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EFFECTS OF FLUORINATION ON CONFORMATION AND BONDING IN DIPHENYL SULPHIDES

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SUMMARY

A survey of the solid-state structures of substituted diphenyl sulphides shows that when there are no more than three ortho substituents the molecules predominantly adopt a conformation in which the ring bearing the more electron-withdrawing substituents is oriented approximately parallel to the central C-S-C plane and the other ring is oriented approximately perpendicular to this plane. Theoretical calculations indicate that this is due to an electronic effect involving some conjugation between sulphur and the more electron-withdrawing ring. In fluorinated compounds interaction of one of the ortho fluoro substituents with the π-electron cloud and carbon 1 of the other ring, which carries a small negative charge, precludes this conformation, the preferred conformation having both rings approximately equally inclined to the C-S-C plane at an angle of ca. 55°. The bond angle at sulphur appears to be affected by the nature of the ring substituents, electron-withdrawing groups (F, NO_2) causing a small decrease in the size of the C-S-C angle.

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INTRODUCTION

The diphenyl sulphides have been extensively studied by X-ray crystallography [1,2] and by theoretical methods [3,4]. The object of these investigations has been to study the overall conformation of the molecules and the geometry of the central C–S–C group with its implications for the bonding state of the sulphur atom. It was noted by van der Heijden et al. [5] that, like the corresponding ethers, in the absence of steric factors, the ring bearing the relatively more electron-withdrawing substituents is oriented nearly parallel to the C–S–C plane, with the other ring, which might bear electron-donating substituents, oriented nearly perpendicular to this plane. Domenicano, Vaciago and Coulson, [3] independently, suggested that this conformation would favour the interaction of the filled $3p_z$ orbital of sulphur with the Π system of the parallel ring which has, relative to the other ring, electron-withdrawing substituents. Further, the empty $3d_{xy}$ orbital of sulphur could interact with the Π system of the other ring oriented perpendicular to the C–S–C plane.

In 1979 we found [6] that while diphenyl sulphides generally adopted the above mentioned conformation, described as 'skew' by van der Heijden et al., [7] even when the compounds were substituted symmetrically (see Fig. 1), bis(2,3,6-trifluoro-4-nitrophenyl) sulphide adopted a different conformation, wherein the two phenyl rings are oriented at approximately the same angle to the C–S–C plane. This conformation is denoted as 'twist' in the nomenclature of van der Heijden et al. [7] (see Fig. 2). Two of the nine non-fluorinated diphenyl sulphides listed by Goodhand and Hamor [6] have the twist conformation, but tending towards skew. One of these is the symmetrically-substituted 4,4'-diaminodiphenyl sulphide [8], dihedral angles 68 and 27° and the other is in the crystal structure of N-(3-dimethylammoniopropyl)-2-amino-4-chlorodiphenyl sulphide maleate [9] where the dihedral angles with respect to the C–S–C plane are 66° (electron-donating ring) and 31° (electron-withdrawing ring). In all cases of unsymmetrical substitution, the ring carrying an electron-withdrawing substituent is oriented at $\leqslant 31^\circ$ to the C–S–C plane. If the dihedral angles are taken to be $< 90^\circ$, and their signs are given in each case by the sign of the smaller C–C–S–C torsion angle, in most cases these signs are the same. Exceptions occur only in a few skew conformers where one of the angles is quite small, or quite close to 90°.

Since 1979, the crystal structures of some fifteen additional diaryl sulphides have been reported [1] and those of the fluorinated derivatives bis(4-trifluoromethyl-tetrafluorophenyl) sulphide and bis(tetrafluoro-4-nitrophenyl) sulphide have been determined [2]. In general these new structures conform to the conformational patterns established previously, both fluorinated compounds adopting twist conformations.

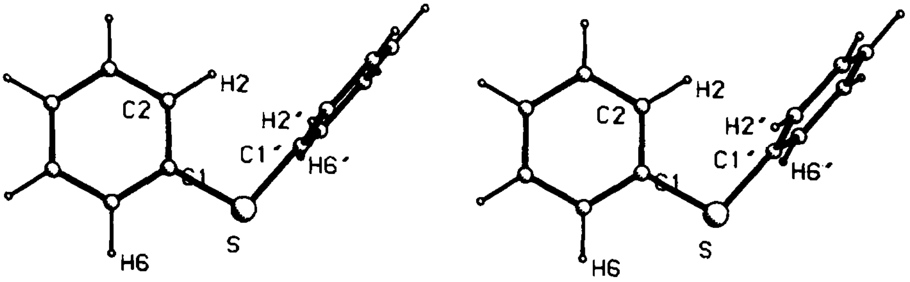

Fig.1. Stereoscopic view of the skew (90,0) conformation of a model of the diphenyl sulphide molecule viewed in a direction rotated 10° from the perpendicular to the C1-S-C1' plane.

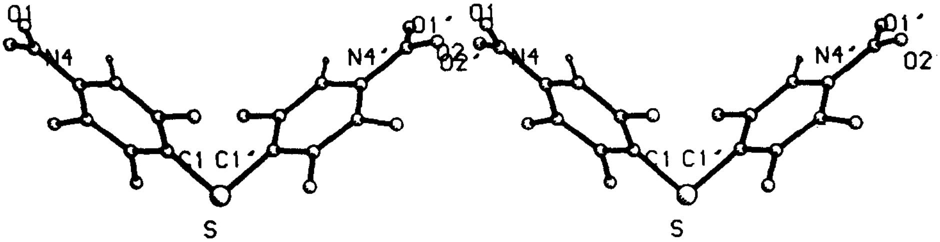

Fig.2. Stereoscopic view of the twist (61,61) conformation of the bis(2,3,6-trifluoro-4-nitrophenyl) sulphide molecule viewed in a direction perpendicular to the C1-S-C1' plane; both rings are inclined at 61° to the C1-S-C1' plane.

In the present paper the results of analysing the energetics of diphenyl sulphide conformation by molecular obital (MNDO), [10] molecular mechanics [11] and simple van der Waals non-bonded interaction [11] calculations are reported, with particular reference to the effects of fluorination on bonding and conformation.

RESULTS AND DISCUSSION

(a) The experimental data

In Tables 1a and 1b are listed the 28 diaryl sulphide systems used in the present analysis together with the references to the crystal structure determinations. Compounds (1)–(18) (Table 1a) are unsymmetrically substituted compounds, so that a distinction can be made between rings bearing electron-withdrawing and electron-donating substituents; or one ring may be more electron withdrawing or more electron donating than the other ring. Under α and β are listed the angles (defined to be $\leq 90^\circ$) which the rings bearing respectively the relatively more electron-donating and the more electron-withdrawing substituents make with the C–S–C plane. The signs of α and β are given by the respective C–C–S–C torsion angles. Compound (18), $\alpha = 90$, $\beta = 0^\circ$ is depicted in Fig. 3. The corresponding C–S bond lengths and C–S–C angles are also listed. Compounds (19)–(28) (Table 1b) are symmetrically substituted, (26)–(28) having fluorine substituents in the four ortho positions. Here there is no distinction betwen the rings and the dihedral angles are listed in order of size.

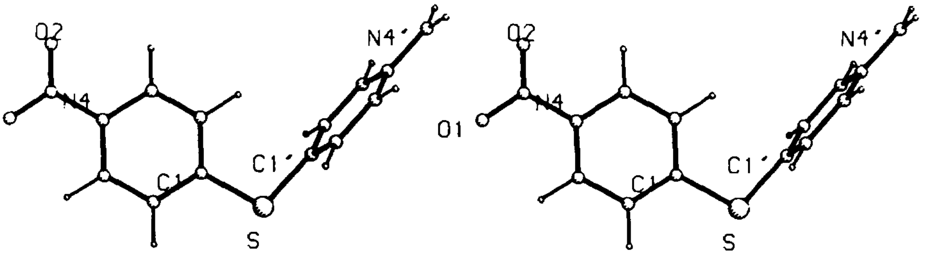

Fig. 3. Stereoscopic view of the skew (90,0) conformation of 4-nitro-4'-aminodiphenyl sulphide [compound (18)] viewed in a direction rotated 10° from the perpendicular to the C1–S–C1' plane.

The dihedral angles for these 28 compounds are plotted in Fig. 4. The horizontal axis represents the larger of the two angles and the vertical axis the smaller angle. It can be seen that the unsymmetrically-substituted compounds fall predominantly into the skew classification; only five are 'twist' and four of these are fairly close (movements of α and $\beta < 10^\circ$) to the twist/skew boundary. In all cases except five,

TABLE 1

Selected structural parameters of diphenyl sulphides as determined by X-ray crystallography. Bond lengths are in A, angles in degrees. Listed are the dihedral angles between the C–S–C plane and the two phenyl rings, and the C–S bond lengths. The dihedral angles are taken to be < 90° with sign defined by the relevant C–C–S–C torsion angle. Multiple entries occur when the crystal contains more than one independent molecule.

(a) Unsymmetrically substituted compounds. The angle between the central C–S–C plane and the relatively more electron-donating ring is denoted α. The corresponding angle involving the other ring is denoted β.

Compound (S denotes 'sulphide')	Ref.	α	β	S-C_β	S-C_α	C_α-S-C_β
N-(3-dimethylammoniopropyl)-2-amino-2'-chlorodiphenyl S maleate (1)	12	75	6	1.781	1.771	104
N-(3-dimethylammoniopropyl)-2-amino-2',4-dichlorodiphenyl sulphide maleate (2)	13	74	-2	1.784	1.777	103
N-(3-dimethylammoniopropyl)-2-amino-4-chlorodiphenyl S maleate (3)	9	66	31	1.786	1.767	103
1,4-bis(phenylthio)benzene (4)	14	57	14	1.777	1.783	105
2,4-bis(phenylthio)nitrobenzene (5)	15	87 79	-6 -14	1.778 1.768	1.781 1.774	102 105
Methyl 2-(2-nitrophenylthio) benzoate (6)	16	82	4	1.757	1.782	103
Methyl 2-(2-nitrophenylthio) phenylacetate (7)	16	68	16	1.768	1.785	103

(continued)

TABLE 1 (cont.)

2-nitro-1,3-bis(phenylthio) benzene	(8)	17	85	-13	1.776	1.786	102
			83	14	1.777	1.781	101
Methyl 2-(4-nitrophenylthio) benzoate	(9)	18	6	80	1.780	1.783	102
2-diazoacetyl-4'-nitrodiphenyl S	(10)	18	32	46	1.766	1.777	102
hexakis(phenylthio)benzene S	(11)	19	56	25	1.772	1.769	103
4-dimethylaminodiphenyl S	(12)	4	85	-5	1.769	1.786	104
4-nitro-4'-dimethylamino-diphenyl S	(13)	20	69	2	1.774	1.791	106
2,4-dinitrodiphenyl S	(14)	21a	77	4	1.756	1.787	103
			86	12	1.751	1.784	103
		21b	76	4	1.758	1.775	103
			86	12	1.743	1.785	102
2-(4'-carbomethoxy-2'-nitro-thiophenyl)-1,3,5-trimethylbenzene	(15)	5	87	4	1.758	1.784	103
4-nitrodiphenyl S	(16)	20	84	-2	1.778	1.780	104
N-(3-diethylammoniopropyl)-2-amino-4-chlorodiphenyl sulphide oxalate	(17)	22	67	39	1.784	1.775	101
4-nitro-4'-aminodiphenyl S	(18)	23	90	0	1.771	1.780	104

(continued)

TABLE 1 (cont.)

(b) Symmetrically substituted compounds. The angles between the C-S-C plane and the phenyl rings are listed in order of magnitude.

		Ref.	Dihedral angles		C-S Bond lengths		C-S-C Angle
2,2'-thiobis(4-methyl)-6-t-butylphenol	(19)	24	68	68	1.780	1.780	105
4,4'-diaminodiphenyl S	(20)	8	27	68	1.808	1.785	104
2,2'-dinitrodiphenyl S	(21)	16	20	65	1.768	1.777	101
bis(3,4-dimethoxyphenyl) S	(22)	25	4	89	1.778	1.764	103
2,2'-dimethyldiphenyl S	(23)	26	7	79	1.776	1.776	103
dimethyl-2,2'-thiodibenzoate	(24)	16	22	82	1.785	1.787	102
4,4'-dimethyldiphenyl S	(25)	27	32	39	1.75	1.74	110
bis(2,3,6-trifluoro-4-nitrophenyl) S	(26)	6	61	61	1.772	1.772	100
bis(4-trifluoromethyl-tetrafluorophenyl) S	(27)	2	47	50	1.757	1.768	102
bis(tetrafluoro-4-nitrophenyl) S	(28)	2	54	61	1.768	1.773	100

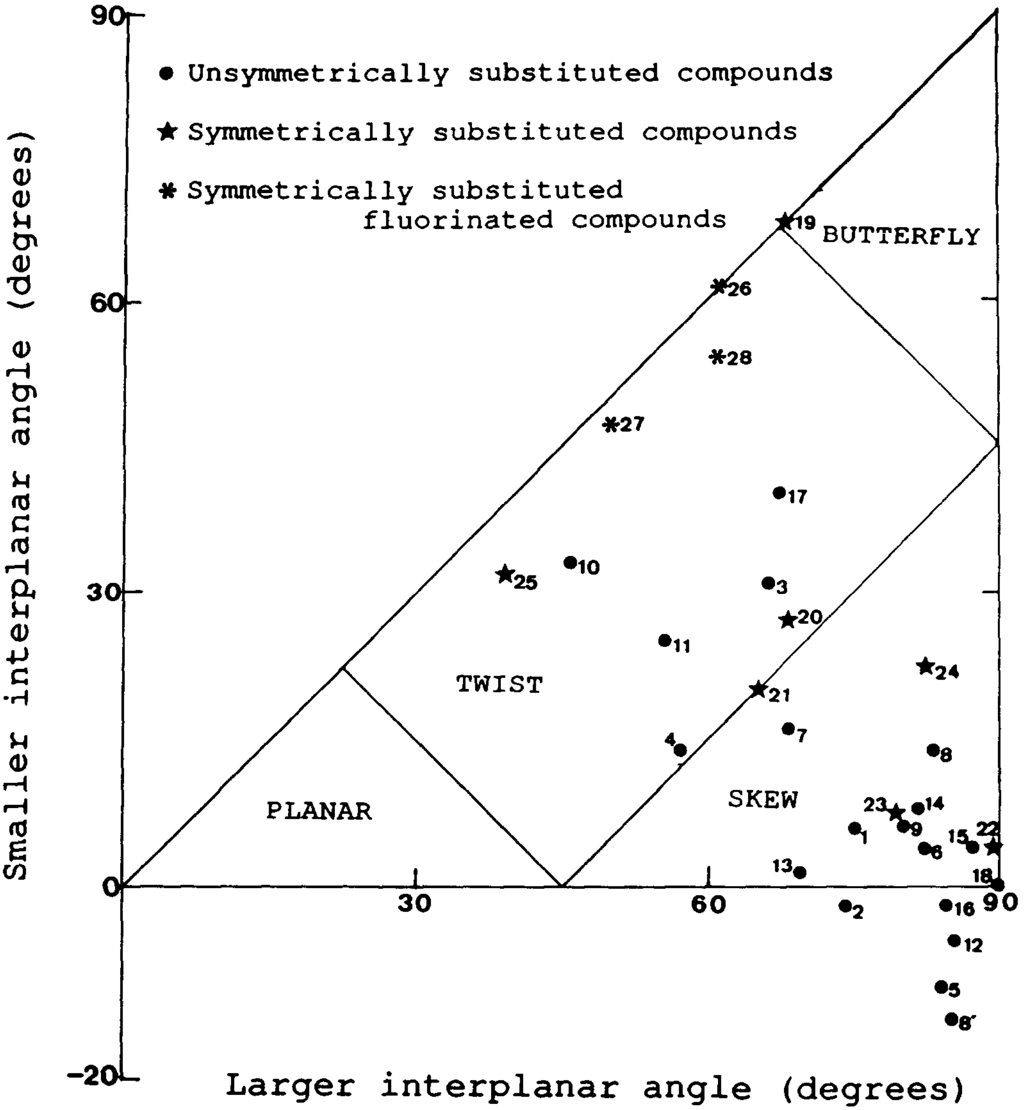

Fig. 4. Conformations of diphenyl sulphides. Plot of the dihedral angles listed in Table 1. The numbers refer to those in Table 1. With the exception of compound (8), multiple entries in Table 1 are represented by mean values.

the signs of α and β are the same. In all of these five compounds one of the angles is quite small, maximum 14.0°. Of the ten symmetrically-substituted compounds (19)-(28), three are skew, one lies on the twist/skew boundary, five are twist and one has a steep twist conformation, described by van der Heijden et al. [5,7] as the 'butterfly' conformation. Thus for the symmetrically-substituted diphenyl sulphides the trend is towards a twist conformation, rather than the skew conformation of the unsymmetrical compounds. It is noteworthy that all three fluorinated compounds have a near ideal twist conformation, with the two phenyl rings inclined at approximately equal angles to the C-S-C plane.

Considering the unsymmetrically substituted compounds, in every case except two [compounds (9) and (10)], the angle α, defined above, is larger than β. In 13 out of the 18 compounds β is less than 20° so that the electron-withdrawing ring can be said to be nearly parallel to the C-S-C plane, and in 10 of these α is greater than 70°; a further four have $\alpha > 65°$. The prediction of van der Heijden et al. [5,7] regarding the orientation of the rings in unsymmetrical diphenyl sulphides, as exemplified by compound (18) (Fig. 3), is therefore, confirmed.

In the two exceptions to this pattern of orientation, both rings bear electron-withdrawing substituents. Compound (9) has a nitro group in one ring competing with an almost-as-strong electron-withdrawing carboxylic ester group in the other ring, while (10) has one ring bearing a nitro group and the other ring a diazoacetyl group. The distinction between the rings regarding their relative electron-withdrawing power is, therefore, rather finely balanced in these compounds.

(b) Theoretical considerations

In terms of simple valence bond theory one can picture the electron distribution in e.g. 4-nitro-4'-aminodiphenyl sulphide as involving conjugation between the sulphur lone pair and the oxygen atoms of the electron-withdrawing nitro group. The S-C($PhNO_2$) bond (S-C_β in our convention) attains partial double bond character thus forcing the ring to orient parallel or nearly parallel to the C-S-C plane. Steric effects would then drive the other ring to a near-perpendicular orientation. The presence of an electron-releasing amino-substituent in this ring, however, enhances the electronic effect of the nitro group.

Inspection of S-C bond lengths (Table 1a) shows that in 13 out of the 18 compounds, the bond to the more electron-withdrawing ring, S-C_β, is shorter than that to the other ring. Mean values are S-C_β 1.773(2)A, S-C_α 1.780(1)A*, a small but

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* Values in parenthesis are the estimated standard deviations in the mean.

significant difference pointing to the relevance of the conjugative effect postulated above. Four of the five exceptions to this pattern of bond length differences are in the cationic compounds (1)–(3) and (17), despite the fact that the orientations of the phenyl rings with respect to the C–S–C plane are consistent with S → C_β conjugation. If the four cationic compounds are excluded from the averaging, the mean values for S–C_β and S–C_α become 1.769(2) and 1.782(1)A, respectively, a much clearer distinction. The fifth case of S–C_β > S–C_α occurs in compound (11), but the difference between the lengths is only 0.003A.

Table 2 shows the results of van der Waals [11], molecular mechanics [11] and MNDO molecular orbital [10] calculations on amino and nitro–substituted diphenyl sulphides using standard bond lengths and angles in modelling the molecules. The geometry at sulphur, (C–S, 1.774A, C–S–C, 103°) is derived from the known structures of diphenyl sulphides. Enthalpies calculated by the MNDO method clearly favour the predominant conformation found in the solid state, α = 90°, β = 0° [Table 1a, see specifically compounds (18), (16) and (12)]. Van der Waals and molecular mechanics calculations give essentially the same energies for the two conformations. It is, therefore, electronic rather than steric factors which influence the orientation of the rings, the nitro group having a greater effect than

TABLE 2

Calculated parameters for amino– and nitro–substituted diphenyl sulphide model molecules. Energies are in kJ mol^{-1}

	4-NO_2-4'-NH_2	4-NO_2	4-NH_2
(a) α=0°, β=90°			
Van der Waals energy	1144	1023	940
Molecular mechanics energy	137	148	109
MNDO enthalpy of formation	349	324	267
Bond order S-C_β	0.972	0.972	0.973
Bond order S-C_α	0.973	0.978	0.975
(b) α=90°, β=0°			
Van der Waals energy	1144	1023	940
Molecular mechanics energy	136	147	110
MNDO enthalpy of formation	341	319	265
Bond order S-C_β	0.994	0.993	0.981
Bond order S-C_α	0.977	0.975	0.975

the amino group. This is further indicated by the higher bond order of the S–C_β bond in the preferred conformation. All three types of energy calculation, however, show lower energies for twist or butterfly conformations with $\alpha = \beta$. For 4–nitro–4'–aminodiphenyl sulphide, van der Waals energy calculations show a minimum of 1138 kJ when $\alpha = \beta = 65^o$, the molecular mechanics energy reaches a minimum of 115 kJ when $\alpha = \beta = 32^o$ and the MNDO enthalpy is at a minimum of 329 kJ at $\alpha = \beta = 90^o$. In agreement with experimental results, conformations of type $\alpha = -\beta$, when β is in the range 20–70° have higher energies.

Figure 5 shows the conformational enthalpy space with respect to dihedral angles between the aromatic rings and the C–S–C plane calculated for an idealised diphenyl sulphide molecule by the MNDO method. Axes are as for Fig. 1; contours are drawn at 8 kJ intervals with the lowest enthalpy taken to be zero (both dihedral angles 90°). The experimental values for the symmetrically substituted diphenyl sulphides listed in Table 1 are plotted on this diagram using the same conventions as for Fig. 1. All the experimental points lie no more than 24 kJ above the global minimum, 225 kJ*. There are, however no experimental points close to the minimum, the closest being compound (19) (dihedral angles both 68°).

The conformational behaviour of the three fluorinated compounds (26)–(28) differs from those of the other compounds in that none of them adopt the skew conformation, and all are close to an ideal twist conformation with equal dihedral angles. Figure 6 is analogous to Fig. 5, but the MNDO molecular orbital enthalpy calculations are based on decafluorodiphenyl sulphide. Here the global minimum is displaced from 90,90 to approximately 70,70 and the enthalpy rises very much more rapidly away from the twist/butterfly equal angles region, but the overall picture is quite similar. The contour lines representing the 80 and 120 kJ enthalpy levels have been included to emphasize the qualitative similarity between Figs. 5 and 6.

Thus the enthalpy at 90,0 is 88 kJ above the global minimum, compared with only 16 kJ for the unfluorinated analogue. The same trend appears also in simple van der Waals energy calculations, the energy at 90,0 being repectively 5 kJ and and 30 kJ above the global minimum for the hydrocarbon and the fluorocarbon. It is evident that a conformation close to 90,0 adopted by many diphenyl sulphides (see Table 1 and Figs. 4 and 5) would be energetically unfavourable for fluorinated diphenyl sulphides, even if one ring is strongly electron–withdrawing relative to the other ring.

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* This value may be compared with the experimental [28] enthalpy of formation of diphenyl sulphide, 231 ± 3 kJ mol^{-1}. The structure of diphenyl sulphide has been studied by gas–phase electron diffraction. Two twist conformations with C_2 symmetry and dihedral angles of 43 and 56° fit the experimental data best [29]. No crystal structure analysis for diphenyl sulphide is, as yet, available [1].

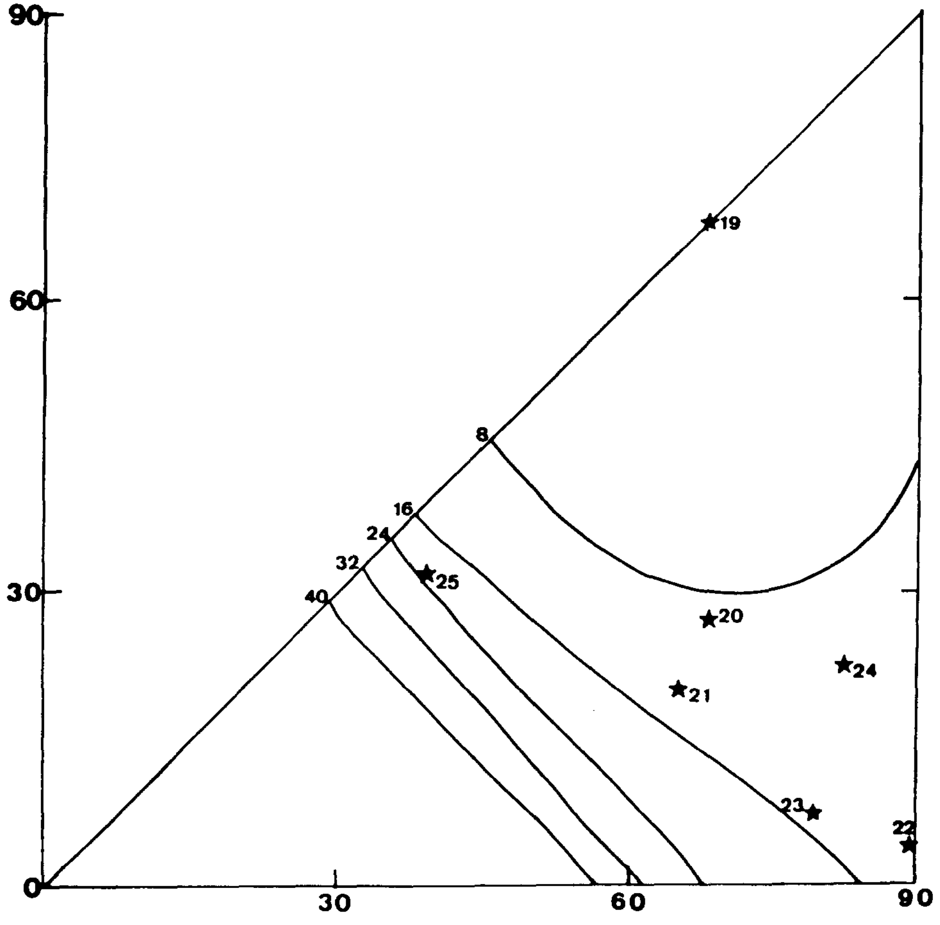

Fig. 5. Conformational enthalpy contour map for diphenyl sulphide. Conformational parameters are the two dihedral angles defined in Table 1. Enthalpies calculated by the MNDO molecular orbital method. Contours at 8, 16, 24, 32 and 40 kJ above global minimum.

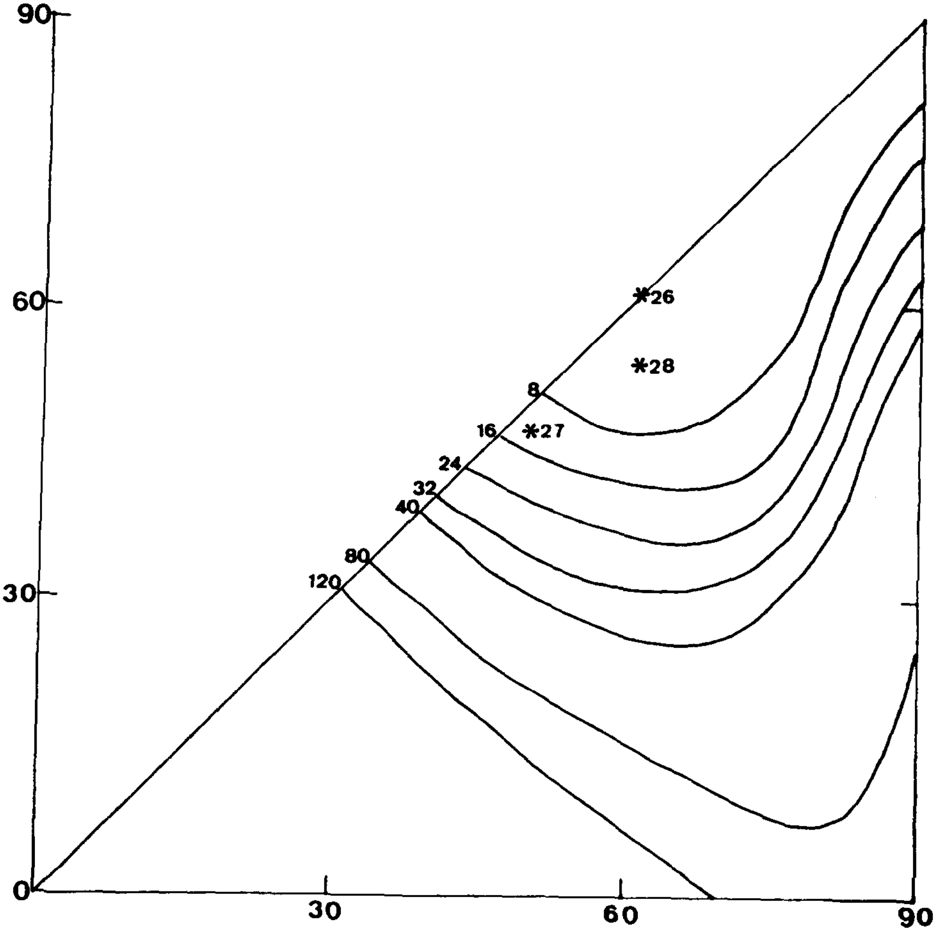

Fig. 6. Conformational enthalpy contour map for decafluorodiphenyl sulphide. Conformational parameters as for Fig. 5. Contours at 8, 16, 24, 32, 40, 80 and 120 kJ above global minimum.

That the skew conformation is energetically unfavourable for the fluorinated compounds does not appear to be due to repulsive interactions between the ortho fluoro substituents. The closest F ... F distances are F2 ... F2' and F2 ... F6' (see Fig. 7), both 3.25 Å, and at least 0.25 Å greater than the sum of the van der Waals radii [30].

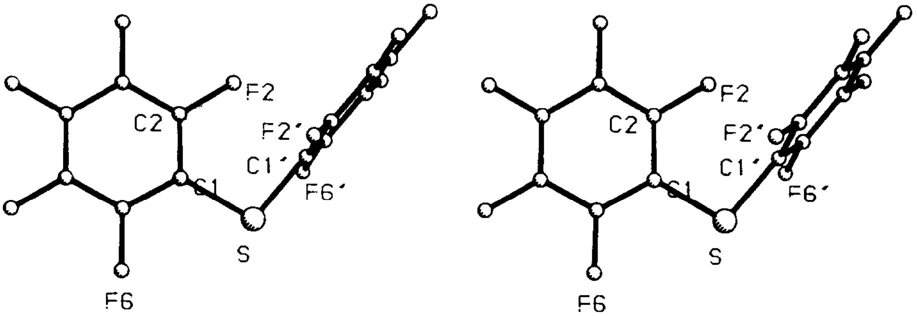

Fig. 7. The skew (90,0) conformation of a model of the decafluorodiphenyl sulphide molecule showing the close contact between F2 and C1'.

Of significance is the ortho F atom of the in-plane ring (F2 in Fig. 7) linked to the carbon atom which is oriented synperiplanar to C1 of the other ring (C1' in Fig. 7). F2 lies above the plane of this ring at a distance of 2.24 Å from C1'. It is presumably the interaction of the electronegative fluorine atom (negative charge calculated by MNDO, 0.18 e) with the π-electron cloud and with C1', which carries a negative charge of 0.26 e, which makes this conformation unfavourable. To confirm the role of this fluorine atom, we replaced it with a hydrogen atom in our model of the fluorinated diphenyl sulphide system. The corresponding short H2 ... C1' distance is only slightly longer at 2.37 Å. However, here we have the favourable situation of a $\delta(+)$ hydrogen atom close to the $\delta(-)$ π-electron cloud and the $\delta(-)$ C1'. The MNDO calculations show a positive charge of 0.08 e on the hydrogen and a negative charge of 0.27 e on C1'. The MNDO enthalpy for this (90,0) skew conformation is only 17 kJ above the global minimum, the butterfly conformation with both dihedral angles 70°, a similar enthalpy difference to that found for diphenyl sulphide itself.

Studies by Gould et al. [31] and by Burley and Petsko [32] have shown that interactions between aromatic rings similar to those of diphenyl sulphides in the skew conformation are common in protein crystal structures. Non-bonded interaction energy calculations [32] lead to an enthalpic contribution of approximately 8 kJ mol^{-1} to the stability of the system when the aromatic rings are oriented as in the skew conformation of diphenyl sulphides, with the significant ortho position occupied by a hydrogen atom. It may be noted that all the compounds with the skew conformation listed in Tables 1a and 1b have a hydrogen atom at this ortho position, although the other ortho sites may be occupied by other atoms.

The additional stabilisation of the skew conformation due to the $\delta(+)$ hydrogen ... π-electron cloud interaction may be the reason for the failure of the MNDO method, which is not sensitive to non-bonded attractive interactions of this type, to predict the skew conformation as the preferred conformation for most diphenyl sulphides. In the case of 4-nitro-4'-aminodiphenyl sulphide (see Table 2), such an interaction would account for ca 8 of the 12 kJ mol^{-1} by which the calculated enthalpy of the observed [23] skew conformation exceeds that of the predicted butterfly (90,90) conformation.

The conformations of the diaryl sulphides discussed above are undoubtedly affected to some extent by crystal packing forces. The fact, however, that the experimentally derived crystal conformations can be largely rationalised by theoretical calculations on the isolated molecules, indicates that packing forces may be considered as 'noise', probably having only a small and random effect on conformation. As far as we are aware, the only gas-phase structural study of a diaryl sulphide [33] is that of diphenyl sulphide [29]. The postulated twist (43,43) or (56,56) conformations (see footnote on page 55) are both in good agreement with solid-state results for related molecules and with theoretical calculations.

(c) The bond angle at sulphur

In our earlier paper [6], we noted that whilst in bis(2,3,6-trifluoro-4-nitrophenyl) sulphide, the bond angle at sulphur was 99.7°, in the nine unfluorinated diaryl sulphides whose crystal structures were known [compounds (1),(2), (3), (12), (13), (15), (16), (20) and (23), but excluding (25) for which structural parameters are of relatively low accuracy] this angle ranged from 102.9 to 105.6°, mean 103.7°. The closing up of this angle by some 4° was rationalised [6] in terms of rehybridization effects [34], the greater electronegatively of the fluorinated rings inducing a greater degree of p-character in the sulphur bonding orbitals directed towards C1 and C1', compared with the unfluorinated sulphides, resulting in a smaller bond angle at sulphur.

Inclusion of the additional two fluorinated and fifteen unfluorinated compounds whose crystal structures are now known gives for the angles at sulphur a range of 99.7 –

102.0, mean 100.5 (8)° in the fluorinated compounds (26)-(28) and 100.8 - 105.6, mean 103.2 (3)° in compounds (1)-(24), a much less clear-cut difference. Five unfluorinated compounds have angles at sulphur in the range 100.8 - 101.8°, i.e. a smaller angle than that found in the fluorinated compound (27). Four of these, however, contain either one or two ortho nitro substituents or a para nitro substituent in one ring and another electron-withdrawing group in the other ring. None of these compounds contains an electron-donating substituent. A similar rehybridization mechanism may, therefore, be operative here, as was postulated [6] for the fluorinated compounds, so that the angle at sulphur might be expected to be relatively small.

This pattern of bond angle variation at sulphur is, however, not replicated by MNDO calculations. Thus for decafluorodiphenyl sulphide in its optimum butterfly (70,70) conformation, the angle at sulphur refines to 106.8°, whilst for diphenyl sulphide in the butterfly (70,70) and optimum (90,90) conformations, the angle at sulphur refines to 105.6 and 105.0°, respectively.

There is no correlation between conformation and the angle at sulphur. Thus the mean C-S-C angle is 103° for both the twist and the skew compounds.

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REFERENCES

1 Cambridge Structural Database, Cambridge Crystallographic Data Centre, Cambridge, England, 1988.

2 N. Goodhand and T.A. Hamor, Acta Crystallogr., C45 (1989) 1609.

3 A. Domenicano, A. Vaciago and C.A. Coulson, Acta Crystallogr., B31 (1975) 1630.

4 G. Bandoli, D.A. Clemente, E. Tondello and A. Dondoni, J. Chem. Soc., (Perkin Trans. 2), (1974) 157.

5 S.P.N. van der Heijden, W.D. Chandler and B.E. Robertson, Can. J. Chem., 53 (1975) 2102.

6 N. Goodhand and T.A. Hamor, J. Fluorine Chem., 14 (1979) 223.

7 S.P.N. van der Heijden, E.A.H. Griffith, W.D. Chandler and B.E. Robertson, Can. J. Chem., 53 (1975) 2084.

8 B.K. Vijayalakshmi and R. Srinivasan, J. Cryst. Mol. Struct., 3 (1973) 147.

9 P. Marsau and M. Cotrait, Acta Crystallogr., B32 (1976) 3135.

10 M.J.S. Dewar and W. Thiel, J. Am. Chem. Soc., 99 (1977) 4899; 4907. Version of AMPAC (QCPE 506) implemented on the CYBER 205 at the University of Manchester Regional Computer Centre.

11 Chem-X, developed and distributed by Chemical Design Ltd., Oxford, England. Version of October 1987.

12 P. Marsau and M. Cotrait, Acta Crystallogr., B32 (1976) 3138.

13 P. Marsau, Acta Crystallogr., B33 (1977) 2897.

14 G.D. Andreetti, J. Garbarczyk and M. Krolikowska, Cryst. Struct. Commun., 10 (1981) 789.

15 J.D. Korp, I. Bernal, R.F. Miller, J.C. Turley, L. Williams and G.E. Martin, J. Cryst. Mol. Struct., 8 (1978) 127.

16 A. Kucsman, I. Kapovits, L. Parkanyi, G. Argay and A. Kalman, J. Mol. Struct., 125 (1984) 331.

17 V.M. Lynch, S.H. Simonsen, R.F. Miller, J.C. Turley and G.E. Martin, Acta Crystallogr., C41 (1985) 1240.

18 A. Kucsman, I. Kapovits, L. Parkanyi and A. Kalman, J. Mol. Struct., 140 (1986) 141.

19 A.D.U. Hardy, D.D. MacNicol and D.R. Wilson, J. Chem. Soc., (Perkin Trans. 2), (1979) 1011.

20 A. Krajewski, L. Riva di Sanseverino, A. Dondoni and A. Mangini, J. Cryst. Mol. Struct., 5 (1975) 345.

21 a. J.D. Korp, I. Bernal and G.E. Martin, J. Cryst. Mol. Struct., 11 (1981) 11;
b. V. Cody and P.A. Lehmann, Cryst. Struct. Commun., 11 (1982) 1671.

22 P. Marsau, M. Cotrait, J.P. Bonte and M. Debaert, Acta Crystallogr., B37 (1981) 1640.

23 H. Abdel-Halim, D.O. Cowan, D.W. Robinson, F.M. Wiygul and M. Kimura, J. Phys. Chem., 90 (1986) 5654.

24 L.A. Chetkina, V.E. Zavodnik, V.K. Bel'skii, I.G. Arzamanova, M.I. Naiman and Y.A. Gurvich, Zh. Strukt. Khim., 25 (1984) 114.

25 K. von Deuten and G. Klar, Cryst. Struct. Commun., 10 (1981) 231.

26 M. Sacerdoti, V. Bertolasi and G. Gilli, Cryst. Struct. Commun., 5 (1976) 477.

27 W.R. Blackmore and S.C. Abrahams, Acta Crystallogr., 8 (1955) 329.

28 J.B. Pedley, R.D. Naylor and S.P. Kirby 'Thermochemical Data of Organic Compounds', Chapman and Hall, London and New York, 1986.

29 B. Rozsondai, J.H. Moore, D.C. Gregory and I. Hargittai, Acta Chim. (Budapest), 94 (1977) 321; cited in ref. 33.

30 A. Bondi, J. Phys. Chem., 68 (1964) 441.

31 R.O. Gould, A.M. Gray, P. Taylor and M.D. Walkinshaw, J. Am. Chem. Soc., 107 (1985) 5921.

32 S.K. Burley and G.A. Petsko, J. Am. Chem. Soc., 108 (1986) 7995.

33 V.A. Naumov, in I. Hargittai and M. Hargittai (eds.), 'Stereochemical Applications of Gas-Phase Electron Diffraction, Part B,' VCH Publishers, New York and Weinheim (1988) p. 93.

34 H.A. Bent, Chem. Rev., 61 (1961) 275.