

Structural Investigations of Ylides. X. Crystal and Molecular Structure of 7-Chloro-3-*p*-tolylbenz-1,2,4-oxadiazine, C₁₄H₁₁N₂OCl

BY A. FORBES CAMERON AND ANDREW A. FREER

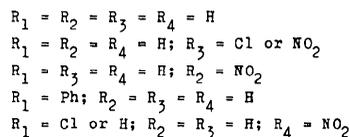
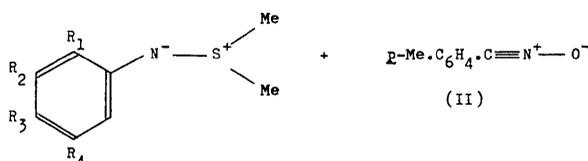
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

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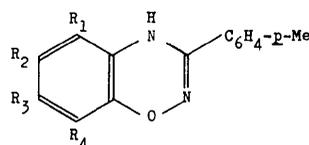
Although not itself an ylide, the title compound is formed directly by the addition of *p*-toluonitrile oxide to the ylide *N*-(*p*-chlorophenyl)-*S,S*-dimethylsulphimide. The structure of the title compound has been determined from 1660 independent diffractometer data, and refined by least squares to a final *R* of 0.043. The crystals are monoclinic, space group *P*2₁/*c*, with *a*=12.801, *b*=9.489, *c*=10.255 Å, β=90.57°, *Z*=4. The analysis confirms that the reactions of *N*-aryl-*S,S*-dimethylsulphimides with *p*-toluonitrile oxide provide a simple synthetic route to the corresponding 1,2,4-benzoxadiazine derivatives, and also reveals that in the solid state the title compound exists in the N(4)-H tautomeric form.

Introduction

The *N*-arylsulphimides (I), isolable as oils or as low-melting solids, possess a highly nucleophilic N atom which bears a good leaving group (dimethyl sulphide). The ylides (I) were found to react rapidly with the other ylide *p*-toluonitrile oxide (II) in dichloromethane at room temperatures, yielding as products the crystalline 1,2,4-benzoxadiazines (III) (Gilchrist, Harris & Rees, 1974). This reaction of *N*-arylsulphimides contrasts with that between a P analogue, *N*-phenyltriphenylphosphimide, and benzonitrile oxide, which results in cycloaddition to the P⁺-N⁻ bond of the phosphimide, followed by extrusion of triphenylphosphine oxide (Huisgen & Wulff, 1967).



(I)



(III)

Since we have a continuing interest in the structures of ylides and their derivatives, we undertook an X-ray

analysis of the title compound (III, R₃=Cl), both to confirm the validity of the relatively rare 1,2,4-benzoxadiazine structure, and also to investigate whether the molecule exists in the N(2)-H or N(4)-H tautomeric form, since chemical and spectroscopic evidence had failed to resolve this feature (Rees, 1975).

Experimental

Crystal data

C₁₄H₁₁N₂OCl, *M*=258.7. Monoclinic, *a*=12.801 (2), *b*=9.489 (1), *c*=10.255 (2) Å, β=90.57 (6)°, *U*=1245.7 Å³, *D_m*=1.37 (by flotation), *D_c*=1.38 g cm⁻³, *Z*=4, *F*(000)=536.0, space group *P*2₁/*c*, Mo *K*α radiation, λ=0.71069 Å, μ(Mo *K*α)=2.99 cm⁻¹.

Crystallographic measurements

Initial cell parameters were determined photographically and later refined by least squares prior to data collection. Intensity measurements were made on a Hilger & Watts Y290 diffractometer with graphite-monochromated Mo radiation, 1660 independent reflexions [*I*≥2σ_{*I*}, σ=√(*I*+*B*₁+*B*₂)] being recorded in the range 2θ=0–50° by the θ, ω-scan technique. Intensities were corrected for Lorentz and polarization effects, but absorption was ignored.

Table 1. Course of refinement

Cycles	Parameters refined	<i>R</i>
1–4	<i>x</i> , <i>y</i> , <i>z</i> , <i>U</i> _{iso} , O, N, C. Unit weights; overall scale factor.	0.139
5–7	<i>x</i> , <i>y</i> , <i>z</i> , <i>U</i> _{<i>ij</i>} , O, N, C; H included, but not refined. Unit weights; overall scale factor.	0.066
8–11	<i>x</i> , <i>y</i> , <i>z</i> , <i>U</i> _{<i>ij</i>} , O, N, C; <i>x</i> , <i>y</i> , <i>z</i> , <i>U</i> _{iso} , H; weighting scheme; overall scale factor.	0.043

Structure determination and refinement

The structure was resolved by the symbolic addition method, an *E* map based on 150 reflexions of |*E*|≥1.53

Table 2. Fractional coordinates ($\times 10^4$) and anisotropic thermal parameters ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cl	5026 (1)	1790 (1)	4721 (1)	925	545	831	-154	-84	-10
O(1)	7526 (2)	5442 (2)	6562 (2)	1125	591	365	-110	-177	45
N(2)	7747 (2)	6950 (3)	6627 (2)	770	550	303	-52	-13	-13
C(3)	7824 (2)	7567 (3)	5507 (3)	507	558	308	15	21	-35
N(4)	7591 (2)	6920 (3)	4343 (2)	689	599	268	-93	17	-6
C(5)	6392 (2)	5232 (3)	3297 (2)	645	570	363	19	-27	-24
C(6)	5792 (3)	4030 (3)	3405 (3)	629	588	489	20	-64	-100
C(7)	5757 (2)	3330 (3)	4580 (3)	601	426	586	4	13	-51
C(8)	6303 (3)	3816 (3)	5665 (3)	780	509	420	-2	22	29
C(9)	6901 (2)	5002 (3)	5528 (3)	665	514	326	11	-29	-52
C(10)	6959 (2)	5723 (2)	4354 (2)	543	487	327	14	28	-31
C(31)	8190 (2)	9030 (3)	5499 (2)	493	570	314	-3	36	-49
C(32)	8943 (3)	9486 (3)	6400 (3)	648	667	383	-30	-64	-10
C(33)	9307 (3)	10844 (3)	6370 (3)	645	731	473	-80	-110	-118
C(34)	8952 (2)	11813 (3)	5455 (3)	579	579	558	-11	43	-125
C(35)	8196 (3)	11355 (4)	4570 (3)	658	546	540	54	-55	-7
C(36)	7819 (3)	10006 (3)	4593 (3)	572	587	415	11	-78	-57
C(341)	9377 (3)	13294 (4)	5406 (4)	784	665	931	-67	-61	-94

Table 2 (cont.)

Hydrogen fractional coordinates ($\times 10^3$) with isotropic temperature factors ($\text{\AA}^2 \times 10^3$)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(4)	768 (3)	742 (3)	367 (3)	68 (10)
H(5)	643 (2)	577 (3)	249 (3)	62 (9)
H(6)	537 (2)	359 (3)	272 (3)	71 (10)
H(8)	630 (3)	333 (4)	647 (4)	77 (10)
H(32)	921 (2)	875 (3)	698 (3)	64 (9)
H(33)	984 (2)	1108 (3)	698 (3)	67 (9)
H(35)	796 (2)	1202 (3)	395 (3)	68 (10)
H(36)	730 (2)	978 (3)	407 (3)	56 (9)
H(341)	1003 (4)	1321 (5)	538 (5)	74 (11)
H(342)	921 (4)	1364 (5)	462 (4)	78 (10)
H(343)	918 (4)	1375 (5)	635 (5)	69 (11)

revealing all non-hydrogen atoms. The refinement by least squares is described in Table 1. After the initial cycles of refinement, examination of a difference synthesis yielded all the H atom positions which were subsequently refined with isotropic thermal parameters. In the latter cycles it was found necessary to apply a weighting scheme of the form $w = (A/F)^2$, the final value of *A* being 12.0. On convergence, when *R* was 0.043, examination of a difference synthesis revealed no errors in the structure, and the refinement was considered complete.

Final fractional coordinates and thermal parameters are given in Table 2; Table 3 contains relevant details of the molecular geometry and conformation. The e.s.d.'s 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.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31665 (14 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion

The analysis has confirmed that the reactions of the ylides (I) and (II) produce the benzoxadiazine systems (III). Moreover, in the case of the present compound (III, $R_3 = \text{Cl}$), the proton associated with the oxadiazine ring is clearly bonded to N(4) [N(4)-H 0.84 (3) Å] rather than to N(2), although adjacent molecules are linked by N(4)-H...N(2) hydrogen bonding [N(4)...N(2) 2.99 Å, N(2)...H 2.18 Å, angle N(4)-H...N(2) 161 (3)°]. However, in the absence of other evidence, the conclusion that the present molecule exists in the N(4)-H tautomeric form must apply only to the solid state, since the observed hydrogen bonding suggests that under different conditions the N(2)-H tautomeric form is at least plausible.

The heterocyclic ring adopts a flattened boat conformation defined by the torsion angles listed in Table 3, with O(1) and N(4) respectively +0.37 and +0.22 Å from the plane of C(3), N(2), C(9) and C(10) (Table 4). The endocyclic valence angles at O(1) and N(4) are respectively 116.1 (2) and 118.5 (2)°. The adoption of

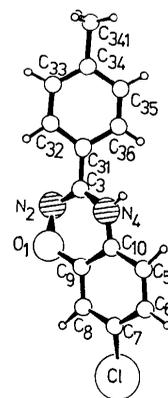


Fig. 1. A view of one molecule showing the atomic numbering. Hydrogen atoms are numbered as the atoms to which they are bonded.

Table 3. Molecular geometry

(a) Bonded distances (Å)			
Cl—C(7)	1.742 (3)	C(7)—C(8)	1.387 (4)
O(1)—N(2)	1.460 (3)	C(8)—C(9)	1.369 (4)
O(1)—C(9)	1.387 (3)	C(9)—C(10)	1.387 (4)
N(2)—C(3)	1.294 (3)	C(31)—C(32)	1.397 (4)
N(4)—C(3)	1.373 (4)	C(31)—C(36)	1.392 (4)
N(4)—C(10)	1.395 (4)	C(32)—C(33)	1.370 (5)
C(3)—C(31)	1.465 (4)	C(33)—C(34)	1.387 (5)
C(5)—C(6)	1.380 (4)	C(34)—C(35)	1.390 (5)
C(5)—C(10)	1.380 (4)	C(34)—C(34I)	1.508 (5)
C(6)—C(7)	1.377 (4)	C(35)—C(36)	1.368 (5)
N(4)—H(4)	0.843 (33)		
Average C—H bond distance 0.956 Å.			
(b) Interbond angles (°)			
N(2)—O(1)—C(9)	116.1 (2)	C(8)—C(9)—C(10)	122.0 (3)
O(1)—N(2)—C(3)	114.8 (2)	N(4)—C(10)—C(5)	124.7 (2)
N(2)—C(3)—N(4)	123.5 (2)	N(4)—C(10)—C(9)	116.5 (2)
N(2)—C(3)—C(31)	117.5 (2)	C(5)—C(10)—C(9)	118.9 (3)
N(4)—C(3)—C(31)	119.0 (2)	C(3)—C(31)—C(32)	120.5 (3)
C(3)—N(4)—C(10)	118.5 (2)	C(3)—C(31)—C(36)	121.8 (3)
C(6)—C(5)—C(10)	120.3 (3)	C(32)—C(31)—C(36)	117.6 (3)
C(5)—C(6)—C(7)	119.5 (3)	C(31)—C(32)—C(33)	120.6 (3)
C(6)—C(7)—C(8)	121.4 (3)	C(32)—C(33)—C(34)	121.9 (3)
Cl—C(7)—C(8)	118.6 (2)	C(33)—C(34)—C(34I)	121.6 (3)
C(7)—C(8)—C(9)	117.9 (3)	C(35)—C(34)—C(34I)	121.3 (3)
O(1)—C(9)—C(8)	119.2 (3)	C(34)—C(35)—C(36)	121.6 (3)
O(1)—C(9)—C(10)	118.6 (3)	C(31)—C(36)—C(35)	121.1 (3)

(c) Intramolecular non-bonded distances (Å)

O(1)···N(4)	2.675
N(2)···C(32)	2.863
N(4)···C(36)	2.937

(d) Intermolecular non-bonded distances (Å)

O(1)···C(34I) ⁱ	3.35	O(1)···N(4) ^{iv}	3.79
C(7)···C(35) ⁱ	3.64	O(1)···C(35) ^{iv}	3.62
C(8)···C(35) ⁱ	3.55	O(1)···C(36) ^{iv}	3.16
Cl···Cl ⁱⁱⁱ	3.44	N(2)···N(4) ^{iv}	2.99
Cl···N(4) ⁱⁱⁱ	3.70	N(2)···C(5) ^{iv}	3.63
Cl···C(3) ⁱⁱⁱ	3.71		
C(6)···C(8) ⁱⁱⁱ	3.51		

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

(i)	x	-y	z	(ii)	1-x	-y	1-z
(iii)	1-x	1-y	1-z	(iv)	x	1.5-y	0.5+z

(e) Selected torsion angles (°)

C(9)—O(1)—N(2)—C(3)	-33.7 (3)
N(2)—O(1)—C(9)—C(10)	+32.2 (4)
O(1)—N(2)—C(3)—N(4)	+7.9 (4)
C(10)—N(4)—C(3)—N(2)	+19.7 (4)
C(3)—N(4)—C(10)—C(9)	-21.1 (4)
O(1)—C(9)—C(10)—N(4)	-5.0 (4)

the N(4)—H tautomeric form is also reflected in the dimensions of this ring. Thus the relative lengths of C(3)—N(2) [1.294 (3) Å] and C(3)—N(4) [1.373 (4) Å] are consistent with the unambiguous location of the double bond between C(3) and N(2), and also with relatively little interaction between this double bond and the lone pair of electrons on N(4). Surprisingly, the length of N(2)—O(1) [1.460 (3) Å] is comparable with the length of the longer [typically 1.479 (5) Å] of the two endocyclic N—O bonds in furoxans [e.g. (IV), Cameron & Freer, 1974], whereas equivalence with

Table 4. Least-squares planes

Equations of least-squares planes in the form $lX' + mY' + nZ' = d$, where X, Y and Z are coordinates in Å with respect to an orthogonalized axial system. Deviations (Å) from the respective planes are given in square brackets.

Plane 1: N(2), C(3), C(9), C(10)

$$0.8876X' - 0.4319Y' - 0.1599Z' = 4.8214$$

[O(1) 0.365; N(2) -0.014; C(3) 0.015; N(4) 0.216; C(9) 0.013; C(10) -0.014]

Plane 2: C(5)—C(10)

$$-0.7846X' + 0.5601Y' + 0.2657Z' = 2.7213$$

[C(5) 0.006; C(6) 0.0; C(7) 0.007; C(8) 0.008; C(9) -0.002; C(10) -0.006]

Plane 3: C(31)—C(36)

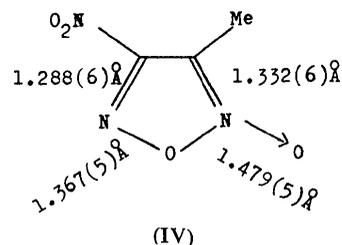
$$0.7260X' - 0.2797Y' - 0.6283Z' = 1.6250$$

[C(31) 0.007; C(32) -0.002; C(33) -0.004; C(34) 0.005; C(35) 0.001; C(36) -0.006]

Dihedral angles (°) between planes

$$(1)-(2) 168.8; (1)-(3) 30.0; (2)-(3) 153.3.$$

the shorter N—O bond [typically 1.367 (5) Å] might be expected. This comparison is made more remarkable when it is considered that C(3)—N(2) is experimentally identical with the shorter C=N bond [1.288 (6) Å] of (IV), since the latter is associated with the shorter N—O endocyclic bond. However, it is possible that this feature of (III) represents a balance between aromatic and N(sp²) substituents of O(1), since the inequality of bonds radiating from O(1) parallels that observed for the endocyclic O atoms in the furoxans.



(IV)

With the exception of those dimensions noted above, other features of the molecular geometry are comparable with literature values for similar bonding situations, while the packing of the molecules appears to be dominated largely by the hydrogen bonding, although we note in particular a relatively short Cl···Cl (3.44 Å) intermolecular contact.

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