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Structure of 1-Tosylimino-1,5-dithiaclooctane

BY FUJIKO IWASAKI*

Department of Materials Science, University of Electro-Communications, Chofu-shi, Tokyo 182, Japan

AND NAOMICHI FURUKAWA

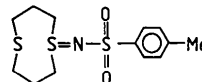
Department of Chemistry, The University of Tsukuba, Sakura-mura, Ibaraki 305, Japan

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Abstract. $C_{13}H_{19}NO_2S_3$, $M_r = 317.48$, triclinic, $P\bar{1}$, $a = 9.2622$ (8), $b = 9.5582$ (6), $c = 9.1289$ (8) Å, $\alpha = 87.199$ (8), $\beta = 111.953$ (6), $\gamma = 105.050$ (7)°, $V = 722.8$ (1) Å³, $Z = 2$, $D_x = 1.459$ Mg m⁻³, $\lambda(\text{Cu } K\alpha_1) = 1.54051$ Å, $\mu = 4.600$ mm⁻¹, $F(000) = 336$, 295 K, $R = 0.034$ for 2361 observed reflexions. The 1,5-dithiaclooctane ring has a boat-chair conformation with a short transannular S^{II}...S^{IV} contact of 3.143 Å. The S^{II}...S^{IV}-N angle is 177.8°. The configuration about the S^{IV} atom is a distorted trigonal bipyramid with two apical S^{IV}-N and S^{II}...S^{IV} contacts. The lengths S^{IV}-N and S^{VI}-N are 1.641 and 1.594 Å, which are normal for *N*-sulfonylsulfilimines. One of the O atoms of the sulfonyl group is *cis* to S^{IV} about the S^{VI}-N bond with a torsion angle of 3.6°. Associated with the *cis* conformation, another short intramolecular contact is observed between S^{IV} and O (2.893 Å).

Introduction. Structures of several *N*-sulfonylsulfilimines have been determined by X-ray analyses (Kálmán, Duffin & Kucsman, 1971; Kálmán & Sasvári, 1972; Cameron, Hair & Morris, 1973; Kálmán, Párkányi & Kucsman, 1980). The S^{IV}=N-S^{VI} bond systems of these compounds show very similar features with long S^{IV}=N and short S^{VI}-N bonds. In the present compound a transannular effect of S^{II} of the

1,5-dithiaclooctane ring on such a S^{IV}=N-S^{VI} system was expected. An X-ray analysis for the title compound was undertaken to investigate the interaction between the sulfonylsulfilimido group and the 1,5-dithiaclooctane ring.



Experimental. Colorless plate, 0.45 × 0.30 × 0.15 mm, unit-cell parameters by least squares from 23 reflexions (70 < 2θ < 74°), Rigaku AFC4 diffractometer, graphite monochromated, 2 ≤ 2θ ≤ 130°, $h = 0 \rightarrow 10$, $k = -11 \rightarrow 11$, $l = -10 \rightarrow 10$, ω -2θ scan, scan range $\Delta\omega = 1.3^\circ + 0.5^\circ \tan\theta$, scan speed 4° min⁻¹ in 2θ, three reflexions monitored (32 $\bar{1}$, 030, 003) every 50 reflexions, variations within 2%. 2777 reflexions measured, 2444 unique, $R_{\text{int}} = 0.03$, 2361 observed, $|F_o| \geq 3\sigma(F)$. Structure was solved by *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). 11 non-H atoms were obtained from the *E* map and the remaining non-H atoms were located from the Fourier synthesis. H atoms were found from the difference map. Block-diagonal least squares with anisotropic temperature factors for non-H, isotropic for H. $\sum w(|F_c| - k^{-1}|F_o|)^2$ was minimized. $w = 1/(0.36055 - 0.02935|F_o| + 0.00132|F_o|^2)$. Absorption correction was applied numerically; range of transmission

* To whom all correspondence should be addressed.

Table 1. Positional parameters ($\times 10^5$) and equivalent isotropic temperature factors (\AA^2) for non-H atoms
$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
S(1)	63988 (6)	54143 (5)	30295 (6)	2.3
S(5)	71666 (8)	82434 (7)	12549 (8)	3.9
S(10)	68759 (6)	27361 (5)	39420 (6)	2.5
O(1)	81024 (20)	32172 (18)	32671 (19)	3.4
O(2)	57384 (22)	13586 (17)	33350 (20)	4.0
N	59279 (24)	39198 (20)	39038 (24)	3.2
C(2)	44342 (26)	58067 (24)	22474 (27)	3.0
C(3)	40836 (29)	66025 (26)	7250 (27)	3.3
C(4)	50774 (31)	81593 (26)	8096 (28)	3.4
C(6)	81668 (33)	90432 (28)	32551 (37)	4.4
C(7)	74522 (32)	82952 (27)	44127 (30)	3.9
C(8)	74981 (30)	67380 (26)	46997 (27)	3.4
C(11)	78832 (25)	25591 (21)	59877 (25)	2.4
C(12)	73522 (26)	13336 (22)	67159 (26)	2.8
C(13)	81322 (29)	12291 (25)	83276 (28)	3.1
C(14)	94325 (28)	23343 (26)	92255 (27)	3.2
C(15)	99476 (27)	35429 (26)	84696 (29)	3.3
C(16)	91955 (27)	36645 (23)	68646 (28)	2.9
C(17)	102474 (37)	22335 (34)	109876 (31)	4.7

factors 0.253–0.547. Extinction parameter $g=2.1 \times 10^{-6}$. $\Delta\rho(\max)=0.32 \text{ e \AA}^{-3}$, $\Delta/\sigma(\max)=0.17$. $R=0.034$, $wR=0.041$, $S=0.989$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All computations were performed on a HITAC M180 Computer of the Data Processing Center of the University of Electro-Communications with the programs UNICSIII (Sakurai & Kobayashi, 1979), MULTAN78, ORTEPII (Johnson, 1971) and GEOM (Motherwell, 1978). The final atomic parameters are given in Table 1.*

Discussion. The molecular structure with atomic numbering is shown in Fig. 1. Bond distances and angles are listed in Table 2. The S(1)–C lengths (1.822 and 1.822 Å) are slightly longer than the S(5)–C lengths (1.803 and 1.811 Å), which corresponds to the difference of covalent radii of S^{IV} and S^{II} (Truter, 1962). The endocyclic torsion angles of the 1,5-dithiacyclooctane ring are close to those in 1-acetonyl-1-thionia-5-thiacyclooctane perchlorate (Johnson, Maier & Paul, 1970). The cyclooctane ring has a boat–chair conformation with an approximate C_s symmetry. A short transannular contact of 3.143(1)† Å is observed between S(1) and S(5), which is shorter than the S...S van der Waals contact (3.50–3.70 Å). The S(5)...S(1)–N angle is

* Lists of structure factors, anisotropic temperature factors for non-hydrogen atoms, atomic parameters of H atoms and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43240 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

† Here and throughout this paper the last decimal figure in parentheses shows the e.s.d.

177.8(1)°. Relatively short transannular S...S contacts in the range 3.121–3.271 Å have also been reported for some sulfur-bonded derivatives of 1,5-dithiacyclooctane as shown in Table 3. The angles C(2)–S(1)...S(5) and C(8)–S(1)...S(5) are 79.4(1) and 79.5(1)°, respectively. The linear N–S(1)...S(5) group is approximately perpendicular to the C(2)–S(1)C(8) plane. The configuration about S(1) is a distorted trigonal bipyramid with two apical S(1)–N and S(1)...S(5) contacts. These structural features indicate the hypervalency of S^{IV} like a σ-sulfurane (Musher, 1969; Paul, Martin & Perozzi, 1972).

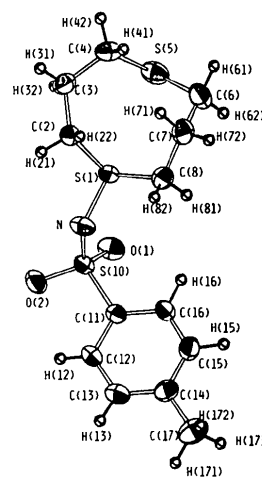


Fig. 1. ORTEPII (Johnson, 1971) drawing with atomic numbering. The thermal ellipsoids for non-H atoms are drawn at 50% probability.

Table 2. Bond lengths (Å) and angles (°) of non-H atoms

S(1)–N	1.641 (2)	C(3)–C(4)	1.521 (4)
S(1)–C(2)	1.822 (3)	C(6)–C(7)	1.506 (4)
S(1)–C(8)	1.822 (3)	C(7)–C(8)	1.507 (4)
S(5)–C(4)	1.803 (3)	C(11)–C(12)	1.387 (3)
S(5)–C(6)	1.811 (3)	C(11)–C(16)	1.387 (3)
S(10)–O(1)	1.451 (2)	C(12)–C(13)	1.387 (4)
S(10)–O(2)	1.437 (2)	C(13)–C(14)	1.387 (4)
S(10)–N	1.594 (2)	C(14)–C(15)	1.386 (4)
S(10)–C(11)	1.771 (2)	C(15)–C(16)	1.381 (4)
C(2)–C(3)	1.518 (4)	C(14)–C(17)	1.511 (4)
N–S(1)–C(2)	98.7 (1)	S(5)–C(6)–C(7)	114.6 (2)
N–S(1)–C(8)	102.1 (1)	C(6)–C(7)–C(8)	116.9 (3)
C(2)–S(1)–C(8)	101.7 (1)	S(1)–C(8)–C(7)	117.8 (2)
C(4)–S(5)–C(6)	103.3 (1)	S(10)–C(11)–C(12)	120.4 (2)
O(1)–S(10)–O(2)	116.4 (1)	S(10)–C(11)–C(16)	119.5 (2)
O(1)–S(10)–N	113.1 (1)	C(12)–C(11)–C(16)	120.1 (2)
O(1)–S(10)–C(11)	107.2 (1)	C(11)–C(12)–C(13)	119.6 (2)
O(2)–S(10)–N	109.4 (1)	C(12)–C(13)–C(14)	121.0 (2)
O(2)–S(10)–C(11)	106.2 (1)	C(13)–C(14)–C(15)	118.3 (2)
N–S(10)–C(11)	103.5 (1)	C(13)–C(14)–C(17)	120.8 (2)
S(1)–N–S(10)	116.2 (1)	C(15)–C(14)–C(17)	120.9 (2)
S(1)–C(2)–C(3)	115.2 (2)	C(14)–C(15)–C(16)	121.6 (2)
C(2)–C(3)–C(4)	117.3 (2)	C(11)–C(16)–C(15)	119.4 (2)
S(5)–C(4)–C(3)	111.4 (2)		

Table 3. Comparison of transannular S...S interaction in derivatives of 1,5-dithiacyclooctane

	X	S...S (Å)	X-S...S (°)	Ring conformation
(a)	N	3.143	177.8	boat-chair
(b)	C	3.121	178.9	boat-chair
(c)	Sn	3.271	171.5	boat-chair
(d)	C	3.259	174.0	chair-chair

(a) Present study. (b) 1-Acetyl-1-thionia-5-thiacyclooctane perchlorate (Johnson, Maier & Paul, 1970). (c) *trans*-Bis(1,5-dithiacyclooctane)tetrachlorotin(IV) (Olmstead, Williams & Musker, 1982). (d) 1-Methyl-5-thia-1-thionia-5-thiacyclooctane iodide (Musker, Olmstead & Goodrow, 1983).

The lengths of S^{IV}(1)-N and S^{VI}(10)-N are 1.641 and 1.594 Å, respectively. The normal S=N and S-N bond lengths are 1.56 and 1.74 Å, respectively (Pauling, 1960). Such an elongation of the S^{IV}=N double bond and a shortening of the S^{VI}-N single bond are typical for *N*-sulfonylsulfilimines as shown in Table 4. This is attributed to the delocalization of the lone pair of the N atom. The S^{IV}(1)-N-S^{VI}(10) angle is 116.2°, while the corresponding angles in the other *N*-sulfonylsulfilimines are 113.4-115.7°. The configuration about S(10) is a distorted tetrahedron. N-S(10)-O(1) (113.1°) and O(1)-S(10)-O(2) (116.4°) are larger than the tetrahedral angle. These bond angles are close to those of other sulfonylsulfilimines. The dihedral angle between the plane of S^{IV}-N-S^{VI} and the phenyl plane of the tosyl group is 88.3 (3)°, which is consistent with those of the other compounds listed in Table 4 (74-96°) except for the β-lactam-fused ylide of 6β-phenylacetamidopenicillanate [(f), 124.9°] (Cameron, Cameron, Campbell & Johnson, 1976).

The conformation about the S(10)-N bond is different from the other *N*-sulfonylsulfilimines, (a)-(e), as shown by the torsion angles S^{IV}-N-S^{VI}-O and S^{IV}-N-S^{VI}-C listed in Table 4. O(1) is *cis* to S(1) about the S(10)-N bond with a torsion angle of 3.6 (2)°, while for most *N*-sulfonylsulfilimines, (a)-(e), the torsion angle S(1)-N-S(10)-O(1) is 34-48°. Associated with the *cis* conformation another short intramolecular contact is observed between S(1) and O(1) [2.893 (2) Å]. The corresponding distance in (f) is 2.861 Å, while those in the other *N*-sulfonylsulfilimines are in the range 2.908-3.046 Å. The angles N-S(1)...O(1), C(2)-S(1)...O(1), C(8)-S(1)...O(1) and S(5)...S(1)...O(1) are 61.0 (1), 145.0 (1), 110.1 (1) and 119.9 (1)°, respectively. S(1) deviates by 0.209 (2) Å from the plane defined by O(1), C(2) and C(8). The lone pair of S^{IV} is nearly in the plane of S(1)-N-S(10)-O(1) and the direction of the lone pair of N is nearly *trans* to that of S^{IV}.

The torsion angles S^{VI}-N-S^{IV}-R,R' are similar to the corresponding angles of (a)-(f). In the six-membered heterocyclic sulfilimides (e) and (f) the cyclic plane is almost perpendicular to the S^{IV}-N bond. This situation is quite different from that of the present

Table 4. Comparison of *N*-sulfonylsulfilimines

Reference	(a)	(b)	(c)	(d)	(e)	(f)	(g)
R	Me	Me	Ph	Ph	N	C	C
R'	Me	Me	Ph	Ph	N	N	C
R''	Me	Tol	Tol	Tol	Tol	Tol	Tol
S ^{IV} ...O(1)	3.009	2.940	2.988	2.908	3.046	2.861	2.893
S ^{IV} =N	1.627	1.636	1.620	1.628	1.618	1.591	1.641
S ^{VI} -N	1.602	1.591	1.618	1.598	1.621	1.612	1.594
S-N-S-O(1)	34.7	36.7	33.9	34.9	-47.5	-5.2	3.6
S-N-S-O(2)	163.2	167.2	163.7	163.9	-176.3	126.2	-127.8
S-N-S ^{VI} -R''	-82.8	-80.4	-82.2	-82.1	68.6	-121.8	119.3
S-N-S-R	-146.4	146.0	132.3	136.1	142.9	-139.6	147.6
S-N-S-R'	118.8	-111.9	-126.6	-118.8	-105.9	119.3	-108.3
ω*		77.5	80.9	73.8	95.5	124.9	88.3

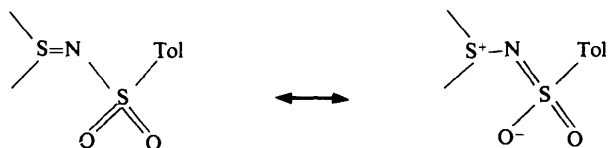
(a) Kálmán, Párkányi & Kucsman (1980). (b) Cameron, Hair & Morris (1973). (c) Kálmán & Sasvári (1972). (d) Kálmán, Duffin & Kucsman (1971). (e) 1,4-Dihydro-3,5-dimethoxy-1-tosylimino-1,2,4,6-thiazine, Kálmán, Argay, Fischer & Teller (1981). (f) 6β-Phenylacetamidopenicillanate sulfilimine ylide, Cameron, Cameron, Campbell & Johnson (1976). (g) Present study.

* Dihedral angle between phenyl plane of tolyl group and S-N-S plane.

compound owing to the hypervalency of the S^{II}...S^{IV}-N linear interaction. The conformations of the molecular moiety are affected by intra- or intermolecular interactions. For (e), N is the acceptor of the intermolecular hydrogen bond and for (f) the molecule suffers overall steric constraints.

The structural features around S^{IV}(1), *i.e.* a boat-chair conformation with a short transannular S^{IV}...S^{II} contact of 1,5-dithiacyclooctane, a distorted trigonal-bipyramidal configuration and another weak contact of S^{IV}...O, are very similar to those in 1-acetyl-1-thionia-5-thiacyclooctane perchlorate, where S⁺...O is 2.81 Å and the torsion angle S⁺-CH₂-C-O is 10°. But the torsion angles OC-CH₂-S⁺-R,R' (176 and -77° for R and R', respectively) are significantly different from those of OS^{VI}-N-S^{IV}-R,R' [147.6 (1) and -108.3 (1)°] in the present compound: the lone pair of S⁺ is *gauche* to C(O) about the S⁺-CH₂ bond. This is attributed to the difference between -N= and -CH₂-.

These structural features of the present compound suggest a contribution of the resonance:



This is consistent with the fact that S(10)-O(1) is longer than S(10)-O(2).

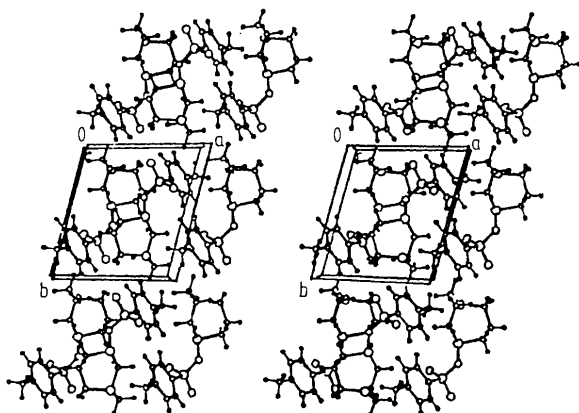


Fig. 2. Stereoscopic view of the crystal structure.

A stereoscopic view of the crystal structure is shown in Fig. 2. The packing contacts are van der Waals type.

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Absolute Configuration of (–)-4-Bromo-*N*-*cis*-2'-phenylcyclopentylbenzamide

BY WOLFGANG WIEHL AND AUGUST W. FRAHM*

Institut für Pharmazeutische Chemie der Universität Bonn, Kreuzbergweg 26, D-5300 Bonn 1, Federal Republic of Germany

AND ARMIN KIRFEL

Lehrstuhl für Mineralogie und Kristallographie, Mineralogisches Institut der Universität Bonn, Poppelsdorfer Schloß, D-5300 Bonn 1, Federal Republic of Germany

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Abstract. C₁₈H₁₈BrNO, $M_r = 344.10$, orthorhombic, $P2_12_12_1$, $a = 5.311(1)$, $b = 16.815(3)$, $c = 17.420(3)$ Å, $Z = 4$, $V = 1555.6(6)$ Å³, $D_x = 1.468$ g cm⁻³, λ (Mo $K\alpha$) = 0.71069 Å, $\mu = 3.02$ cm⁻¹, $F(000) = 704$, $T = 293$ K, final $R = 0.039$ for 1819

observed reflections. Under enantiomeric and diastereomeric control 2-substituted cyclopentanones are converted by reductive amination and hydrogenolysis to *cis*-2-substituted cyclopentylamine hydrochlorides. The absolute configuration of one of these products, (+)-*cis*-2-phenylcyclopentylamine hydrochloride, could be elucidated as (1*S*, 2*S*) via its 4-bromo-*N*-benzamide,

* To whom correspondence should be addressed.