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Structural Investigations of Ylides. XV.[*] Structures of *S*,*S*-Dimethyl-*N*-(*m*-nitrophenyl)sulphimide, *S*,*S*-Dimethyl-*N*-(*p*-nitrophenyl)sulphimide and the Picrate Salt of *N*-(*p*-Chlorophenyl)-*S*,*S*-dimethylsulphimide

BY A. FORBES CAMERON, ANDREW A. FREER AND ABRAHAM MALTZ

*Department of Chemistry, University of Glasgow, Glasgow G*12 8*QQ, Scotland*

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Abstract

The structure of *S*,*S*-dimethyl-*N*-(*m*-nitrophenyl)-sulphimide (I), of its *p*-nitro analogue (II) and of the picrate salt of the *p*-chloro analogue (III) have been determined. Crystals of (I) are orthorhombic, space group $P2_12_12_1$, with a = 13·663 (3), b = 13·850 (3), c = 5·008 (1) Å, Z = 4, U = 947·68 Å^3. (II) is monoclinic, space group $P2_1/c$, with a = 4·811 (1), b = 9·874 (2), c = 19·947 (4) Å, β = 97·45 (3)°, Z = 4, U = 939·6 Å^3. Crystals of (III) are also monoclinic, space group $P2_1/n$, with a = 7·924 (1), b = 9·406 (1), c = 23·078 (2) Å, β = 92·19 (6)°, Z = 4, U = 1718·8 Å^3. For 1348, 868 and 3687 independent diffractometer data for (I), (II) and (III), respectively, the final R = 0·030 for (I), 0·052 for (II) and 0·033 for (III). The S–N lengths are 1·622 (2) in (I), 1·640 (4) in (II) and 1·631 (1) Å in (III), while the N–C(aryl) lengths are, respectively, 1·391 (2), 1·366 (6) and 1·415 (2) Å. The solid-state conformations of (I) and (II) are virtually identical, but differ from that of (III). The analysis of (III) confirms that salt formation occurs with protonation of the ylide at N, the latter atom being planar and trigonal.

Introduction

The stabilities and reactivities of stabilized ylides, X^+-Y^--R, are in part determined by the extent to which the electron pair(s) on Y^- interact both with the onium group X^+, and also with the stabilizing group R. We have previously described the structures of several second-row ylides including two *N*-sulphonylimino-sulphuranes ($>S^+-N^--SO_2R$) (Cameron, Cameron, Campbell & Johnson, 1976; Cameron, Hair & Morris, 1973) and an *N*-acyliminosulphurane ($>S^+-N^--COR$) (Cameron, Duncanson & Morris, 1976). *N*-Sulphonyl and *N*-acyl examples are relatively unreactive and long-lived at room temperature, whereas *N*-aryliminosulphuranes ($>S^+-N^--C_6H_4-Y$) with strongly electron-withdrawing groups (Y = CN, NO_2) on the aromatic ring are only moderately stable (1–12 months at room temperature), and halogenated examples are hygroscopic and decompose within a few days at room temperature (Varkey, Whitfield & Swern, 1974). Thus crystals of (I) and (II) prepared for the analyses survived for several months, but are nevertheless sufficiently reactive to be of chemical interest. In a subsequent publication (A. F. Cameron & A. Maltz, to be published), we shall report the structures of several of their reaction products. In contrast to (I) and (II), *N*-(*p*-chlorophenyl)-*S*,*S*-dimethylsulphimide is

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[*] Part XIV: Cameron & Duncanson (1981).

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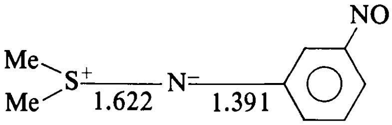
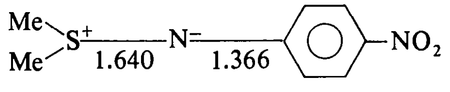
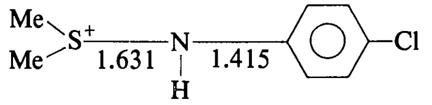
hygroscopic and decomposes within a few days at room temperature, being stable only at lower temperatures or in the form of salts such as the picrate (III). Our analyses of (I), (II) and (III) were undertaken to provide details of the geometries and conformations of the three compounds.



(I)



(II)



(picrate)−

(III)

Having completed the analysis of (II) it was brought to our attention that this compound had been the subject of a crystallographic study (Eliel, Koskimies, McPhail & Swern, 1976). However, the latter workers report a unit cell of dimensions $a = 4{\cdot}845$, $b = 9{\cdot}886$, $c = 21{\cdot}018$ Å, $\beta = 109{\cdot}49°$, and the choice of space group $P2_1/c$ is supported by quoted systematic absences in the $0k0$ and $h0l$ spectra. This cell differs from that found by ourselves, but since there is the possibility of two crystalline forms of (II), we note that reindexing our cell would yield a cell of dimensions $a = 4{\cdot}811$, $b = 9{\cdot}874$, $c = 21{\cdot}117$ Å, $\beta = 110{\cdot}51°$, very similar to that quoted by Eliel *et al.*, but that our space group would then change to $P2_1/n$. We therefore feel justified in including details of our analysis of (II), although the molecular geometries resulting from the two analyses are virtually identical.

Experimental

Preparation of crystals

Ylides (I) and (II) and the ylide moiety of (III) were prepared by the procedure described by Claus, Rieder, Hofbauer & Vilsmaier (1975), with *m*-nitroaniline, *p*-nitroaniline and *p*-chloroaniline respectively as reagents. Crystallization from an ether–hexane–dichloromethane mixture yielded red needle-shaped crystals of (I), while yellow crystals of (II) were produced from an ether–dichloromethane mixture.

A solution of picric acid in ether was added dropwise in excess to an ether solution of ylide (III), and the mixture was stirred for one hour. The filtrate was recrystalized from acetone–ether to give needle-shaped crystals of the picrate (III).

Crystal data

$C_8H_{10}N_2O_2S$ (I), $M_r = 198{\cdot}2$, $D_m = 1{\cdot}38$, $D_c = 1{\cdot}39$ Mg m^{-3}, $F(000) = 416$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu(\text{Mo}\,K) = 0{\cdot}296$ mm^{-1}.

$C_8H_{10}N_2O_2S$ (II), $M_r = 198{\cdot}2$, $D_m = 1{\cdot}40$, $Z = 4$, $D_c = 1{\cdot}40$ Mg m^{-3}, $F(000) = 416$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu(\text{Mo}\,K) = 0{\cdot}296$ mm^{-1}.

$C_8H_{11}ClNS^+.C_6H_2N_3O_7^-$ (III), $M_r = 416{\cdot}8$, $D_m = 1{\cdot}61$, $D_c = 1{\cdot}61$ Mg m^{-3}, $F(000) = 856$, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}7107$ Å, $\mu(\text{Mo}\,K) = 0{\cdot}394$ mm^{-1}.

Crystallographic measurements and structure determinations

Small crystals of the three compounds were exposed to Mo radiation [graphite-monochromated for (I) and (III), Zr-filtered for (II)] on a Hilger & Watts Y290 diffractometer. Intensity measurements were made with the θ,ω-scan technique in the range 2θ 0–60°, and yielded 1348 independent reflexions [$I \geq 2{\cdot}5\sigma_I$, $\sigma_I = \sqrt{(I + B_1 + B_2)}$] for (I), 868 independent reflexions ($I \geq 2{\cdot}5\sigma_I$) for (II), and 3687 independent reflexions ($I \geq 3\sigma_I$) for (III). The three sets of intensities were corrected for Lorentz and polarization effects, but not for absorption.

The structures of (I) and (II) were solved with *MULTAN* (Main, Woolfson, Lessinger, Germain &

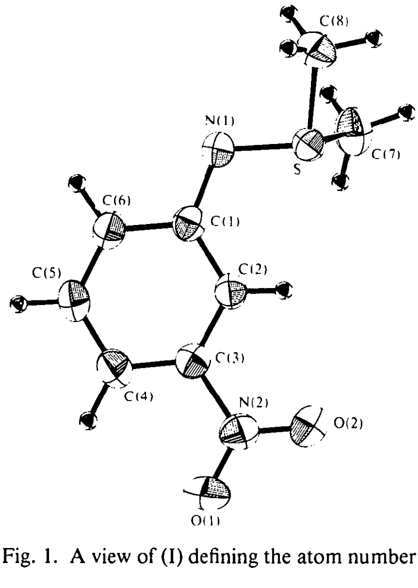


Fig. 1. A view of (I) defining the atom numbering.

Declercq, 1976). The structure of (III) was solved with quartets in a modified version of *PHASE* (Cameron, Freer & Gilmore, 1981) incorporated in XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). 1031 quartets were produced with QGEN for $E \geq 2{\cdot}10$ with $P^+ \geq 0{\cdot}90$ ($P^- \leq 0{\cdot}10$), from both the $P_7^{\pm}$ and $P_{13}^{\pm}$ formulae. After elimination of groups of invariants with

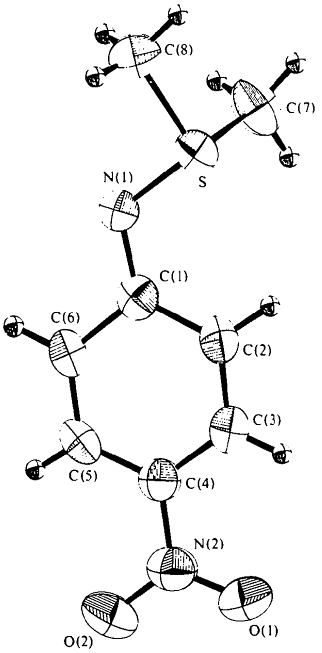


Fig. 2. A view of (II) defining the atom numbering.

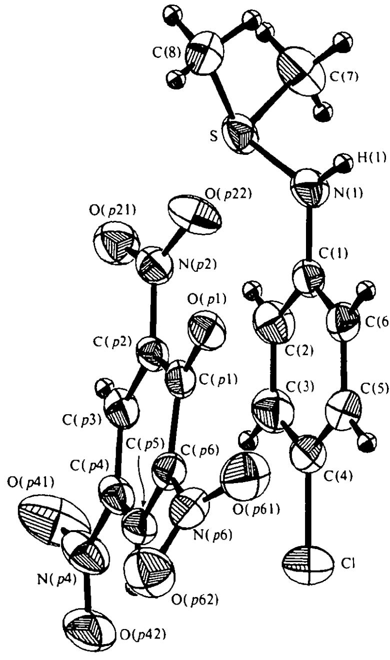


Fig. 3. A view of the two residues of (III) defining the atom numbering.

Table 1. *Positional parameters* ($\times 10^4$, *for* H $\times 10^3$) *and equivalent isotropic thermal parameters* (Å^2 $\times 10^3$) *for* (I)

$U_{eq} = (U_1 U_2 U_3)^{1/3}$.

	x	y	z	U_{eq}
C(1)	3054 (1)	7970 (1)	8192 (4)	37 (1)
C(2)	3690 (1)	7613 (1)	10145 (4)	38 (1)
C(3)	3469 (1)	6757 (1)	11449 (4)	39 (1)
C(4)	2645 (2)	6207 (1)	10904 (5)	49 (1)
C(5)	2031 (2)	6555 (2)	8948 (5)	53 (1)
C(6)	2219 (1)	7408 (1)	7608 (5)	47 (1)
C(7)	5043 (2)	9344 (2)	5674 (6)	57 (1)
C(8)	3610 (2)	10665 (2)	6594 (6)	55 (1)
N(1)	3156 (1)	8827 (1)	6769 (4)	45 (1)
N(2)	4152 (1)	6416 (1)	13507 (4)	46 (1)
O(1)	3960 (2)	5672 (1)	14705 (4)	69 (1)
O(2)	4888 (1)	6890 (1)	13964 (5)	71 (1)
S	4019 (1)	9532 (1)	7831 (1)	39 (1)
H(2)	425 (2)	792 (2)	1058 (5)	
H(4)	257 (2)	560 (2)	1186 (6)	
H(5)	147 (2)	614 (2)	847 (7)	
H(6)	177 (2)	759 (2)	617 (5)	
H(71)	554 (2)	986 (2)	598 (7)	
H(72)	485 (2)	936 (2)	388 (7)	
H(73)	528 (2)	863 (2)	592 (6)	
H(81)	416 (2)	1115 (2)	665 (7)	
H(82)	348 (2)	1056 (2)	472 (7)	
H(83)	304 (2)	1087 (2)	755 (7)	

Table 2. *Positional parameters* ($\times 10^4$, *for* H $\times 10^3$) *and equivalent isotropic thermal parameters* (Å^2 $\times 10^3$) *for* (II)

$U_{eq} = (U_1 U_2 U_3)^{1/3}$.

	x	y	z	U_{eq}
C(1)	−1420 (9)	8492 (5)	1949 (2)	42 (3)
C(2)	−499 (10)	7407 (5)	2390 (2)	46 (3)
C(3)	−1386 (10)	7296 (6)	3013 (3)	49 (3)
C(4)	−3266 (10)	8233 (5)	3216 (2)	45 (3)
C(5)	−4251 (11)	9279 (6)	2793 (3)	48 (3)
C(6)	−3381 (10)	9419 (5)	2171 (3)	45 (3)
C(7)	80 (17)	6324 (7)	662 (4)	69 (5)
C(8)	2681 (16)	8684 (8)	396 (3)	72 (5)
N(1)	−711 (8)	8711 (4)	1316 (2)	49 (3)
N(2)	−4183 (9)	8089 (5)	3864 (2)	59 (3)
O(1)	−3440 (10)	7083 (4)	4207 (2)	86 (3)
O(2)	−5646 (10)	8974 (4)	4070 (2)	87 (3)
S	1782 (3)	7738 (1)	1096 (1)	48 (1)
H(2)	74 (10)	671 (6)	227 (3)	
H(3)	−75 (9)	660 (5)	329 (2)	
H(5)	−545 (10)	987 (5)	289 (3)	
H(6)	−407 (10)	1014 (5)	188 (2)	
H(71)	143 (11)	581 (6)	45 (3)	
H(72)	−128 (13)	667 (7)	33 (3)	
H(73)	−77 (16)	574 (8)	100 (4)	
H(81)	335 (14)	951 (8)	58 (3)	
H(82)	100 (12)	882 (6)	8 (3)	
H(83)	393 (14)	809 (9)	20 (4)	

all four principal terms in common, 955 quartets remained. Triplet phase relationships were generated for $E \geq 1{\cdot}60$. The probabilities for acceptance of a triplet, a positive quartet and a negative quartet were 0·8, 0·95 and 0·07 respectively. The program arbitrarily selected three reflexions for origin definition, which were expanded to phase 341 reflexions (156+, 185−). The resulting E map revealed the complete structure.

All three structures were refined by least-squares calculations which were terminated at $R = 0{\cdot}030$ for (I), 0·052 for (II) and 0·033 for (III).* In each case all H atoms were located from difference syntheses, and their positions refined in later cycles.

Figs. 1, 2 and 3 show views of (I), (II) and (III) respectively, and define the atom numbering. Atomic coordinates are presented in Tables 1, 2 and 3. Table 4 contains details of the molecular geometries.

Discussion

The analysis of the picrate confirms that it may be formulated as in (III), with the ylide protonated at N(1), which is planar and trigonal. Picrate and protonated-ylide ions are paired by strong N—H···O

Table 3. *Positional parameters* ($\times 10^4$, *for* H $\times 10^3$) *and equivalent isotropic thermal parameters* (Å$^2 \times 10^3$) *for* (III)

$U_{eq} = (U_1 U_2 U_3)^{1/3}$.

	x	y	z	U_{eq}
Cl	7707 (1)	5009 (1)	3161 (1)	69 (1)
S	11200 (1)	11683 (1)	3567 (1)	41 (1)
O(*p*1)	6164 (1)	8733 (1)	5256 (1)	40 (1)
C(*p*1)	5689 (1)	8387 (1)	4756 (1)	32 (1)
C(*p*2)	6130 (1)	9135 (1)	4231 (1)	32 (1)
N(*p*2)	7200 (1)	10382 (1)	4268 (1)	38 (1)
O(*p*21)	7999 (2)	10644 (1)	4722 (1)	54 (1)
O(*p*22)	7300 (1)	11144 (1)	3838 (1)	53 (1)
C(*p*3)	5572 (2)	8751 (2)	3682 (1)	35 (1)
C(*p*4)	4533 (2)	7577 (2)	3612 (1)	38 (1)
N(*p*4)	3975 (2)	7172 (2)	3032 (1)	51 (1)
O(*p*41)	4268 (2)	7993 (2)	2633 (1)	74 (1)
O(*p*42)	3199 (2)	6049 (2)	2963 (1)	65 (1)
C(*p*5)	4006 (2)	6807 (1)	4080 (1)	37 (1)
C(*p*6)	4547 (2)	7204 (1)	4629 (1)	35 (1)
N(*p*6)	3894 (2)	6375 (1)	5101 (1)	44 (1)
O(*p*61)	4762 (2)	6232 (1)	5546 (1)	60 (1)
O(*p*62)	2492 (2)	5827 (2)	5028 (1)	64 (1)
N(1)	11369 (2)	10202 (1)	3932 (1)	44 (1)
C(1)	10489 (2)	8972 (1)	3738 (1)	41 (1)
C(2)	10019 (2)	8781 (2)	3154 (1)	37 (1)
C(3)	9150 (2)	7564 (2)	2983 (1)	34 (1)
C(4)	8786 (2)	6542 (2)	3383 (1)	42 (1)
C(5)	9252 (2)	6710 (2)	3963 (1)	54 (1)
C(6)	10100 (2)	7937 (2)	4140 (1)	53 (1)
C(7)	10882 (3)	13016 (2)	4099 (1)	44 (1)
C(8)	13308 (2)	12081 (3)	3368 (1)	48 (1)
H(1)	1191 (3)	1019 (2)	423 (1)	
H(*p*3)	589 (2)	927 (2)	336 (1)	
H(*p*5)	327 (2)	602 (2)	405 (1)	
H(6)	1040 (3)	809 (2)	454 (1)	
H(2)	1034 (3)	950 (2)	289 (1)	
H(3)	886 (4)	746 (3)	255 (1)	
H(71)	1402 (3)	1205 (2)	370 (1)	
H(72)	1331 (3)	1300 (3)	322 (1)	
H(73)	1358 (3)	1138 (3)	106 (1)	
H(81)	988 (4)	1287 (3)	424 (1)	
H(82)	1180 (3)	1301 (3)	438 (1)	
H(83)	1097 (3)	1390 (3)	390 (1)	

Table 4. *Molecular geometries of* (I), (II) *and* (III)

(*a*) Bond lengths (Å)

	(I)	(II)	(III)
S–C(7)	1·787 (3)	1·785 (8)	1·780 (2)
S–C(8)	1·777 (2)	1·780 (8)	1·788 (2)
S–N(1)	1·622 (2)	1·640 (4)	1·631 (1)
N(1)–C(1)	1·391 (2)	1·366 (6)	1·415 (2)
C(1)–C(2)	1·399 (3)	1·420 (7)	1·396 (2)
C(2)–C(3)	1·386 (3)	1·370 (7)	1·386 (3)
C(3)–C(4)	1·387 (3)	1·390 (7)	1·374 (2)
C(4)–C(5)	1·376 (3)	1·378 (7)	1·383 (2)
C(5)–C(6)	1·382 (3)	1·368 (8)	1·390 (2)
C(6)–C(1)	1·412 (3)	1·426 (7)	1·386 (2)
C(3)–N(2)	1·468 (3)		
N(2)–O(1)	1·221 (2)	1·233 (6)	
N(2)–O(2)	1·222 (3)	1·226 (7)	
C(4)–N(2)		1·426 (7)	
C(4)–Cl			1·743 (2)

Picrate residue of (III)

C(*p*1)–C(*p*2)	1·453 (2)	N(*p*2)–O(*p*21)	1·229 (2)
C(*p*2)–C(*p*3)	1·375 (2)	N(*p*2)–O(*p*22)	1·229 (2)
C(*p*3)–C(*p*4)	1·383 (2)	C(*p*4)–N(*p*4)	1·443 (2)
C(*p*4)–C(*p*5)	1·378 (2)	N(*p*4)–O(*p*41)	1·231 (2)
C(*p*5)–C(*p*6)	1·373 (2)	N(*p*4)–O(*p*42)	1·230 (2)
C(*p*6)–C(*p*1)	1·457 (2)	C(*p*6)–N(*p*6)	1·452 (2)
C(*p*1)–O(*p*1)	1·244 (2)	N(*p*6)–O(*p*61)	1·222 (2)
C(*p*2)–N(*p*2)	1·448 (2)	N(*p*6)–O(*p*62)	1·231 (2)

(*b*) Bond angles (°)

	(I)	(II)	(III)
C(7)–S–C(8)	99·5 (1)	100·0 (4)	100·8 (1)
C(7)–S–N(1)	106·5 (1)	106·4 (3)	104·8 (1)
C(8)–S–N(1)	100·9 (1)	99·4 (3)	104·6 (1)
S–N(1)–C(1)	114·7 (1)	115·7 (3)	120·4 (1)
N(1)–C(1)–C(2)	126·7 (2)	126·6 (4)	121·4 (1)
N(1)–C(1)–C(6)	116·4 (2)	116·1 (4)	118·9 (1)
C(2)–C(1)–C(6)	116·8 (2)	117·2 (4)	119·8 (1)
C(1)–C(2)–C(3)	119·8 (2)	120·9 (5)	119·7 (2)
C(2)–C(3)–C(4)	123·6 (2)	120·2 (5)	120·2 (2)
C(3)–C(4)–C(5)	116·3 (2)	120·4 (5)	121·2 (2)
C(4)–C(5)–C(6)	122·1 (2)	120·7 (5)	119·1 (2)
C(5)–C(6)–C(1)	121·4 (2)	120·6 (5)	120·3 (2)
C(2)–C(3)–N(2)	117·9 (2)		
C(4)–C(3)–N(2)	118·6 (2)		
C(3)–C(4)–N(2)		119·2 (4)	
C(5)–C(4)–N(2)		120·5 (4)	
O(1)–N(2)–C(3)	118·7 (2)		
O(2)–N(2)–C(3)	118·8 (2)		
O(1)–N(2)–O(2)	122·5 (2)	121·7 (5)	
O(1)–N(2)–C(4)		118·8 (4)	
O(2)–N(2)–C(4)		119·5 (5)	
Cl–C(4)–C(3)			119·6 (1)
Cl–C(4)–C(5)			119·2 (1)

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* Lists of structure factors and anisotropic thermal parameters for the three compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35910 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4 (*cont.*)

Picrate residue of (III)

O(*p*1)–C(*p*1)–C(*p*2)	124·9 (1)	C(*p*5)–C(*p*6)–N(*p*6)	116·0 (1)
O(*p*1)–C(*p*1)–C(*p*6)	123·3 (1)	C(*p*1)–C(*p*6)–N(*p*6)	119·7 (1)
C(*p*2)–C(*p*1)–C(*p*6)	111·7 (1)	C(*p*2)–N(*p*2)–O(*p*21)	119·6 (1)
C(*p*1)–C(*p*2)–C(*p*3)	124·2 (2)	C(*p*2)–N(*p*2)–O(*p*22)	118·8 (1)
C(*p*1)–C(*p*2)–N(*p*2)	120·2 (1)	O(*p*21)–N(*p*2)–O(*p*22)	121·7 (1)
C(*p*3)–C(*p*2)–N(*p*2)	115·7 (1)	C(*p*4)–N(*p*4)–O(*p*41)	117·9 (1)
C(*p*2)–C(*p*3)–C(*p*4)	119·1 (1)	C(*p*4)–N(*p*4)–O(*p*42)	118·7 (1)
C(*p*3)–C(*p*4)–C(*p*5)	121·7 (1)	O(*p*41)–N(*p*4)–O(*p*42)	123·3 (2)
C(*p*3)–C(*p*4)–N(*p*4)	118·6 (1)	C(*p*6)–N(*p*6)–O(*p*61)	119·0 (1)
C(*p*5)–C(*p*4)–N(*p*4)	119·8 (1)	C(*p*6)–N(*p*6)–O(*p*62)	117·9 (1)
C(*p*4)–C(*p*5)–C(*p*6)	119·1 (1)	O(*p*61)–N(*p*6)–O(*p*62)	123·1 (1)
C(*p*5)–C(*p*6)–C(*p*1)	124·3 (1)		

(*c*) Selected torsion angles (°)

	(I)	(II)	(III)
S–N(1)–C(1)–C(2)	−9·3 (3)	−9·0 (6)	25·4 (2)
S–N(1)–C(1)–C(6)	170·4 (1)	173·9 (3)	−155·0 (1)
C(7)–S–N(1)–C(1)	99·6 (2)	93·2 (4)	134·4 (1)
C(8)–S–N(1)–C(1)	−157·1 (2)	−163·5 (4)	−120·0 (1)
C(2)–C(3)–N(2)–O(1)	178·8 (2)		
C(2)–C(3)–N(2)–O(2)	−0·9 (3)		
C(3)–C(4)–N(2)–O(1)		−5·2 (7)	
C(3)–C(4)–N(2)–O(2)		173·7 (5)	

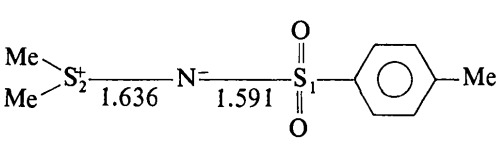
hydrogen bonds [N(1)–H(1) 0·80 (2), O(*p*1)···H(1) 2·15 (2) Å]. In three dimensions these pairs are arranged such that there is face-to-face stacking of aromatic residues in adjacent pairs.

The S–N bonds in (I), (II) and (III) [respectively 1·622 (2), 1·640 (4) and 1·631 (1) Å] are similar within experimental error, and compare to values reported for similar bonds elsewhere (Cameron, Duncanson & Morris, 1976). That (III) does not differ greatly from (I), (II), (IV) (Cameron, Hair & Morris, 1973) and (V) (Cook, Glick, Rigau & Johnson, 1971) in this respect, confirms the earlier observation, based on comparison of (IV) and (V), that protonation or alkylation of N$^-$ in salt formation does not have a gross effect on the length of the S–N ylide bond in such compounds. However, the N–S(sulphonyl) bond of (V) [1·681 (5) Å] is considerably longer than the corresponding bond of (IV) [1·591 (8) Å]. Because of the differing nature of the aryl substituents in (I)–(III), such a direct comparison is not possible for the corresponding bond in (III). However, the N(1)–C(1) length of 1·415 (2) Å in (III) is only slightly longer than the 1·391 (2) and 1·366 (6) Å in (I) and (II) respectively.

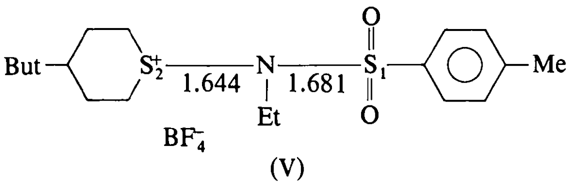
Comparison of the dimensions of (I) and (II) suggests that there may be discernible differences between the two molecules, particularly in the lengths of the S(1)–N(1), N(1)–C(1) and N(2)–C(4) bonds, although these differences are slight and border on the level of significance. Nevertheless, in every instance they are compatible with there being slightly more interaction of N(1)$^-$ with the *p*-nitrophenyl ring of (II) than with the *m*-nitrophenyl ring of (I), in accordance with expectations. Moreover, the aromatic ring of (II) shows slightly more perturbation from idealized geometry than does that of (I).

The torsion angles in Table 4 reveal that the conformations of (I) and (II) are closely similar, but differ from that of the ylide moiety in (III), in particular with respect to the orientation of the S–N bond relative to the aromatic ring. However, not only is the electronic configuration of N(1) in (III) necessarily different from that in (I) and (II) as a result of the N protonation, but the N(1)–H(1) bond of (III) is involved also in interionic hydrogen bonding. One consequence of the small deviations from coplanarity of the S–N bonds and aromatic rings in (I) and (II) is that the S atoms approach relatively close to an aromatic proton. Moreover, in (I), the *cisoid* relationship of the S and *m*-nitro groups (Fig. 1) means that this proton exists in a potentially overcrowded environment. Thus we observe similar angular distortions at C(1) in (I) and (II) which are not so pronounced in (III), while in (I) there is additional out-of-plane bending of the N(1)–C(1) bond, an effect which is absent in (II) and (III).

We thank Professor C. W. Rees for his interest, help and advice, and for extending experimental facilities to AM.



(IV)



(V)

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Structure of a Novel Type of Heteropolyanion: Dicupro(II)-18-molybdodisilicate(12−), $[Cu_2Si_2Mo_{18}O_{66}]^{12-}$

BY H. F. FUKUSHIMA,* A. KOBAYASHI AND Y. SASAKI

Department of Chemistry and Research Centre for Spectrochemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, *Japan*

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Abstract. $(NH_4)_{12}[Cu_2Si_2Mo_{18}O_{66}].14H_2O$, $M_r = 3434{\cdot}2$, triclinic, $P\bar{1}$, $a = 12{\cdot}19$ (2), $b = 15{\cdot}78$ (2), $c = 10{\cdot}81$ (2) Å, $\alpha = 91{\cdot}3$ (6), $\beta = 74{\cdot}6$ (3), $\gamma = 75{\cdot}8$ (2)°, $U = 1989$ Å^3, $Z = 1$, $D_x = 2{\cdot}87$, $D_m = 2{\cdot}91$ Mg m^{-3}, μ(Mo $K\alpha$) = 2·47 mm^{-1}. Block-diagonal least-squares calculations based on 4602 independent intensities reduced the R factor to 0·048. The X-ray structure determination of $(NH_4)_6[CuSiMo_9O_{33}].7H_2O$ has shown that the compound has a dimeric structure and contains the polyanion $[Cu_2Si_2Mo_{18}O_{66}]^{12-}$. Each SiO_4 tetrahedron is surrounded by nine MoO_6 octahedra. The two CuO_6 octahedra, which have a common edge, are attached to both Si atoms. These CuO_6 octahedra are elongated by the static Jahn–Teller effect.

Introduction. Many kinds of heteropolymolybdates and -tungstates containing two different hetero-atoms have recently been prepared and investigated. Anions of the general formula $[H_2X^{m+}Y^{n+}M_{11}O_{40}]^{(12-m-n)-}$ (where M = Mo^{6+} or W^{6+}; X^{m+} = Si^{4+}, Ge^{4+}, P^{5+}, As^{5+}, Co^{2+}, or Co^{3+}; Y^{n+} = transition metals) have the Keggin structure in which one of the Mo or W atoms in the MO_6 octahedra is substituted by Y^{n+} (Baker, Baker, Eriks, Pope, Shibata, Rollins, Fang & Koh, 1966; Weakley & Malik, 1967; Tourné & Tourné, 1969; Tourné, Tourné, Malik & Weakley, 1970; Zonnevijlle, 1976). The $[H_2X_2^{m+}Y^{n+}M_{17}O_{62}]^{(20-2m-n)-}$-type anions ($X^{m+}$ = P^{5+} or As^{5+}; M = Mo^{6+} or W^{6+}; Y^{n+} = transition metals) (Malik & Weakley, 1968) can be regarded as substitution derivatives of the well known $[X_2^{m+}M_{18}O_{62}]^{(16-2m)-}$ anion, in which the geometrical arrangement of the MO_6 octahedra around each XO_4 tetrahedron is common to that found in the Dawson structure.

The $[P_2Co_4(H_2O)_2W_{18}O_{68}]^{10-}$ anion (Weakley, Evans, Showell, Tourné & Tourné, 1973) likewise contains two fragments of the Keggin ion, PW_9O_{34}, but lacks one of the four W_3O_{13} units contained in the Keggin structure. The present paper reports a new type of heteropolyanion containing two different kinds of hetero-atoms (Si and Cu^{II}) with a structure having no resemblance to the Keggin or Dawson structure. The ammonium salt of the present complex was first prepared by Leyrie, Fournier & Massart (1971) together with $[H_2CuSiMo_{11}O_{40}]^{6-}$ salts, and Fournier & Massart (1974) later gave the ammonium salt the monomeric formula $(NH_4)_6[CuSiMo_9O_{34}H_2(H_2O)_3]$. The crystals were prepared by a procedure similar to that described by Leyrie, Fournier & Massart (1971).

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* Present address: Tokyo University of Agriculture and Technology, Koganei, Tokyo 184, Japan.

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