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Structural Investigations of Ylides. IX. Crystal and Molecular Structure of a Sulphonyl-Stabilized Pyridinium Ylide: *N*-(1-Pyridinio)chlorobenzene-*p*-sulphonamidate

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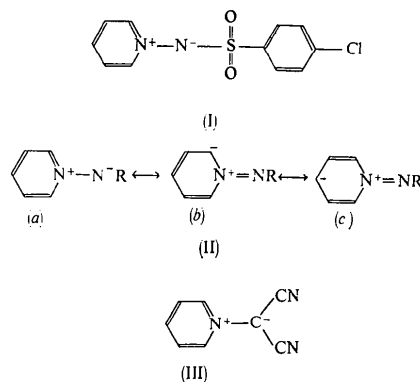
The structure of the title compound has been determined from 1634 independent data collected on a diffractometer. The crystals are monoclinic, space group $P2/c$, with $Z=4$, $a=11.613$, $b=7.372$, $c=15.462$ Å, $\beta=111.85^\circ$. The structure was solved by direct methods, and refined by least squares to a final R of 0.037. The analysis has revealed a molecular conformation that has not previously been observed in sulphonyl-stabilized imines. The $\overset{+}{N}-\overset{-}{N}$ and $\overset{-}{N}-\text{SO}_2$ lengths are respectively 1.419 (3) and 1.584 (2) Å, while the $\overset{+}{N}-\overset{-}{N}-\text{S}$ valence angle is 111.9 (1)°.

Introduction

Preparative chemistry of pyridinium ylides (Johnson, 1966) has shown that these compounds have greater stability than corresponding ammonium compounds. This increased stability has been postulated as arising from a resonance interaction of the anionic species with the pyridinium ring as in (II) [(a) \leftrightarrow (b) \leftrightarrow (c)].

We have described several ylides of the type $\overset{+}{X}-\overset{-}{N}-\text{SO}_2\text{R}$ (Cameron, Hair & Morris, 1973; Cameron, Hair & Morris, 1974; Cameron, Cameron, Campbell & Johnson, 1976; Cameron, Duncanson & Morris, 1976) and compared these with other examples (Kálmán, 1967; Kálmán, Duffin & Kucsman, 1971; Kálmán & Sasvári, 1972), with particular reference to the delocalization possibilities of each molecule in relation to the observed molecular geometries. However, one feature of these examples has been that where delocalization is possible between the 'onium and imine groupings (*e.g.* in sulphonium and phosphonium compounds), it is necessary to invoke *d*-orbital participation, in contrast to the interactions proposed in (II) [(a) \leftrightarrow (b) \leftrightarrow (c)].

We have therefore extended the above series by studying the sulphonyl-stabilized pyridinium-imine (I), with the object of investigating both the delocalization possibilities between the pyridinium and imine species, and also of studying the imine-sulphonyl system in the presence of yet another 'onium grouping.



Experimental

Crystal data

N-(1-Pyridinio)chlorobenzene-*p*-sulphonamidate, $\text{C}_{11}\text{H}_9\text{N}_2\text{SCl}$, $M=268.7$. Monoclinic, $a=11.613$, $b=7.372$, $c=15.462$ Å, $\beta=111.85^\circ$, $U=1228.5$ Å³, $D_m=1.41$ (by flotation), $Z=4$, $D_c=1.45$ g cm⁻³, $F(000)=552$. Space group $P2/c$. Mo $K\alpha$ radiation, $\lambda=0.7107$ Å, $\mu(\text{Mo } K\alpha)=4.67$ cm⁻¹.

Crystallographic measurements

The cell parameters were initially determined photographically and were subsequently refined by least

Table 1. Course of refinement

Cycles	Parameters refined	Final R	Final R'
1-4	x, y, z, U_{iso} for S, O, N, C and Cl, scale factor. Unit weights, full matrix.	0.107	0.0102
5-10	x, y, z, U_{ij} for S, O, N, C and Cl, scale factor. H atom contributions included but not refined. Unit weights, blocked matrix. Correction for anomalous dispersion included. Correction made to data for counter saturation.	0.045	0.0017
11-13*	x, y, z, U_{ij} for S, O, N, C and Cl, x, y, z, U_{iso} for H, scale factor. Unit weights, full matrix.	0.038	0.0014
14-16	x, y, z, U_{ij} for S, O, N, C and Cl, x, y, z, U_{iso} for H, scale factor. Weighting scheme applied, full matrix.	0.037	0.0021

* The space group was changed from Pc to $P2/c$ prior to cycle 11.

squares prior to the diffractometer data collection. Systematic absences suggested the two possible space groups Pc and $P2/c$, the latter subsequently being chosen on the basis of trial refinements. Intensity measurements were made on a Hilger & Watts Y290 diffractometer. A small crystal was exposed to graphite-monochromated Mo radiation, and the $2\theta, \omega$ -scan technique used to record the intensities of 1643 independent reflexions [$I > 2\sigma_I$, $\sigma_I = \sqrt{(I + B_1 + B_2)}$] in the range 2θ $0 \rightarrow 60^\circ$. The intensities were corrected with Lorentz and polarization factors, but not for absorption.

Structure determination

Patterson methods failed to reveal positions for the Cl and S atoms, while direct phasing for both the centrosymmetric and non-centrosymmetric space groups yielded E maps which showed partial pseudosymmetry, and from which no recognizable molecular fragments could be derived. Inspection of the data set suggested that such features could well result from systematic trends within the intensities. In particular, the four parity groups (eeo, eoe, oeo, ooe) representing all reflexions for which $k+l$ is odd, were systematically weak, and present in smaller numbers than the other four groups, with only three members present in a list of the hundred highest $|E|$ values. It was therefore apparent that two largely non-interacting phase subsets existed, since the triplet relationships rarely included members of both subsets. This difficulty was overcome by renormalizing the data in individual parity groups, scaling each group such that $\langle |E|^2 \rangle = 1$. Phase determination was then carried out, in space group Pc , by the automatic multiresolution tangent method (*MULTAN*) with 350 reflexions with $|E| \geq 1.20$. A resulting E map revealed the complete structure.

Structure refinement

Details of the least-squares refinement are given in Table 1. Convergence was achieved when R was 0.037 and R' ($= \sum w\Delta^2 / \sum w|F_o|^2$) 0.0021. Initial refinement assumed space group Pc (in which the structure had eventually been solved), with two molecules per asymmetric unit, although it was apparent that the two molecules were related by an approximate centre of inversion. After several cycles of refinement there appeared certain shortcomings in the refined model, in particular C–C bonds in the pyridinium rings of the two molecules with lengths of 1.54 and 1.21 Å. On changing to space group $P2/c$, all such irregularities vanished, and the refinement was completed on the basis of this space group.

Difference syntheses calculated after the preliminary cycles of refinement revealed all the H atoms, positional and isotropic thermal parameters being refined for these atoms in later cycles. The weighting scheme applied in the later stages was $w = (A + B|F_o| + C|F_o|^2)^{-1}$, the final values of A , B and C being 0.5189, 0.0258 and 0.00128 respectively.

Fractional coordinates and thermal parameters are given in Table 2; Table 3 contains bond lengths, valence angles, non-bonded distances and selected torsion angles, Table 4 gives the least-squares planes. The estimated standard deviations given in Tables 2

Table 2. Atomic coordinates and thermal parameters

(a) Fractional coordinates

	x	y	z
S	0.34435 (6)	0.23542 (9)	1.02985 (4)
Cl	−0.09345 (9)	0.76769 (18)	0.83024 (9)
O(1)	0.4008 (2)	0.2894 (3)	1.1262 (1)
O(2)	0.2917 (2)	0.0554 (3)	0.0113 (1)
S(1)	0.4484 (2)	0.2724 (3)	0.9888 (1)
N(2)	0.4059 (2)	0.2354 (3)	0.8919 (1)
C(1)	0.2191 (2)	0.3842 (4)	0.9725 (2)
C(2)	0.1011 (3)	0.3185 (5)	0.9252 (3)
C(3)	0.0052 (3)	0.4359 (6)	0.8814 (3)
C(4)	0.0284 (3)	0.6181 (5)	0.8843 (2)
C(5)	0.1450 (3)	0.6871 (5)	0.9301 (2)
C(6)	0.2413 (3)	0.5689 (4)	0.9735 (2)
C(7)	0.3868 (3)	0.3788 (4)	0.8341 (2)
C(8)	0.3495 (3)	0.3514 (5)	0.7397 (2)
C(9)	0.3337 (3)	0.1783 (5)	0.7050 (2)
C(10)	0.3569 (3)	0.0336 (4)	0.7656 (2)
C(11)	0.3929 (2)	0.0640 (4)	0.8591 (2)

(b) H atom fractional coordinates and isotropic thermal parameters ($\text{Å}^2 \times 10^3$)

	x	y	z	U_{iso}
H(2)	0.087 (3)	0.190 (5)	−0.076 (2)	75 (10)
H(3)	−0.072 (4)	0.390 (6)	−0.151 (3)	120 (15)
H(5)	0.160 (3)	0.810 (5)	−0.067 (2)	67 (10)
H(6)	0.321 (3)	0.614 (4)	0.002 (2)	66 (9)
H(7)	0.403 (2)	0.493 (4)	−0.136 (2)	40 (7)
H(8)	0.341 (3)	0.453 (4)	−0.296 (2)	67 (10)
H(9)	0.311 (3)	0.154 (4)	−0.360 (2)	67 (9)
H(10)	0.349 (3)	−0.082 (4)	−0.252 (2)	60 (9)
H(11)	0.412 (3)	−0.023 (4)	−0.096 (2)	56 (8)

(c) Anisotropic thermal parameters ($\text{Å}^2 \times 10^4$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	526	393	401	−14	160	−1
Cl	675	1219	1249	420	218	266
O(1)	749	609	371	36	145	−27
O(2)	741	399	638	−86	309	4
N(1)	427	433	389	−14	81	−28
N(2)	377	368	413	10	129	22
C(1)	440	464	421	−15	166	−48
C(2)	519	586	872	−132	172	−24
C(3)	438	879	1126	−54	130	13
C(4)	499	820	678	158	187	62
C(5)	632	471	671	44	184	32
C(6)	482	445	546	−29	103	−76
C(7)	503	409	581	28	256	72
C(8)	602	670	532	99	274	182
C(9)	564	810	413	53	193	−14
C(10)	509	525	524	−9	171	−93
C(11)	460	394	491	25	177	17

Mean estimated standard deviations ($\text{Å}^2 \times 10^4$)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	4	3	3	3	3	3
Cl	6	10	9	6	6	7
O	13	12	11	11	10	9
N	10	12	11	9	9	9
C	17	19	19	15	14	16

and 3 are derived from the least-squares calculations, and should be regarded as minimum values. The atomic numbering is shown in Fig. 1.*

Discussion

The length of $\overset{+}{\text{N}}(2)\text{---}\overset{-}{\text{N}}(1)$ in (I) is of particular interest in relation to the suggestion that pyridinium ylides owe their stability in part to delocalization between the aromatic ring and the anionic species. The present

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31598 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

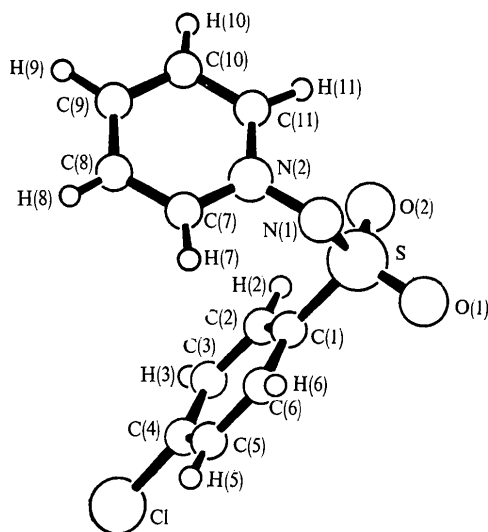


Fig. 1. A view of one molecule showing the atomic numbering.

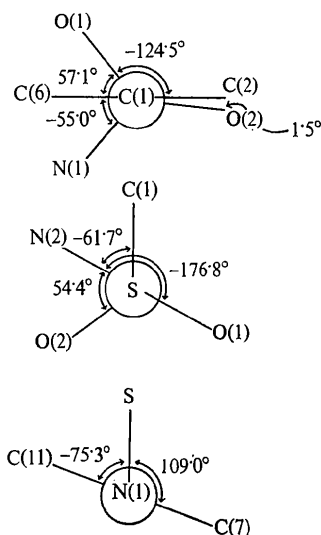


Fig. 2. The three Newman projections illustrating the molecular conformation.

analysis reveals a value of 1.419 (3) Å for this bond, which although shorter than the value of 1.472 (2) Å typically observed for $\overset{+}{\text{N}}\text{---}\overset{-}{\text{N}}$ in ammonium imines (Cameron, Duncanson & Morris, 1976), is not unduly short when the change in hybridization at N(2) is considered, and a plausible interpretation is that this

Table 3. *Interatomic distances and angles*

(a) Bonded distances (Å)

S—O(1)	1.443 (2)	C(10)—C(11)	1.366 (4)
S—O(2)	1.445 (2)	C(1)—C(2)	1.379 (5)
S—N(1)	1.584 (2)	C(2)—C(3)	1.374 (6)
S—C(1)	1.773 (3)	C(3)—C(4)	1.367 (6)
N(1)—N(2)	1.419 (3)	C(4)—C(5)	1.371 (5)
N(2)—C(7)	1.348 (4)	C(5)—C(6)	1.379 (5)
N(2)—C(11)	1.349 (3)	C(1)—C(6)	1.385 (4)
C(7)—C(8)	1.373 (4)	C(4)—Cl	1.743 (4)
C(8)—C(9)	1.370 (5)		
C(9)—C(10)	1.378 (5)		
		Mean C—H	0.93 (3)

(b) Interbond angles (°)

O(1)—S—O(2)	117.0 (1)	C(5)—C(6)—C(1)	120.2 (2)
N(1)—S—O(1)	104.2 (1)	C(6)—C(1)—C(2)	119.7 (2)
N(1)—S—O(2)	114.1 (1)	C(3)—C(4)—Cl	119.4 (2)
N(1)—S—C(1)	107.4 (1)	C(5)—C(4)—Cl	118.8 (2)
C(1)—S—O(1)	108.6 (1)	N(1)—N(2)—C(7)	117.2 (2)
C(1)—S—O(2)	105.1 (1)	N(1)—N(2)—C(11)	121.5 (2)
S—N(1)—N(2)	111.9 (1)	N(2)—C(7)—C(8)	119.9 (2)
S—C(1)—C(2)	121.1 (2)	C(7)—C(8)—C(9)	119.7 (2)
S—C(1)—C(6)	119.2 (1)	C(8)—C(9)—C(10)	119.4 (2)
C(1)—C(2)—C(3)	120.2 (3)	C(9)—C(10)—C(11)	119.8 (2)
C(2)—C(3)—C(4)	119.3 (3)	C(10)—C(11)—N(2)	119.9 (2)
C(3)—C(4)—C(5)	121.7 (2)	C(7)—N(2)—C(11)	121.2 (2)
C(4)—C(5)—C(6)	118.8 (2)		

(c) Intramolecular non-bonded distances (Å)

S·····N(2)	2.49	O(2)···N(2)	2.96
S·····C(7)	3.41	O(2)···C(2)	2.87
S·····C(11)	3.16	O(1)···C(6)	3.16
O(1)···O(2)	2.46	O(2)···C(11)	3.00
O(1)···N(1)	2.39	C(1)···C(7)	3.39
O(2)···N(1)	2.54	C(6)···C(7)	3.49

(d) Intermolecular distances (Å) < 3.90 Å

C(5)···O(2) ⁱ	3.20	Cl·····Cl ^{iv}	3.86
C(6)···O(2) ⁱ	3.65	Cl·····C(10) ^v	3.47
O(2)···C(9) ⁱⁱ	3.33	C(7)·····C(8) ^{vi}	3.65
O(1)···C(10) ⁱⁱ	3.37	C(8)·····C(8) ^{vi}	3.39
O(1)···C(8) ⁱⁱⁱ	3.35	C(8)·····C(9) ^{vi}	3.68
C(8)···C(3) ^{iv}	3.89	C(9)·····C(10) ^{vi}	3.61
C(5)···Cl ^{iv}	3.89	C(9)·····C(11) ^{vi}	3.75
C(4)···Cl ^{iv}	3.83	C(10)·····C(10) ^{vi}	3.53

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

(i)	x	1+y	z	(ii)	x	-y	$\frac{1}{2}+z$
(iii)	x	1-y	$\frac{1}{2}+z$	(iv)	-x	y	$\frac{3}{2}-z$
(v)	-x	1+y	$\frac{3}{2}-z$	(vi)	1-x	y	$\frac{3}{2}-z$

(e) Selected torsion angles (°)

O(1)—S—N(1)—N(2)	-176.8	O(2)—S—C(1)—C(6)	-176.9
O(2)—S—N(1)—N(2)	54.4	N(1)—S—C(1)—C(2)	123.4
C(1)—S—N(1)—N(2)	-61.7	N(1)—S—C(1)—C(6)	-55.0
O(1)—S—C(1)—C(2)	-124.5	S—N(1)—N(2)—C(7)	109.0
O(1)—S—C(1)—C(6)	57.1	S—N(1)—N(2)—C(11)	-75.3
O(2)—S—C(1)—C(2)	1.5		

Mean e.s.d. 0.2°

Table 4. *Least-squares planes*

(a) Equations of planes

$$(I) \quad 0.5394X - 0.0773Y - 0.8385Z - 13.558 = 0$$

$$(II) \quad -0.9959X + 0.0150Y - 0.0893Z - 0.7119 = 0$$

X , Y and Z are orthogonal coordinates in Å.

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

(I)	S	-0.008	Cl	-0.032	O(2)	0.045
	C(1)	-0.010*	C(2)	0.004*	C(3)	0.001*
	C(4)	-0.002*	C(5)	-0.004*	C(6)	0.009*
(II)	N(1)	-0.046	N(2)	0.011*	C(7)	-0.009*
	C(8)	-0.001*	C(9)	0.008*	C(10)	-0.006*
	C(11)	-0.004*				

* Denotes atom used to define plane.

value indicates minimal delocalization across N(2)-N(1) of (I). This conclusion is supported by the essentially normal dimensions of the pyridinium ring, in which the N-C lengths [average 1.349 (4) Å] and C-C lengths [average 1.372 (5) Å] are little different from those observed in free pyridine (Bak, Hansen & Rastrup-Andersen, 1954). Moreover, the C(7)-N(2)-N(1)-S torsion angle (75.3°) indicates that the pyridinium ring is not ideally aligned for effective overlap with either of the lone pairs on N(1). This orientation of the pyridinium ring is in marked contrast to that in pyridiniumdicyanomethylide (III) (Bart, 1969), in which exact coplanarity with the trigonal methylide species is observed. However, the N-C length of (III), 1.42 (1) Å, again suggests relatively little delocalization, despite the favourable overlap geometry in this case.

The length, 1.584 (2) Å, of the N(1)-S imine-sulphonyl bond compares with the range of values [1.581 (10)-1.618 (7) Å] previously observed for ylides containing this grouping. The present value, although clearly tending towards the lower end of this range and perhaps defining the range more precisely, adds further weight to the suggestion (Cameron, Duncanson & Morris, 1976) that the length of the imine-sulphonyl bond in ylides of the type X-N-SO₂R, is not grossly influenced by the presence of different 'onium groups.

The conformation of (I) is illustrated by the three Newman projections in Fig. 2. We have previously commented on the apparent uniformity in the conformations of ylides of the type X-N-SO₂R, although one aberrant example has been recorded (Cameron, Cameron, Campbell & Johnson, 1976), in which the anomalies are attributed to internal steric constraints. However, the present molecule constitutes yet another exception. In particular, the sulphonyl-bonded aromatic ring is only 1.5° removed from coplanarity with S=O(2) (usual value *ca* 11°), while N(2)-N(1) is only 3.2° removed from *trans*-coplanarity with S=O(1)

(usual value *ca* 12°). Although slight, the significance of these differences is nevertheless heightened by the regularity observed in most other examples. In seeking an explanation for the anomalous behaviour of (I), we note that the steric requirements of the pyridinium ring are in contrast to those of the 'onium species (ammonium, sulphonium and phosphonium) in the previous examples. Moreover, the folding of these molecules is such that the substituents or sterically significant lone pairs associated with the 'onium groups, are in close proximity to the sulphonyl-bonded aromatic ring. It is plausible, therefore, that while there probably exists an ideal conformation for such molecules related to the delocalization requirements, in particular within the imine-sulphonyl moiety, the fine details of individual conformations represent a compromise between bonding and steric requirements, and that slight deviations should not be unexpected when major changes are effected in the steric requirements of the 'onium group.

Of the other aspects of the geometry of (I), the valence angle at the imino-nitrogen atom N(1) [111.9 (1)°] is the smallest value yet reported for ylides of the type X-N-SO₂R [previous range 113.4 (5)-126.4 (2)°]. It is possible that this feature may also be related to the detailed steric interactions within individual molecules, since the largest value [126.4 (2)°] is associated with the bulky triphenylphosphonium group, while there is little difference between the values associated with sulphonium [113.4 (5)-116.2 (6)°] and ammonium [118.0 (1)°] groups.

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