

## Structural Investigations of Ylides. XI. Crystal and Molecular Structure of *N*-Benzoyliminodimethylsulphur(IV)

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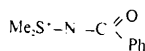
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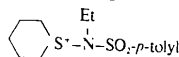
The structure of the title compound has been determined from 1481 independent diffractometer data, and refined by least squares to a final  $R$  of 0.034. Crystals are monoclinic, space group  $P2_1/c$ , with  $Z=4$ ,  $a=9.595$ ,  $b=8.632$ ,  $c=11.617$  Å,  $\beta=92.60^\circ$ . The lengths of the  $S^+-N^-$  and  $N^- - C(O)$  bonds are 1.659(2) and 1.544(3) Å respectively while the  $S^+-N^- - C$  valence angle is  $110.4(1)^\circ$ . The  $S^+-N^- - C=O$  moiety is planar, with  $S^+$  and O relatively *cis*.

### Introduction

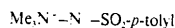
The involvement of  $\pi$ -bonding interactions between lone-pair electrons of the anionic atom and vacant  $d$ -orbitals of the 'onium atom in the stabilization of sulphonium imines ( $>S^+-N^- - R$ ) has been suggested by structural studies of several of this class of compound with sulphonyl stabilizing groups ( $R = -SO_2 - X$ ) (Kálmán, 1967; Kálmán, Duffin & Kucsman, 1971; Kálmán & Sasvári, 1972; Cameron, Hair & Morris, 1973; Cameron, Cameron, Campbell & Johnson, 1976) and with halogen-containing carbonyl stabilizing groups (Kálmán, Sasvári & Kucsman, 1971, 1973). In addition, comparative examination of the above sulphonyl-stabilized compounds with the *N*-alkylated derivative (X) (Cook, Glick, Rigau & Johnson, 1971), extended to include the sulphonyl-stabilized ammonium and pyridinium imines (XI) and (XII) (Cameron, Duncanson & Morris, 1976; Cameron & Duncanson, 1976), suggests the importance of a delocalizing interaction between the imino (anionic) atom and the sulphonyl stabilizing group, which is relatively unaffected by the nature of the 'onium species.



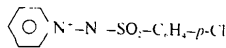
(I)



(X)



(XI)



(XII)

Despite the latter conclusion, there remains the possibility that the  $\pi$ -bonding interaction between the sulphonium and imino groups of sulphonium imines may be influenced by the nature of the stabilizing group. In order to investigate this effect we have determined the structure of *N*-benzoyliminodimethylsulphur(IV), (I), which differs from previous carbonyl-stabilized examples in which the carbonyl groupings are additionally bonded to highly electronegative substituents ( $-CCl_3$  and  $-CHCl_2$ ).

### Experimental

#### Crystal data

*N*-Benzoyliminodimethylsulphur(IV),  $C_9H_{11}NOS$ ,  $M=181.3$ ; monoclinic,  $a=9.595$ ,  $b=8.632$ ,  $c=11.617$  Å,  $\beta=92.60^\circ$ ,  $U=961.1$  Å<sup>3</sup>;  $D_m=1.24$  (by flotation),  $Z=4$ ,  $D_c=1.27$  g cm<sup>-3</sup>;  $F(000)=384$ ; space group  $P2_1/c$  ( $C_{2h}^2$ , No. 14); Mo  $K\alpha$  radiation,  $\lambda=0.7107$  Å,  $\mu(\text{Mo } K\alpha)=2.88$  cm<sup>-1</sup>.

#### Crystallographic measurements

The cell parameters were initially determined photographically and were subsequently refined by least squares prior to the diffractometer data collection. Intensity measurements were made on a Hilger & Watts Y290 diffractometer, exposure of a small crystal to Zr-filtered Mo radiation producing 1481 independent reflexions [ $I > 2\sigma_I$ ,  $\sigma_I = \sqrt{(I + B_1 + B_2)}$ ], measured by the  $\theta, \omega$ -scan technique in the range  $2\theta=0 \rightarrow 60^\circ$ . The intensities were corrected for Lorentz and polarization factors, but not for absorption.

#### Structure determination and refinement

The structure was determined by direct phasing with the multi-symbolic approach. Triplet relationships were generated for those 144 reflexions with  $|E| \geq 1.50$  and a solution for the 60 strongest reflexions was obtained with a set of three origin-determining phases chosen by the program and relationships of probability  $\geq 0.85$ . All 144 reflexions were then phased from this solution, and the resulting  $E$  map revealed all non-hydrogen atoms.

Details of the least-squares refinement are given in Table 1. All H atoms were located from a difference synthesis calculated after the initial cycles of refinement, parameters for these atoms being refined in later cycles. The weighting scheme was  $w = (A + B|F_o| + C|F_o|^2)^{-1}$ , final values of the parameters  $A$ ,  $B$  and  $C$  being 0.2627,  $-0.0423$  and 0.0027 respectively. On convergence, examination of a difference synthesis

Table 1. *Course of refinement*

Cycles	Parameters refined	Final <i>R</i>	Final <i>R'</i>
1-3	<i>x, y, z, U<sub>iso</sub></i> for S, O, N and C; scale factor. Unit weights.	0.106	0.0112
4	<i>x, y, z, U<sub>iso</sub></i> for S, O, N and C; scale factor. H atom contributions included but not refined. Unit weights.	0.089	0.0069
5-6	<i>x, y, z, U<sub>ij</sub></i> for S, O, N and C; scale factor. H atom contributions included but not refined. Unit weights.	0.045	0.0026
7-8	<i>x, y, z, U<sub>ij</sub></i> for S, O, N and C; scale factor. H atom contributions included but not refined. Weighting scheme applied.	0.043	0.0022
9-11	<i>x, y, z, U<sub>ij</sub></i> for S, O, N and C; <i>x, y, z</i> for H; scale factor. Weighting scheme applied.	0.035	0.0018
12-14	<i>x, y, z, U<sub>ij</sub></i> for S, O, N and C; <i>x, y, z, U<sub>iso</sub></i> for H; scale factor. Weighting scheme applied.	0.034	0.0017
15-17	<i>x, y, z, U<sub>ij</sub></i> for S, O, N and C; <i>x, y, z, U<sub>iso</sub></i> for H; scale factor. Anomalous dispersion correction included; weighting scheme modified.	0.034	0.0012

revealed no errors in the structure, and the refinement was considered complete.

Final coordinates and thermal parameters are given in Table 2, details of the molecular geometry and conformation in Table 3. Estimated standard deviations quoted in Tables 2 and 3 derive from the least-squares calculations, and should be regarded as minimum values. Fig. 1 shows a view of one molecule and defines the atomic numbering.\*

### Discussion

Comparisons of the main features of the ylidic geometry of (I) with various other examples are made in Table 4. Considering the sulphonium-imine [S<sup>+</sup>-N<sup>-</sup>] bond, it is apparent that the value observed in (I) [1.659 (2) Å] is experimentally identical with the values in the other carbonyl-stabilized examples (II) and (III). Moreover, the average length of the S<sup>+</sup>-N<sup>-</sup> bond in (I)-(III) [1.666 Å] is significantly longer than the average length [1.629 Å] for the corresponding bond in the sulphonyl-stabilized examples (IV)-(VI) and (VIII). [(VII) has been excluded from this comparison because the unusual sulphonium substitution probably further perturbs the length of the S<sup>+</sup>-N<sup>-</sup> bond.] It would therefore appear from those examples studied to date, that the differences in bonding within the -N<sup>-</sup>-C(=O)R and -N<sup>-</sup>-SO<sub>2</sub>R groupings are sufficient to induce differences in the S<sup>+</sup>-N<sup>-</sup> bonds. We identify two inter-related factors which may plausibly produce such an effect. Firstly, delocalization in the -N<sup>-</sup>-C(=O)R groupings may take place only *via* *p*<sub>π</sub>-*p*<sub>π</sub> interactions, whereas *d*-orbitals are available in the sulphonyl examples, and secondly the extent to which delocalization takes place within the two types of stabilizing groups. Thus we note that the N<sup>-</sup>-C lengths in (I)-(III) are comparable with the value [1.340 (5) Å] observed in free pyridine (Bak, Hansen & Rastrup-Andersen, 1954), while the range of values for the N<sup>-</sup>-S(sul-

Table 2. *Fractional coordinates and thermal parameters*

#### (a) Fractional coordinates

	<i>x</i>	<i>y</i>	<i>z</i>
S	0.94523 (6)	0.79026 (7)	0.14911 (5)
N	0.8318 (2)	0.9268 (2)	0.1081 (2)
O	0.8397 (2)	0.9923 (2)	0.3008 (1)
C(1)	0.6922 (2)	1.1375 (3)	0.1702 (2)
C(2)	0.6210 (3)	1.1445 (3)	0.0638 (2)
C(3)	0.5195 (3)	1.2562 (4)	0.0432 (3)
C(4)	0.4890 (3)	1.3626 (4)	0.1266 (3)
C(5)	0.5607 (3)	1.3577 (3)	0.2313 (3)
C(6)	0.6613 (3)	1.2456 (3)	0.2537 (2)
C(7)	0.7961 (2)	1.0117 (3)	0.1992 (2)
C(8)	0.8391 (4)	0.6319 (4)	0.1890 (4)
C(9)	0.9975 (4)	0.7281 (4)	0.0119 (3)

#### (b) H atom fractional coordinates and isotropic thermal parameters (Å<sup>2</sup> × 10<sup>3</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>iso</sub></i>
H(2)	0.640 (2)	1.066 (3)	0.009 (2)	63 (7)
H(3)	0.469 (3)	1.254 (3)	-0.025 (3)	80 (9)
H(4)	0.422 (3)	1.436 (3)	0.114 (2)	77 (9)
H(5)	0.544 (3)	1.437 (3)	0.284 (2)	69 (8)
H(6)	0.714 (3)	1.242 (3)	0.332 (2)	60 (7)
H(81)	0.775 (3)	0.613 (4)	0.127 (3)	91 (11)
H(82)	0.798 (4)	0.661 (4)	0.270 (3)	130 (15)
H(83)	0.898 (3)	0.547 (4)	0.200 (3)	95 (11)
H(91)	0.910 (3)	0.695 (3)	-0.037 (2)	85 (10)
H(92)	1.062 (3)	0.642 (4)	0.027 (2)	83 (9)
H(93)	1.045 (3)	0.816 (4)	-0.016 (3)	89 (11)

#### (c) Anisotropic thermal parameters (Å<sup>2</sup> × 10<sup>4</sup>)

	<i>U<sub>11</sub></i>	<i>U<sub>22</sub></i>	<i>U<sub>33</sub></i>	<i>U<sub>12</sub></i>	<i>U<sub>13</sub></i>	<i>U<sub>23</sub></i>
S	495	432	519	67	-50	-24
N	570	425	486	127	-45	-22
O	572	633	456	110	-79	-20
C(1)	404	375	462	-676	64	42
C(2)	643	543	479	147	2	-15
C(3)	769	808	527	295	-71	51
C(4)	648	626	689	266	129	107
C(5)	672	580	646	155	142	-74
C(6)	545	553	490	66	29	-47
C(7)	392	374	495	-50	10	15
C(8)	680	540	1068	19	20	233
C(9)	837	547	624	167	82	-49

#### Mean estimated standard deviations (Å<sup>2</sup> × 10<sup>4</sup>)

	<i>U<sub>11</sub></i>	<i>U<sub>22</sub></i>	<i>U<sub>33</sub></i>	<i>U<sub>12</sub></i>	<i>U<sub>13</sub></i>	<i>U<sub>23</sub></i>
S	3	3	3	3	2	3
N	12	11	11	9	9	9
O	10	11	9	8	7	8
C	16	16	17	13	13	13

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31670 (10 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

phenyl) bonds [1.581 (10)–1.618 (7) Å] must be compared with the formal single-bond value of 1.772 (1) Å in sulphamic acid (Cameron & Duncanson, 1975). However, since the S<sup>+</sup>–N<sup>–</sup> bonds of (I)–(III) are con-

Table 3. *Interatomic distances and angles*

(a) Bonded distances (Å)			
S—N	1.659 (2)	C(1)—C(2)	1.385 (3)
S—C(8)	1.779 (4)	C(2)—C(3)	1.384 (4)
S—C(9)	1.776 (3)	C(3)—C(4)	1.377 (4)
N—C(7)	1.344 (3)	C(4)—C(5)	1.371 (4)
O—C(7)	1.246 (3)	C(5)—C(6)	1.383 (4)
C(7)—C(1)	1.502 (3)	C(6)—C(1)	1.388 (3)
(b) Interbond angles (°)			
S—N—C(7)	110.4 (1)	C(7)—C(1)—C(2)	121.8 (2)
N—S—C(8)	104.2 (1)	C(7)—C(1)—C(6)	119.3 (2)
N—S—C(9)	99.5 (1)	C(1)—C(2)—C(3)	120.0 (2)
C(8)—S—C(9)	101.0 (2)	C(2)—C(3)—C(4)	120.9 (2)
N—C(7)—O	125.9 (1)	C(3)—C(4)—C(5)	119.4 (2)
C(1)—C(7)—O	120.0 (2)	C(4)—C(5)—C(6)	120.4 (2)
N—C(7)—C(1)	114.1 (1)	C(5)—C(6)—C(1)	120.5 (2)
		C(6)—C(1)—C(2)	118.9 (2)
(c) Intramolecular non-bonded distances (Å)			
S·····O	2.71	S·····C(7)	2.47
N·····O	2.31	N·····C(2)	2.79
O·····C(6)	2.81	O·····C(8)	3.37
C(7)·····C(8)	3.31		
(d) Intermolecular distances (Å)			
C(5)·····C(8) <sup>i</sup>	3.61	C(4)·····C(1) <sup>ii</sup>	3.82
C(6)·····C(8) <sup>i</sup>	3.84	C(5)·····C(7) <sup>ii</sup>	3.79
C(4)·····O <sup>ii</sup>	3.49	C(5)·····C(1) <sup>ii</sup>	3.64
C(4)·····C(7) <sup>ii</sup>	3.71	O·····C(9) <sup>iii</sup>	3.40

Roman numeral superscripts refer to the following equivalent positions relative to a molecule at (x, y, z):

$$\begin{array}{ll} \text{(i)} & x \quad 1+y \quad z \\ \text{(iii)} & x \quad -\frac{1}{2}-y \quad \frac{1}{2}+z \end{array} \quad \begin{array}{ll} \text{(ii)} & -1-x \quad \frac{1}{2}+y \quad \frac{1}{2}-z \end{array}$$

(e) Torsion angles (°)

S—N—C(7)—O	–0.5
S—N—C(7)—C(1)	–179.4
N—C(7)—C(1)—C(2)	11.7
N—C(7)—C(1)—C(6)	–171.5
O—C(7)—C(1)—C(2)	–167.3
O—C(7)—C(1)—C(6)	9.5
C(7)—N—S—C(8)	87.4
C(7)—N—S—C(9)	–168.6

Mean e.s.d. 0.2°

(f) Least-squares planes

Planes are in the form  $lX + mY + nZ - d = 0$ , where X, Y and Z refer to an orthogonalized set of axes. An asterisk denotes atoms used to define plane.

(1) Equations of planes

$$\begin{array}{l} \text{(I)} \quad 0.7105X + 0.6161Y - 0.3400Z + 10.0379 = 0 \\ \text{(II)} \quad 0.7593X + 0.6329Y - 0.1512Z + 10.8922 = 0 \end{array}$$

(2) Deviations of atoms from the planes (Å)

(I)	S	–0.036	N	0.095	O	–0.336
	C(7)	–0.091	C(9)	0.583	C(8)	–1.774
	C(1)	–0.005*	C(2)	0.007*	C(3)	–0.002*
	C(4)	–0.004*	C(5)	0.006*	C(6)	–0.002*
(II)	S	–0.010	C(9)	0.327	C(1)	–0.002*
	C(7)	0.006*	O	–0.002*	N	–0.002*

(3) Dihedral angle between planes (I) and (II): 11.2°

sistently longer than in the sulphonyl-stabilized examples, it may possibly be concluded that there is significantly less delocalization in the S<sup>+</sup>–N<sup>–</sup> bonds of (I)–(III), thus implying that delocalization in the N<sup>–</sup>–C(=O)R system is more efficient than in the N<sup>–</sup>–SO<sub>2</sub>R system when both are bonded to similar sulphonium groupings.

We also note that although there is no significant difference between the lengths of N<sup>–</sup>–C bonds of (I)–(III), the value quoted for (II) suggests that a more accurate analysis would possibly reveal a significant effect resulting from the highly electronegative –CCl<sub>3</sub> moiety. Comparison of the N<sup>–</sup>–C bonds in (I) and (IX) does reveal a significant difference which suggests relatively more delocalization in the N<sup>–</sup>–C(=O)R fragment of (IX). This effect is consistent with there being no delocalization possible in the N<sup>+</sup>–N<sup>–</sup> moiety of (IX), whereas a significant degree of delo-

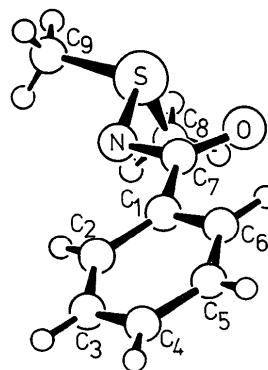


Fig. 1. A view of one molecule of (I), defining the atomic numbering used in the X-ray analysis. Hydrogen atoms are numbered as the atoms to which they are bonded.

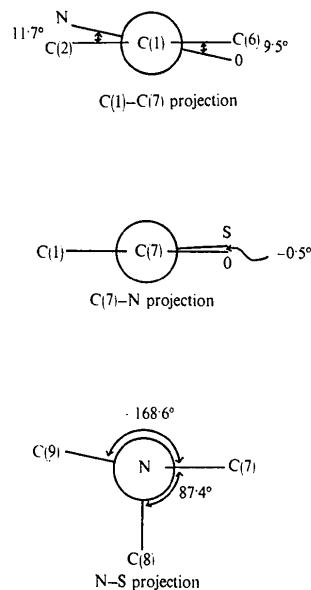


Fig. 2. Three Newman projections defining the solid-state conformation of (I).

Table 4. Geometries of various sulphonium ylides and related compounds

	S <sup>+</sup> -N <sup>-</sup>	N <sup>-</sup> -C/N <sup>-</sup> -S	C=O	N̂-
(I) Me <sub>2</sub> S <sup>+</sup> -N <sup>-</sup> -C(=O)-Ph	1.659 (2) (Å)	1.344 (3) (Å)	1.246 (3) (Å)	110.4 (1)°
(II) Me <sub>2</sub> S <sup>+</sup> -N <sup>-</sup> -C(=O)-CCl <sub>3</sub>	1.667 (7)	1.320 (10)	1.227 (10)	110.0 (6)
(III) Et <sub>2</sub> S <sup>+</sup> -N <sup>-</sup> -C(=O)-CHCl <sub>2</sub>	1.673	1.344	1.212	112.6
(IV) Me <sub>2</sub> S <sup>+</sup> -N <sup>-</sup> -SO <sub>2</sub> - <i>p</i> -tolyl	1.636 (8)	1.591 (8)	-	113.4 (5)
(V) Ph <sub>2</sub> S <sup>+</sup> -N <sup>-</sup> -SO <sub>2</sub> - <i>p</i> -tolyl	1.628 (7)	1.598 (8)	-	113.4 (5)
(VI) $\begin{matrix} \text{Ph} \\ \text{n Pr} \end{matrix} \text{S}^+ \text{-N}^- \text{-SO}_2 \text{-}i\text{-tolyl}$	1.620 (7)	1.618 (7)	-	115.7 (4)
(VII) R <sub>2</sub> S <sup>+</sup> -N <sup>-</sup> -SO <sub>2</sub> - <i>p</i> -tolyl (penicillin derivative)	1.592 (5)	1.613 (4)	-	116.3 (2)
(VIII) Me <sub>2</sub> S <sup>+</sup> -N <sup>-</sup> -SO <sub>2</sub> -Me	1.633 (9)	1.581 (10)	-	116.2 (6)
(IX) Me <sub>3</sub> N <sup>+</sup> -N <sup>-</sup> -C(=O)-Ph	-	1.313 (6)	1.24 <sup>1</sup> (5)	114.2 (3)

(I) Present work. (II) Kálmán, Sasvári & Kucsman (1973). (III) Kálmán, Sasvári & Kucsman (1971). (IV) Cameron, Hair & Morris (1973). (V) Kálmán, Duffin & Kucsman (1971). (VI) Kálmán & Sasvári (1972). (VII) Cameron, Cameron, Campbell & Johnson (1976). (VIII) Kálmán (1967). (IX) Cameron, Hair & Morris (1972).

calization is usually attributed to the S<sup>+</sup>-N<sup>-</sup> bonds of (I) and similar examples.

The conformation of (I) is illustrated by the three Newman projections given in Fig. 2, which reveals the approximately staggered arrangement of the sulphonium methyl groups relative to the C-N bond, an arrangement which is also common to (II) and (III). Another feature common to all three molecules is the almost planar geometry of the S<sup>+</sup>-N<sup>-</sup>-C=O groupings [torsion angle -0.5° for (I)], which in each case adopt a configuration such that the S<sup>+</sup> and O atoms are *cis* [S<sup>+</sup>...O 2.71 Å for (I)]. It has already been noted (Kálmán, Sasvári & Kucsman, 1971) that this configuration results in expansion of the N<sup>-</sup>-C=O valence angles to *ca* 130° in (II) and (III), although this effect is less pronounced in (I) [125.9 (1)°].

The valence angle at the imino atom of (I) [110.4 (1)°] is experimentally identical with the value observed in (II), and adds further weight to the suggestion (Cameron & Duncanson, 1976) that this angle is sensitive to the steric requirements of the groups bonded to the central N<sup>-</sup> atom. Other features of the molecular geometry of (I) are similar to literature values for similar bonding situations, and there are no abnormally short intermolecular contacts.

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