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THE MOLECULAR STRUCTURE OF METHYLPHENYL(DIPHENYLSULFILIMINO)SULFONIUM PERCHLORATE

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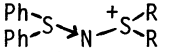
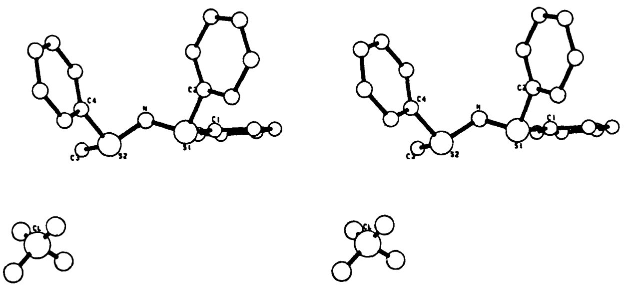
The structure of the titled compound (I) has been determined by X-ray crystallographic techniques. (I) crystallizes in a triclinic space group P$\bar{1}$ with a=9.98, b=11.06, c=9.71 Å, α=81.0, β=76.1, γ=75.3° and Z=2. The cationic charge of (I) localizes predominantly on the sulfur atom (S(2)) of methyl phenyl sulfide. The bond length between the nitrogen atom and the sulfur atom (S(1)) of diphenyl sulfide is shorter than that of N-S(2) (1.60 and 1.67 Å, respectively).

Recently, we found a convenient and versatile procedure to prepare diphenylsulfiliminosulfonium salts ( $Ph_2S \rightarrow N - \overset{+}{S}R_2\ X^-$), by treating diphenyl N-halogenated sulfilimine with the corresponding sulfides.[1,2] The nature of the bond between sulfur and nitrogen atom of these sulfiliminosulfonium salts is quite interesting since the compounds belong to a group of sulfilimines with the imino nitrogen atom flanked by two similar sulfur functional groups and hence the S-N bond would be somewhat different from those of other S-N compounds.

In this communication, we wish to report the structure of (I).

Results: (I) was prepared according to the procedure reported previously,[1] and recrystallized from chloroform-n-hexane. Oscillation and Weissenberg photographs showed the crystals to be triclinic, P1 or P$\bar{1}$. From angular settings of 13 reflections on a diffractometer, the cell dimensions were determined as follows: a=9.98, b=11.06, c=9.71 Å, α=81.0, β=76.1, γ=75.3°. Assuming that Z=2, the calculated density is 1.41 g cm^{-3}. An observed density determined by flotation is 1.40 g cm^{-3}. Intensity data were collected on a Rigaku automatic four-circle diffractometer using Zr-filtered Mo-Kα radiation in the ω-2θ scanning mode at a speed of 4° min^{-1} in 2θ. 2991 independent reflections with 2θ < 45° were measured, of which 830 were too weak to be observed. The positions of chlorine and two sulfur atoms were determined from a Patterson function. Subsequent Fourier synthesis revealed the positions of all non-hydrogen atoms. The positional and anisotropic thermal parameters were refined by block-diagonal least squares method. The refinements with space group P$\bar{1}$ gave satisfactory results. Electron density map indicated that perchlorate ions are oriented in disorder. The conventional R value was 0.10 for non-zero reflections.

Figure 1 illustrates the molecular structure. Positional and thermal parameters for the non-hydrogen atoms, and principal bond lengths and bond angles are presented in Tables 1 and 2, respectively.



(Perchlorate ions are oriented in disorder)

Figure 1. A stereoscopic view of the molecule (I).

Table 1. Positional and thermal parameters for the non-hydrogen atoms of (I)

The thermal parameters($\times 10^4$) are defined by $T = \exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.
Estimated standard deviations are given in parentheses.

Atom	x/a	y/b	z/c	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	0.6788 (3)	0.0563 (3)	0.1538 (3)	150 (4)	121 (3)	178 (4)	-44 (5)	-98 (7)	-87 (6)
S(1)	0.8631 (3)	0.1850 (3)	0.6435 (3)	147 (4)	96 (3)	143 (4)	-91 (5)	0 (6)	-27 (5)
S(2)	0.5839 (3)	0.2024 (3)	0.6998 (3)	146 (4)	132 (4)	180 (5)	-109 (6)	23 (7)	-76 (7)
O(1)	0.7554 (18)	0.1660 (18)	0.0430 (17)	439 (36)	501 (40)	383 (30)	-624 (67)	355 (54)	-221 (55)
O(2)	0.7468 (31)	-0.0061 (24)	0.2393 (40)	748 (60)	451 (38)	1253 (99)	-59 (86)	-1562 (141)	578 (103)
O(3)	0.6061 (25)	-0.0072 (22)	0.1154 (15)	1121 (85)	798 (61)	275 (25)	-1654 (136)	-140 (71)	-160 (60)
O(4)	0.5847 (27)	0.1288 (19)	0.2314 (24)	718 (62)	382 (36)	564 (52)	-14 (73)	569 (95)	-428 (71)
N	0.7201 (9)	0.2534 (9)	0.5888 (10)	130 (12)	134 (11)	174 (14)	-58 (19)	-10 (21)	-63 (21)
C(1)	1.1304 (13)	0.1419 (11)	0.4750 (13)	172 (17)	115 (13)	180 (18)	-100 (24)	-23 (28)	-14 (25)
C(11)	1.2278 (13)	0.1245 (11)	0.3450 (15)	158 (17)	114 (12)	253 (24)	-90 (23)	70 (34)	-144 (29)
C(12)	1.1780 (13)	0.1277 (11)	0.2215 (14)	186 (19)	109(13)	215 (21)	-96 (26)	75 (33)	-114 (28)
C(13)	1.0389 (14)	0.1465 (11)	0.2261 (13)	217 (21)	127 (14)	166 (18)	-135 (28)	-8 (31)	-58 (26)
C(14)	0.9380 (12)	0.1671 (10)	0.3538 (11)	158 (16)	105 (11)	129 (14)	-71 (22)	18 (25)	-42 (21)
C(15)	0.9845 (11)	0.1677 (9)	0.4741 (11)	134 (14)	68 (9)	156 (19)	-56 (18)	-15 (24)	-75 (19)
C(2)	0.9191 (11)	0.3026 (9)	0.7075 (11)	134 (14)	84 (10)	133 (14)	-75 (20)	15 (23)	-18 (20)
C(21)	0.8843 (14)	0.4270 (11)	0.6489 (12)	235 (23)	133 (15)	133 (16)	-123 (30)	34 (32)	5 (25)
C(22)	0.9426 (15)	0.5137 (12)	0.7013 (14)	252 (26)	146 (16)	188 (20)	-177 (33)	53 (36)	-146 (29)
C(23)	1.0237 (16)	0.4752 (14)	0.7976 (14)	241 (24)	190 (19)	189 (21)	-232 (35)	48 (36)	-131 (32)
C(24)	1.0533 (17)	0.3502 (16)	0.8537 (14)	278 (29)	234 (24)	168 (20)	-224 (44)	-60 (39)	-71 (36)
C(25)	1.0014 (13)	0.2593 (13)	0.8092 (12)	174 (19)	177 (18)	135 (16)	-89 (29)	-17 (29)	-47 (27)
C(3)	0.4806 (15)	0.2036 (19)	0.5718 (17)	149 (20)	379 (33)	283 (28)	-145 (42)	-81 (39)	-383 (52)
C(4)	0.4829 (11)	0.3313 (11)	0.7917 (11)	122 (14)	125 (13)	133 (14)	-73 (21)	11(22)	-47 (22)
C(41)	0.4291 (13)	0.3052 (13)	0.9347 (13)	184 (19)	178 (17)	164 (18)	-117 (29)	-116 (30)	-48 (27)
C(42)	0.3505 (16)	0.4046 (16)	1.0130 (18)	230 (25)	243 (25)	242 (03)	-144 (40)	-74 (40)	-204 (39)
C(43)	0.3322 (14)	0.5286 (15)	0.9486 (19)	143 (18)	179 (19)	380 (34)	-41 (29)	-35 (40)	-234 (43)
C(44)	0.3832 (17)	0.5504 (15)	0.8030 (18)	216 (25)	157 (18)	301 (31)	-54 (34)	23 (45)	-69 (39)
C(45)	0.4600 (15)	0.4528 (13)	0.7236 (15)	210 (24)	130 (16)	233 (24)	-21 (31)	-33 (38)	-61 (32)

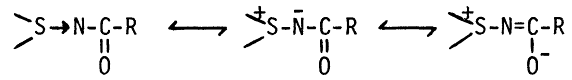
Table 2. Bond lengths (Å) and angles (°) of (I)*

S_1-N	1.60(1)	S_1-N-S_2	109.6(5)
S_2-N	1.67(1)		
		N-S_1-C_1	100.1(5)
S_1-C_1	1.81(1)	N-S_1-C_2	106.6(5)
S_1-C_2	1.78(1)	Mean	103.4
Mean	1.80		
		N-S_2-C_3	99.2(7)
S_2-C_3	1.80(2)	N-S_2-C_4	105.4(5)
S_2-C_4	1.75(1)		
		C_1-S_1-C_2	100.5(5)
Non-bonded distance		C_3-S_2-C_4	100.2(6)
S_2··········Cl	4.23(1)		

*) Estimated standard deviations are given in parentheses.

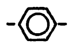
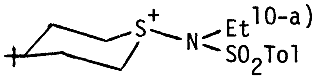
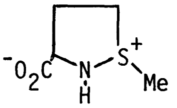
Bond lengths and angles in each benzene ring of (I) are usual values.

Discussion: The sulfilimines ($\overset{R}{\underset{R}{>}}S \to NX$), are trivalent sulfur compounds like sulfoxides, and have a semipolar bond between sulfur and nitrogen atom.3,4) The structural analyses of a few crystalline N-acyl (sulfonyl and carbonyl) and N-aryl substituted sulfilimines have been carried out.4,5) All these compounds have such electron-withdrawing group as acyl or sulfonyl group on the nitrogen atom, and hence the S-N semipolar bond would resonate or interact with the N-substituted group as shown below.



Thus, the S(III)-N bond distance in N-substituted sulfilimines is expected to be substantially shorter than the normal S-N single bond. A few examples are tabulated in Table 3.

Table 3. Bond distances and angles of some N-substituted sulfilimines.

$\overset{R}{\underset{R}{>}}S \to N-X$ R	X	Bond distance (S→N) Å	Bond distance (N-X) Å	Bond angle (S-N-X)
Ph	$-SO_2Tol$ 6)	1.628	1.598	113.4°
Me	$-SO_2Me$ 7)	1.633	1.581	116.2°
Me	-  $-NO_2$ 5)	1.651	1.341	116.1°
Me	$-COCCl_3$ 8)	1.667	1.320	110.0°
Ph	$-\overset{+}{S}<^{Me}_{Ph}$ *)	1.60	1.67	109.6°
Me	$-\overset{+}{S}<^{Me}_{Me}$ 9)	1.63	1.64	110.8°
 10-a)		1.644		
 10-b)		1.679		

*) present work.

Both S(1)-N and S(2)-N bond distances obtained for (I) (1.60 and 1.67 Å, respectively) are significantly different from that of the S-N single bond (1.74 Å) and also from that of the double bond (1.56 Å) calculated from Pauling's bond radii.11)

The S-N bond distances of N-acyl (sulfonyl) and N-arylsulfilimines are usually longer than the N-X bond distances and 1.628 Å (See Table 3). One interesting feature is that the S(1)-N bond distance (1.60 Å) in (I) is the shortest among those appeared in the literature. However, the other S(2)-N bond is somewhat longer than that of the symmetrical dimethyl(dimethylsulfilimino)-sulfonium bromide (II),9) and the average value of the S-N bonds in (I) is nearly the same as in (II), which is also nearly the same as other S-N bonds in N-sulfonylsulfilimines, despite the higher electron-withdrawing ability of the sulfonio group than the sulfonyl group. Perhaps the negative ligand, in this case, perchlorate ion is compensating the strong inductive effect of the sulfonio group by a direct field interaction. The unequal distances of the two S-N bonds in (I) are probably due to the unsymmetrical nature of the two sulfonio group, both electronically and sterically. Since the S(1)-N bond distance of (I) is apparently shorter than that of S(2)-N bond of (I), the cationic charge should be localized on S(2) atom. This seems to be supported from the fact that (I) was easily hydrolyzed with aqueous alkaline solution to afford methyl phenyl sulfoxide and diphenyl free sulfilimine in quantitative yields, giving practically no diphenyl sulfoxide.$^{1)}$ The bond angle of the S(1)-N-S(2) of (I) (109.6°) is similar to that of other N-substituted sulfilimines and the configurations around the S(1), S(2) atom and also N atom are approximately tetrahedral, supporting that pπ-dπ type conjugation through N atom is significant.

References and Notes:

1) T. Yoshimura, N. Furukawa, T. Akasaka, and S. Oae, Tetrahedron, 33, 1061 (1977).
2) Preparation of dimethyl(dimethylsulfilimino)sulfonium bromide (II); P. Y. Blanc, Experimentia, 21, 308 (1965); the chloride; M. Becke-Goering and H. P. Latscha, Angew. Chem., 74, 695 (1962).
3) D. W. J. Cruickshank, J. Chem. Soc., 1961, 5486.
4) A. Kucsman and I. Kapovitz, Phosphorus and Sulfur, 3, 9 (1977); T. L. Gilchrist and C. J. Moody, Chem Rev., 77, 409 (1977), references cited therein.
5) E. L. Eliel, J. Koskimies, A. T. Mcphail, and D. Swern, J. Org. Chem., 41, 2137 (1976).
6) A. Kalman, B. Duffin, and A. Kucsman, Acta Crystallogr., B27, 586 (1971).
7) A. Kalman, ibid., B22, 501 (1967).
8) A. Kalman, K. Sasvari, and A. Kucsman, Acta Crystallogr., B29, 1241 (1973).
9) A. M. Griffin and G. M. Scheldrick, Acta Crystallogr., B31, 893 (1975); In the case of (II) determined by X-ray analysis, the S-N bond distances are 1.63 and 1.64 Å, and the predominant structure is represented by $\mathrm{Me_2\ddot{S}^{+}\text{-}\underset{\cdot\cdot}{\ddot{N}}^{-}\text{-}{}^{+}\ddot{S}Me_2}$ in which two lone pairs on N atom and one on each S atom are localized.
10) a) R. E. Cook, M. D. Glick, J. J. Rigau, and C. R. Johnson, J. Am. Chem. Soc., 93, 924 (1971); In the case of trans-4-t-butyl-1-(N-ethyl-N-p-toluenesulfonylamino)-1-thioniacyclohexane fluoroborate, the sulfonium sulfur-nitrogen bond distance is 1.644 Å, suggesting the existence of significant pπ-dπ bonding. b) R. S. Glass and J. R. Duchek, J. Am. Chem. Soc., 98, 965 (1976); In the case of dehydromethionine, the geometry about the nitrogen atom suggests the the absence of pπ-dπ bonding between the sulfur-nitrogen bond, and the S-N bond distance is 1.68 Å.
11) L. Pauling, "The Nature of the Chemical Bond", Cornell Univ. Press, Ithaca, N. Y., 3rd Ed., 1960, p.224.

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