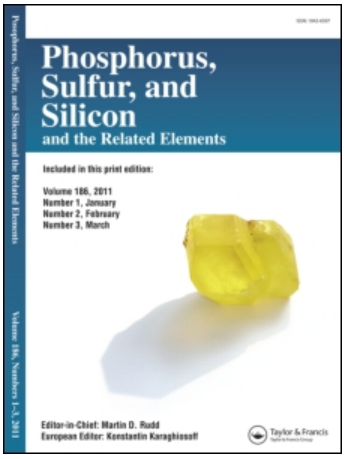

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THE CRYSTAL AND MOLECULAR STRUCTURE OF OCTAFLUORODIBENZOTHIOPHENE

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THE CRYSTAL AND MOLECULAR STRUCTURE OF OCTAFLUORODIBENZOTHIOPHENE

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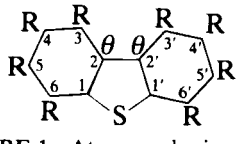
The X-ray crystal structure of octafluorodibenzothiophene is reported. Despite the larger size of fluorine relative to hydrogen there is surprisingly little change in molecular dimensions when the hydrogen atoms of dibenzothiophene are replaced by fluorine. The 3 and 3′ fluorine atoms are closer together (2.549 Å) than the sum of the accepted van der Waals radii. Dibenzothiophene and octafluorodibenzothiophene form a 1:1 crystalline "complex".

Key Words: Octafluorodibenzothiophene; perfluorodibenzothiophene; dibenzothiophene.

INTRODUCTION AND DISCUSSION

The slightly larger size of fluorine (van der Waals radius, 1.35 Å) compared with hydrogen (1.2 Å) might be expected to cause considerable distortion in 3,3′,4,4′,5,5′,6,6′-octafluorodibenzothiophene, (I), because of the close proximity of the 3 and 3′ fluorine atoms. The hydrogen analogue (II) was found[1] to be somewhat distorted in that the angles θ were 129.3° rather than the "ideal" value of 120°, but at least part of this increase in θ is probably due to the restrictions imposed on the molecular geometry by the presence of the five-membered C_4S ring. Scale models show that the 3,3′ hydrogens in dibenzothiophene are only just in "contact" when θ is 120°, the H—H distance being about 2.4 Å.



I; R = F

II; R = H

FIGURE 1 Atom numbering in the dibenzothiophenes.

Atom numbering in the $C_{12}F_8S$ molecule is shown in Figure 1, bond lengths and angles in Figure 2, contact distances and displacements from the least squares molecular plane in Figure 3, and unit cell contents in Figure 4. Atomic coordinates and equivalent isotropic thermal parameters are listed in Table I.

The two aromatic rings and the C_4S ring are all planar in both (I) and (II), but the former has a crystallographically imposed 2-fold rotation axis in the C_4S plane passing through S. The CSC angle in (I) is 89.8(2)° (Figure 2), only slightly less than the value of 91.5° found in (II). Somewhat surprisingly there are no very pronounced differences in the molecular dimensions of (I) relative to (II). The angles θ, which would be expected to show most change, are increased only slightly to 131.5(3)° suggesting that the impositions placed on θ by the C_4S ring

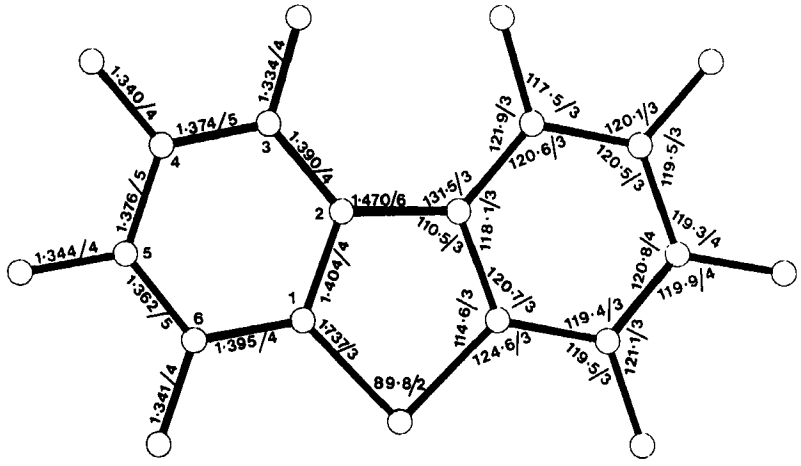


FIGURE 2 Bond lengths (Å) and bond angles (°) in octafluorodibenzothiophene with esd.

are either almost sufficient to relieve F—F strain or severely restrict any gross increase in θ; there is an apparent elongation of the inter-ring C—C bond of 0.029 Å in (I) but this value is very close to the confidence limit of 3σ (0.021 Å). As in (II), the value of θ and the C_4S ring make angle C(1)–C(2)–C(3) somewhat less than 120° (118.1°) but the other aromatic ring angles are close to the sp^2 value.

Notwithstanding the increase in θ the 3,3′ fluorines are still closer together [2.549(16) Å; Figure 3] than the sum of their van der Waals radii (2.7 Å). Presumably as a consequence of this: (i) the angle C(2)–C(3)–F(3) is 121.9° and the angle F(3)–C(3)–C(4) is correspondingly less than 120° at 117.5° (Figure 2); (ii) F(3) and F(3′) are displaced by −0.011 Å and +0.011 Å from the mean plane of the $C_{12}S$ atoms. All other F—F distances are close to the value 2.7 Å (Figure 3). The five- and six-membered rings are virtually co-planar, the angle between them being only 0.4(2)°.

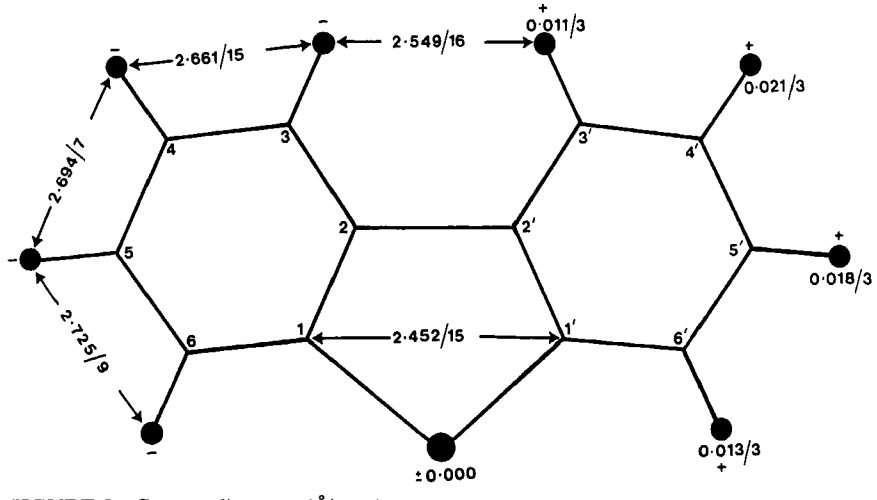


FIGURE 3 Contact distances (Å) and atom displacements in octafluorodibenzothiophene.

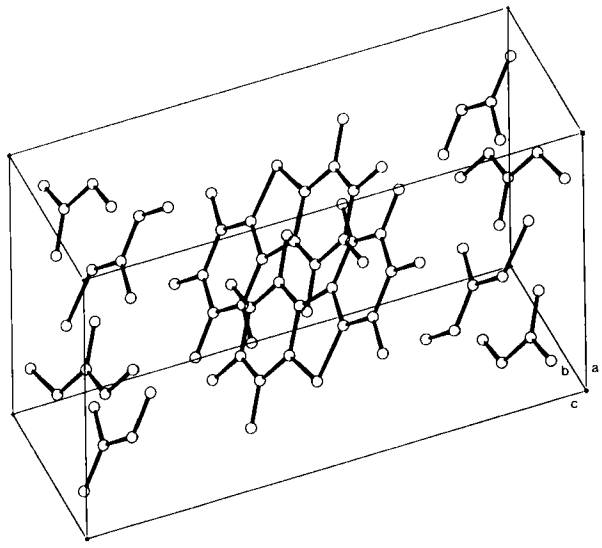


FIGURE 4 Contents of the unit cell.

TABLE I

Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters

ATOM	X/a	Y/b	Z/c	Beq ($Å^2$)
		Beq = $\frac{1}{3}\Sigma_i B_{ii}$		
C1	0.7024	1.1387	0.0608	2.9(1)
C2	0.7213	0.9694	0.0364	2.7(1)
C3	0.6852	0.8354	0.0819	3.1(1)
C4	0.6314	0.8687	0.1483	3.4(2)
C5	0.6132	1.0356	0.1711	3.6(2)
C6	0.6475	1.1706	0.1283	3.4(2)
F3	0.6986	0.6708	0.0625	5.8(1)
F4	0.5947	0.7385	0.1909	5.0(1)
F5	0.5592	1.0649	0.2359	5.6(1)
F6	0.6288	1.3335	0.1496	5.4(1)
S	0.7500	1.2971	0.0000	3.55(6)

Crystal data. $C_{12}F_8S$, $M_r = 328.179$, monoclinic, A2/a, $a = 8.797(2)$, $b = 7.77(2)$, $c = 16.724(2)$ Å, $\beta = 110.21(2)°$, $U = 1072.75$ $Å^3$, $Z = 4$, $D_x = 2.033$ g cm^{-3}, $D_m = 1.998$ g cm^{-3}, $\lambda(MoK\alpha) = 0.71069$ Å, $\mu = 3.34$ cm^{-1}, $F(000) = 640$, $T = 293$ K, $R = 0.043$ for 899 observed reflections with $I > 3\sigma(I)$.

EXPERIMENTAL

Octafluorodibenzothiophene, prepared by heating sulphur with 2,2′-diiodo-octafluorobiphenyl in a sealed tube[2], was recrystallized from 60–80° petrol ether. The selected crystal was sealed in a Lindemann-glass capillary and mounted about b. Preliminary lattice constants were determined from oscillation and Weissenberg

phorographs and refined constants from a Stoe Stadi-2 two-circle diffractometer using axial-row reflections. The intensities of 1,381 reflections were measured out to a maximum 2θ of 60° using Mo Kα radiation; 899 had $I > 3\sigma(I)$ and were classed as observed. A standard check reflection was measured, every 50 reflections, for each layer and no significant variation in intensity was noted. Corrections were applied for Lp but not for absorption or extinction. The position of the S atom on the 2-fold axis was found by direct methods which also located four C and two F atoms. The coordinates of the remaining atoms were obtained from a ΔF synthesis. Anisotropic refinement by full-matrix least squares on F with unit weights gave a final $R = 0.043$, $\Delta/\sigma < 0.02$ and $\Delta\rho$ excursions = $+0.23$ to $-0.38\,e\text{Å}^{-3}$. Scattering factors were those of Cromer and Mann, and calculations were carried out with SHELX76, implemented at Loughborough University of Technology Computer Centre, and with XRAY72 implemented at the University of Manchester Regional Computer Centre. A copy of the list of structure factors and anisotropic temperature factors is available on request from J.B.J.

When a hexane solution containing non-stoichiometric amounts of $C_{12}H_8S$ and $C_{18}F_8S$ was set aside at room temperature for 24 hours colourless, but opaque, crystals of the 1:1 "complex" separated out; [Found: C, 56.3; H, 1.6; F, 29.3; S, 12.6%. calcd. for $C_{24}H_8F_8S_2$: C, 56.2; H, 1.6; F, 29.7; S, 12.5%]. The infrared spectrum of the needle crystals was essentially a superposition of the spectra of the two components with only very slight shifts ($<5\,cm^{-1}$) of a few bands; the crystals melted at 137° compared with 97–100° for dibenzothiophene and 102.5–104° for octafluorodibenzothiophene.

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