COLEMAN, L. B., COHEN, J. A., GARITO, A. F. & HEEGER, A. J. (1973). *Phys. Rev. B*, 7, 2122–2128.

EPSTEIN, A. J., ETAMAD, S., GARITO, A. F. & HEEGER, A. J. (1972). *Phys. Rev. B*, 5, 952–977.

EPSTEIN, A. J. & MILLER, J. S. (1978). *Solid State Commun.* 27, 325–329.

FRITCHIE, C. J. JR (1966). *Acta Cryst.* 18, 892–898.

GOLDBERG, I. & SHMUELI, U. (1973). *Acta Cryst.* B29, 421–431.

HATFIELD, W. A. (1979). *Molecular Metals*, NATO Conference Series VI, Materials Science, Vol. 1. New York: Plenum.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

KELLER, H. J. (1977). *Chemistry and Physics of One-Dimensional Metals*. NATO-ASI Series B25. New York: Plenum.

KELLER, H. J., MORONI, W., NÖTHE, D., SCHERZ, M. & WEISS, J. (1978). *Z. Naturforsch. Teil B*, 33, 838–842.

KELLER, H. J., MORONI, W., NÖTHE, D., SEIFRIED, V. & WERNER, M. (1979). *Molecular Metals*, edited by W. A. HATFIELD, NATO Conference Series VI, Materials Science, Vol. 1, pp. 75–79 and references cited therein. New York: Plenum.

KELLER, H. J., NÖTHE, D., MORONI, W. & SOOS, Z. G. (1978). *J. Chem. Soc. Chem. Commun.* pp. 331–332.

KELLER, H. J., NÖTHE, D. & WERNER, M. (1979). *Can. J. Chem.* 57, 1033.

KOBAYASHI, H. (1975). *Bull. Chem. Soc. Jpn*, 48, 1373–1377.

MAIN, P., GERMAIN, G. & WOOLFSON, M. M. (1971). *MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univ. of York, England.

MEGTERT, S., POUGET, J. P. & COMÈS, R. (1979). *Molecular Metals*, edited by W. A. HATFIELD, NATO Conference Series VI, Materials Science, Vol. 1, pp. 87–103. New York: Plenum.

MILLER, J. S. & EPSTEIN, A. J. (1978a). *J. Am. Chem. Soc.* 100, 1639–1641.

MILLER, J. S. & EPSTEIN, A. J. (1978b). *Synthesis and Properties of Low-Dimensional Materials, Ann. NY Acad. Sci.* 313.

MILLER, J. S. & EPSTEIN, A. J. (1979). In *Molecular Metals*, edited by W. A. HATFIELD, NATO Conference Series VI, Materials Science, Vol. 1. New York: Plenum.

MORONI, W. (1977). Dissertation, Univ. of Heidelberg.

NÖTHE, D., MORONI, W., KELLER, H. J., SOOS, Z. G. & MAZUMDAR, S. (1978). *Solid State Commun.* 26, 713–716.

SANDMAN, D. J. (1978). *J. Am. Chem. Soc.* 100, 5230–5232.

SANDMAN, D. J. (1979). *Mol. Cryst. Liq. Cryst.* 50, 235–258.

SCHERZ, M. (1977). Dissertation, Univ. of Heidelberg.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

A Reinvestigation of the Structure of S,S-Dimethyl-N-methylsulphonylsulphilimine*

BY ALAJOS KÁLMÁN AND LÁSZLÓ PÁRKÁNYI

Central Research Institute of Chemistry, Hungarian Academy of Sciences, H-1525 Budapest, POB 17, Hungary

AND ÁRPÁD KUCSMAN

Institute of Organic Chemistry, Eötvös University, H-1088 Budapest, Muzeum krt. 4/B, Hungary

Abstract

The structure of S,S-dimethyl-N-methylsulphonyl-sulphilimine (Me_2SNSO_2Me), $C_3H_9NO_2S_2$, has been reinvestigated with diffractometer data. The crystals are monoclinic, $a = 5\cdot809$ (1), $b = 13\cdot518$ (2), $c = 9\cdot212$ (2) Å, $\beta = 105\cdot17$ (2)°, $Z = 4$, space group $P2_1/c$. The atomic parameters obtained from film data ($R = 0\cdot105$) have been refined by least squares to $R = 0\cdot048$ for 1115 independent reflexions. The $S^{IV}N$ and $S^{VI}N$ bond lengths are discussed.

---

* IUPAC name: S,S-dimethyl-N-methylsulphonylsulphimide.

Introduction

An X-ray structure determination of the title compound was carried out (Kálmán, 1967) to study the chemical bonds and stereochemistry of organosulphur compounds of the N-sulphonylsulphilimine type ($R^1R^2SNSO_2R^3$). Later, the conclusions gained further support from subsequent X-ray investigations of related molecules: $Me_2SNSO_2C_6H_4Me$ (Cameron, Hair & Morris, 1973), $Ph_2SNSO_2C_6H_4Me$ (Kálmán, Duffin & Kucsman, 1971), $PrPhSNSO_2C_6H_4Me$ (Kálmán & Sasvári, 1972) and [*tert*-$BuC_5H_9SN(Et)SO_2C_6H_4Me$]⁺-[$BF_4$]⁻ (Cook, Glick, Rigau & Johnson, 1971).

Furthermore, X-ray data of N-sulphonylsulphilimines provided a means to construct models for EHMO, SCF and CNDO/2 calculations (Náray-Szabó & Kucsman, 1979 and references therein).

$S^{IV}N$ and $S^{VI}N$ bond lengths obtained from earlier X-ray analyses of N-sulphonylsulphilimines pointed to a π bonding delocalized to the $S^{IV}NS^{VI}$ moiety (Kucsman, Kálmán & Kapovits, 1967). The same conclusion could be drawn from a semi-empirical CNDO/2 calculation of bond localizabilities for H_2SN-SO_2H and its conjugated acid (Náray-Szabó & Kucsman, 1979).

Since the original structure refinement of Me_2SN-SO_2Me (carried out by differential synthesis) had been based on intensities collected from films, it seemed worthwhile to perform a new refinement of the parameters with diffractometer data.

Experimental

A needle of maximum dimension (d_{max}) 0·4 mm was mounted on a Syntex $P2_1$ computer-controlled four-circle diffractometer equipped with a graphite mono-chromator. Cell constants were determined by least squares from the setting angles of 15 centred reflexions. During data collection the intensities of 54 reflexions were lower than a preset limit and these were skipped rather than measured. 1123 reflexions were retained in the final set. Since $\mu d_{max} = 0·24$ for Mo $K\alpha$ radiation no absorption correction was applied.

Crystal data

$C_3H_9NO_2S_2$, $M_r = 155·15$, monoclinic, $a = 5·809$ (1), $b = 13·518$ (2), $c = 9·212$ (2) Å, $\beta = 105·17$ (2)°, $V = 698·17$ Å^3, $D_x = 1·477$, $Z = 4$, $D_m = 1·473$ Mg m^{-3}, $F(000) = 328$, $\mu[\lambda(Mo\ K\alpha) = 0·7107$ Å] = 61 mm^{-1}, space group $P2_1/c$.

Structure refinement

Anisotropic refinement was started with the parameters obtained for non-hydrogen atoms in the first analysis ($R = 0·106$ for 1027 observed reflexions). Full-matrix least-squares refinement of 73 variables, with a program incorporated in the XTL-system 74 provided by Syntex, was terminated at $R = 0·063$ for 1085 observed reflexions $[I - 2\sigma(I) > 0]$; R_{tot} was 0·064. The maximum shift in the parameters was <0·001 Å. At this stage an attempt was made to locate the H atoms in a difference map. However, owing to the vigorous thermal motion of the methyl groups, especially C(2), the positions of the H atoms were not

Table 1. *Fractional coordinates* $(\times 10^4)$ *for non-hydrogen atoms and* B_{eq} (Å^2)

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

	x	y	z	B_{eq}
S^{IV}	1662 (3)	−781 (1)	2887 (2)	3·51 (9)
S^{VI}	1297 (2)	1177 (1)	2138 (2)	2·74 (8)
O(1)	1721 (8)	2097 (3)	2935 (5)	4·84 (27)
O(2)	−1140 (6)	972 (3)	1356 (5)	4·13 (25)
N	2509 (8)	350 (3)	3342 (5)	3·09 (29)
C(1)	2908 (9)	1203 (4)	774 (6)	3·46 (32)
C(2)	4189 (16)	−1369 (6)	2571 (10)	8·49 (65)
C(3)	1790 (12)	−1298 (4)	4683 (7)	4·73 (41)

Table 2. *Fractional coordinates* $(\times 10^3)$ *for the* H *atoms with a common isotropic temperature factor* $B = 8·3$ Å^2

	x	y	z
H(11)	477	126	137
H(12)	240	184	6
H(13)	262	54	10
H(21)	415	−112	145
H(22)	402	−217	257
H(23)	586	−116	334
H(31)	144	−208	461
H(32)	43	−93	509
H(33)	351	−116	545

revealed. These were generated, therefore, by *SHELX* (Sheldrick, 1976), assuming regular tetrahedral configurations for C atoms with C—H = 1·08 Å. These moieties were treated through the refinement as rigid groups.

Further anisotropic refinement for 101 variables (an average isotropic temperature factor was refined for the H atoms) was carried out with *SHELX*, using 1115 of the 1123 reflexions. This resulted in a final R of 0·048 $[R_G = (\sum w\Delta^2/\sum w|F_o|^2)^{1/2} = 0·051]$ while k and g in the weighting scheme $w = k/[\sigma^2(F) + gF_o^2]$ refined to 1·000 and 0·000213, respectively. The maximum shifts in bond distances and angles were then 0·001 Å and 0·2°, respectively. In the final calculations, a bonded H-atom scattering factor (Stewart, Davidson & Simpson, 1965) was employed with complex neutral scattering factors (Cromer & Liberman, 1970; Cromer & Mann, 1968) for the remaining atoms. Final coordinates for the non-hydrogen and H atoms are given in Tables 1 and 2, bond distances and angles in Table 3.* The numbering of the molecule is shown in Fig. 1. An analysis of the thermal parameters of the

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35129 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond distances (Å) and angles (°)

	I	II	III	(I – II) × 10³
S^{IV}–C(2)	1·74 (7)	1·759 (9)	1·779	19
S^{IV}–C(3)	1·74 (3)	1·780 (5)	1·786	40
S^{IV}–N	1·633 (9)	1·627 (4)	1·641	6
S^{VI}–N	1·581 (10)	1·602 (4)	1·610	21
S^{VI}–O(1)	1·438 (9)	1·432 (4)	1·448	6
S^{VI}–O(2)	1·455 (12)	1·437 (4)	1·453	18
S^{VI}–C(1)	1·749 (12)	1·753 (5)	1·766	4
C(2)–S^{IV}–C(3)	98·0 (19)	98·2 (6)		0·2
C(2)–S^{IV}–N	106·4 (17)	105·0 (4)		1·4
C(3)–S^{IV}–N	102·6 (7)	101·1 (4)		1·5
S^{IV}–N–S^{VI}	116·2 (6)	115·4 (4)		0·8
N–S^{VI}–C(1)	106·4 (5)	106·9 (4)		0·5
N–S^{VI}–O(1)	106·0 (6)	105·4 (4)		0·6
N–S^{VI}–O(2)	114·7 (6)	114·2 (4)		0·5
C(1)–S^{VI}–O(1)	107·4 (6)	107·3 (4)		0·1
C(1)–S^{VI}–O(2)	105·3 (6)	106·6 (4)		1·3
O(1)–S^{VI}–O(2)	116·4 (6)	116·0 (4)		0·4

Column I: obtained from film data by differential synthesis.
Column II: obtained from final refinement with *SHELX* including H-atom positions.
Column III: corrected for thermal motion.

Table 4. Rigid-body librational analysis

Centre which gives symmetric **S** is 0·1633, 0·0670, 0·2320. Tensors and e.s.d.'s are given with respect to orthogonal axes.

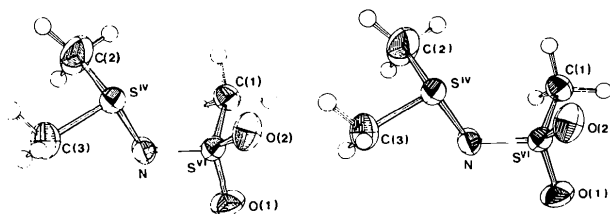| **L** (rad² × 10⁴)	32 (9)	6 (10)	1 (9)
		101 (22)	–84 (12)
			122 (10)
S (rad Å × 10⁴)	18 (13)	3 (10)	10 (9)
	3 (14)	–19 (15)	37 (15)
	10 (10)	37 (11)	1 (13)
T (Å × 10⁴)	303 (36)	0 (27)	–17 (31)
		318 (27)	–47 (26)
			330 (34)

Fig. 1. *ORTEP* (Johnson, 1965) stereodrawing for S,S-dimethyl-N-methylsulphonylsulphilimine.

non-hydrogen atoms was performed assuming rigid-body motion of the molecule (Schomaker & Trueblood, 1968). The generalized $R_{UG} = [\sum (U_c - U_o)^2 / \sum U_o^2]^{1/2}$ was 0·120. The results, Table 4, were used for applying the libration correction to the bond lengths given in Table 3.

Discussion

The results of the earlier analysis (Kálmán, 1967) have been essentially confirmed, Table 3. Owing to the vigorous thermal vibration of both C(2) and C(3), the refined $S^{IV}C$ bond lengths could be expected to differ from those given earlier. Significant shifts for $S^{VI}O(2)$ and $S^{VI}N$ distances were also observed. Nevertheless, these shifts (0·018 and 0·021 Å) are in the range of the original e.s.d.'s (0·012 and 0·010 Å). As for the bond angles, the largest shifts (1·4–1·5°) found for the $CS^{IV}N$ angles are also in the range of their original e.s.d.'s.

Table 5 shows that in all N-sulphonylsulphilimines the corresponding bond lengths and angles and the relevant torsion angles are rather similar. Thus Me_2SN-SO_2Me can be regarded as a simple but typical sulphilimine model. Although the difference in bond lengths found for $S^{IV}N$ (1·627 Å) and $S^{VI}N$ (1·602 Å) has become smaller in the new refinement, 0·025 Å, it is significant enough to point to the different character of these SN bonds. Only the $S^{VI}N$ bond in the $S^{IV}NS^{VI}$ moiety has been found to elongate considerably when an alkyl group is linked to the N atom {[tert-BuC₅H₉SN(Et)SO₂C₆H₄Me]⁺; Cook, Glick, Rigau & Johnson, 1971}.

The exclusive elongation of the $S^{VI}N$ bond seemed to be qualitatively explainable by the failure of the delocalization of the N-atom lone pair (Kálmán, 1974). Theoretical considerations on bond-length controlling factors (Náray-Szabó & Kucsman, 1979) suggest, however, that $S^{VI}N$ bond lengthening in sulphilimine cations may be attributed primarily to the decrease of total bond localizabilities in this moiety and to the decrease of bond polarity.

In all sulphilimines listed in Table 5 the N–S^{IV}–O(2) angle is significantly greater than the N–S^{VI}–O(1) angle (mean value 112·8 vs 105·2°); here O(2) and S^{IV} are in a synclinial (Klyne & Prelog, 1960) position [the mean value of the S^{IV}–N–S^{VI}–O(2) torsion angles is 35°], while an approximately antiperiplanar arrangement is attributed to O(2) and the N-atom lone pair. For the $NS^{VI}O$ angles a similar difference could be observed in other structures having the RSO_2–N= moiety [e.g. in sulfaguanidine 114·1 (1) vs 105·4 (1)° (Alléaume, Gulko, Herbstein, Kapon & Marsh, 1976)]. On the other hand, in compounds having a three-coordinate N atom, e.g. [tert-BuC₅H₉SN(Et)SO₂-C₆H₄Me]⁺[BF₄]⁻ (Table 5) or methanesulphonamide derivatives (Kálmán, Párkányi & Schawartz, 1977), the N–S^{VI}–O(2) and N–S^{VI}–O(1) angles are nearly the same. No explanation for this phenomenon could be found.

Table 5. *Typical bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *in N-sulphonylsulphilimines*

E.s.d.'s are in parentheses; e.s.d.'s for torsion angles are $<1°$.

	I	II	III	IV	V	VI
$S^{IV}-N$	1·627 (4)	1·636 (8)	1·628 (7)	1·620 (7)	1·628	1·644 (5)
$S^{VI}-N$	1·602 (4)	1·591 (8)	1·598 (8)	1·618 (7)	1·602	1·681 (5)
$S^{VI}-O(1)$	1·432 (4)	1·425 (8)	1·430 (8)	1·436 (7)	1·431	1·417 (5)
$S^{VI}-O(2)$	1·437 (4)	1·438 (7)	1·435 (8)	1·441 (7)	1·438	1·405 (5)
$S^{IV}-N-S^{VI}$	115·4 (4)	113·4 (5)	113·4 (5)	115·7 (4)	114·5	114·5 (3)
$N-S^{VI}-O(1)$	105·4 (4)	104·6 (4)	104·8 (4)	105·9 (4)	105·2	104·7 (3)
$N-S^{VI}-O(2)$	114·2 (4)	112·8 (4)	111·8 (4)	112·5 (4)	112·8	106·3 (3)
$O(1)-S^{VI}-O(2)$	116·0 (4)	118·8 (5)	118·1 (5)	117·6 (4)	117·6	121·1 (3)
$C(2)S^{IV}NS^{VI}$	112	112	119	127	118	110
$C(3)S^{IV}NS^{VI}$	−146	−146	−136	−132	−140	−143
$S^{IV}NS^{VI}C(1)$	−83	−80	−82	−83	−82	−64
$S^{IV}NS^{VI}O(1)$	163	167	164	163	165	180
$S^{IV}NS^{VI}O(2)$	35	37	34	34	35	51

Column I: Present work.
Column II: $Me_2SNSO_2C_6H_4Me$; Cameron, Hair & Morris (1973).
Column III: $Ph_2SNSO_2C_6H_4Me$; Kálmán, Duffin & Kucsman (1971).
Column IV: $PrPhSNSO_2C_6H_4Me$; Kálmán & Sasvári (1972).
Column V: Mean values (the average of data found for I–IV).
Column VI: $[tert\text{-}BuC_5H_9SN(Et)SO_2C_6H_4Me]^+BF_4^-$; Cook, Glick, Rigau & Johnson (1971).

References

ALLÉAUME, M., GULKO, A., HERBSTEIN, F. H., KAPON, M. & MARSH, R. E. (1976). *Acta Cryst.* B32, 669–682.
CAMERON, A. F., HAIR, N. J. & MORRIS, D. G. (1973). *J. Chem. Soc. Perkin Trans.* 2, pp. 1951–1954.
COOK, R. E., GLICK, M. D., RIGAU, J. J. & JOHNSON, C. R. (1971). *J. Am. Chem. Soc.* 93, 924–928.
CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* 53, 1891–1898.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A24, 321–324.
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.
KÁLMÁN, A. (1967). *Acta Cryst.* 22, 501–507.
KÁLMÁN, A. (1974). Thesis, Degree of Doctor in Chemical Sciences (DSc), MTA Budapest.

KÁLMÁN, A., DUFFIN, B. & KUCSMAN, Á. (1971). *Acta Cryst.* B27, 586–594.
KÁLMÁN, A., PÁRKÁNYI, L. & SCHAWARTZ, J. (1977). *Acta Cryst.* B33, 3097–3102.
KÁLMÁN, A. & SASVÁRI, K. (1972). *Cryst. Struct. Commun.* 1, 243–246.
KLYNE, W. & PRELOG, V. (1960). *Experientia*, 16, 521–523.
KUCSMAN, Á., KÁLMÁN, A. & KAPOVITS, I. (1967). *Acta Chim. Acad. Sci. Hung.* 53, 97–104.
NÁRAY-SZABÓ, G. & KUCSMAN, Á. (1979). *J. Chem. Soc. Dalton Trans.* pp. 891–894.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B24, 63–76.
SHELDRICK, G. M. (1976). *SHELX.* Crystal-structure calculation program, Univ. of Cambridge, England.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.