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Crystal and Molecular Structure of *S,S*-Diphenyl-*N-p*-tolylsulphonyl Sulphilimine*

BY A. KÁLMÁN†

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, England

B. DUFFIN

Unilever Research Laboratory, Port Sunlight, Cheshire, England

AND Á. KUCSMAN

Institute of Organic Chemistry, L. Eötvös University, Budapest, Hungary

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The crystal structure of *S,S*-diphenyl-*N-p*-tolylsulphonyl sulphilimine has been solved by the symbolic addition method and refined by least-squares analysis of three-dimensional data collected by the multiple-film technique to the final residual, $R=0.095$. The S-N(sp^2) bond lengths (1.598 and 1.628 Å) indicate a π -bond system delocalized to the S-N-S moiety. The S-N-S bond angle of 113.4° is considerably less than the theoretical 120° . The S(VI)-C(11) distance of 1.756 Å is in a good agreement with the calculated 1.75 Å for the S(VI)-C(sp^2) single bond. Due to the different S(IV)-C(sp^2) π -bonding one of the S(IV)-C(sp^2) bonds is significantly shorter (1.769 Å) than the other (1.799 Å) and than the theoretical 1.80 Å value. The mean S(VI)-O distance is 1.432 Å. The conformation of the molecule, which is fairly similar to that of the *S,S*-dimethyl-*N*-methylsulphonyl sulphilimine, is discussed in detail.

Introduction

N-Sulphoacyl sulphilimines (RR'SNSO₂Q) containing different SN bonds are compounds of theoretical interest. In the course of the structure investigation of *N*-acyl sulphilimines, started by Kuczman, Ruff & Kapovits (1966),‡ the crystal structure of *S,S*-dimethyl-*N*-methylsulphonyl sulphilimine (DMMSS; Me₂SNSO₂Me) has been determined (Kálmán, 1967). On this basis the electronic structure and conformation of *N*-sulphoacyl sulphilimines were discussed in detail (Kuczman, Kálmán & Kapovits, 1967).§ In order to get more information about the fine-structure of sul-

philimines, the crystal and molecular structure of the *S,S*-diphenyl-*N-p*-tolylsulphonyl sulphilimine (DPTSS; Ph₂SNSO₂C₆H₄Me) of the *S*-aryl-*N*-arylsulphonyl type has been determined.

Experimental

DPTSS was prepared by the method of Kuczman, Kapovits & Balla (1962) and crystallized from ethanol. Infrared and melting point data showed that the product was of analytical purity. The crystals were colourless transparent needles the main axis of which was parallel to the monoclinic unique axis, *b*. The lattice parameters were determined from precession photographs and the density was measured by flotation.

Crystal data

C₁₉H₁₇NO₂S₂, $M=355.48$. Monoclinic;
 $a=10.616 \pm 0.011$, $b=10.540 \pm 0.006$,
 $c=15.931 \pm 0.013$ Å,
 $\beta=100.90 \pm 0.09^\circ$;

* This paper is to be regarded as part XI of the series: *The Bond System of the N-Acyl Sulphilimines*, published by Kuczman *et al.* (Part X: Mezey, 1970a).

† Permanent address: Central Research Institute for Chemistry Hungarian Academy of Sciences, Budapest, Pf. 114/17, Hungary.

‡ Part I of the series.

§ Part IV of the series.

$V=1750.39 \text{ \AA}^3$, $Z=4$,
 $D_c=1.348$, $D_x=1.342 \text{ g.cm}^{-3}$,
 $F(000)=744$;
 μ for Cu $K\alpha$ ($\lambda=1.5418 \text{ \AA}$) 28.1 cm^{-1} .
 Space group, $P2_1/c$ (No. 14).

Reflexions were collected on integrated equi-inclination Weissenberg photographs taken with Ni-filtered Cu $K\alpha$ radiation using the multiple-film technique. The DPTSS crystals similarly to other sulphilimines are rather sensitive to X-ray irradiation. In order to dim-

inish the errors caused by their decomposition during the long exposures the samples were changed after every second layer. From the long needles, small cylinder-like samples were prepared and shaped properly by an instrument (Kálmán & Argay, 1965) to the diameter of 0.1 mm. Thus absorption correction was neglected ($\mu R=0.3$). Photographs were taken from the following layers; $h0l-h8l$, $hk0-hk4$ and $0kl-1kl$. The observed structure factors were derived from the integrated intensities, measured by a Zeiss photometer, in a data reduction program which also corrected for vari-

Table 1. Fractional coordinates and anisotropic thermal parameters ($\times 10^4$) for non-hydrogen atoms

Estimated standard deviations are given in parentheses. The anisotropic thermal parameters are in the form:
 $\exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]$.

	x/a	y/b	z/c	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
S(1)*	-154 (2)	1268 (2)	2447 (1)	96 (2)	93 (2)	47 (1)	2 (3)	22 (2)	4 (2)
S(2)*	-2529 (2)	528 (2)	1689 (1)	103 (2)	155 (3)	41 (1)	-42 (4)	7 (2)	13 (3)
N	-1127 (6)	89 (7)	2149 (5)	95 (7)	115 (8)	67 (4)	-22 (12)	2 (9)	-1 (10)
O(1)	-3104 (7)	-585 (7)	1267 (5)	173 (9)	221 (11)	55 (3)	-165 (16)	32 (9)	-95 (3)
O(2)	-2488 (7)	1653 (8)	1186 (5)	191 (10)	218 (11)	60 (4)	-5 (17)	38 (9)	119 (10)
C(11)	-3379 (8)	912 (7)	2499 (5)	92 (8)	96 (8)	50 (4)	-28 (13)	-5 (9)	25 (10)
C(12)	-4210 (8)	15 (8)	2744 (6)	108 (9)	94 (8)	51 (4)	-12 (13)	2 (10)	23 (10)
C(13)	-4837 (8)	284 (9)	3403 (6)	109 (10)	125 (10)	67 (5)	-19 (16)	26 (11)	33 (12)
C(14)	-4699 (8)	1441 (9)	3801 (6)	106 (9)	138 (11)	68 (5)	67 (16)	52 (11)	39 (13)
C(15)	-3910 (9)	2331 (9)	3547 (7)	133 (11)	113 (10)	83 (6)	35 (17)	22 (14)	4 (14)
C(16)	-3260 (9)	2071 (9)	2891 (6)	128 (11)	114 (10)	75 (6)	-28 (17)	42 (13)	33 (12)
C(17)	-5354 (13)	1805 (13)	4537 (8)	204 (18)	216 (18)	79 (7)	91 (29)	113 (18)	19 (18)
C(21)	629 (8)	837 (8)	3489 (5)	115 (9)	108 (8)	32 (3)	-12 (14)	25 (9)	-5 (9)
C(22)	630 (10)	1742 (9)	4126 (7)	168 (13)	106 (9)	66 (5)	-7 (18)	30 (14)	-28 (12)
C(23)	1188 (10)	1436 (10)	4957 (6)	156 (13)	172 (13)	57 (5)	-71 (21)	19 (13)	-50 (14)
C(24)	1692 (9)	270 (10)	5136 (6)	124 (11)	215 (15)	42 (4)	-39 (21)	9 (11)	-9 (13)
C(25)	1725 (10)	-606 (10)	4523 (6)	140 (12)	162 (13)	57 (5)	40 (20)	14 (12)	44 (13)
C(26)	1177 (9)	-335 (8)	3678 (6)	141 (11)	99 (8)	47 (4)	35 (16)	26 (11)	-12 (10)
C(31)	1113 (7)	1032 (7)	1856 (5)	92 (8)	85 (8)	43 (4)	11 (12)	14 (9)	23 (9)
C(32)	2209 (8)	1759 (8)	2066 (5)	103 (9)	130 (10)	44 (4)	-30 (15)	12 (10)	7 (10)
C(33)	3149 (9)	1629 (9)	1590 (6)	111 (10)	152 (11)	47 (4)	-42 (17)	14 (10)	25 (12)
C(34)	3010 (9)	826 (9)	906 (6)	124 (10)	121 (10)	63 (5)	42 (16)	40 (12)	41 (12)
C(35)	1897 (10)	120 (9)	715 (6)	180 (13)	109 (10)	52 (5)	22 (19)	45 (13)	-13 (11)
C(36)	937 (9)	229 (8)	1169 (6)	125 (10)	107 (9)	53 (4)	-35 (15)	24 (11)	-5 (10)

* In the discussion S(1)=S(IV), S(2)=S(VI).

Table 2. Fractional coordinates ($\times 10^3$) isotropic temperature parameters (\AA^2) and bond distances (\AA) for the hydrogen atoms

Estimated standard deviations are given in parentheses.

	x/a	y/b	z/c	B_i	C-H distances
H(12)	-428 (9)	-77 (8)	247 (6)	4.45	0.93 (9)
H(13)	-538 (9)	-38 (9)	359 (6)	5.08	0.99 (10)
H(15)	-385 (10)	318 (9)	387 (6)	5.86	1.03 (10)
H(16)	-278 (10)	257 (9)	263 (6)	5.70	0.90 (10)
H(17.1)	-610 (11)	165 (10)	432 (7)	7.11	0.82 (12)
H(17.2)	-496 (11)	247 (10)	506 (7)	7.11	1.11 (11)
H(17.3)	-537 (11)	133 (10)	487 (7)	7.11	0.73 (11)
H(22)	1 (10)	258 (9)	395 (6)	5.74	1.11 (10)
H(23)	95 (10)	187 (10)	559 (7)	6.08	1.18 (10)
H(24)	196 (10)	6 (9)	585 (7)	5.88	1.14 (10)
H(25)	218 (10)	-151 (9)	472 (6)	5.67	1.09 (10)
H(26)	116 (9)	-97 (9)	323 (6)	4.57	0.97 (9)
H(32)	248 (9)	222 (8)	261 (6)	4.48	0.99 (9)
H(33)	388 (9)	221 (9)	176 (6)	4.82	0.98 (9)
H(34)	378 (10)	70 (9)	61 (6)	5.27	1.03 (10)
H(35)	169 (10)	-39 (9)	21 (7)	5.43	0.95 (10)
H(36)	125 (9)	-23 (9)	112 (6)	4.88	0.98 (10)

Table 3. Observed and calculated structure factors (x 10)

Reflexions indicated by asterisks have intensity values less than the threshold value for an observed reflexion; those indicated by an E were thought to be affected by extinction. Both sets were omitted from the final least-squares and R calculations.

Table with multiple columns for h, k, l, F_o, F_c, and various reflection indices. The table lists observed and calculated structure factors for various reflections, including intensity values and extinction indicators.

ideal method of phase determination for the structure. A computer program was used to place the film data on an absolute scale by Wilson's (1942) method and to determine the overall temperature factor as $B=4.09 \text{ \AA}^2$. Normalized structure factor magnitudes, $|E|$, were computed from the observed structure factor values, $|F|$, with the formula (Karle & Karle, 1964):

$$E_h^2 = F_h^2 / \varepsilon \sum_{j=1}^N f_{jh}^2$$

where N is the number of atoms in the unit cell, f is the atomic scattering factor for the j th atom corrected for the overall temperature factor B and $\varepsilon=1$ except for $h0l$ and $0k0$ where $\varepsilon=2$. All triplet interactions E_h , E_k and E_{h-k} with E_h values greater than $|E|=1.5$ were listed and allowed 321 reflexions to be used for the symbolic addition procedure. A lower limit of $|E|=2.0$ was used for the E_k and E_{h-k} values to ensure a number of statistically preferable E_k , E_{h-k} pairs related to each E_h .

Three linearly independent reflexions $\bar{7}84$, 145 and $\bar{6}42$ were given positive signs to specify the origin and further reflexion, 467 , was assigned the symbol a . All four reflexions had large $|E|$ values and entered into many relationships applicable to the \sum_2 formula (Hauptman & Karle, 1953):

$$sE_h \approx s \sum_k E_k E_{h-k}$$

During the course of phase determination, by the symbolic addition procedure, of the 74 reflexions with $|E_h| > 2.0$, it was found necessary to increase the number of phased reflexions in the starting set by including the reflexions 625, 539 and 021, with assigned symbols b , c and d . In this way, all but six reflexions could be phased in terms of signs or symbols. From the many indications of phase found in the individual phase determinations, the symbols a , b , c and d were assigned the negative sign. This set of 68 phases was used to determine the signs of the remaining reflexions with $|E_h| > 1.5$. A three-dimensional E map was computed using 295 E values as coefficients in a Fourier synthesis and showed the positions of all non-hydrogen atoms in the molecule. A structure factor calculation, based on the fractional atomic coordinates obtained from the E map and applying isotropic temperature factors of $B=4.09 \text{ \AA}^2$ to all atoms as given by the Wilson plot, resulted in an agreement value R of 0.30 for the observed reflexions.

The structure was refined by the method of least-squares with the block-diagonal approximation where the function minimized was $w(|F_o| - |F_c|)^2$. Two cycles of refinement of the scale factor, positional parameters

Table 4. *Interatomic distances and bond angles with their e.s.d.'s*

The estimated standard deviations are in parentheses.

S(IV)-N	1.628 (7) \AA	O(1)-S(VI)-O(2)	118.07 (45)°
S(IV)-C(21)	1.769 (8)	O(1)-S(VI)-C(11)	107.51 (42)
S(IV)-C(31)	1.799 (8)	O(1)-S(VI)-N	104.84 (42)
S(VI)-N	1.598 (8)	O(2)-S(VI)-C(11)	107.08 (42)
S(VI)-O(1)	1.430 (8)	O(2)-S(VI)-N	111.81 (42)
S(VI)-O(2)	1.435 (8)	C(11)-S(VI)-N	107.00 (39)
S(VI)-C(11)	1.756 (8)	S(VI)-C(11)-C(12)	119.26 (62)
S(IV)..S(VI)	2.696 (3)	S(VI)-C(11)-C(16)	121.70 (67)
C(11)-C(12)	1.399 (12)	C(12)-C(11)-C(16)	119.03 (78)
C(11)-C(16)	1.367 (12)	C(11)-C(12)-C(13)	119.74 (79)
C(12)-C(13)	1.374 (13)	C(12)-C(13)-C(14)	120.82 (86)
C(13)-C(14)	1.369 (13)	C(13)-C(14)-C(15)	119.46 (89)
C(14)-C(15)	1.369 (14)	C(14)-C(15)-C(16)	120.48 (92)
C(15)-C(16)	1.384 (14)	C(15)-C(16)-C(11)	120.38 (88)
C(14)-C(17)	1.521 (16)	C(13)-C(14)-C(17)	123.82 (92)
C(21)-C(22)	1.392 (12)	C(15)-C(14)-C(17)	116.70 (91)
C(21)-C(26)	1.374 (12)	S(IV)-C(21)-C(22)	116.33 (66)
C(22)-C(23)	1.382 (14)	S(IV)-C(21)-C(26)	122.78 (64)
C(23)-C(24)	1.348 (16)	C(22)-C(21)-C(26)	120.86 (80)
C(24)-C(25)	1.349 (15)	C(21)-C(22)-C(23)	118.68 (90)
C(25)-C(26)	1.391 (13)	C(22)-C(23)-C(24)	119.68 (98)
C(31)-C(32)	1.381 (12)	C(23)-C(24)-C(25)	122.36 (99)
C(31)-C(36)	1.368 (12)	C(24)-C(25)-C(26)	119.71 (93)
C(32)-C(33)	1.371 (13)	C(25)-C(26)-C(21)	118.66 (82)
C(33)-C(34)	1.365 (13)	S(IV)-C(31)-C(32)	118.38 (60)
C(34)-C(35)	1.380 (14)	S(IV)-C(31)-C(36)	120.12 (62)
C(35)-C(36)	1.362 (14)	C(32)-C(31)-C(36)	121.26 (75)
S(IV)-N-S(VI)	113.43 (45)°	C(31)-C(32)-C(33)	118.60 (79)
C(21)-S(IV)-N	103.72 (38)	C(32)-C(33)-C(34)	121.56 (86)
C(31)-S(IV)-N	103.77 (37)	C(33)-C(34)-C(35)	118.00 (88)
C(21)-S(IV)-C(31)	101.01 (37)	C(34)-C(35)-C(36)	122.19 (90)
		C(35)-C(36)-C(31)	118.32 (82)

and isotropic temperature factors of the 24 non-hydrogen atoms reduced R to 0.21. All observations were given unit weights during these cycles. A further cycle using the weighting scheme suggested by Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) improved the agreement to 0.17. The positions of the 14 phenyl hydrogen atoms were calculated assuming them to lie on the ring diagonals with C–H equal to 1.05 Å; they were included, as fixed atoms with a temperature factor equal to that of carbon atom to which they were attached, in a further cycle which reduced R to 0.15. Three cycles of anisotropic refinement of the non-hydrogen atoms, with fixed isotropic hydrogen atoms, improved the agreement to 0.109. The positions of the methyl group hydrogen atoms and improved coordinates of the phenyl hydrogen atoms were determined from a three-dimensional difference Fourier synthesis using coefficients obtained from a structure factor calculation for which the contributions of the hydrogen atoms were omitted.

At this stage it was seen that twelve large, low order reflexions were probably affected by extinction; these were omitted from the subsequent refinement cycles. Three further anisotropic cycles were performed; in the last of these cycles the positional parameters of the hydrogen atoms were allowed to vary also. Calculated shifts in parameters were now less than the corre-

sponding standard deviations and refinement was terminated. The final agreement R was 0.095 for the 1758 observed reflexions. Inclusion of the reflexions affected by extinction and the 922 unobserved reflexions gave an R value of 0.124.

In all structure factor and least-squares calculations, the atomic scattering factors for all atoms were those given in *International Tables for X-ray Crystallography* (1962). All calculations in the structure determination and refinement were performed on an IBM 360/50 computer using programs supplied by Dr F. R. Ahmed. The final fractional coordinates and anisotropic thermal parameters for the non-hydrogen atoms are given in Table 1 and the hydrogen atomic coordinates and isotropic temperature factors are shown in Table 2. Estimated standard deviations given in these Tables have been calculated from the inverse diagonal elements of the final least-squares matrix. F_o and F_c values listed in Table 3.

The interatomic distances and bond angles along with their estimated standard deviations are given in Table 4. Bond lengths involving hydrogen atoms are shown in Table 2.

Discussion

S(IV)–N(sp^2) and S(VI)–N(sp^2) bond lengths (1.628 and 1.598 Å, respectively) show that DPTSS, like DMMSS, contains SN bonds of intermediate π -bond order; thus both sulphilimines can be characterized by a π -bond system involving the S(IV)–N(sp^2)–S(VI) group of atoms (Table 5). Although the difference in SN bond lengths (0.03 Å) is less than that found in DMMSS (0.05 Å) it may be still regarded as significant (*cf.* Cruickshank & Robertson, 1953). The longer S(IV)–N bond can be attributed to the electronegativity and atomic radius of the S(IV) atom differing from those of the S(VI) atom (*cf.* Truter, 1962; Kucsmán, Kálmán & Kapovits, 1967). It is noteworthy that N(sp^2) forms a bond angle of 113.4° (in DMMSS 116.1°) with the sulphur atoms. In both cases the SNS bond angles are considerably less than the expected 120°. The S(VI)–O distances (1.430 and 1.435 Å) correspond to those in DMMSS. The S(VI)–C(11) bond length (1.756 Å) is in agreement with the theoretical S(VI)–C(sp^2) value (1.75 Å) calculated from the atomic radii and electronegativities given by Truter (1962) and with the experimental data obtained for sulphanyl amides (O'Connor

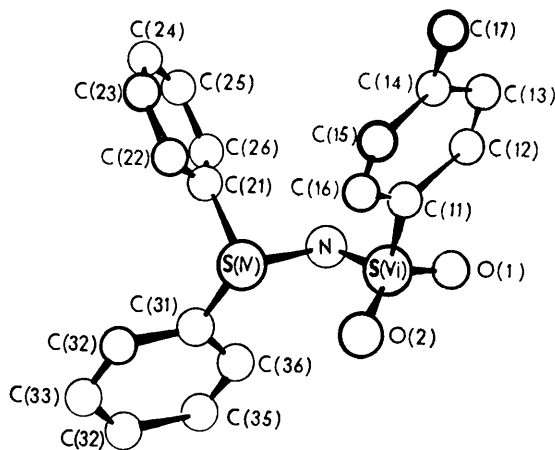


Fig. 1. Clinographic projection of DPTSS molecule indicating the labelled non-hydrogen atoms.

Table 5. S–N bond lengths

Compounds	Bond type	Bond lengths with e.s.d.'s	Reference
H ₃ N ⁽⁺⁾ –SO ₃ ⁽⁻⁾	S(VI)–N(sp^3)	1.764 (20) Å	Sass (1960)
(FSN) ₄	S(IV)–N(sp^2)	1.660 (10)	Wiegiers & Vos (1963)
DMMSS	S(IV)–N(sp^2)	1.633 (9)	Kálmán (1967)
DPTSS	S(IV)–N(sp^2)	1.628 (7)	Present work
(CISN) ₃	S(IV)–N(sp^2)	1.614 (7)	Wiegiers & Vos (1966)
DPTSS	S(VI)–N(sp^2)	1.598 (8)	Present work
DMMSS	S(VI)–N(sp^2)	1.581 (10)	Kálmán (1967)
α -(CISNO) ₃	S(VI)–N(sp^2)	1.574 (11)	Hazell, Wiegiers & Vos (1966)
(FSN) ₄	S(IV)–N(sp^2)	1.540 (10)	Wiegiers & Vos (1963)

& Maslen, 1965; O'Connell & Maslen, 1967; Alléaume & Decap, 1965*a, b*).

The S(IV)–C(*sp*²) bond lengths in DPTSS are different (1.799 and 1.769 Å). The larger value corresponds to the interatomic distance calculated by Truter (1962) for a S(IV)–C(*sp*²) bond. A similar phenomenon has been observed in several compounds of the S(IV)–C(H)₃ type (Table 6). In these compounds one of the chemically equivalent methyl groups forms a considerably shorter bond with the S(IV) atom than the other. In the case of diphenyl sulphoxide (Abrahams, 1957) both the S(IV)–C(*sp*²) bonds were found to be significantly shorter than 1.80 Å (see Table 6). From bond length data it may be concluded that additional π -bonding should be taken into account for one or both of the S(IV)–C σ -bonds when a tetravalent sulphur atom is surrounded by three appropriate ligands.

The equations of the 'least-squares' planes of the phenyl rings calculated according to Blow (1960) and the deviations of the atoms from these planes are listed in Table 7. The χ^2 test for the atoms defining the phenyl rings I, II, and III gave values $\chi^2 = 7.61$, 4.57 and 4.95 respectively; thus each ring can be regarded as planar within experimental error. The mean C(*sp*²)–C(*sp*²) bond lengths, 1.377, 1.373 and 1.371 Å for phenyl rings I, II, and III respectively, are shorter than expected, but similar values have been reported in the literature. The bond angles in the phenyl rings differ only slightly from the theoretical value of 120°. The mean C(*sp*²)–H bond distances for all three phenyl rings is 1.02 Å.

Conformation of the molecule

In the (C₆H₅)₂SN group the C(21), C(31) and N(*sp*²) atoms are linked to the S(IV) atom according to the bond orientation of a trigonal pyramid. The bond angles in the S(C, C, N) pyramid are very similar to the corresponding ones in DMMSS, dimethyl sulphoxide and diphenyl sulphoxide, indicating the same hybridization of the S(IV) atom in all of these compounds. The relative position of the S(IV)-phenyl rings in DPTSS differs from that in diphenyl sulphoxide. The planes of phenyl rings II and III are nearly perpendicular (86.9°) to each other; the dihedral angle between plane II (or plane III) and the plane containing the atoms C(21), S(IV) and C(31) is 56.8° (or 39.8°). The S–N–S plane is almost perpendicular (89°) to the plane of atoms C(21), S(IV) and C(31) and bisects the C–S–C angle (101.0°) in two non-equal parts (42.4 and 58.6°). The 'perpen-

dicular' position of phenyl rings II and III is favourable, because there is no steric hindrance between them and, according to quantum chemical calculations (Mezey, 1970*b*) this conformation allows considerable (though significantly different) S(IV)–C(21) and S(IV)–C(31) *d-p* overlaps (*cf.* the actual bond lengths). The quantum chemical calculations were based on the assumption (*cf.* Kucsman, Kálmán & Kapovits, 1967) that if there is a maximum S(IV)–N(*sp*²) *d-p* overlap in the energetically most favourable, crystalline state of

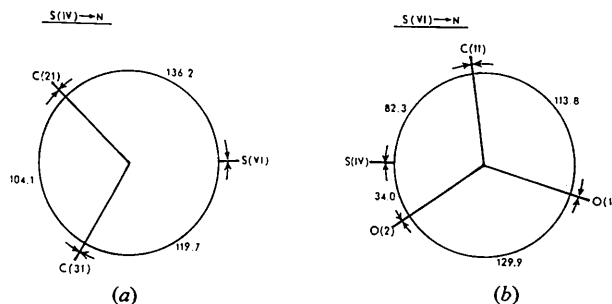


Fig. 2. Newman projections down the S–N bonds in DPTSS, showing the conformation angles, in degrees.

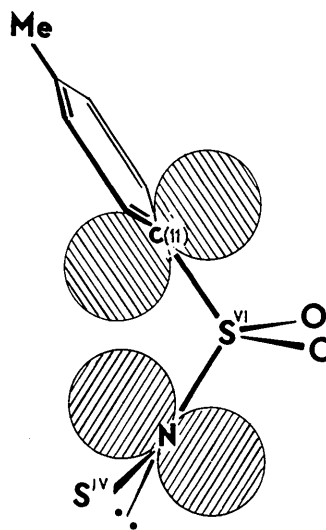


Fig. 3. The actual conformation of the S(VI) [C(11), O(1), O(2), N(*sp*²)] moiety. Case II of conjugation, according to Koch & Moffitt.

Table 6. S(IV)–C bond lengths in R¹R²S(IV) groups

E.s.d.'s are given in parentheses.

Compounds	S(IV)–R ¹	S(IV)–R ²	Reference
(CH ₃) ₂ SO	1.827 (11) Å	1.766 (8) Å	Thomas, Shoemaker & Eriks (1966)
(CH ₃) ₂ SC(CN) ₂	1.841 (10)	1.810 (10)	Christensen & Withmore (1969)
DMMSS	1.822 (70)	1.772 (30)	Kálmán (1967)*
DPTSS	1.799 (8)	1.769 (8)	Present work
(C ₆ H ₅) ₂ SO	1.763 (15)	1.756 (15)	Abrahams (1957)

* The present data are corrected for thermal vibration.

the molecule, the strong S(IV)–N(*sp*²) bond fixes* the *d* orbitals of the S(IV) atom. Thus the S(IV)–C *d*–*p* overlaps are expected to be dependent on the S(IV)–C bond directions, and in the case of C_{ar} atoms, on spatial positions of the phenyl rings, as well. Comparison of S(IV)–C(21) and S(IV)–C(31) *d*–*p* overlap integrals actually shows that C(21) is in a more favourable position for π -bonding than C(31) when the actual conformation of DPTSS is taken into account. Maximum S(IV)–C_{ar} *d*–*p* overlap would be established if the phenyl rings were nearly coplanar, but this conformation is obviously hindered by steric factors, *i.e.* by perturbation of (C_{ar})–H atoms.

Fig. 1 and the corresponding Newman projection [Fig. 2(a)] show the tosyl group to be bonded asymmetrically to the nitrogen atom of the (C₆H₅)₂SN group. As a consequence, the actual conformation of the DPTSS molecule is asymmetric, similar to that of

* It may be mentioned, however, that a free rotation about the SN axis should be taken into account in solution.

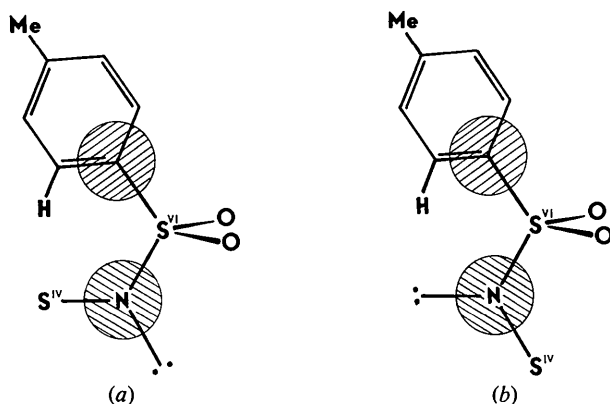


Fig. 4. Possible conformations of the S(VI) [C(11), O(1), O(2), N(*sp*²)] moiety. Case I of conjugation, according to Koch & Moffitt.

DMMSS. In the crystalline state the lattice of both compounds (the space group of DMMSS is also *P*2₁/*c*) contains not only the asymmetric form shown in Fig. 1, but also the enantiomeric one. It has been established, however (Ruff, Kucsmán, Schuster & Kapovits, 1968),[†] that the molecular asymmetry of sulphilimines containing two identical S(IV)-substituents is a result only of the constraints imposed by the crystalline state. Since the rotation around the S(IV)–N(*sp*²) axis was found to be free in solution, optical isomerism of such sulphilimines does not exist.

The C(11), O(1), O(2) and N atoms form an irregular tetrahedron around the S(VI) atom. The bond angles are rather similar to those in DMMSS. Fig. 3 shows that the axis of the *p* orbitals of N(*sp*²) and C(11) atoms lie in the plane which is perpendicular to the OSO plane and bisects the O–S–O angle. Thus, the N(*sp*²) atom in DPTSS was found to be oriented with respect to the SO₂Q moiety in the same way as in DMMSS [Fig. 2(b)]. According to Koch & Moffitt (1951) such a conformation of compounds containing SO₂ group can be described as ‘case II of conjugation’. It should be mentioned that the actual conformation of the molecule (Fig. 3) could be previously predicted on the base of infrared data of *N*-arylsulphonyl sulphilimines (Kucsmán, Kapovits & Ruff, 1967).[‡] Fig. 4(a) and (b) shows possible conformations of DPTSS according to the ‘case I of conjugation’ (Koch & Moffitt, 1951). In Fig. 4(a) can be seen the steric interaction of the S(IV) atom and the *ortho*-hydrogen atom of phenyl ring I. Fig. 4(b) presents the unfavourable position of the S(IV) and oxygen atoms [*cf.* the Δ_2 effect in carbohydrates, published by Reeves (1957)].

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[†] Part VII of the series.

[‡] Part V of the series.

Table 7. Equations for the atomic planes of the DPTSS molecule

For S(IV), N, and S(VI) atoms:	
	$-0.4652X - 0.0211Y + 0.8850Z = 3.8348$
For C(21), S(IV) and C(31) atoms:	
	$0.2641X + 0.9475Y + 0.1806Z = 1.7180$
For the phenyl rings (least-squares planes):	
I	$-0.6525X + 0.2582Y - 0.6676Z = 0.5803$
II	$0.9251X + 0.3493Y - 0.1490Z = -0.8536$
III	$-0.3149X + 0.7331Y - 0.6029Z = -1.1339$
	where <i>X</i> , <i>Y</i> and <i>Z</i> are orthogonal coordinates in Å.

Atomic deviations (Å) from the planes
* identifies the atoms defining the planes.

S*N*S*		Ph I		Ph II		Ph III	
O(1)	0.383	C(11)	-0.014*	C(21)	-0.006*	C(31)	-0.009*
O(2)	0.761	C(12)	0.015*	C(22)	0.002*	C(32)	0.007*
C(11)	-1.664	C(13)	-0.007*	C(23)	0.011*	C(33)	-0.003*
C(21)	-1.192	C(14)	-0.003*	C(24)	-0.015*	C(34)	0.003*
C(31)	1.532	C(15)	0.002*	C(25)	0.008*	C(35)	-0.008*
		C(16)	0.010*	C(26)	0.004*	C(36)	0.012*
		S(IV)	-0.061	S(IV)	-0.081	S(IV)	0.095

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Crystal Structure of Thaumasite, $[\text{Ca}_3\text{Si}(\text{OH})_6 \cdot 12\text{H}_2\text{O}](\text{SO}_4)(\text{CO}_3)$

BY R. A. EDGE AND H. F. W. TAYLOR

Department of Chemistry, University of Aberdeen, Old Aberdeen, Scotland

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Thaumasite (hexagonal, $P6_3$, a 11.04, c 10.39 Å, $Z=2$) has a structure based on columns of empirical composition $[\text{Ca}_3\text{Si}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]^{4+}$ running parallel to c , between which occur the CO_3^{2-} and SO_4^{2-} groups. The present results confirm Moenke's [*Naturwissenschaften* (1964) **51**, 239] conclusion, based on the infrared absorption spectrum, that thaumasite contains octahedral $\text{Si}(\text{OH})_6^{2-}$ groups; it is the first structure in which these have been shown to occur. It is isostructural with jouravskite, $[\text{Ca}_3\text{Mn}(\text{OH})_6 \cdot 12\text{H}_2\text{O}](\text{SO}_4)(\text{CO}_3)$, and, so far as the columns are concerned, with ettringite, $[\text{Ca}_3\text{Al}(\text{OH})_6 \cdot 12\text{H}_2\text{O}]_2(\text{SO}_4)_3 \cdot 2\text{H}_2\text{O}$, with which it probably forms solid solutions. The $\text{Si}(\text{OH})_6^{2-}$ octahedra in thaumasite are somewhat distorted, with Si-O distances of 1.731 and 1.835 Å; the conditions under which octahedral coordination of Si by O can arise in phases produced at ordinary pressures are discussed.

Introduction

Thaumasite is a mineral of approximate composition $3\text{CaO} \cdot \text{SiO}_2 \cdot \text{SO}_3 \cdot \text{CO}_2 \cdot 15\text{H}_2\text{O}$. There has been some uncertainty as to whether the number of moles of water in the formula should be 15 or 14; the results to be presented support the value of 15. The only

previous investigation of the crystal structure was made by Welin (1956), who found a structure based on chains of Ca^{2+} and SiO_4^{4-} ions running parallel to the hexagonal c axis, between which occurred the SO_4^{2-} and CO_3^{2-} ions and H_2O molecules. Welin considered the constitutional formula to be

