

Structural Investigations of Ylides. XII. Crystal and Molecular Structure of *N*-(*p*-Nitrobenzoyl)-2-iminophenyldimethylsulphur(IV), C₁₅H₁₄N₂O₃S

BY A. FORBES CAMERON, FERGUS D. DUNCANSON AND DAVID G. MORRIS

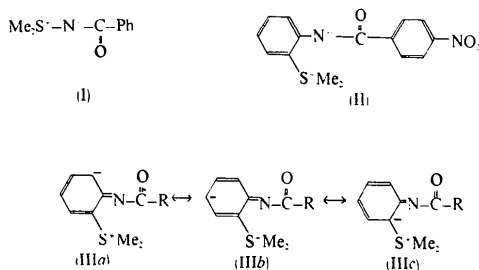
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

(Received 13 January 1976; accepted 10 February 1976)

The structure of the title compound has been determined from 2209 independent diffractometer data, and refined by least squares to a final *R* of 0.040. The crystals are orthorhombic, space group *Pbca*, with *Z* = 8, *a* = 25.971, *b* = 8.822, *c* = 13.310 Å. The S⁺-C(ar) and C(ar)-N⁻ lengths are 1.772 (2) and 1.385 (3) Å respectively, which in conjunction with the observed conformation suggest little delocalizing interaction between the sulphonium and imine species *via* the intervening aromatic ring.

Introduction

We have recently discussed the structure of the sulphonium-imine ylide (I), comparing the main features of the ylidic geometry with other available examples (Cameron, Duncanson & Morris, 1976). We now describe the structure of the unusual compound (II), which may be regarded as a structural variant of ylides of the type represented by (I), in which an aromatic ring is interposed between the sulphonium and imine species.



Whereas in the simpler sulphonium-imines [*e.g.* (I)], delocalization in the S⁺-N⁻ moiety is thought to take place by interaction between the vacant S *d*-orbitals and the lone pair(s) of electrons on the N atom, in (II) such a simple interaction is impossible. However, it is possible to write several canonical forms [(IIIa) ↔ (IIIb) ↔ (IIIc)] showing interaction between the aromatic system and the imine atom, with the additional possibility of interaction between the vacant S *d*-orbitals and the perturbed aromatic system.

Experimental

Crystal data

N-(*p*-Nitrobenzoyl)-2-iminophenyldimethylsulphur(IV), C₁₅H₁₄N₂O₃S, *M* = 302.4. Orthorhombic, *a* = 25.971, *b* = 8.822, *c* = 13.310 Å, *U* = 3046.7 Å³, *D_m* = 1.31 (by flotation), *Z* = 8, *D_c* = 1.32 g cm⁻³, *F*(000) = 1264. Space group *Pbca* (*D*_{2h}¹⁵, No. 61).

Mo *Kα* radiation, λ = 0.7107 Å, μ(Mo *Kα*) = 2.23 cm⁻¹.

Crystallographic measurements

The cell parameters were initially determined photographically and were refined by least squares prior to the diffractometer data collection. Intensity measurements were made on a Hilger & Watts Y290 diffractometer with a small crystal exposed to graphite-monochromated Mo radiation and with the θ, ω -scan technique to measure the intensities of 2209 independent reflexions [*I* > 3σ_{*I*}, σ_{*I*} = √(*I* + *B*₁ + *B*₂)] in the range 2θ = 0 → 60°. The intensities were corrected for Lorentz and polarization factors, but not for absorption.

Structure determination and refinement

The structure was determined by direct methods with the multi-symbolic technique, triplet relationships being derived for those 256 reflexions with |*E*| ≥ 1.40, and a solution for the 60 strongest reflexions being obtained with relationships of probability ≥ 0.8. 231 phases were then determined from this solution, and the resulting *E* map yielded all but four of the non-hydrogen atom positions. A subsequent structure factor and electron density calculation revealed the remaining four atoms.

Refinement by least squares was terminated when *R* was 0.040. Details of the refinement are presented in Table 1, from which it will be seen that some effort was devoted to examining subsets of the data. This was undertaken to investigate marked anisotropy with high values of thermal parameters for the nitro group and neighbouring ring atoms. It was eventually concluded that the anomalous thermal motion of the nitrobenzoyl group is a property of the whole data set, and this will be discussed later in relation to the molecular packing.

All H atoms were located from difference syntheses, and parameters for these atoms were refined in later cycles. The weighting scheme was *w* = (*A* + *B*|*F_o*| + *C*|*F_o*|²)⁻¹, the final values of the parameters *A*, *B* and *C* being 2.701, -0.241 and 0.0105 respectively. On

Table 2 (cont.)

(c) Anisotropic thermal parameters ($\text{\AA}^2 \times 10^4$)						
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	382	442	369	0	16	-16
N(1)	413	493	377	58	-9	-48
N(2)	488	3298	1556	-167	-268	-48
O(1)	572	982	434	98	22	-201
O(2)	445	6783	2037	282	-214	-530
O(3)	828	3867	1496	-413	-545	33
C(1)	398	455	365	-41	-7	-8
C(2)	453	472	298	-655	-10	25
C(3)	602	511	388	-66	8	-20
C(4)	653	671	458	-212	-68	-49
C(5)	441	849	612	-175	-87	-25
C(6)	404	670	565	-2	-27	-28
C(7)	425	510	524	38	-11	-4
C(8)	469	692	554	-51	-49	61
C(9)	605	1003	697	-173	-192	92
C(10)	401	1478	1154	-39	-174	78
C(11)	425	2417	1068	140	29	-395
C(12)	497	1617	796	154	38	-291
C(13)	463	452	414	50	-8	-16
C(14)	679	573	372	8	-40	25
C(15)	510	611	489	100	82	-36

Mean estimated standard deviations ($\text{\AA}^2 \times 10^4$)						
	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	4	4	4	2	2	2
N	14	45	25	21	16	29
O	17	70	30	32	16	40
C	14	14	14	14	14	16

1969) and (VI) [1.707 (4) Å] (Christensen & Thom, 1971). There would thus appear to be negligible delocalizing interaction between the sulphonium and aromatic species. Possibly conflicting with these con-

Table 3. Interatomic distances and angles

(a) Bonded distances (Å)			
S—C(1)	1.772 (2)	C(5)—C(6)	1.381 (4)
S—C(14)	1.793 (3)	C(6)—C(1)	1.392 (3)
S—C(15)	1.789 (3)	C(7)—C(8)	1.389 (4)
N(1)—C(2)	1.385 (3)	C(8)—C(9)	1.387 (4)
N(1)—C(13)	1.324 (3)	C(9)—C(10)	1.362 (5)
O(1)—C(13)	1.245 (3)	C(10)—C(11)	1.377 (7)
C(13)—C(7)	1.511 (3)	C(11)—C(12)	1.373 (5)
C(1)—C(2)	1.405 (3)	C(12)—C(7)	1.380 (4)
C(2)—C(3)	1.405 (3)	C(10)—N(2)	1.470 (5)
C(3)—C(4)	1.382 (4)	N(2)—O(2)	1.187 (7)
C(4)—C(5)	1.371 (4)	N(2)—O(3)	1.187 (8)

Mean		Mean	
C—H (methyl)	0.95 (3)	C—H (aryl)	0.94 (4)

(b) Interbond angles (°)			
C(1)—S—C(14)	102.5 (1)	C(4)—C(5)—C(6)	120.0 (2)
C(1)—S—C(15)	105.0 (1)	C(5)—C(6)—C(1)	118.5 (2)
C(14)—S—C(15)	100.4 (1)	C(13)—C(7)—C(8)	121.8 (2)
S—C(1)—C(2)	113.0 (1)	C(13)—C(7)—C(12)	119.2 (2)
S—C(1)—C(6)	124.0 (1)	C(7)—C(8)—C(9)	120.5 (2)
C(1)—C(2)—N(1)	116.0 (1)	C(8)—C(9)—C(10)	118.4 (3)
C(3)—C(2)—N(1)	127.4 (2)	C(9)—C(10)—C(11)	122.7 (3)
C(2)—N(1)—C(13)	120.4 (1)	C(10)—C(11)—C(12)	118.1 (3)
N(1)—C(13)—O(1)	128.2 (1)	C(11)—C(12)—C(7)	121.3 (3)
N(1)—C(13)—C(7)	114.1 (2)	C(9)—C(10)—N(2)	118.2 (3)
O(1)—C(13)—C(7)	117.7 (2)	C(11)—C(10)—N(2)	119.1 (3)
C(6)—C(1)—C(2)	122.9 (2)	C(10)—N(2)—O(2)	118.5 (4)
C(1)—C(2)—C(3)	116.4 (2)	C(10)—N(2)—O(3)	119.6 (3)
C(2)—C(3)—C(4)	120.5 (2)	O(2)—N(2)—O(3)	121.9 (4)
C(3)—C(4)—C(5)	121.7 (2)	C(12)—C(7)—C(8)	119.0 (2)

Table 3 (cont.)

(c) Intramolecular non-bonded distances (Å)			
S—N(1)	2.73	O(1)···C(3)	2.93
N(1)···C(14)	3.19	O(1)···C(12)	2.76
N(1)···O(1)	2.31	O(2)···C(11)	2.71
N(1)···C(8)	2.78	O(3)···C(9)	2.70
O(1)···C(2)	2.81	O(2)···O(3)	2.08

(d) Intermolecular distances (Å)			
N(1)···C(14) ⁱ	3.42	C(14)···C(2) ⁱⁱⁱ	3.72
C(9)···C(4) ⁱ	3.69	C(14)···C(3) ⁱⁱⁱ	3.55
C(9)···C(5) ⁱ	3.45	C(15)···C(4) ⁱⁱⁱ	3.57
C(14)···O(1) ⁱ	3.86	S···O(1) ^{iv}	2.98
C(14)···C(13) ⁱ	3.41	C(1)···O(1) ^{iv}	3.27
C(14)···C(3) ⁱ	3.70	C(6)···O(1) ^{iv}	3.63
C(14)···C(7) ⁱ	3.74	C(15)···O(1) ^{iv}	3.05
S···S ⁱⁱ	3.48	O(2)···C(5) ^v	3.58
S···C(15) ⁱⁱ	3.71	O(2)···C(15) ^{vi}	3.27
C(15)···C(8) ⁱⁱⁱ	3.55	O(3)···C(6) ^{vi}	3.48
C(14)···O(1) ⁱⁱⁱ	3.40		

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

(i)	-x	-y	1-z
(ii)	-x	1-y	1-z
(iii)	x	½-y	½+z
(iv)	-x	½+y	½-z
(v)	½+x	y	½-z
(vi)	½+x	½-y	1-z

(e) Torsion angles (°)	
C(2)—N(1)—C(13)—O(1)	7.5
C(2)—N(1)—C(13)—C(7)	-174.2
N(1)—C(13)—C(7)—C(8)	3.8
N(1)—C(13)—C(7)—C(12)	-176.8
O(1)—C(13)—C(7)—C(8)	-177.6
O(1)—C(13)—C(7)—C(12)	1.8
N(1)—C(2)—C(1)—S	3.3
N(1)—C(2)—C(1)—C(6)	-177.6
N(1)—C(2)—C(3)—C(4)	175.7
C(2)—C(1)—S—C(14)	-80.3
C(2)—C(1)—S—C(15)	175.2
C(6)—C(1)—S—C(14)	100.6
C(6)—C(1)—S—C(15)	-4.0
C(9)—C(10)—N(2)—O(2)	179.8
C(9)—C(10)—N(2)—O(3)	2.3
C(11)—C(10)—N(2)—O(2)	-0.9
C(11)—C(10)—N(2)—O(3)	178.4
C(13)—N(1)—C(2)—C(1)	-149.5
C(13)—N(1)—C(2)—C(3)	36.3
Mean e.s.d.	0.3°

(f) Least-squares planes	
X, Y and Z are orthogonal coordinates in Å. An asterisk denotes atoms used to define plane.	

(1) Equations of planes	
(I)	-0.1430X - 0.5847Y + 0.7986Z + 3.1678 = 0
(II)	0.0736X + 0.9699Y - 0.2322Z - 0.0846 = 0
(III)	-0.0917X - 0.9578Y + 0.2723Z + 0.2374 = 0

(2) Deviations of atoms from the planes (Å)						
(I)	S	0.041	N(1)	0.056	C(13)	-0.535
	C(15)	-0.072	C(1)	0.013*	C(2)	-0.014*
	C(3)	0.002*	C(4)	0.012*	C(5)	-0.013*
	C(6)	0.001*				
(II)	N(1)	0.053	O(1)	-0.052	C(13)	-0.012
	N(2)	-0.022	O(2)	-0.040	O(3)	-0.058
	C(7)	-0.001*	C(8)	-0.006*	C(9)	0.010*
	C(10)	-0.008*	C(11)	-0.001*	C(12)	0.003*
(III)	C(7)	-0.002*				
	O(1)	-0.003*				

(3) Dihedral angles between planes: (I) and (II) 139.7°; (II) and (III) 2.6°; (I) and (III) 37.8°.	
--	--

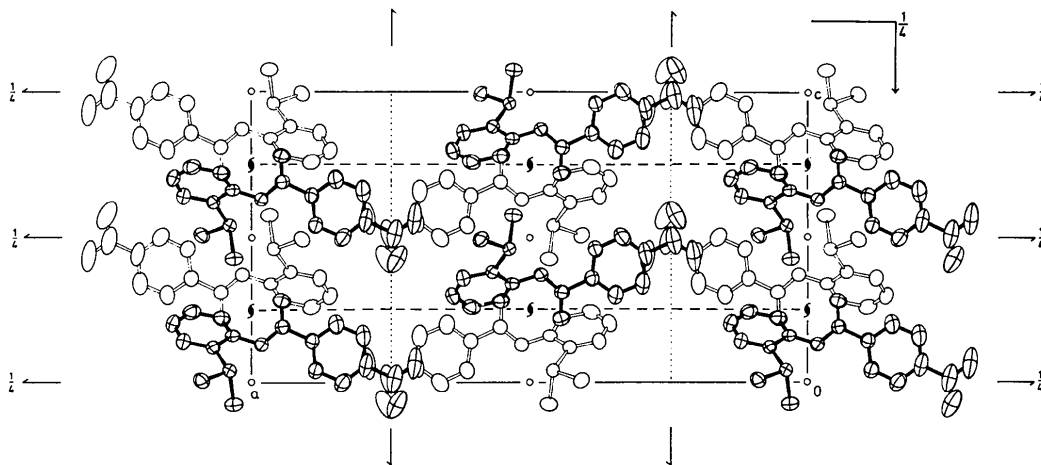


Fig. 2. The molecular packing viewed down **b**.

clusions is the perceptible lengthening of C(1)-C(2) [1.405 (3) Å] and C(2)-C(3) [1.405 (3) Å] in relation to the other values within this ring. However, if significant, the effect is slight and could well be a reflexion of the *ortho* substitution rather than evidence for extended delocalization.

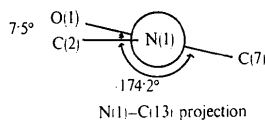
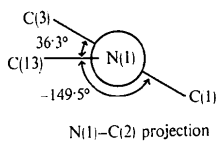
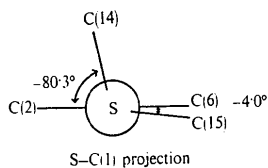
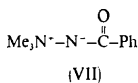
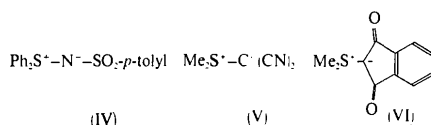


Fig. 3. Newman projections illustrating the molecular conformation.

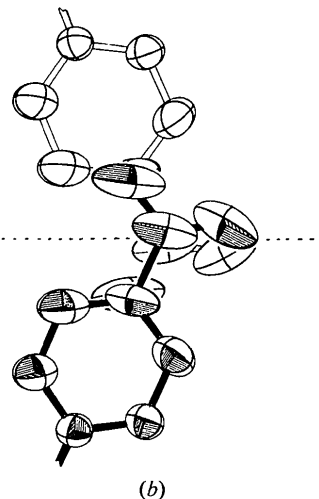
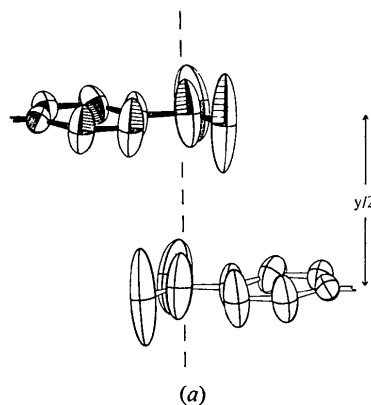


Fig. 4. The overlap of adjacent nitrobenzene groups viewed (a) perpendicular to **b**, and (b) parallel to **b**.

It would appear, therefore, that the major delocalization of the negative charge should take place into the carbonyl group, and in this respect we note the short N(1)-C(13) [1.324 (3) Å], indicative of high double-bond character, in conjunction with the length

of the carbonyl bond [1.245 (3) Å]. Moreover, the C(2)–N(1)–C(13)=O(1) grouping is close to planarity [torsion angle 7.5°]. Since we have suggested minimal delocalization of the negative charge into the sulphonium-aromatic system, there should therefore be a similarity between (II) and (VII) (Cameron, Hair & Morris, 1972), in which there is no delocalization between the σ onium and imine species, in contrast to (I) where some delocalization across the S⁺–N[–] bond is postulated. Thus in (VII) the N[–]–C and C=O lengths are 1.313 (6) and 1.243 (5) Å respectively, while the corresponding values in (I) are 1.344 (3) and 1.246 (3) Å. In particular, therefore, there is an apparent progression of values for the N[–]–C(O) bonds in the three molecules, which may well reflect the degree of delocalization between the σ onium and imine groups in each case.

The major conformational features of (II) are illustrated by the Newman projections in Fig. 3. The 36° torsion about N(1)–C(2) may well arise from steric interactions involving the carbonyl group, the sulphonium-substituted aromatic ring and the sulphonium group itself [O(1)···C(3) 2.93 Å, S⁺···N(1) 2.73 Å]. As a further possible consequence of such interactions, the valence angle at N(1) [120.4 (1)°] is considerably larger than the corresponding angles in (I) [110.0 (1)°] and similar molecules, while the value of 128.2 (1)° for N(1)–C(13)–O(1) is similar to that observed elsewhere.

One interesting feature of the crystal structure of (II) is related to the large thermal motion of the terminal nitro-aromatic group, and is illustrated by the thermal ellipsoid plots in Fig. 4, which shows the over-

lap of pairs of *b*-glide related molecules viewed parallel to and perpendicular to *b*. The nature and direction of the motion thus viewed, suggests a tendency for overlapped nitrobenzene groups to associate closely in pairs by the out-of-phase flexing of adjacent molecules, to give rise to stacks of pairs of associated molecules extending throughout the crystal. Consideration of the r.m.s. amplitude of vibration in relation to the *b* spacing, indicates a closest possible approach of overlapped nitro groups of the order of 3.2–3.3 Å, such that the possibility of charge-transfer interaction cannot be excluded. However, it must be noted that although the colour of the crystals is intense orange, this colour not only persists in solution, but is solvent invariant. Whatever the exact nature of the above interaction, it would seem to be the dominant feature of the crystal packing, although several short intermolecular contacts involving the sulphonium group [S···S 3.48, S···O(1) 2.98 Å] must be noted.

References

- BAK, B., HANSEN, L. & RASTRUP-ANDERSEN, J. (1954). *J. Chem. Phys.* **22**, 2013–2017.
 CAMERON, A. F., DUNCANSON, F. D. & MORRIS, D. G. (1976). *Acta Cryst.* **B32**, 1998–2001.
 CAMERON, A. F., HAIR, N. J. & MORRIS, D. G. (1972). *J. Chem. Soc. Perkin II*, pp. 1071–1076.
 CHRISTENSEN, A. T. & THOM, E. (1971). *Acta Cryst.* **B27**, 581–586.
 CHRISTENSEN, A. T. & WITMORE, W. G. (1969). *Acta Cryst.* **B25**, 73–78.
 KÁLMÁN, A., DUFFIN, B. & KUCSMAN, Á. (1971). *Acta Cryst.* **B27**, 586–594.

Acta Cryst. (1976). **B32**, 2006

The Crystal Structure of the Methanesulphonamide of Piperidine-4-spiro-1'-(2',5'-dioxolane) (C₈H₁₅NSO₄)

BY P. SMITH-VERDIER, S. GARCÍA-BLANCO AND F. FLORENCIO

Instituto 'Rocasolano', Consejo Superior de Investigaciones Científicas, Serrano 119, Madrid-6, Spain

(Received 24 December 1975; accepted 13 January 1976)

Crystals of the methanesulphonamide of piperidine-4-spiro-1'-(2',5'-dioxolane) are monoclinic, space group *P2₁/c* with *a* = 10.373 (2), *b* = 5.449 (1), *c* = 18.049 (4) Å and β = 91.87 (1)°. The structure has been refined to *R* = 0.076 for 2936 independent reflexions measured on an automatic four-circle diffractometer. The piperidine ring has a chair conformation and the S–N bond length of 1.634 Å shows a certain amount of double-bond character.

Introduction

It is difficult to carry out the conformational analysis of *N*-methylsulphonyl compounds by liquid phase methods (dipole moments and NMR) owing to (a)

the flattening at the nitrogen atom involving a not completely tetrahedral arrangement of substituents and (b) the possible existence of rotamers around the N–S bond. For these reasons Dr Moreno Mañas of Universidad Autónoma de Barcelona, suggested