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THE CRYSTAL AND MOLECULAR STRUCTURE OF DODECAFLUOROTRIPHENYLENE, $C_{18}F_{12}$

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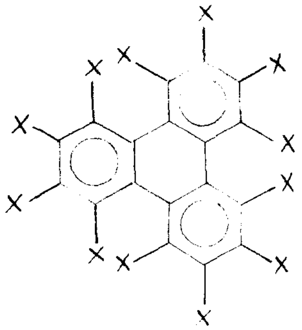
SUMMARY

The dodecafluorotriphenylene molecule is considerably distorted from planarity by steric interactions between the "ortho" fluorine atoms which approach to within 2.41 Å of each other (or about 0.3 Å closer than the sum of the van der Waals radii for two fluorine atoms, 2.70 Å).

Ahmed and Trotter[1] have shown that triphenylene (I) is somewhat distorted from planarity in the solid state, presumably due to steric interaction of the hydrogen atoms in the "ortho" positions. Since the van der Waals radius of hydrogen (1.2Å) is less than that generally accepted for fluorine (1.35 Å), it was suggested[2] that dodecafluorotriphenylene (II) would probably be too unstable to exist due to the substantial increase in steric interaction. In apparent agreement with this view several reactions[2,3] which might have been expected to yield (II) gave other products. However, when 1,2-diiodotetrafluorobenzene is heated in a sealed tube with copper, a mixture of perfluorophenylenes results of which dodecafluorotriphenylene is the principal component[4]. The mass spectra of pentafluorophenyl-metal derivatives containing three or more rings often exhibit a peak due to the ion $C_{18}F_{12}^{+}$, which is presumably ionized dodecafluorotriphenylene produced in fluorine-migration reactions. Typically, the mass spectrum of tris(pentafluorophenyl)boron has a strong metastable peak



(I) : X = H

(II) : X = F

due to the transition:

$$B(C_6F_5)_3^+ \longrightarrow BF_3 + (C_6F_4)_3^+.$$

Obviously the adverse steric interactions in (II) do not preclude its existence. A spectral examination of the molecule suggested[4] that the strain is releaved partially in solution by the adoption of a "propellor-like" distortion. Unexpectedly, this is not the conformation adopted in the crystal studied in this work. As noted in the Experimental section, two crystal modifications of dodecafluorotriphenylene occur and it could be that the compound assumes the propellor form in the second type of crystal.

EXPERIMENTAL

1,2-Diiodotetrafluorobenzene (1g) and copper powder (1g) were heated at 200° for 18 hr in a sealed, evacuated tube. The contents were then extracted with ether, the solution filtered and the ether removed at 0° to give a pale yellow solid which was subjected to fractional vacuum sublimation at 10^{-4} mm.

At room temperature 30 mg of white octafluorobiphenylene was obtained, m.pt. 97-98° (lit^{5}, 100-101.5°). [Found : C, 48.6; H,0.1;F,51.4%; MW(mass spectrum) 296. $C_{12}F_{8}$ calcd. : C,48.7; H,0.0; F,51.3%, MW,296].

Dodecafluorotriphenylene sublimed as a white solid at 80° and was recrystallized from hexane, m.pt. 105-107° (lit^{5}, 102-104°); yield, 60 mg (15%). [Found: C,48.8, H,0.0, F,51.4%, $C_{18}F_{12}$ calcd.,: C,48.7; H,0.0; F,51.3%]. An accurate mass determination on the parent peak at 444 in the mass spectrum gave the value 443.9793; that calculated for $^{12}C_{18}\ ^{19}F_{12}$ is 443.9809.

When the temperature was raised to 160°, 20 mg of perfluoro-tetraphenylene were collected, m.pt. 249-251° (lit^{5}, 249-251°). [Found: C, 48.6; H, 0.0; F,51.2%, MW(mass spectrum) 592; $C_{24}\ F_{16}$ calcd.: C,48.7: H,0.0; F,51.3%; MW,592]

The mass spectrum of the remaining product indicated the presence of several higher members of the polyphenylene series, $(C_{6}F_{4})_{x}$.

Dodecafluorotriphenylene also occurs as one of the products when 1,2-diiodotetrafluorobenzene is heated with lead, bismuth or silver, but the copper reaction appears to give the highest yield. The copper coupling reaction can also be carried out in dry dimethylformamide at 100° for 6 hr, when the yield of dodecafluorotriphenylene is about 10%.

The crystal used in the X-ray work was grown from hexafluorobenzene, a different modification occurs if the crystals are grown from hexane or by slow vacuum sublimation.

Crystal Data: $C_{18}F_{12}$, M.wt 443.98; orthorhombic, $\underline{a}$=20.228(6); $\underline{b}$=13.500(5), $\underline{c}$=10.927(5)Å, U=2984Å^{3}, $\underline{D}_{\underline{m}}$(by flotation), 1.87, z=8, $\underline{D}_{\underline{c}}$ 1.90 g.cm^{-3}, space group Fdd2 (from systematic absences).

Intensity data were recorded on a G.E. XRD6 manual diffractometer using the stationary-crystal-stationary-counter technique and Cu-Kα radiation. Each reflection was counted for 10s, as were the individual backgrounds at $2\theta + 1^{\circ}$.

From a total of 812 reflections measured to a 2θ limit of 140°, 603 had intensities for which $I>3\sigma(I)$, where $\sigma(I)$ was calculated according to the formula $\sigma(I)=[I + 2B + (0.03I)^2]^{\frac{1}{2}}$, and these were used for the structure analysis and refinement.

With eight molecules per unit cell, each molecule must be on a two-fold axis, and in Fdd2, these are parallel to c. A three-dimensional, origin-removed Patterson map clearly showed the gross orientation of the molecule. Using a Dreiding model, distorted to allow for the ortho F...F repulsions, but with D_3 symmetry, suitably oriented in the unit cell, co-ordinates for all atoms were calculated. These were subjected to least-squares refinement with the z co-ordinate of one carbon atom fixed to define the origin, but no convergence could be obtained with this model. Not until it was realised that an alternative distorted model, still with C_2 symmetry, could be chosen (see later) was progress made. Using this new model structure solution and refinement were completed very quickly. Least squares refinement with isotropic temperature factor coefficients gave R=0.134; with anisotropic coefficients, R was reduced to its final value of 0.078. During the last stages of refinement, a Hughes-type weighting scheme $w=1$ for $F<F^*$ and $\sqrt{w}=F^*/F$ for $F>F^*$, was used, with a value for F^* of 35 on an absolute scale giving satisfactory agreement analyses. The final list of atomic fractional co-ordinates are given in Table 1. Lists of $|F_o|$ and F_c can be obtained from the authors (at Q.M.C.). All computations were made on the University of London CDC6600 computer, using the X-ray 70 program system.[6] Scattering factors were taken from ref. 7.

RESULTS AND DISCUSSION

Bond lengths and angles computed from the data of Table 1 are given in Figure 1. The distortions from planarity are given in Figure 2, where the deviations are from the best plane defined by the central C_6 ring (C(3), C(4), C(9) and their

TABLE 1

Dodecafluorotriphenylene:- Final positional parameters (x, y, z) expressed as fractions (x 10^4) of the a, b and c unit cell dimensions respectively, with estimated standard deviations in parentheses, (fractional x 10^4). The numbering system is shown in Figure 1.

Atom	x	y	z
C(1)	306(6)	216(10)	6671(14)
C(2)	601(5)	495(8)	5594(13)
C(3)	270(4)	312(8)	4470(12)
C(4)	428(5)	852(8)	3315(13)
C(5)	706(4)	186(8)	3281(14)
C(6)	708(5)	2335(8)	2248(14)
C(7)	443(5)	2010(8)	1209(13)
C(8)	132(5)	1107(8)	1198(12)
C(9)	153(4)	507(6)	2210(0)
F(1)	610(4)	431(7)	7735(10)
F(2)	1197(3)	913(5)	5643(11)
F(3)	913(3)	2261(4)	4295(10)
F(4)	1006(3)	3270(4)	2271(11)
F(5)	437(3)	2561(5)	173(11)
F(6)	-207(3)	847(4)	181(10)

Table I (Continued overleaf)

Table 1 (cont.)

Perfluorotriphenylene:- Final anisotropic temperature factors

($Å^2 \times 10^4$) as they appear in exp - ($\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl$).

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	36(3)	101(9)	91(11)	-2(4)	-11(5)	-9(8)
C(2)	32(8)	78(6)	85(10)	4(4)	4(4)	-3(7)
C(3)	21(2)	68(6)	67(8)	-1(3)	3(3)	-1(6)
C(4)	26(2)	73(7)	75(9)	-4(3)	-6(4)	1(6)
C(5)	23(2)	65(6)	96(11)	-7(3)	-2(4)	-7(7)
C(6)	24(2)	59(7)	123(11)	-5(3)	-3(4)	-10(8)
C(7)	24(2)	56(5)	111(10)	4(3)	-4(4)	27(7)
C(8)	23(2)	70(7)	82(11)	3(3)	3(4)	4(6)
C(9)	22(3)	54(5)	68(7)	-3(3)	3(3)	1(6)
F(10)	51(3)	136(7)	77(6)	6(3)	-13(3)	-11(6)
F(11)	35(2)	99(5)	124(7)	-13(2)	-24(3)	3(5)
F(3)	37(2)	75(4)	110(6)	-13(2)	-9(3)	-18(4)
F(4)	35(2)	54(3)	185(10)	-14(2)	8(3)	6(5)
F(5)	41(2)	77(4)	125(7)	-2(2)	0(3)	35(5)
F(6)	42(2)	71(3)	89(5)	-3(2)	-18(3)	9(4)

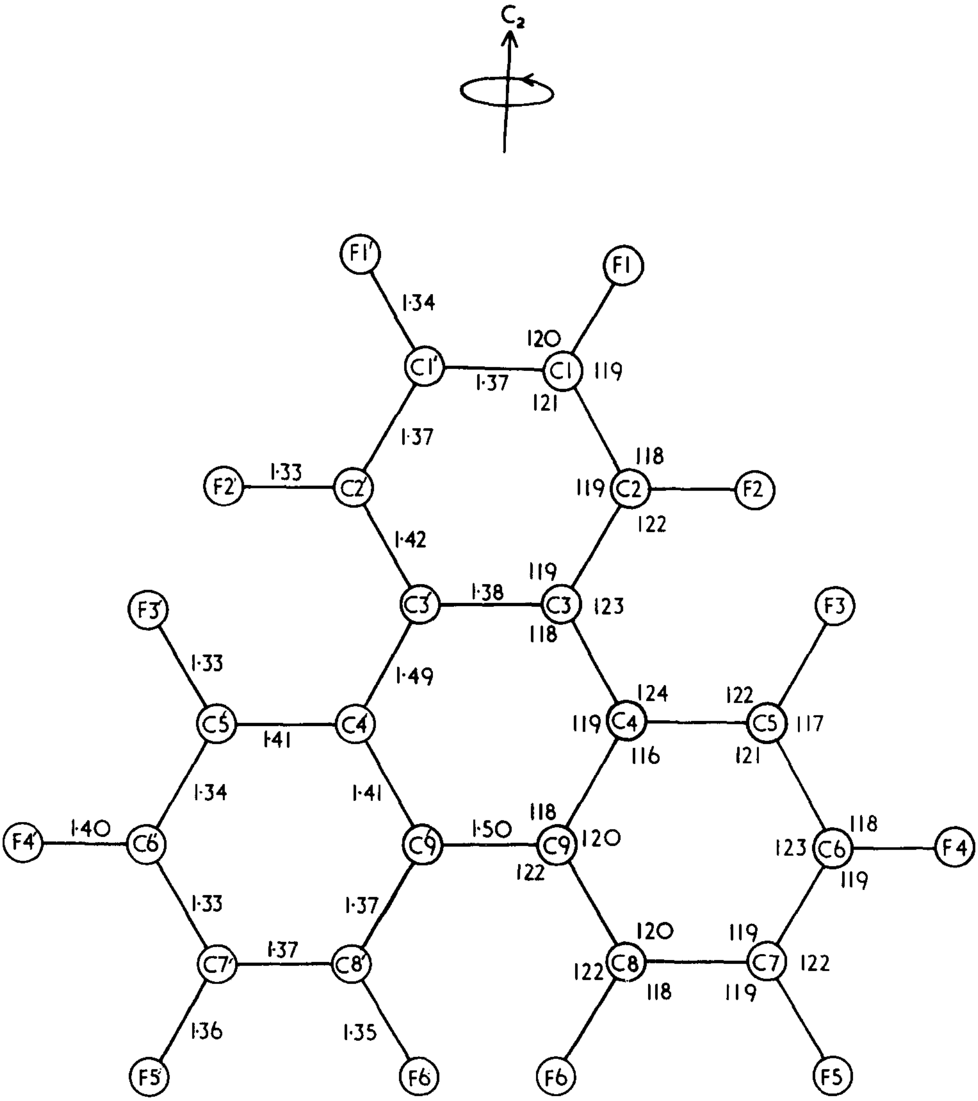


Figure 1 Dodecafluorotriphenylene :- Bond lengths and Angles.

Estimated standard deviations are in the ranges 0.012 - 0.020 Å in bond lengths 0.6 - 1.2° in angles.

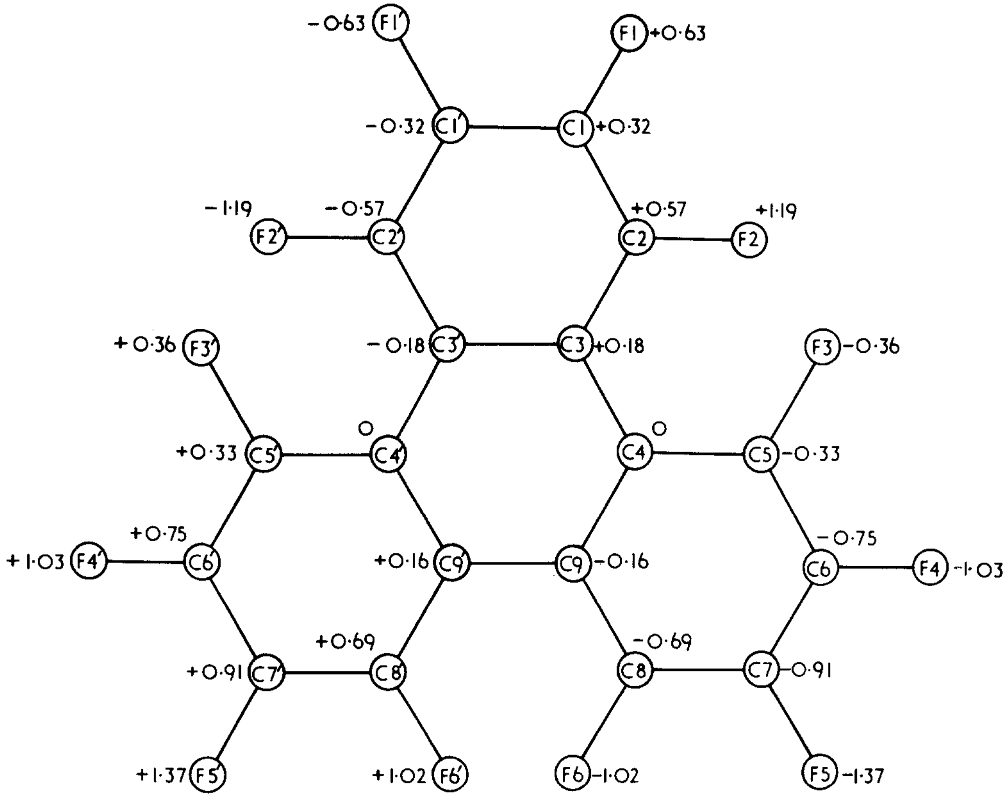


Figure 2 Dodecafluorotriphenylene. Deviations in Å from the best plane defined by C(3), C(4), C(9), C(9′), C(4′), C(3′)

2-fold axis relatives). The magnitude of the distortions are also well demonstrated in Figure 3, a view down the two-fold axis.

The data in Figure 2 shows that in this crystal structure at least, the dodecafluorotriphenylene molecule does not have the "propellor-like" distortion, giving rise to D_3 symmetry (IV) which ^{19}Fnmr spectroscopy suggested to be present in solution[4], but that shown in V, (where + and - indicate the distortion of the

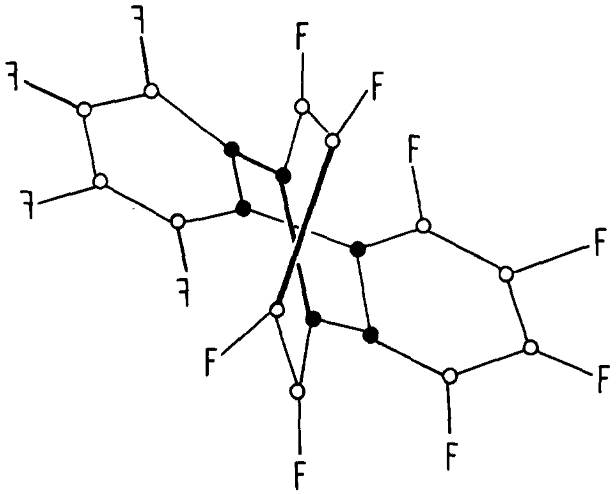
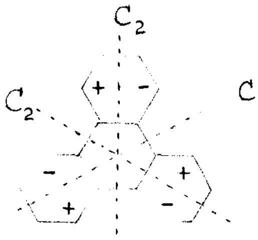
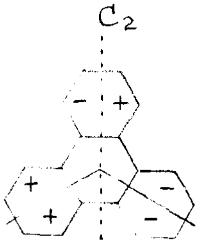


Figure 3. Sketch of the perfluorotriphenylene molecule. The twisted state of the central ring (closed circles) results in the top of the right hand C_6F_4 ring and the underside of the left hand C_6F_4 ring being presented to the viewer.

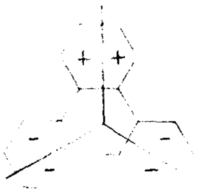


(IV) D_3 distortion



(V) observed distortion in the solid

rings from the mean plane). Crystalline triphenylene (I) shows yet another kind of distortion[1] (VI):



(VI) distortion shown by triphenylene

The distortion from planarity of dodecafluorotriphenylene, best seen in Figure 4, is very much greater than that of its hydrogen analogue. The fluorine-fluorine contacts between F(1′)-F(1); F(1)-F(2); F(3)-F(4); F(4)-F(5) and F(5)-F(6) all correspond to the normally expected van der Waals radius for fluorine of 1.35 Å by showing F-F distances of between 2.6 and 2.7 Å; similarly the shortest

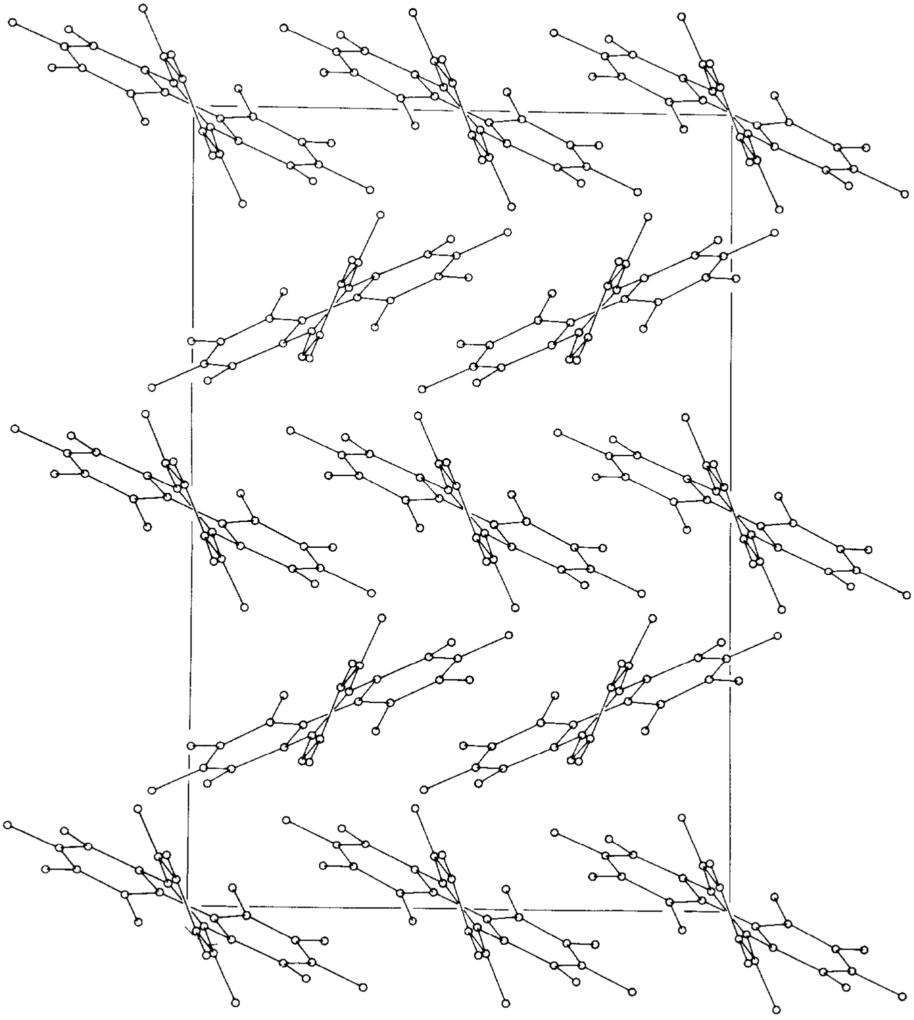
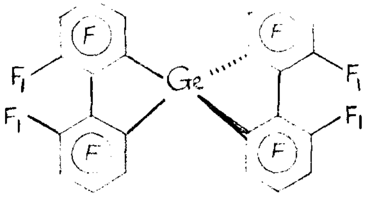


Figure 4: The Contents of the Unit Cell in Dodecafluorotriphenylene.

F-F distance between fluorine atoms in different molecules is 2.8 Å. The greatest steric interaction is expected between F(2)-F(3) and F(6)-F(6') and correspondingly short F-F distances of 2.41 and 2.43 Å, respectively, are found. These values compare well with the short F_1-F_1, distances of 2.45 Å observed[8] for fluorine atoms in a similar position in the germanium heterocycle (VII):



bis(octafluorobiphenylene)germane, (VII)

The rather long C-C bonds in the central ring of dodecafluorotriphenylene between C(9)-C(9) and C(3)-C(4) are probably due to the partial relief of interaction between F(2)-F(3) and F(6)-F(6'). A similar effect is possibly just visible in triphenylene[1]. The three long bonds in the central ring, corresponding to almost C-C single bonds, would cause considerable loss of overlap of the $p\pi$ orbitals in this ring, and its aromaticity could thus be expected to be considerably reduced. This is indicated in the UV spectrum of $C_{18}F_{12}$, in both the solid state and in solution, which shows a considerably lower extinction coefficient than that observed for triphenylene.

Nyberg and Szymanski[9] have suggested that the fluorine atom has an oblate spheroidal shape, the smallest van der Waals radius (1.35 Å) being diametrically opposite the bonded atom. This model suggests even more steric interaction in the dodecafluorotriphenylene molecule because the F-F contacts are at the "fattest" parts of the fluorine atoms. This work shows that F-F distances which are considerably less than twice the van der Waals radius can be tolerated by fluoroaromatic molecules with little adverse effect on their general stability.

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