STRUCTURES OF POLYFLUOROAROMATIC COMPOUNDS.   PART VI [1].   CRYSTAL
STRUCTURE OF 3H,3'H-4,4'-DINITROHEXAFLUORODIPHENYL SULPHIDE

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SUMMARY

    Crystals of the title compound are tetragonal, with unit cell
dimensions a = b = 6.10(1), c = 37.16(2) Å, space group $P4_12_12$.   The
structure has been determined from 780 three–dimensional counter data
and refined to a value of 4.5% for the conventional discrepancy factor R.
Estimated standard deviations average 0.006 Å for bond lengths and 0.5°
for bond angles.   The molecule has C_2 symmetry.   The symmetry–related
aromatic rings are each inclined at an angle of 61° to the C—S—C plane.
The length of the C—S bond, 1.771(4) Å, corresponds closely to that
expected for a single bond between sulphur and sp^2–hybridized carbon.
The bond angle at sulphur is 99.7(3)°, some 4° smaller than the angle in
unfluorinated diaryl sulphides.

INTRODUCTION

    The crystal structures of a number of diaryl sulphides have been
determined by X-ray methods, to study both the geometry of the C—S—C
group, with its implications for the bonding state of the sulphur atom,
and the overall conformation of the molecules [2-9].   We have now
determined the structure of 3H,3'H-4,4'-dinitrohexafluorodiphenyl
sulphide [10] by a single crystal X-ray analysis in order to assess the
effects of the electron-withdrawing substituents on the geometry of the
C—S—C group, and as part of a continuing study of highly fluorinated
organic molecules.

TABLE 1

Atomic coordinates and thermal parameters.
Coordinates are expressed as fractions (x 10^4) of the corresponding unit cell edges. The U_{ij} values ($\mathring{A}^2$ x 10^4) are parameters in the temperature factor expression $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S	-2034(2)	-2034(2)	0	783(8)	783(8)	743(11)	-58(7)	58(7)	-229(11)
C(1)	-1643(7)	225(7)	293(1)	586(28)	670(28)	502(24)	67(22)	10(22)	-72(25)
C(2)	169(8)	449(8)	509(1)	647(31)	671(30)	609(25)	89(25)	-34(25)	18(25)
C(3)	435(9)	2141(9)	742(1)	703(32)	855(35)	547(27)	-6(28)	-48(27)	-144(33)
C(4)	-1197(9)	3701(8)	770(1)	798(35)	647(31)	622(28)	40(25)	148(29)	-96(31)
C(5)	-3055(9)	3515(8)	564(1)	705(34)	736(36)	787(32)	170(28)	263(32)	103(31)
C(6)	-3261(7)	1797(9)	324(1)	547(29)	834(35)	626(27)	133(28)	15(24)	-11(31)
F(2)	1730(5)	-1087(5)	487(1)	809(19)	947(21)	917(19)	-62(16)	-144(16)	247(18)
F(5)	-4737(5)	4927(5)	584(1)	933(23)	1041(24)	1346(26)	141(20)	271(20)	323(17)
F(6)	-5067(4)	1678(6)	122(1)	668(18)	1341(28)	1052(20)	87(21)	-169(17)	111(20)
N	-890(12)	5530(9)	1026(1)	1245(45)	835(39)	713(31)	-56(30)	290(32)	-237(37)
O(1)	565(11)	5357(10)	1235(1)	1639(46)	1353(44)	1331(39)	-513(34)	-369(39)	-242(40)
O(2)	-2116(10)	7065(8)	1002(1)	2076(55)	822(27)	1042(33)	-61(25)	502(33)	217(35)
H	1646(63)	2294(57)	888(9)	394(97)					

RESULTS AND DISCUSSION

Atomic coordinates and thermal parameters obtained from the X-ray
analysis are listed in Table 1.   Bond lengths and angles with their
estimated standard deviations are in Table 2.   The conformation of the
molecule and the atom numbering are shown in Fig. 1.   The molecule
possesses exact C_2 symmetry, with the sulphur atom lying on the 2-fold
axis.   The angle between the mean planes of the phenyl rings is 88.1°
(Table 3) and the angle between the plane of the nitro group and the
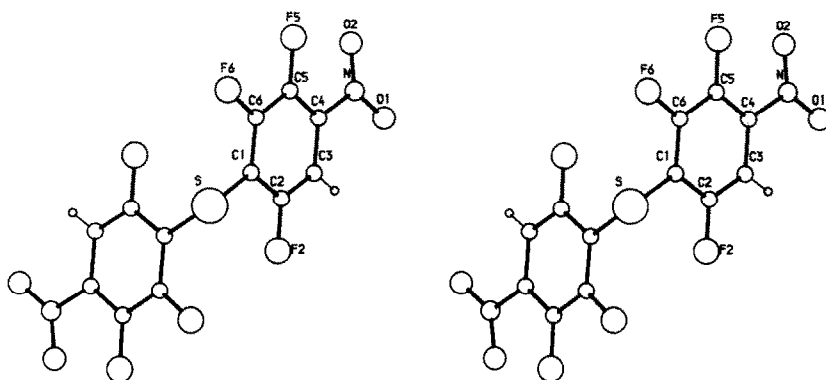phenyl ring to which is bonded is 12.6°.

Fig. 1.   Stereoscopic view of the molecule along the two-fold axis.
Atoms related by the symmetry axis to those labelled 1-6 are denoted
by primed numbers.

Analysis of the thermal parameters for rigid-body thermal motion [11]
gave good agreement between observed and calculated U_{ij} values when the
molecule was treated as having independent phenyl groups with only
fluorine substituents (r.m.s. deviation 0.003 Å^2).   Inclusion of
S, N or NO_2 resulted in significantly worse agreement.   Bond lengths
corrected for thermal libration are included in Table 2.   Both oxygen
atoms have abnormally large thermal parameters, and this could be an

TABLE 2   Molecular dimensions

(a) Bond lengths (Å) with estimated standard deviations in parentheses.
    Values in the second column are corrected for thermal libration.

C(1) – S	1.771(4)		C(2) – F(2)	1.338(5)	1.351
C(1) – C(2)	1.373(6)	1.387	C(5) – F(5)	1.342(5)	1.354
C(2) – C(3)	1.357(6)	1.366	C(6) – F(6)	1.336(5)	1.349
C(3) – C(4)	1.381(7)	1.394	C(3) – H	0.922(37)	
C(4) – C(5)	1.373(7)	1.387	C(4) – N	1.478(7)	
C(5) – C(6)	1.380(7)	1.390	N – O(1)	1.184(7)	
C(6) – C(1)	1.381(6)	1.394	N – O(2)	1.202(7)	

(b) Bond angles (°) with estimated standard deviations in parentheses.

C(1) – S – C(1')	99.7(3)	N – C(4) – C(3)	118.5(5)
C(6) – C(1) – C(2)	117.1(4)	N – C(4) – C(5)	121.8(6)
S – C(1) – C(2)	123.0(4)	C(6) – C(5) – C(4)	119.9(5)
S – C(1) – C(6)	119.8(3)	F(5) – C(5) – C(4)	123.2(5)
C(3) – C(2) – C(1)	123.1(5)	F(5) – C(5) – C(6)	116.9(5)
F(2) – C(2) – C(1)	117.9(4)	C(5) – C(6) – C(1)	121.1(4)
F(2) – C(2) – C(3)	119.1(4)	F(6) – C(6) – C(1)	120.2(5)
C(4) – C(3) – C(2)	119.1(5)	F(6) – C(6) – C(5)	118.7(5)
H – C(3) – C(2)	123.3(23)	C(4) – N – O(1)	116.7(6)
H – C(3) – C(4)	117.5(23)	C(4) – N – O(2)	117.4(6)
C(5) – C(4) – C(3)	119.6(5)	O(1) – N – O(2)	125.8(6)

(c) Torsion angles (°)

C(1') – S – C(1) – C(2)   [= C(1) – S – C(1') – C(2')]   −63.3

C(1') – S – C(1) – C(6)   [= C(1) – S – C(1') – C(6')]   120.3

TABLE 3   Mean plane calculations

(a) Deviations (Å) of atoms from mean plane of phenyl ring C(1)–(6)

C(1)	−0.004,	C(2)	0.008,	C(3)	−0.004
C(4)	−0.005,	C(5)	0.008,	C(6)	−0.004
S	0.070,	F(2)	0.038,	H	0.009
N	−0.012,	F(5)	0.048,	F(6)	−0.016

(b) Equations of planes (x,y,z are fractional coordinates)

I   Phenyl ring C(1) – (6) $2.6935x + 3.3066y - 26.5686z = -1.1499$

II Phenyl ring C(1') – (6') [symmetry related to I]
              $-3.3066x - 2.6935y - 26.5686z = 1.1499$

III Nitro group N, O(1) and O(2) $3.7919x + 2.6454y - 24.2401z = -1.3623$

IV S, C(1) and C(1') $-3.4656x + 3.4656y - 22.1237z = 0$

Interplanar angles (°)
        I – II : 88.1   I – IV (= II – IV) : 61.1
        I – III : 12.6

indication of some freedom of rotation about the C(4)—N bond, or some degree of disorder in the orientation of the nitro group.

The aromatic C—C bond lengths are in the range 1.366-1.394 Å, mean 1.386 Å (corrected for thermal libration). This compares well with means of 1.381 Å for the nitro-substituted ring of 2-nitrononafluorobiphenyl [12] and 1.382 Å for the fluorinated ring of 2,3,5,6-tetrafluorobiphenyl [13]. No crystallographic studies of fluorinated diaryl sulphides are available for comparison with the present structure. Structural results have, however, been reported for three nitro-substituted diphenyl sulphides, 4-nitrodiphenyl sulphide [3], 4-nitro-4'-dimethylamino-diphenyl sulphide [3] and 2,4,6-trimethyl-2'-nitro-4'-carbomethoxy-diphenyl sulphide [4]. The mean aromatic C—C bond lengths in the nitro-substituted rings of these compounds are 1.378, 1.386 and 1.387 Å, respectively (uncorrected for thermal effects). The uncorrected mean value in the present structure is 1.374 Å. A slight shortening of C—C bonds in unsaturated fluorocarbons has been noted previously [12-14] and is consistent with the effect of hybridization changes induced by the electronegative fluoro-substituents [15].

The C—F bonds are all in the range 1.349-1.354 Å (corrected). The mean length (1.351 Å) is intermediate between the means in 2-nitrononafluorobiphenyl (1.342 Å) and 2,3,5,6-tetrafluorobiphenyl (1.360 Å). Bond lengths and angles in the nitro group are similar to those in other, comparable structures [3,4,12]. The angle of inclination of the nitro group to the phenyl ring (12.6°) is, however, larger than the corresponding angles in 4-nitrodiphenyl sulphide and 4-nitro-4'-dimethylaminodiphenyl sulphide, which are 6.3 and 1.2°, respectively. This can be attributed to the need to relieve a close contact between O(2) and F(5).

Of particular interest in this structure is the bonding of the sulphur atom to the nitrotrifluorophenyl ring in comparison with that found in diarylsulphides not carrying highly electronegative fluoro-substituents. To assess any effects due to fluorine substitution, pertinent structural parameters determined by X-ray crystallography for the diaryl sulphides (1)-(9) are listed in Table 4. This list is derived from a search of the literature aided by the compilations of the Cambridge Crystallographic Data Centre [16]. Excluded are a number of early studies not based on full three-dimensional data.

TABLE 4

Comparison of selected structural parameters in diaryl sulphides.

Bond lengths are in Å, angles in degrees. The angle between the plane of the bonded atoms C(1),S,C(1') and that of the mean plane of the phenyl ring whose substituents are labelled by unprimed numbers is denoted α. The corresponding angle involving the other phenyl ring plane is denoted β, and the angles between the planes of the phenyl rings are listed under γ. For the symmetrically substituted compounds (8)–(10) the choice of α and β is arbitrary. In (10) $\alpha = \beta$ by crystallographic symmetry.

Compound (S denotes "sulphide")		Ref.	C(1)-S	C(1')-S	C(1)-S-C(1')	C(6)-C(1)-C(2)	C(6')-C(1')-C(2')	α	β	γ
4-Dimethylaminodiphenyl S	(1)	[2]	1.786(4)	1.769(4)	104(0.2)	118(0.4)	118(0.4)	85	5	82
4-Nitrodiphenyl S	(2)	[3]	1.778(5)	1.779(5)	104(0.2)	120(0.5)	120(0.5)	2	84	84
4-Nitro-4'-dimethylaminodiphenyl S	(3)	[3]	1.780(6)	1.795(6)	105(0.3)	120(0.6)	120(0.6)	2	69	68
2,4,6-Trimethyl-2'-nitro-4'-carbomethoxy diphenyl S	(4)	[4]	1.785(3)	1.759(2)	103(0.1)	122(0.2)	116(0.2)	87	4	88
N-(3-Dimethylammoniopropyl)-2-amino-4-chlorodiphenyl S maleate	(5)	[5]	1.767(5)	1.789(5)	103(0.2)	119(0.4)	120(0.4)	66	31	79
N-(3-Dimethylammoniopropyl)-2-amino-2'-chlorodiphenyl S maleate	(6)	[6]	1.773(5)	1.781(6)	104(0.3)	120(0.5)	119(0.5)	75	6	77
N-(3-Dimethylammoniopropyl)-2-amino-2',4-dichlorodiphenyl S maleate	(7)	[7]	1.78(1)	1.78(1)	103(0.4)	120(0.9)	118(0.8)	74	2	75
4,4'-diaminodiphenyl S	(8)	[8]	1.785(8)	1.807(7)	104(0.3)	119(0.9)	121(0.8)	68	26	81
2,2'-Dimethyldiphenyl S	(9)	[9]	1.776(6)	1.777(6)	103(0.3)	121(0.5)	122(0.6)	7	79	83
3H,3'H,4,4'-Dinitrohexafluorodiphenyl S	(10)	Present work	1.771(4)	1.771(4)	100(0.3)	117(0.4)	117(0.4)	61	61	88

The overall conformation of the title compound (10) is such that the planar phenyl rings are each inclined at an angle of 61.1° to the plane defined by atoms C(1), S and C(1') (Table 3). This corresponds to the "twist" conformation in the notation of van der Heijden et al. [17]. Compounds (1)-(4), (6), (7) and (9) adopt a different conformation, denoted "skew" [17], wherein one ring is nearly perpendicular, and the other ring is nearly parallel to the C(1), S, C(1') plane. Only sulphides (5) and (8) have a conformation somewhat similar to (10) (twist, but tending towards skew).

In the unfluorinated compounds (1)-(9) the C—S bonds have lengths 1.759-1.807 Å, with a mean of 1.780 Å, slightly, but not significantly longer than the length of 1.771(4) Å in the present structure (10). These lengths correspond closely to the sum of the single bond covalent radii [18] of sulphur (1.04 Å) and sp^2-hybridized carbon (0.74 Å).[†] There is, however, a significant difference between sulphides (1)-(9) and the fluorinated compound (10) when the bond angles at sulphur are considered. In (10) the C(1)-S-C(1') angle is 99.7 ± 0.3°, compared with 103-105°, mean 103.7° in the unfluorinated sulphides. The closing up of this angle by some 4° can be rationalised on the basis of rehybridization effects [15]. The greater electronegativity of the partially fluorinated rings induce a greater degree of p-character in the sulphur bonding orbitals directed towards C(1) and C(1') compared with the unfluorinated sulphides, resulting in a smaller bond angle at sulphur. The relatively small endocyclic angles at C(1) and C(1') can be rationalised by similar arguments.

The arrangement of the molecules in the unit cell as viewed along the x axis is shown in Fig. 2. All intermolecular contact distances correspond to normal van der Waals interactions.

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† Examination of the structural parameters of the unsymmetrically substituted sulphides (1)-(7) confirms an earlier observation [4], that the phenyl ring which is near-coplanar with the C-S-C plane is an electron acceptor relative to the other ring. This geometry is such as to favour conjugation between the sulphur atom and the π-systems of the aromatic rings. The observed lengths of the C—S bonds, however, exclude any appreciable involvement of the sulphur atom in such conjugative interactions (with the possible exception of the 2'-nitro-4'-carbomethoxy-substituted ring (4) where the C(1')—S bond is 1.759 Å). Contrary to this conclusion, analysis of the X-ray fluorescence spectra of derivatives of perfluorodiphenyl sulphide with para substituents which are π-acceptors (such as CN,NO$_2$), indicate considerable π-coupling of sulphur to the aromatic rings [19].
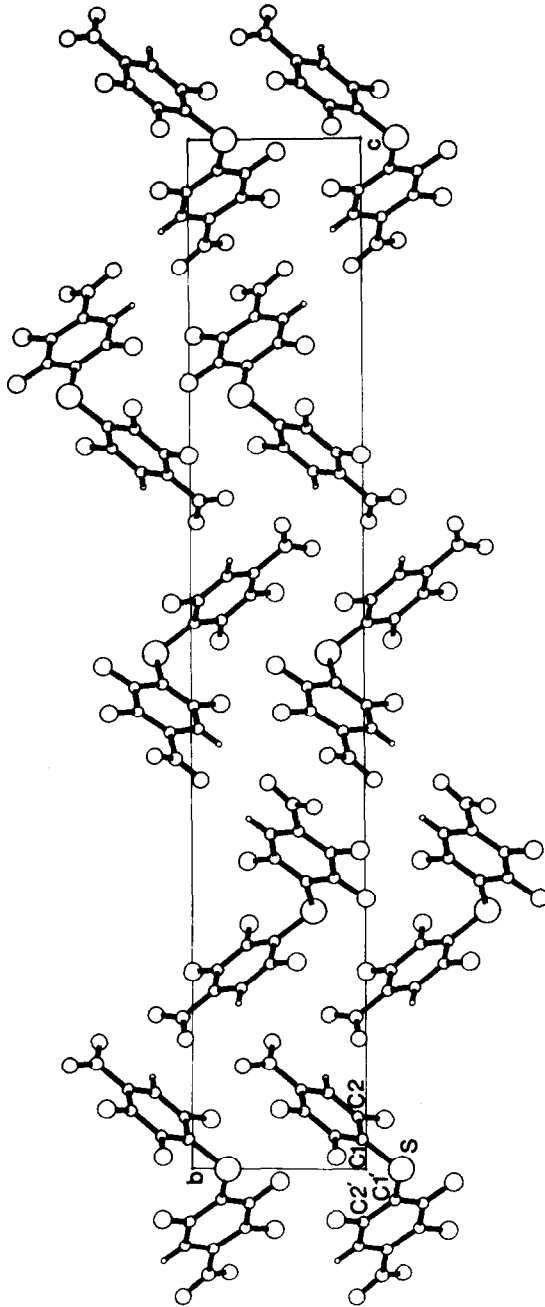
Fig. 2. Projection of the contents of the unit cell along the x axis.

EXPERIMENTAL

X-Ray measurements

Crystals were obtained by recrystallisation from acetone/methanol and a fragment with dimensions 0.6 x 0.4 x 0.2 mm was sealed in a Pantak capillary tube and aligned about the y axis. From oscillation and Weissenberg photographs the space group was determined as $P4_12_12$. Cell dimensions and intensity data were measured on a Stoe computer-controlled, two-circle diffractometer, operating in the ω scan mode, with graphite monochromated Mo-Kα radiation and a scintillation counter. For layers h0ℓ – h2ℓ, 120 counts of 1 s at 0.01° intervals were taken for each reflection. For layers h3ℓ – h7ℓ, a variable scan range was used as previously described [12,13]. Backgrounds were measured for 30 s at each end of a scan. Four zero layer reflections were remeasured after each layer of data collection to monitor the stability of the system, and layer scale factors were calculated from these reflections. These showed only small variations from unity. Of 1721 unique reflections measured in the range $0.1 \leqslant \sin\theta/\lambda \leqslant 0.7$ Å^{-1}, 780 with $I > 2.5\sigma(I)$ were considered to be observed and used in the analysis. Absorption corrections were not applied in the conversion of intensities to structure amplitudes.

Crystal data

$C_{12}H_2F_6N_2O_4S$. Tetragonal, a = b = 6.10(1), c = 37.16(2) Å, U = 1383 Å^3, Z = 4, D_c = 1.85 g cm^{-3}. Space group $P4_12_12$. Molecular symmetry 2(C_2). Absorption coefficient for Mo-Kα radiation (λ = 0.71069 Å) = 2.71 cm^{-1}.

Structure determination

The structure was solved by direct methods using the SHELX system of programs [20]. From the E-map with the highest figure of merit, all atoms except the NO_2 group, C(4) and the hydrogen atom, were located. Six cycles of full matrix least-squares refinement of coordinates and isotropic thermal parameters reduced the discrepancy factor, R, from 43% to 33% and the remaining heavier atoms were located from a Fourier map.

Refinement with isotropic thermal parameters reduced R to 13.4%.   With
the introduction of anisotropic thermal parameters and a further three
cycles of least squares refinement, the hydrogen atom was located from a
difference Fourier.   The refinement was terminated with R = 4.5% for
780 observed structure amplitudes.   The weighting scheme employed was

$$w = 1/[\sigma^2(F) + 0.0002F^2]$$

where $\sigma(F)$ is the standard deviation in the observed amplitudes based on
counting statistics.

Computations were carried out on the CDC 7600 computer at the
University of Manchester Regional Computer Centre and on the Birmingham
University ICL 1906A.

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