indicates that both the constrained refinements I and II are significantly poorer than the unconstrained refinement III. Thus we conclude that (i) there are significant distortions from the idealized molecular geometry assumed in Fig. 1 and (ii) there are significant internal vibrations of the molecule, the atomic thermal parameters not being completely determined by the external rigid-body vibrations of the molecule. The results from the constrained refinements are:

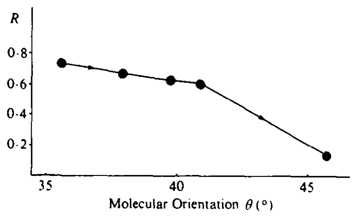

Fig. 2. Variation of the R factor in four successive cycles of the constrained refinement with only two parameters, the molecular orientation angle θ and the scale factor.

model I,

$$\theta = 45{\cdot}39\,(1)^\circ,\ r_{\rm C} = 1{\cdot}386\,(1),\ r_{\rm F} = 1{\cdot}318\,(2),$$
$$r_{\rm Cl} = 1{\cdot}718\,(1)\ \text{Å};$$

model II,

$$T_{11} = T_{22} = 0{\cdot}0326\,(5),\ T_{33} = 0{\cdot}0424\,(12),$$
$$T_{23} = T_{31} = T_{12} = 0\ \text{Å}^2,$$
$$L_{11} = L_{22} = 9{\cdot}9\,(4),\ L_{33} = 11{\cdot}4\,(2),$$
$$L_{23} = L_{31} = L_{12} = 0\ (^\circ)^2.$$

T and **L** are expressed in the orthogonal coordinate system described earlier.

The results of the unconstrained refinement III are given in Table 2. None of the results presented above or in Table 2 have been corrected for librational motion, but this correction has been made to the bond lengths presented in the *Discussion*.

The value of the extinction parameter in the refinement with the three models I, II and III was respectively 0·00003 (3), 0·00005 (5) and 0·00010 (2), and the corresponding scale factors were 0·484 (4), 0·486 (5) and 0·497 (3). Throughout the refinement the atomic scattering factors given in *International Tables for X-ray Crystallography* (1969) were used, but the anomalous-dispersion contribution was omitted.

Fig. 1(*b*) shows the distortion of the molecule from the idealized molecular geometry of the constrained refinement, enlarged 50 times. This compliant distortion of the molecule gives some indication of the nature of internal vibrations of the molecule expected at

Table 1. *Residuals and residual ratios for the three refinements, all using M = 401 reflections*

Model	Atom positions	Thermal parameters	Number of variables	R	R_w	$R_{w(c/u)}$	$S_{(c/u)}$
I	Constrained	Unconstrained	22	5·4	10·7	1·5	1·02
II	Unconstrained	**TL**	14	6·2	14·1	2·0	1·04
III	Unconstrained	Unconstrained	26	3·9	7·0	–	–

Table 2. *Atomic positions* (Å) *and thermal parameters* (Å^2) *from the unconstrained refinement* III

The molecule lies on the plane $Z = c/4$. The orthogonal axes are such that X is along the a axis, Y along the b^* axis. The coordinates are related to fractional coordinates $\mathbf{x}$ through $\mathbf{X} = \mathsf{A}.\,\mathbf{x}$, defining A. The temperature factor is exp $\{-2\pi^2 \sum_i \sum_j U_{ij} H_i H_j\}$ where $\mathbf{H} = \mathbf{h}.\mathsf{A}^{-1}$.

	X_u	Y_u	U_{11}	U_{22}	U_{33}	U_{12}
C(1)	5·2344 (13)	3·4395 (13)	0·0406 (6)	0·0378 (7)	0·0449 (6)	−0·0054 (5)
C(2)	3·9002 (13)	3·8146 (13)	0·0406 (7)	0·0349 (6)	0·0453 (6)	0·0033 (5)
F	6·1786 (10)	4·3806 (9)	0·0486 (6)	0·0464 (6)	0·0782 (6)	−0·0146 (4)
Cl	3·4440 (5)	5·4578 (4)	0·0632 (3)	0·0357 (3)	0·0712 (4)	0·0095 (1)

Table 3. *Distortion of the molecule from the idealized configuration,* $\Delta X = X_u - X_c$ *and* $\Delta Y = Y_u - Y_c$ (Å)

Out-of-plane distortions are forbidden by symmetry.

	ΔX	ΔY
C(1)	−0·009 (2)	−0·013 (2)
C(2)	−0·003 (2)	0·013 (2)
F	0·010 (2)	−0·009 (2)
Cl	−0·003 (1)	−0·001 (1)

Table 4. *Parameters for the powder diffraction constrained refinement*

The small value of r_F shows the inadequacies of the quick powder diffraction experiment.

Overall scale factor	0·087 (2)
Variable flat background	335 (5)
Scan zero (°)	0·07 (1)
U Peak-shape parameters (Å^2), see Rietveld (1969)	1·25 (32)
V	−1·07 (24)
W	0·32 (4)
a Unit-cell edges (Å)	8·4412 (21)
c	6·0516 (18)
B Isotropic temperature factor (varying this made no improvement)	0
θ Molecule orientation (°)	47·11 (05)
r_C (Å)	1·46 (2)
r_F (Å)	1·01 (5)
r_{Cl} (Å)	1·68 (2)

low frequencies. The numerical values of the distortions are given in Table 3.

Low-temperature structure

It is of considerable interest in such systems as *sym*-$C_6Cl_3F_3$ to establish whether phase changes exist. Crystals grown from the melt show no evidence of a transition on cooling to room temperature. Such a sample was finely ground to a powder and packed into a vanadium cylinder of approximate diameter 8 mm, and was then plunged directly into liquid helium. Such treatment can cause supercooling of the higher phase when a transition exists, but subsequent Raman scattering studies on a 0·5 g single crystal cooled slowly to helium temperatures (unpublished) indicate no phase change. A powder diffraction pattern was obtained in 4 h on the PANDA instrument at AERE, Harwell. About 20 mm of the sample tube received the neutron beam, which was set at 1·55 Å. Measurements out to a maximum $2\theta_{\text{Bragg}}$ of 60° were taken at 0·2° intervals (Fig. 3).

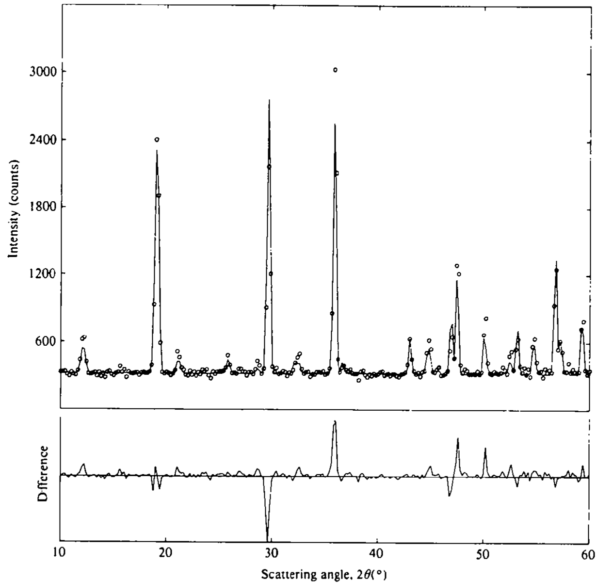

Fig. 3. The powder diffraction scan. The continuous line is the calculated scan, and the points are the observed values. The differences between these are plotted separatelv below.

The powder diffraction pattern was indexed on the assumption that the structure was similar to that at room temperature. This indexing was successful, and a constrained refinement using the program *EDINP* (Pawley, 1980) was immediately successful, giving the results of Table 4. The value of R as defined above was 0·084 where y_i is the intensity at the ith scan point, but it must be appreciated that the sum is over the whole of the scan without an arbitrary background removed, giving an R factor different from that used by Rietveld (1969).

Discussion

Fig. 1(b) shows two large deviations from the idealized molecular geometry which have both chemical and physical origins. The distortion of the benzene ring is expected to be fundamental to the molecule even in the free state and must have a chemical origin. The bond lengths in the unconstrained refinement III are therefore of interest, and after a librational correction are C—C = 1·432 (3) and 1·427 (3), C—F = 1·377 (2) and C—Cl = 1·761 (2) Å. The greatest part of the distortion involving the C atoms is radial, and is consistent with the molecular symmetry. However there is a slight distortion in the C—C bonds, the longer bond listed above being that outlined in Fig. 1(*a*). Also there is tangential distortion, predominantly involving the F atoms, and this must surely have its origin in the anisotropy of the crystalline forces.

The structure evidently undergoes no phase change on cooling to 4·2 K as evidenced by the powder diffraction refinement. Table 4 serves to show that such a refinement on data very rapidly taken (4 h) gives a very accurate unit-cell measurement, a tolerable estimate of the gross structure (the value of θ) but a poor estimate of the fine structure. Such a technique is thus ideal for searching for the existence of different phases and for establishing expansion coefficients. These coefficients, assumed linear over 300 K, are 39×10^{-6} K^{-1} in the plane containing the molecules, but 130×10^{-6} K^{-1} perpendicular to the molecular planes. There is a 2° reorientation of the molecules as a function of temperature.

The thermal motion at 300 K is evidently not well represented by rigid-body motion alone. The comparison of refinements II and III shows that the internal motion contributes most significantly to the Debye–Waller factor, and this is consistent with the ease of distortion of the molecule, especially the F-atom bonds, as shown in Fig. 1(*b*). Internal modes involving such distortions are expected to have low frequencies, and we plan to study such motions with Raman scattering and coherent inelastic neutron scattering.

As the molecule has been shown to suffer a considerable distortion from the free-state symmetry, it should be recognized that an out-of-plane distortion could exist, reducing the symmetry to $P6_3$. The distinction between this space group and $P6_3/m$ can only be made in the refinement stage of the work. No significant distortion was found on allowing this distortion in the refinement, and Table 5 has been prepared to show that there is no evidence for such a distortion in the individual intensity measurements. The distortion would manifest itself most in those reflections with weak intensities and high *l* indices, but the agreement achieved in these cases with the unconstrained $P6_3/m$ refinement is seen to be remarkably good.

Table 5. *The weakest reflections with* $l \geq 5$

Those listed have observed or calculated intensities, I^o or I^c less than 200, on a scale where the largest reflection $(1\bar{1}1)$ has I^o = 27309 and I^c = 27493. The calculated values come from the final unconstrained refinement in $P6_3/m$.

h k l	I^o	I^c	*h k l*	I^o	I^c	*h k l*	I^o	I^c
$2\,\bar{4}\,5$	135	144	$6\,\bar{7}\,5$	38	30	$1\,\bar{3}\,6$	17	18
$3\,\bar{4}\,5$	76	78	$0\,8\,5$	12	9	$3\,\bar{4}\,6$	15	17
$1\,\bar{5}\,5$	48	43	$1\,\bar{8}\,5$	28	26	$2\,\bar{5}\,6$	130	138
$2\,\bar{5}\,5$	33	29	$3\,\bar{8}\,5$	1	0	$3\,\bar{5}\,6$	102	104
$4\,\bar{5}\,5$	120	132	$6\,\bar{8}\,5$	51	49	$4\,\bar{5}\,6$	4	4
$5\,\bar{5}\,5$	5	9	$1\,\bar{9}\,5$	8	2	$3\,\bar{6}\,6$	59	58
$1\,\bar{6}\,5$	110	109	$2\,\bar{9}\,5$	74	73	$2\,\bar{2}\,7$	70	70
$1\,\bar{7}\,5$	153	153	$0\,1\,6$	2	0	$0\,3\,7$	31	37
$4\,\bar{7}\,5$	83	94	$2\,\bar{2}\,6$	49	52			
$5\,\bar{7}\,5$	24	26	$0\,3\,6$	8	2			

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