Crystal, Molecular, and Electronic Structure of 4-Dimethylaminophenyl Phenyl Sulphide

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The crystal structure of the title compound has been determined by three-dimensional *X*-ray analysis. Crystals are monoclinic, space group $P2_1/c$, with cell dimensions a = 7·963(6), b = 12·297(7), c = 13·254(7) Å, β 97° 18′(5), Z 4. The structure has been solved by the symbolic-addition procedure from 1322 reflections collected by counter, and refined by least-squares methods to R 0·053. The S–C bond lengths are equivalent [1·769(4) and 1·786(4) Å] and significantly shorter than the S–C distance in other diaryl sulphides, and than the sum of Pauling's single-bond covalent radii; C–S–C is 104·1(2)°. The normals to the two aromatic rings form an angle of 82·2°. The electronic distribution of the ground state of the molecule is discussed in terms of the CNDO method.

THE nature of the orbitals used in bonding by the sulphur atom in diaryl sulphides has not yet been completely elucidated. A partial summary of the various determinations of the S–C bond length and the C–S–C bond angle was presented by Blackmore and Abrahams in 1955.[1] Thereafter, the distribution of the valency bonds in divalent sulphur in various environments received considerable attention,[2] but the role of 3d sulphur orbitals (and also the 4s orbital) on structure and reactivity of organic sulphides [3] is still a matter of controversy. In order to gain some insight into this problem, we have carried out an *X*-ray structural determination of 4-dimethylaminophenyl phenyl sulphide with the aim of evaluating the influence of the NMe_2 group on the C–S bond length and on the degree of conjugation. The electronic distribution in the ground state of the molecule has been evaluated by the CNDO/2 method. A partial report on the molecular structure of the title compound has appeared previously.[4]

EXPERIMENTAL

The sulphide, prepared as reported,[5] was crystallized from light petroleum as prisms, m.p. 65—66°. For the *X*-ray analysis, a small prismatic crystal of dimensions 0·08 × 0·15 × 0·21 mm was mounted with its length (the a axis) along the direction of a glass fibre. Weissenberg and procession photographs were taken for preliminary determination of the space group, but the cell dimensions and intensity data were measured on a Siemens AED automated four-circle diffractometer, with Cu-target tube at a take-off angle 4·5° equipped with a Na(Tl)I scintillation counter. Accurate values of lattice and orientation parameters were derived by least-squares refinements.[6]

Crystal Data.—$C_{14}H_{15}NS$, M = 229·3. Monoclinic, a = 7·963(6), b = 12·297(7), c = 13·254(7) Å, β = 97° 18(5)′, U = 1287·4 Å^3, D_c = 1·182 g cm^{-3}, Z = 4, D_m (by flotation) = 1·17 g cm^{-3}, $F(000)$ = 488. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 19·3 cm^{-1}. Space group $P2_1/c$ from systematic absences: $h0l$ for l odd, $0k0$ for k odd.

Intensity data were measured using the θ—2θ scan method and $1/Lp$ corrections were applied to net counts, but absorption corrections were ignored since $(\mu t)_{av.}$ =

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0·29.[7] In the reciprocal space corresponding to $2\theta_{\text{max.}} = 100°$ ($\sin\theta/\lambda$ 0·50), there are 1322 non-equivalent lattice sites excluding those prohibited by the space group, and of these 1058 were observed and found to be above threshold. All reflections were re-measured with the same tube-current setting; the $|F_o|$ data were the best least-squares values derived from the two sets of measurements, using the method of ref. 8.

Structure Determination and Refinement.—The structure was determined by the symbolic-addition procedure for centrosymmetric crystals,[9] using a multiple-solution computer program.[10] Scattering factor curves were those of ref. 11(*a*), except for hydrogen which were taken from ref. 11(*b*). Normalized structure factor amplitudes $|E|$ were calculated according to Karle and Hauptman.[12]

TABLE 1

Final fractional co-ordinates and anisotropic parameters with their standard deviations (all $\times 10^4$)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	−759(1)	3467(1)	666(1)	245(3)	53(1)	76(1)	−19(2)	89(2)	−14(1)
N	−5111(4)	248(3)	2515(3)	214(7)	98(3)	72(2)	−26(8)	35(7)	17(4)
C(1)	477(5)	2716(3)	−108(3)	171(8)	66(3)	44(2)	−5(7)	2(7)	18(4)
C(2)	322(5)	1609(3)	−300(3)	185(8)	73(4)	82(3)	−19(8)	65(8)	8(5)
C(3)	1319(6)	1091(4)	−941(3)	295(10)	64(4)	80(3)	24(10)	69(9)	1(5)
C(4)	2487(6)	1670(4)	−1381(3)	224(9)	114(5)	63(3)	72(10)	61(8)	7(5)
C(5)	2661(5)	2776(4)	−1213(3)	182(8)	96(4)	71(3)	−35(9)	18(8)	26(6)
C(6)	1701(5)	3294(3)	−571(3)	202(8)	63(3)	71(3)	−45(8)	27(8)	18(5)
C(7)	−2019(5)	2462(3)	1188(3)	220(9)	66(3)	54(3)	3(8)	2(7)	−16(4)
C(8)	−1534(5)	2054(4)	2154(3)	184(8)	93(4)	60(3)	−14(9)	−1(7)	−8(5)
C(9)	−2540(5)	1314(4)	2593(3)	205(9)	102(4)	51(3)	−9(9)	24(8)	10(5)
C(10)	−4109(5)	987(3)	2083(3)	165(7)	64(3)	58(3)	5(7)	50(7)	−15(4)
C(11)	−4595(5)	1402(4)	1093(3)	205(8)	84(4)	59(3)	−4(9)	10(8)	−5(5)
C(12)	−3554(5)	2137(3)	676(3)	199(8)	76(3)	58(3)	24(8)	−19(7)	1(5)
C(13)	−4565(7)	−228(4)	3502(3)	336(12)	98(4)	74(3)	−40(12)	77(10)	45(6)
C(14)	−6685(6)	−142(5)	1964(4)	253(10)	130(5)	109(4)	−120(12)	13(11)	2(7)

The computed values for the distribution of $|E|$ for this structure, and the corresponding theoretical values which were calculated by Karle *et al.*[13] (in parentheses), were as follows: $\langle|E|\rangle = 0{\cdot}819$ (0·798), $\langle|E|^2\rangle = 0{\cdot}972$ (1·000), $\langle|E^2 - 1|\rangle = 0{\cdot}924$ (0·968); reflections with $|E| > 3$ were 0·38% (0·3%), reflections with $|E| > 2$ were 4·69% (5·0%), and reflections with $|E| > 1$ were 28·60% (32·0%).

The 272 reflections with $|E| \geqslant 1{\cdot}2$ (corresponding to 17 reflections per non-hydrogen atom) were separated from the rest of the data and their signs were deduced in terms of three signs for the origin-specifying reflections and four symbolic signs. The three-dimensional E-map, corresponding to the largest value of the consistency index (0·88),[10] gave the structure without ambiguity and there were no spurious peaks $> 1{\cdot}3$ in the map as large as those selected for the molecule (2·1—8·1). R, Corresponding to these starting parameters, was 0·23.

The assumed structure was refined by successive cycles of block-diagonal least-squares, employing only the observed reflections; R was reduced to 0·10 after four cycles with anisotropic thermal parameters, in the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

The positions of the hydrogen atoms were derived from a difference Fourier map. The peak heights for the hydrogen atoms were between 0·4 and 0·7 eÅ^{-3}, the residual electron densities on some of the bonds were as high as 0·25 eÅ^{-3}, and the background elsewhere was quite flat and within $\pm 0{\cdot}15$ eÅ^{-3}.

Three final cycles of refinement with full-matrix least-squares method (isotropic temperature factors for the hydrogen atoms) were carried out, giving R 0·053 for all observed data.

During the first cycles the weighting scheme was of the form: $w = 1/\sigma(|F_o|)$; in the last five cycles this was changed to: $w = (A|F_o|^2 + |F_o| + C)^{-1}$ where $A = 2/|F_o|_{\text{max.}}$ and $C = 2|F_o|_{\text{min.}}$. Final parameters for sulphur, nitrogen, and carbon atoms are listed in Table 1, and those for hydrogen atoms in Table 2. The σ values quoted in Tables 1 and 2 were calculated by use of 'International Tables for X-Ray Crystallography,' 1959, vol. II, p. 330. Observed and calculated structure factors are listed in Supplementary Publication SUP No. 20864 (6 pp.).*

Theoretical Calculations.—We have carried out a CNDO/2 calculation, according to the method of ref. 14 adapted to double precision for the CDC 6600 computer. The orthogonal co-ordinates of all atoms were assumed to be those derived from the X-ray structure determination. The arbitrary numbering scheme adopted for the atoms is shown in Figure 1 together with their total electronic densities from the first (Hückel type) and the last (self-consistent) cycle.

RESULTS AND DISCUSSION

A perspective drawing of the molecule is presented in Figure 2; bond lengths and their σ values, as calculated by the expression of ref. 15, are in Table 3, bond angles and their σ values in Table 4. These results are based on the refined co-ordinates and do not include corrections for thermal vibration. Equations of the least-squares planes, calculated by the procedure of ref. 16

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* For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1972, Index Issue. Items less than 10 pp. are supplied as full-size copies.

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and the deviations of atoms from these planes are in Table 5. Excluding hydrogen atoms, intramolecular non-bonded contacts <3·5 Å are in Table 6.

TABLE 2

Fractional co-ordinates ($\times 10^3$) and isotropic temperature factors of the hydrogen atoms, with estimated standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*	*B*/Å^2
H(2)	−69(6)	120(4)	0(3)	6·7(1·4)
H(3)	121(6)	34(4)	−108(3)	4·5(1·1)
H(4)	332(6)	131(4)	−188(3)	9·5(1·8)
H(5)	355(5)	309(3)	−150(3)	5·3(1·2)
H(6)	169(5)	402(4)	−41(3)	3·7(1·0)
H(8)	−2(7)	229(5)	240(5)	7·8(1·6)
H(9)	−208(5)	108(3)	330(3)	3·8(1·0)
H(11)	−578(7)	107(5)	80(4)	7·7(1·6)
H(12)	−405(5)	245(3)	0(3)	3·2(0·9)
H1(13)	−560(8)	−70(6)	368(4)	8·8(1·7)
H2(13)	−428(8)	43(6)	402(5)	9·6(1·8)
H3(13)	−337(6)	−65(5)	359(4)	2·8(0·9)
H1(14)	−732(7)	−68(6)	244(4)	7·3(1·5)
H2(14)	−629(9)	−46(7)	128(6)	4·9(1·1)
H3(14)	−756(7)	55(5)	178(4)	9·6(1·9)

TABLE 3

Bond lengths (Å), with estimated standard deviations in parentheses. Hydrogen atoms are numbered according to the carbon atom to which they are bonded

S–C(1)	1·769(4)	C(2)–H(2)	1·07(5)
S–C(7)	1·786(4)	C(3)–H(3)	0·94(5)
N–C(10)	1·380(5)	C(4)–H(4)	1·09(5)
N–C(13)	1·449(6)	C(5)–H(5)	0·93(4)
N–C(14)	1·450(6)	C(6)–H(6)	0·91(5)
C(1)–C(2)	1·387(6)	C(8)–H(8)	1·24(6)
C(2)–C(3)	1·389(6)	C(9)–H(9)	1·00(4)
C(3)–C(4)	1·360(7)	C(11)–H(11)	1·06(5)
C(4)–C(5)	1·382(7)	C(12)–H(12)	1·01(4)
C(5)–C(6)	1·371(6)	C(13)–H1(13)	1·06(7)
C(1)–C(6)	1·408(6)	C(13)–H2(13)	1·07(7)
C(7)–C(8)	1·384(6)	C(13)–H3(13)	1·08(5)
C(8)–C(9)	1·388(6)	C(14)–H1(14)	1·08(6)
C(9)–C(10)	1·402(6)	C(14)–H2(14)	1·07(8)
C(10)–C(11)	1·415(5)	C(14)–H3(14)	1·11(6)
C(11)–C(12)	1·388(6)		
C(7)–C(12)	1·380(6)		

TABLE 4

Bond angles (°), with estimated standard deviations in parentheses

C(1)–S–C(7)	104·1(0·2)	C(1)–C(2)–H(2)	116·6(2·6)
S–C(1)–C(2)	125·1(0·3)	C(3)–C(2)–H(2)	121·8(2·6)
S–C(1)–C(6)	117·1(0·3)	C(2)–C(3)–H(3)	121·5(2·9)
C(2)–C(1)–C(6)	117·8(0·4)	C(4)–C(3)–H(3)	118·7(2·9)
C(1)–C(2)–C(3)	121·2(0·4)	C(3)–C(4)–H(4)	123·7(2·6)
C(2)–C(3)–C(4)	119·8(0·4)	C(5)–C(4)–H(4)	115·9(2·6)
C(3)–C(4)–C(5)	120·4(0·4)	C(4)–C(5)–H(5)	114·1(2·6)
C(4)–C(5)–C(6)	120·3(0·4)	C(6)–C(5)–H(5)	125·1(2·6)
C(1)–C(6)–C(5)	120·5(0·4)	C(5)–C(6)–H(6)	128·1(2·7)
S–C(7)–C(8)	120·3(0·3)	C(1)–C(6)–H(6)	111·3(2·7)
S–C(7)–C(12)	121·1(0·3)	C(7)–C(8)–H(8)	108·1(3·0)
C(8)–C(7)–C(12)	118·4(0·4)	C(9)–C(8)–H(8)	129·2(3·0)
C(7)–C(8)–C(9)	121·1(0·4)	C(8)–C(9)–H(9)	114·8(2·2)
C(8)–C(9)–C(10)	120·8(0·4)	C(10)–C(9)–H(9)	124·3(2·2)
C(9)–C(10)–C(11)	117·8(0·4)	C(10)–C(11)–H(11)	109·0(3·0)
C(10)–C(11)–C(12)	119·8(0·4)	C(12)–C(11)–H(11)	131·2(3·0)
C(7)–C(12)–C(11)	122·0(0·4)	C(11)–C(12)–H(12)	114·7(2·4)
N–C(10)–C(9)	121·0(0·3)	C(7)–C(12)–H(12)	123·2(2·4)
N–C(10)–C(11)	121·1(0·3)	N–C(13)–H1(13)	105·6(3·6)
C(10)–N–C(13)	121·1(0·3)	N–C(13)–H2(13)	106·7(3·6)
C(10)–N–C(14)	121·1(0·4)	N–C(13)–H3(13)	117·0(2·9)
C(13)–N–C(14)	117·6(0·4)	N–C(14)–H1(14)	110·2(3·3)
		N–C(14)–H2(14)	102·8(4·2)
		N–C(14)–H3(14)	109·6(2·9)

The S–C(1) and S–C(7) bond distances [1·769(8) and 1·786(8) Å respectively] and the C(1)–S–C(7) angle (104·1°) are in agreement with those for di-*p*-tolyl sulphide[1] (1·75 Å, 109°) and bis-*p*-bromophenyl sulphide[2] (1·75 Å, 109·5°) obtained from two-dimensional *X*-ray data. However, some disagreement exists between the values of the dihedral angle between the normals to the planes of the aromatic rings; in our

TABLE 5

Equations of least-squares planes, with deviations (Å) of the atoms in square brackets. Equations, in the form $AX' + BY' + CZ' - D = 0$, are referred to the orthogonal set of axes: $X' = ax + cz \cos \beta$, $Y' = by$, and $Z' = cz \sin \beta$

Plane	*A*	*B*	*C*	*D*
(1) C(1)—(6)	−0·5942	0·1889	−0·7818	0·5005
[C(1) 0·005, C(2) −0·001, C(3) 0·003, C(4) −0·008, C(5) 0·011, C(6) −0·010, S 0·045]				
(2) C(7)–(12)	0·5104	−0·7618	−0·3989	−3·8550
[C(7) 0·003, C(8) −0·006, C(9) 0·010, C(10) −0·010, C(11) 0·007, C(12) −0·004, S −0·108, N 0·011, C(13) 0·077, C(14) 0·074]				
(3) C(1), S, C(7)	−0·6175	0·1131	−0·7784	0·2428
[N −0·008, C(13) −1·251, C(14) 1·219, C(4) 0·037, C(10) −0·001]				
(4) C(13), N, C(14)	0·5621	−0·7040	−0·4340	−4·1744

Angles (deg.) between planes:

(1)–(2)	*82·2*	(1)–(3)	4·5	(2)–(3)	*84·8*
(1)–(4)	*82·7*	(2)–(4)	4·9	(3)–(4)	*84·9*

TABLE 6

Intramolecular non-bonded distances (Å) <3·5 Å. Contacts with hydrogen atoms are excluded

S · · · C(2)	2·81	C(2) · · · C(7)	3·06
S · · · C(6)	2·72	C(3) · · · C(5)	2·38
S · · · C(8)	2·76	C(3) · · · C(6)	2·76
S · · · C(12)	2·76	C(4) · · · C(6)	2·39
N · · · C(9)	2·42	C(7) · · · C(9)	2·41
N · · · C(11)	2·43	C(7) · · · C(10)	2·82
C(1) · · · C(3)	2·42	C(7) · · · C(11)	2·42
C(1) · · · C(4)	2·78	C(8) · · · C(10)	2·43
C(1) · · · C(5)	2·41	C(8) · · · C(11)	2·77
C(1) · · · C(7)	2·80	C(8) · · · C(12)	2·38
C(2) · · · C(4)	2·38	C(9) · · · C(11)	2·41
C(2) · · · C(5)	2·75	C(9) · · · C(12)	2·76
C(2) · · · C(6)	2·39	C(9) · · · C(13)	2·85

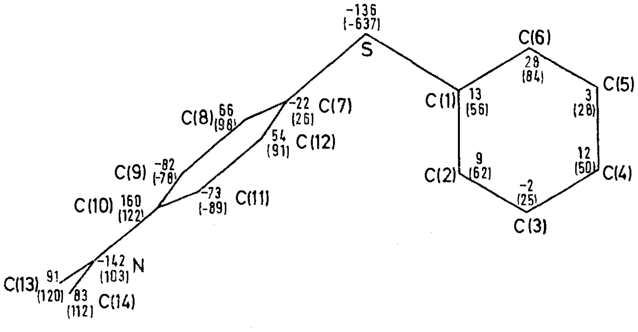

FIGURE 1 Atomic charges in 10^{-3} unit calculated by the CNDO method, with values calculated by the Hückel method in parentheses. Hydrogen atoms are omitted. The arbitrary numbering scheme adopted is shown

case the angle is 82·2° whereas for di-*p*-tolyl and bis-*p*-bromophenyl sulphide the reported values are 56 and 72° respectively.[1,2] It is noteworthy that in our unsymmetrically substituted diaryl sulphide, the two S–C bonds have the same length within experimental error, but this is $<1{\cdot}812$ Å, the mean of 11 experimental values from compounds containing the S–C single bond.[17] The sum of Pauling's single bond covalent radii[18] of carbon and sulphur gives 1·812 Å. The N–C(13) [1·449(12) Å] and N–C(14) [1·450(12) Å] distances are equal;[19] the NMe_2 group is twisted out of the aromatic plane about the N–C(10) bond by 4·9° (Figure 3). The N–C(10) bond [1·380(10) Å] is shorter than that for a pure C–N single bond (1·47 Å),[18] but is similar to that in related compounds (1·36—1·39 Å) in which the amino- or alkylamino-group is adjacent to the aromatic ring.[19,20] This indicates that some double-bond character may be present in the carbon–nitrogen bond and that a conjugative interaction is occurring between the electron-donating NMe_2 group and the aromatic ring. The phenyl rings have the usual bond lengths[21] and are essentially planar. There are no intermolecular contacts $<3{\cdot}5$ Å (except for those involving hydrogen atoms).

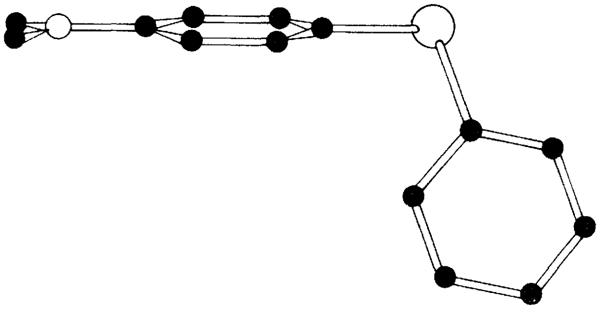

FIGURE 2 A perspective view of the molecule

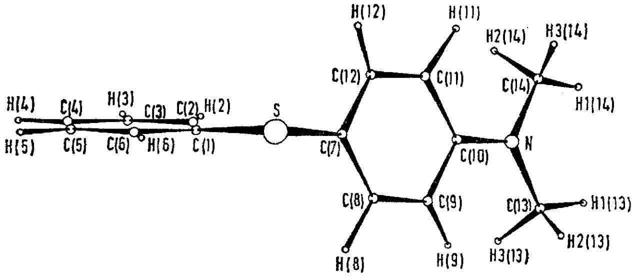

FIGURE 3 The projection of the molecule on the mean plane through the ring bearing the NMe_2 substituent

From the theoretical calculations the electronic configuration of the sulphur is $3s^{1\cdot797}3p^{3\cdot890}3d^{0\cdot449}$, thus indicating low occupancy of the *d* orbitals. The S–C(1) and S–C(7) bonds, with 'bond indices'[22] of 1·088 and 1·122 (Table 7), are practically equivalent, as found in the *X*-ray determination (1·769 and 1·786 Å respectively). The higher value (1·076) of the bond index for the N–C(10) bond in comparison with that of N–C(13) (1·023) and N–C(14) (1·016) may account for the shortening of the first bond (1·380 Å) with respect to the others (1·449 and 1·450 Å respectively). The bond indices for the atoms of the phenyl rings are consistent with those expected on the basis of the electronic distribution, for C(1)–C(4) 1·413, for C(2)–H(2) 0·960. The CNDO results on the electronic distribution of the ground state of the molecule show that the sulphur atom does not affect appreciably the electronic situation of the unsubstituted phenyl ring, whereas the NMe_2 group induces a negative charge on the *ortho*- and *para*-positions of the other phenyl ring with the *ortho*-value greater than the *para* (see Figure 1). These results are similar to those for aniline[23] and consequently suggest that the sulphur atom contributes little to the electronic distribution of the substituted phenyl ring, so that its influence on the ground state of both phenyl rings appears negligible.

TABLE 7

Bond indices between S, and C(1) and C(7)

		C(1)		C(7)	
		2*s*	2*p*	2*s*	2*p*
S	3*s*	0·022	0·073	0·020	0·069
	3*p*	0·216	0·567	0·208	0·608
	3*d*	0·054	0·156	0·052	0·165

A conclusion of the theoretical calculations is that the 3*d* sulphur orbitals affect, to a small extent only, the carbon atoms adjacent to sulphur and are not, therefore, involved in conjugative processes with the nearby π-systems.

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