

References

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7,7,9,9-Tetramethyl-8-thiosulphinyliminothio-1,4-dioxaspiro[4,5]decane

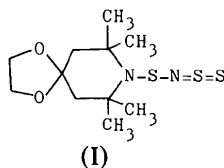
BY CHIHIRO TAMURA, KIMIE AIBA, SADA0 SATO, TADASHI HATA,
SYOJI MORIMURA AND TAKAO YOSHIOKA

Central Research Laboratories, Sankyo Co., Ltd, Hiromachi Shinagawa-ku, Tokyo 140, Japan

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Abstract. $\text{C}_{11}\text{H}_{20}\text{N}_2\text{O}_2\text{S}_3$, $M_r = 308.5$, monoclinic, $P2_1/n$, $Z = 4$, $a = 15.310$ (2), $b = 9.477$ (1), $c = 10.860$ (2) Å, $\beta = 104.58$ (2)°, $D_x = 1.32$ g cm⁻³. Final residual $R = 0.067$. A new bonding system consisting of one N and three S atoms has been determined. The bonding system is $-\text{S}=\text{N}=\text{S}=\text{S}$ wherein the S=S double-bond distance is 1.912 Å and the N=S=S bond angle is 114.85°.

Introduction. Red crystals of the title compound (I)* were grown from a dilute ether solution. A crystal with dimensions 0.5 × 0.4 × 0.5 mm was selected for the data collection on a Rigaku four-circle diffractometer. 1508 independent reflexions [$F = 3\sigma(F)$] were collected with the $\omega-2\theta$ scanning technique with graphite-monochromatized Mo $K\alpha$ radiation. The intensities were corrected for Lorentz-polarization but not for absorption. The structure was solved by symbolic addition procedures using 546 reflexions



with $E \geq 1.54$ and refined by block-diagonal least-squares procedures. On a subsequent difference Fourier map the positions of all the H atoms were discernible. The final coordinates with their estimated

Table 1. Final atomic coordinates ($\times 10^4$ for non-hydrogen atoms and $\times 10^3$ for H atoms) with e.s.d.'s in parentheses

	x	y	z
S(1)	4589 (1)	4815 (2)	6653 (2)
S(2)	4639 (2)	3130 (3)	8767 (2)
S(3)	5400 (2)	1961 (2)	8046 (3)
O(1)	3066 (4)	9750 (6)	3865 (5)
O(2)	2599 (3)	9271 (5)	5656 (5)
N(1)	4060 (3)	6258 (6)	6069 (5)
N(2)	4286 (4)	4498 (7)	7987 (6)
C(1)	3093 (4)	6125 (7)	5333 (7)
C(2)	2901 (5)	7352 (8)	4370 (6)
C(3)	3181 (4)	8787 (7)	4897 (6)
C(4)	4151 (5)	8784 (7)	5627 (7)
C(5)	4419 (4)	7654 (7)	6641 (7)
C(6)	2477 (7)	10790 (9)	4016 (9)
C(7)	2319 (8)	10613 (10)	5274 (9)
C(8)	2984 (6)	4760 (9)	4552 (8)
C(9)	2440 (5)	6088 (9)	6196 (8)
C(10)	5460 (5)	7604 (9)	6962 (10)
C(11)	4112 (5)	8032 (9)	7845 (7)
H(C2a)	231 (4)	721 (7)	410 (6)
H(C2b)	328 (4)	716 (6)	367 (5)
H(C4a)	432 (3)	975 (6)	592 (5)
H(C4b)	448 (3)	853 (5)	494 (5)
H(C6a)	196 (5)	1065 (8)	346 (7)
H(C6b)	264 (5)	1178 (8)	356 (7)
H(C7a)	171 (5)	1098 (9)	578 (8)
H(C7b)	266 (6)	1125 (10)	563 (8)
H(C8a)	237 (4)	485 (6)	383 (5)
H(C8b)	294 (4)	402 (7)	517 (6)
H(C8c)	346 (4)	476 (6)	413 (5)
H(C9a)	190 (4)	580 (7)	569 (6)
H(C9b)	238 (4)	700 (7)	658 (6)
H(C9c)	263 (4)	513 (7)	688 (6)
H(C10a)	549 (6)	721 (7)	769 (6)
H(C10b)	578 (6)	869 (9)	700 (8)
H(C10c)	575 (5)	696 (9)	641 (8)
H(C11a)	351 (4)	794 (7)	781 (6)
H(C11b)	424 (5)	714 (8)	843 (7)
H(C11c)	447 (4)	884 (7)	831 (6)

* (I) was prepared by reaction of the corresponding N-unsubstituted piperidine with sulphur monochloride followed by treatment with aqueous ammonia. The details will be published elsewhere.

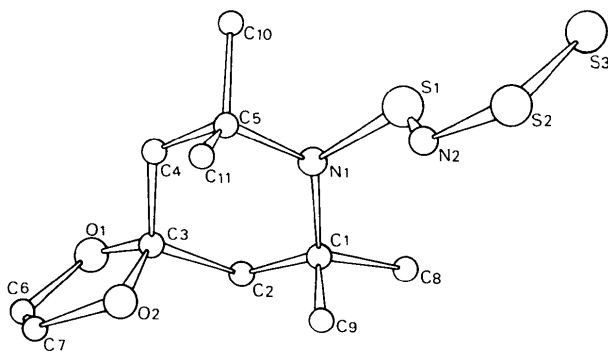
Fig. 1. The molecule projected perpendicular to *c*.

Table 2. Bond lengths (Å)

S(1)–N(1)	1.634 (5)	C(1)–C(2)	1.542 (10)
S(1)–N(2)	1.657 (6)	C(1)–C(8)	1.533 (11)
S(2)–S(3)	1.912 (3)	C(1)–C(9)	1.535 (9)
S(2)–N(2)	1.569 (7)	C(2)–C(3)	1.495 (10)
O(1)–C(3)	1.421 (8)	C(3)–C(4)	1.498 (8)
O(1)–C(6)	1.373 (10)	C(4)–C(5)	1.517 (10)
O(2)–C(3)	1.433 (7)	C(5)–C(10)	1.545 (7)
O(2)–C(7)	1.373 (11)	C(5)–C(11)	1.538 (9)
N(1)–C(1)	1.500 (7)	C(6)–C(7)	1.456 (13)
N(1)–C(5)	1.505 (8)		

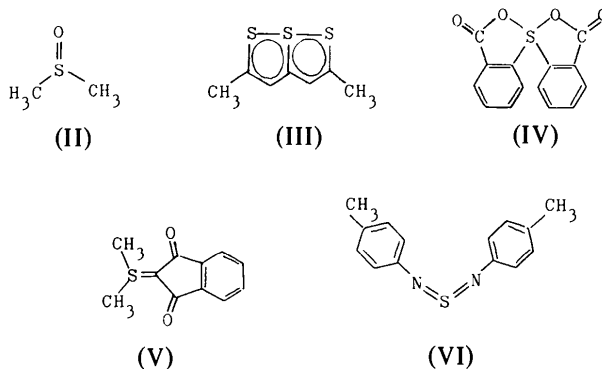
Table 3. Bond angles (°)

N(1)–S(1)–N(2)	105.7 (1)	N(1)–C(1)–C(9)	112.6 (5)
C(3)–O(2)–C(7)	108.3 (3)	N(1)–C(1)–C(8)	108.7 (4)
C(3)–O(1)–C(6)	108.8 (3)	N(1)–C(1)–C(2)	107.0 (4)
C(1)–N(1)–C(5)	120.1 (4)	N(1)–C(5)–C(11)	113.5 (4)
S(3)–S(2)–N(2)	114.9 (1)	N(1)–C(5)–C(10)	108.3 (4)
S(1)–N(1)–C(5)	118.8 (3)	N(1)–C(5)–C(4)	108.5 (5)
C(10)–C(5)–C(11)	109.5 (4)	S(1)–N(1)–C(1)	117.6 (4)
C(4)–C(5)–C(11)	111.6 (4)	S(1)–N(2)–S(2)	119.2 (4)
C(4)–C(5)–C(10)	105.0 (3)	O(1)–C(3)–C(4)	109.2 (4)
C(3)–C(4)–C(5)	115.9 (4)	O(1)–C(3)–C(2)	108.4 (5)
C(8)–C(1)–C(9)	108.7 (4)	O(2)–C(3)–C(4)	111.9 (5)
C(2)–C(3)–C(4)	110.6 (5)	O(2)–C(3)–C(2)	110.6 (4)
C(1)–C(2)–C(3)	116.0 (5)	O(1)–C(3)–O(2)	106.1 (5)
C(2)–C(1)–C(9)	112.9 (4)	O(1)–C(6)–C(7)	107.4 (7)
C(2)–C(1)–C(8)	106.6 (4)	O(2)–C(7)–C(6)	106.1 (7)

standard deviations are given in Table 1.* Fig. 1 shows a drawing of the molecule. The bond lengths and angles are listed in Tables 2 and 3 with their estimated standard deviations.

Discussion. A new stable –S–N=S=S bond system has been unequivocally determined by X-ray

analysis.* The S(2)–S(3) bond length of 1.912 Å obtained for this compound is significantly shorter than the usual S–S single-bond distance of 2.0–2.1 Å (Tamura, 1971). Therefore this bond system is thought to exhibit considerable double-bond character. Since no S=S double bond is found in the literature, the observed value may be compared with the P=S double bond whose length is in the range 1.94–1.98 Å (Lee & Goodacre, 1971). It should be noted that although S(3) is divalent, S(2) is tetravalent and both atoms are directly bonded. The N=S=S bond angle of 114.9° is smaller than O=S=O or N=S=N, which are 120.4 and 117.0° respectively (Sime & Abrahams, 1960; Leandri, Busetti, Valle & Mammi, 1970). This may be due to the repulsive force between N(2) and S(3) being weaker than those between the two O or the two N atoms. Tetravalent or hyper-tetravalent S atoms occur in dimethyl sulphoxide (II) (Thomas, Shoemaker & Eriks, 1966), dimethylthiathiothene (III) (Bezzi, Garbuglio, Traverso & Mammi, 1958), bis(2-carboxyphenyl)sulphur dihydroxide dilactone (IV) (Kálmán, Sasvári & Kapovits, 1973), and 2-dimethylsulphuranylidene-1,3-indandione (V) (Christensen & Thom, 1971). The bond system of the present compound has a topology at the tetravalent S(2) atom different from those in the above compounds since the linkages on both sides of S(2) show double-bond character.



Therefore, it can be said that the bond system at the S atom in the *p,p'*-ditolyl derivative (VI) (Leandri *et al.*, 1970) is similar to that of the present compound.

Very few data on the S=N bond distance have been published. The present value can only be compared with the results of Leandri *et al.* (1970) of 1.56 and 1.53 Å. These values are shorter than other reported S–N bonds, ranging from 1.60 to 1.76 Å (Tamura, 1971).

S(1), N(2), S(2) and S(3) are fairly planar with a maximum deviation of 0.001 Å from the least-squares plane. N(1) deviates 0.084 Å from this plane. The

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32888 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

* An analogous bond system has been reported for *p*-dimethylaminoaniline (Barton & Robson, 1974) and hindered aniline derivatives (Inagaki, Okazaki & Inamoto, 1977).

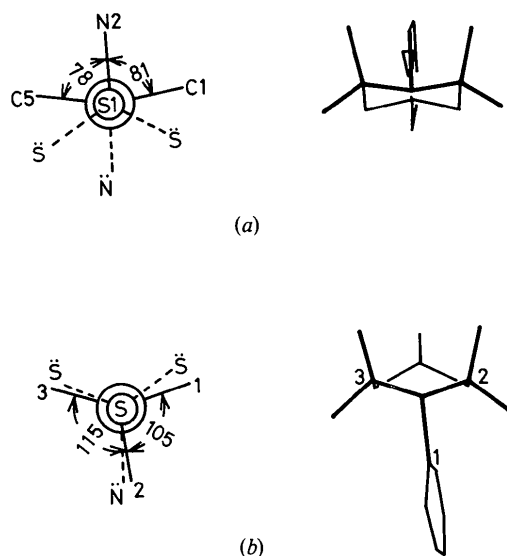
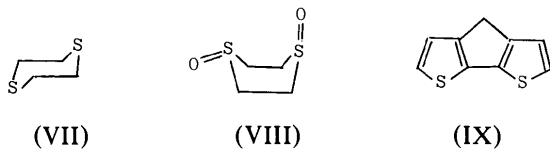


Fig. 2. Newman projections and molecular structures viewed down the S(1)—N(1) bond.

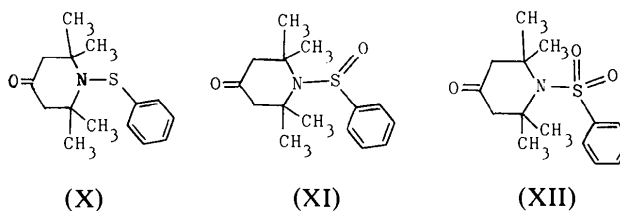
torsional angle S(1)—N(2)—S(2)—S(3) is 0.2° which is *cis* with respect to the N(2)—S(2) bond. This may be due to the presence of some sort of S...S intramolecular interaction, as the nonbonded distance of 3.194 Å is shorter than corresponding distances in the compounds 1,4-dithiane (VII) (Marsh, 1955), 1,4-dithiane 1,4-dioxide (VIII) (Montgomery, 1960) and 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (IX) (Koster, van Bolhuis & Visser, 1970) whose two S atoms are *cis* or *gauche*. In addition, the shortest intermolecular S...S distance published is given as 3.36 Å (Johnson & Paul, 1970).



Sletten (1975, 1976) has studied intramolecular S...S bonding and partial-bonding systems extensively. Values for these atomic distances are continuously distributed from 2.06 to 3.00 Å. Therefore, all the S—S interatomic distances, including the single bond, double bond, partial-bonding and nonbonding interactions, are continuously spread over a very wide range of values, from 1.91 to 3.4 Å, which may be due to special characteristics of the *d*-orbital electrons of the S atoms.

Conformational studies of the related 2,2,6,6-tetramethylpiperidine derivatives (X), (XI), and (XII) have been made (Sato, Yoshioka & Tamura, 1975). The six-membered-ring system in the present compound has nearly a chair form wherein the best four-atom plane is made up by C(1), C(2), C(4) and C(5), and

the maximum deviation is 0.004 Å. N(1) and C(3) deviate 0.540 and -0.608 Å from this plane. The conformational aspects of this ring system are similar to those of 1-benzenesulphenyl-2,2,6,6-tetramethyl-4-piperidinone (X). As shown in Fig. 2, the Newman projection of the present compound viewed down the S(1)—N(1) bond is *gauche* while (X) is eclipsed. The deviation of the N atom from the S(1), C(1), C(5) least-squares plane is 0.168 Å, which is more similar to that in 1-benzenesulphenyl-2,2,6,6-tetramethyl-4-piperidinone (XI), 0.144 Å, and that in 1-benzenesulphonyl-2,2,6,6-tetramethyl-4-piperidinone (XII), 0.175 Å, than to that in (X), 0.343 Å.



Short intermolecular atomic contacts are S(2)...C(9), 3.734, N(2)...O(2), 3.562, N(2)...C(7), 3.613, and C(8)...O(1), 3.654 Å, values which are within the range of normal van der Waals contacts.

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