where X, (Y), and Z are the coordinates in Å referred to axes parallel to **a**, (**b**), and **c***. As may be seen from Fig. 3, the equatorial planes of successive bipyramids along the chain are necessarily parallel and very nearly coincident. The substantial difference from ideal D_{5h} geometry lies in the irregularity of the equatorial pentagon, as shown by the angles (in Table 3) scattered widely about the ideal value of 72°. Of course the difference in size between the oxygen and bromine atoms would be expected to lead to unequal angles; it may be considered, however, that the three oxygens and two bromines in the equatorial coordination zone of the protactinium are equivalent in their spatial requirements to the five chlorines in $PaCl_5$.

The double chain structure is an unusual one and it is all the more surprising to find it also in the non-stoichiometric oxide material $Cs_xUO_3Cl_x$ ($x \sim 0{\cdot}9$). The disorder resultant on the non-stoichiometry of this compound was not determined by Allpress & Wadsley (1964), but, as all the chlorines are bridging, their shortfall must result either in a reduction of the multiple bridging of the chains or in chain terminations. In the present compound, termination of the chains at irregular intervals could well account for the difficulties we experienced with the upper level data; we have observed no evidence for non-stoichiometry but, as suggested by Allpress and Wadsley, occasional termination of the chains need not introduce any. Irregularities of this sort could well account also for the difficulty of growing sizable crystals and for the poor quality of the few crystals which have been observed.

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The Crystal Structures of 2,2,6,6-Tetramethyl-4-oxopiperidine Derivatives

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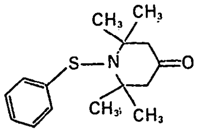
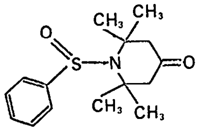
The crystal structures of a series of compounds, 1-benzenesulphenyl-2,2,6,6-tetramethyl-4-oxopiperidine (TMPS), 1-benzenesulphinyl-2,2,6,6-tetramethyl-4-oxopiperidine (TMPSO) and 1-benzenesulphonyl-2,2,6,6-tetramethyl-4-oxopiperidine (TMPSO2), have been determined by the three-dimensional Patterson method. The crystals of all three compounds are monoclinic, space group $P2_1/c$, with four molecules in each unit cell of dimensions: $a=17{\cdot}46$, $b=7{\cdot}86$, $c=15{\cdot}51$ Å and $\beta=136{\cdot}0°$ for TMPS, $a=14{\cdot}89$, $b=6{\cdot}31$, $c=21{\cdot}01$ Å and $\beta=130{\cdot}8°$ for TMPSO and $a=7{\cdot}60$, $b=15{\cdot}73$, $c=17{\cdot}08$ Å and $\beta=131{\cdot}2°$ for TMPSO2. Refinements were carried out by the block-diagonal least-squares procedure, and the respective final R values were 0·113, 0·120 and 0·113 for the three molecules. The conformations of the piperidine rings in each compound observed here are a chair form, a twisted form and a boat form. The nitrogen atom in TMPS is sp^3 hybridized, whereas those in TMPSO and TMPSO2 are partly sp^2 hybridized.

Introduction

To study the stereochemistry and the variation of molecular conformation, some tetramethyl piperidine derivatives, (I) 1-benzenesulphenyl-2,2,6,6-tetramethyl-4-oxopiperidine (hereafter designated as TMPS), (II) 1-benzenesulphinyl-2,2,6,6-tetramethyl-4-oxopiperidine (TMPSO) and (III) 1-benzenesulphonyl-2,2,6,6-tetramethyl-4-oxopiperidine (TMPSO2), have been examined by X-ray analysis.



(I)



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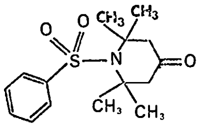
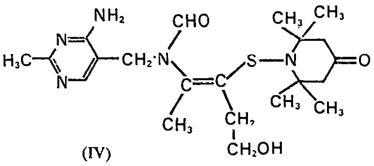


(III)

Analogous compounds with four methyl substituents have been reported by several authors: (IV) S-(2,2,6,6-

tetramethyl-4-oxopiperidino)thiamine (Tamura, Sato & Yoshioka, 1969), (V) 2-bromo-3,3,5,5-tetramethylcyclohexanone (Goaman & Grant, 1964), (VI) 2,6-dibromo-3,3,5,5-tetramethylcyclohexanone (Goaman & Grant, 1964), (VII) 2,2,6,6-tetramethyl-4-piperidone (Rees & Weiss, 1971) and (VIII) 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl (Lajzérowicz-Bonneteau, 1968; Berliner, 1970). In all these cases the six-membered ring with four methyl groups generally takes a chair conformation, except for another orthorhombic form of (VIII) (Bordeaux & Lajzérowicz, 1974).



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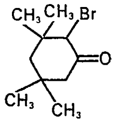

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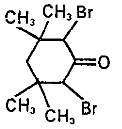

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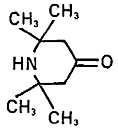
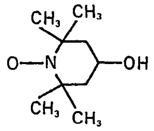


(VII)



(VIII)

With the three compounds in this study there seems to be a similar molecular skeleton except for the number of oxygens attached to the sulphur atom. However, the molecular conformations differ significantly from each other. The piperidine ring in TMPS is in the usual chair form but those in TMPSO and TMPSO2 are flexible, *i.e.* a twisted form and a boat form. Hence the oxygen atom(s) attached to the sulphur atom contribute to some extent to the conformation of these molecules.

Experimental

All compounds recrystallized from ether as colourless, needle-like crystals. The cell constants were measured by oscillation and Weissenberg photographs, and the densities were determined by the flotation method. All intensity data were estimated visually from several sets of multiple-film equi-inclination Weissenberg photographs taken with Cu *Kα* radiation, and corrected for Lorentz and polarization factors, but not for absorption. The crystal data are summarized in Table 1.

Table 1. *Crystal data for TMPS, TMPSO and TMPSO2*

	TMPS	TMPSO	TMPSO2
Formula	$C_{15}H_{21}NOS$	$C_{15}H_{21}NO_2S$	$C_{15}H_{21}NO_3S$
M.W.	263·4	279·4	295·4
a (Å)	17·46 (1)	14·89 (1)	7·60 (1)
b	7·86 (1)	6·31 (1)	15·73 (1)
c	15·51 (1)	21·01 (2)	17·08 (1)
β (°)	136·0 (2)	130·8 (2)	131·2 (2)
Volume (Å^3)	1478·6	1494·3	1536·3
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
Z	4	4	4
D_{obs} (g cm^{-3})	1·19	1·26	1·29
D_{calc}	1·18	1·24	1·28
Collected data	*h0l–h6l*	*h0l–h5l*	*0kl–7kl*
Number of reflexions	2012	2216	2648

Structure determination

The positional parameters of the sulphur atoms in each of the crystals could be obtained from sharpened Patterson syntheses. All three molecular structures were obtained through successive Fourier syntheses using Sim's weighting scheme. Several cycles of block-diagonal least-squares refinement with anisotropic temperature factors for the sulphur atoms and isotropic temperature factors for others gave the *R* values 0·19, 0·18 and 0·18 for TMPS, TMPSO and TMPSO2 respectively. At this stage the difference Fourier syntheses were computed to obtain the hydrogen-atom positions. Almost all of hydrogens for the respective compounds were revealed at the expected positions in each difference map. Subsequent anisotropic refinements for the non-hydrogen atoms, and isotropic for hydrogen atoms, gave the final *R* values 0·113, 0·120 and 0·113 for TMPS, TMPSO and TMPSO2, respectively. The final fractional coordinates and anisotropic thermal parameters for these three molecules are given in Table 2 together with their standard deviations.*

Results and discussion

The bond lengths and angles for the three molecules are shown in Tables 3 and 4 together with their standard deviations. The stereo pairs in Fig. 1 illustrate the geometrical aspects to the molecules and the atomic numbering used throughout this paper.

Coordination around the S *atom*

The S–C bond lengths in TMPS (1·774 Å) and TMPSO2 (1·777 Å) are in agreement with the expected value for the S–Csp^2 bond, but in TMPSO (1·846 Å) the length seems to be slightly high. The S–N bond lengths in TMPS, TMPSO and TMPSO2 are somewhat shorter than the calculated single-bond length of 1·73 Å, which is derived from the conventional radii and the electronegativity correction (Schomaker & Stevenson, 1941). For these bond lengths, the decrease in S–N corresponds to the increase in the number of oxygen atoms attached to the sulphur atom. This indicates that S–O bonding electrons are partially localized on the oxygen atom resulting in the sulphur atom being more positively charged and the lone-pair electrons of

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30867 (48 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

nitrogen participate in S–N bonding. Thus the S–N bond lengths in TMPSO and TMPSO2 would be shortened and there is more double-bond character. This tendency appears systematically at the S–N bond rather than at the S–C bond. Consequently the atomic configuration of nitrogen in these molecules may be changed substantially: this will be discussed below. The S–O bond length of the sulphoxide group in

Table 2. *Fractional coordinates and anisotropic thermal parameters* (× 10^4)

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

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
TMPS									
S(1)	1501 (2)	4419 (3)	1536 (1)	59 (1)	164 (5)	26 (1)	40 (2)	22 (1)	3 (2)
C(2)	1541 (5)	5571 (10)	2551 (5)	54 (5)	113 (16)	37 (5)	1 (7)	30 (4)	−8 (7)
C(3)	594 (6)	6472 (11)	1995 (6)	61 (6)	118 (18)	62 (6)	13 (7)	43 (5)	−8 (8)
C(4)	536 (7)	7388 (12)	2700 (8)	77 (7)	154 (20)	103 (8)	13 (9)	72 (7)	2 (10)
C(5)	1398 (8)	7381 (12)	3972 (8)	106 (8)	185 (21)	111 (9)	−29 (10)	97 (8)	−46 (11)
C(6)	2340 (7)	6525 (12)	4521 (7)	89 (7)	180 (20)	56 (6)	−22 (9)	55 (6)	−29 (9)
C(7)	2430 (6)	5587 (12)	3840 (6)	71 (6)	167 (19)	43 (5)	7 (9)	40 (5)	−12 (9)
N(8)	2666 (4)	3229 (12)	2467 (4)	53 (4)	61 (12)	37 (4)	16 (5)	31 (4)	8 (5)
C(9)	3440 (6)	3709 (7)	2387 (6)	61 (5)	83 (15)	51 (5)	−17 (7)	41 (5)	−17 (7)
C(10)	4506 (7)	2682 (10)	3320 (7)	60 (6)	175 (21)	82 (8)	1 (9)	44 (6)	−15 (10)
C(11)	4264 (6)	825 (12)	3242 (7)	59 (7)	214 (23)	58 (6)	42 (9)	30 (5)	9 (10)
C(12)	3560 (8)	444 (13)	3434 (8)	94 (7)	101 (18)	88 (8)	33 (10)	59 (7)	37 (10)
C(13)	2472 (6)	1382 (12)	2494 (6)	60 (5)	119 (17)	59 (6)	−1 (7)	45 (5)	−4 (8)
C(14)	3750 (8)	5592 (10)	2733 (8)	109 (8)	188 (22)	100 (8)	−38 (11)	80 (8)	−30 (12)
C(15)	2946 (7)	3443 (14)	1072 (7)	99 (8)	188 (20)	64 (7)	1 (10)	68 (7)	5 (9)
O(16)	4612 (6)	−247 (12)	3038 (7)	117 (7)	264 (19)	160 (9)	59 (9)	95 (7)	11 (11)
C(17)	1739 (8)	437 (10)	1236 (9)	116 (9)	219 (24)	110 (9)	−59 (12)	90 (9)	−83 (13)
C(18)	1869 (9)	1209 (14)	2905 (9)	125 (10)	236 (26)	149 (11)	−47 (13)	119 (10)	−34 (14)
TMPSO									
S(1)	1569(2)	1935 (3)	2866 (1)	82 (2)	187 (6)	40 (1)	−30 (2)	43 (1)	−19 (2)
C(2)	2196 (6)	2806 (12)	3925 (6)	72 (6)	157 (23)	42 (3)	−12 (9)	39 (4)	−16 (7)
C(3)	1953 (7)	4821 (14)	4029 (5)	98 (8)	243 (28)	48 (4)	7 (11)	50 (5)	5 (8)
C(4)	2293 (7)	5375 (14)	4797 (5)	110 (8)	275 (30)	50 (4)	−10 (12)	57 (5)	−22 (8)
C(5)	2884 (7)	3932 (16)	5461 (5)	100 (8)	410 (34)	42 (4)	−40 (13)	53 (5)	−20 (9)
C(6)	3116 (7)	1940 (15)	5355 (5)	108 (8)	331 (31)	43 (4)	2 (13)	51 (5)	29 (9)
C(7)	2743 (7)	1309 (13)	4563 (5)	102 (8)	224 (28)	46 (4)	−4 (11)	49 (5)	10 (8)
N(8)	2195 (5)	3612 (10)	2564 (4)	61 (5)	194 (20)	37 (3)	−5 (7)	32 (3)	−1 (5)
C(9)	1342 (7)	4434 (13)	1749 (4)	81 (7)	250 (27)	32 (3)	19 (10)	34 (4)	3 (7)
C(10)	1893 (8)	6362 (15)	1671 (5)	104 (8)	306 (32)	50 (4)	−5 (12)	54 (5)	13 (9)
C(11)	3108 (8)	5992 (17)	2009 (6)	123 (10)	416 (37)	52 (4)	−38 (15)	60 (6)	7 (10)
C(12)	3771 (6)	4119 (20)	2609 (6)	88 (8)	599 (47)	63 (5)	−13 (16)	57 (6)	−10 (13)
C(13)	3489 (7)	3782 (12)	3174 (5)	75 (6)	173 (25)	47 (4)	3 (9)	42 (4)	−2 (7)
C(14)	242 (8)	5342 (16)	1537 (6)	85 (8)	360 (35)	52 (4)	61 (13)	43 (5)	41 (9)
C(15)	1007 (7)	2664 (17)	1128 (5)	121 (10)	363 (38)	44 (4)	−19 (15)	41 (5)	−40 (10)
O(16)	3533 (8)	6985 (15)	1782 (5)	211 (11)	628 (38)	108 (5)	−58 (17)	121 (7)	53 (12)
C(17)	4211 (8)	1888 (20)	3777 (7)	102 (9)	592 (49)	78 (6)	77 (18)	65 (7)	92 (15)
C(18)	3941 (8)	5774 (17)	3803 (7)	91 (8)	361 (36)	54 (4)	−12 (14)	43 (5)	−5 (10)
O(19)	1975 (5)	−301 (9)	2988 (4)	136 (7)	181 (18)	72 (3)	−17 (8)	78 (4)	−17 (6)
TMPSO2									
S(1)	2391 (2)	3600 (1)	2219 (1)	72 (4)	12 (1)	43 (1)	−11 (1)	23 (2)	−6 (1)
C(2)	1521 (10)	4654 (3)	2198 (5)	128 (18)	18 (2)	43 (4)	4 (5)	46 (8)	2 (2)
C(3)	−595 (12)	4944 (4)	1294 (5)	193 (22)	33 (3)	43 (4)	20 (6)	50 (9)	8 (3)
C(4)	−1342 (12)	5734 (5)	1285 (6)	198 (22)	30 (3)	74 (6)	50 (7)	67 (10)	24 (3)
C(5)	−17 (14)	6227 (4)	2167 (7)	347 (28)	19 (3)	99 (7)	28 (7)	147 (13)	11 (3)
C(6)	2147 (14)	5925 (4)	3074 (6)	356 (29)	22 (3)	76 (6)	−11 (7)	123 (12)	−8 (3)
C(7)	2924 (11)	5140 (4)	3098 (5)	172 (20)	22 (2)	43 (4)	−1 (5)	49 (8)	−3 (2)
N(8)	5211 (8)	3633 (3)	2895 (4)	69 (13)	16 (2)	39 (3)	1 (4)	21 (6)	1 (2)
C(9)	6819 (11)	3023 (4)	3818 (5)	175 (20)	17 (2)	39 (4)	8 (5)	34 (8)	6 (2)
C(10)	9290 (12)	3039 (4)	4192 (6)	152 (21)	32 (3)	59 (5)	18 (6)	43 (9)	11 (3)
C(11)	10103 (12)	3901 (5)	4214 (6)	169 (22)	35 (3)	58 (6)	−20 (7)	35 (10)	−8 (3)
C(12)	8413 (11)	4426 (4)	3268 (6)	150 (20)	28 (3)	61 (5)	−27 (6)	52 (9)	−5 (3)
C(13)	6053 (10)	4005 (4)	2393 (5)	135 (19)	26 (2)	40 (4)	3 (5)	43 (8)	5 (2)
C(14)	7027 (14)	3320 (5)	4705 (6)	294 (27)	39 (3)	43 (5)	38 (8)	57 (10)	16 (3)
C(15)	5993 (14)	2097 (4)	3521 (7)	303 (27)	14 (2)	86 (7)	12 (6)	86 (12)	8 (3)
O(16)	11968 (11)	4193 (5)	4949 (6)	285 (23)	76 (4)	102 (7)	−82 (8)	−2 (10)	−5 (4)
C(17)	6138 (14)	3338 (5)	1771 (6)	279 (27)	46 (4)	59 (6)	22 (8)	80 (11)	−1 (4)
C(18)	4462 (13)	4740 (5)	1608 (6)	276 (25)	34 (3)	54 (5)	29 (7)	80 (10)	21 (3)
O(19)	1134 (8)	3362 (3)	1165 (4)	151 (14)	33 (2)	58 (4)	−6 (4)	29 (6)	−24 (2)
O(20)	1993 (9)	3126 (3)	2785 (5)	240 (17)	26 (2)	104 (5)	−7 (5)	119 (8)	10 (2)

TMPSO is comparatively longer than that in the sulphone in TMPSO2. This tendency is observed in similar bond systems, such as dimethyl sulphoxide (1·531 Å; Thomas, Schoemaker & Eriks, 1966) and dimethyl sulphone (1·446 Å: Langs, Silverton & Bright, 1970).

The C(2)–S(1)–N(8) bond angles for TMPS, TMPSO and TMPSO2 are 105·6, 101·8 and 106·3° respectively; these values are similar to C–S–C and C–S–N angles in open-chain molecules (Blackmore & Abrahams, 1955; Kálmán, Duffin & Kucsman, 1971;

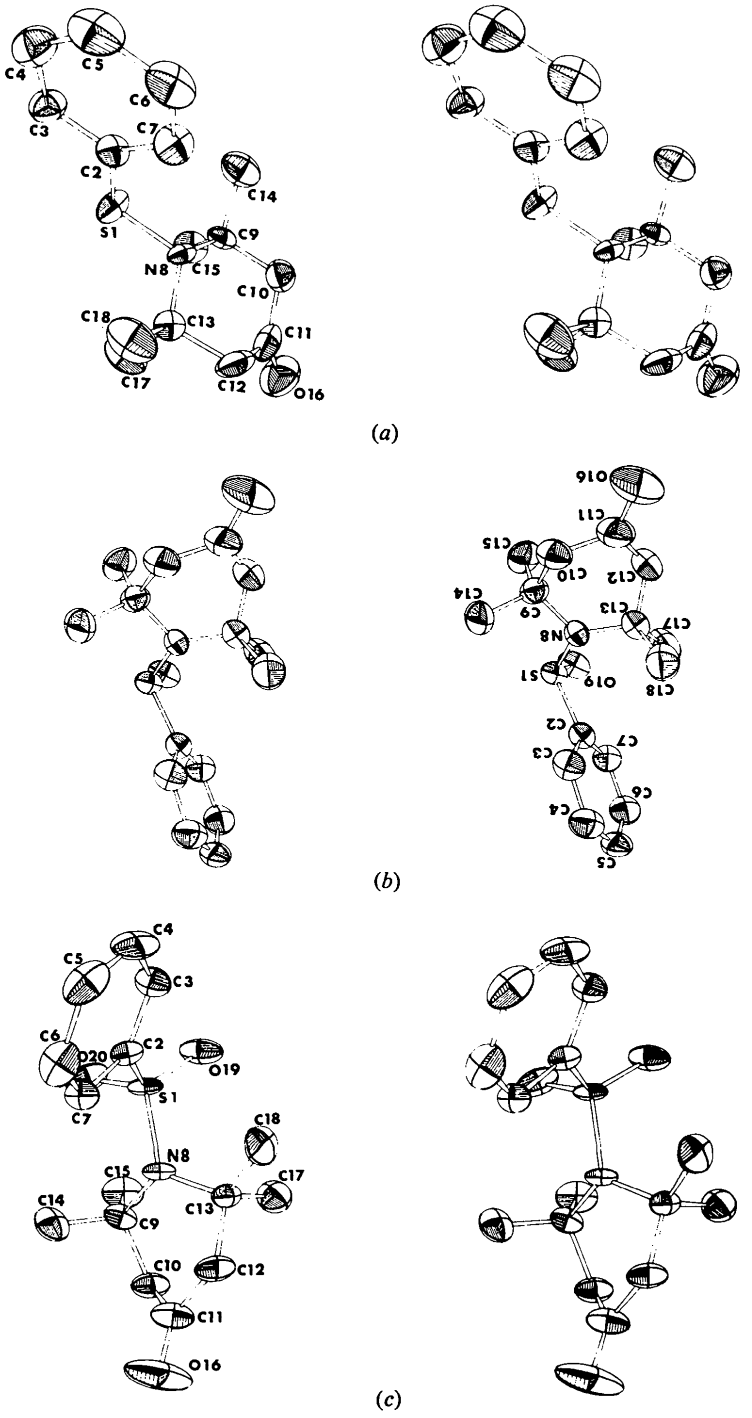


Fig. 1. Stereoscopic views of the three compounds showing the atomic numbering used throughout this study. (*a*) TMPS. (*b*) TMPSO. (*c*) TMPSO2.

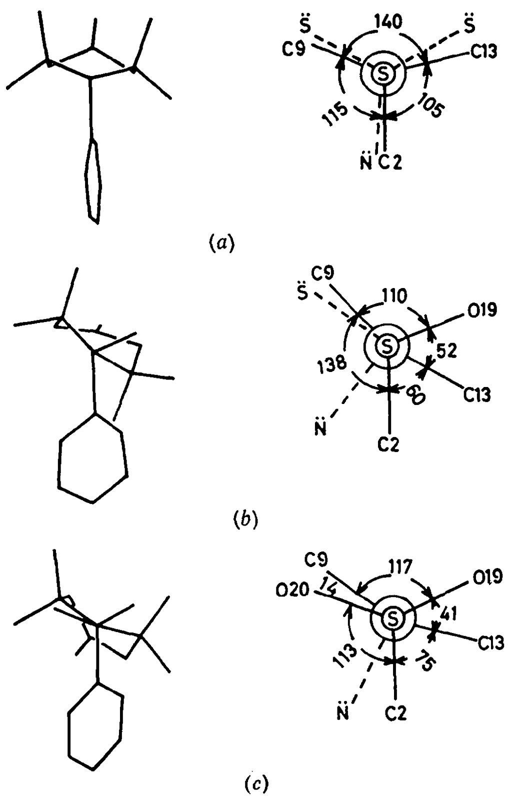


Fig. 2. Molecular structures and conformational angles (°) viewed down the S-N bond. (*a*) TMPS. (*b*) TMPSO. (*c*) TMPSO2.

Table 3. *Bond lengths* (Å)

Standard deviations are in parentheses.

	TMPS	TMPSO	TMPSO2
S(1)—C(2)	1·774 (10)	1·846 (9)	1·777 (6)
S(1)—N(8)	1·694 (6)	1·652 (9)	1·634 (5)
S(1)—O(19)		1·490 (6)	1·424 (6)
S(1)—O(20)			1·402 (9)
C(2)—C(3)	1·389 (13)	1·378 (13)	1·381 (7)
C(2)—C(7)	1·393 (8)	1·389 (11)	1·378 (8)
C(3)—C(4)	1·372 (18)	1·386 (16)	1·362 (11)
C(4)—C(5)	1·373 (11)	1·395 (12)	1·372 (11)
C(5)—C(6)	1·366 (16)	1·360 (15)	1·405 (9)
C(6)—C(7)	1·386 (17)	1·423 (15)	1·359 (10)
N(8)—C(9)	1·492 (15)	1·530 (9)	1·537 (7)
N(8)—C(13)	1·498 (10)	1·471 (10)	1·487 (13)
C(9)—C(10)	1·528 (11)	1·535 (15)	1·535 (13)
C(9)—C(14)	1·534 (13)	1·502 (15)	1·492 (15)
C(9)—C(15)	1·554 (14)	1·533 (14)	1·533 (8)
C(10)–C(11)	1·500 (14)	1·468 (16)	1·481 (11)
C(11)–C(12)	1·489 (21)	1·529 (15)	1·486 (10)
C(11)–O(16)	1·207 (17)	1·189 (20)	1·205 (9)
C(12)–C(13)	1·514 (11)	1·511 (20)	1·535 (8)
C(13)–C(17)	1·550 (13)	1·553 (13)	1·524 (14)
C(13)–C(18)	1·582 (23)	1·617 (13)	1·569 (9)

Table 4. *Bond angles* (°)

Standard deviations are in parentheses.

	TMPS	TMPSO	TMPSO2
C(2)—S(1)—N(8)	105·6 (3)	101·8 (4)	106·3 (3)
C(2)—C(1)—O(19)		104·2 (4)	106·8 (3)
C(2)—S(1)—O(20)			105·3 (4)
N(8)—S(1)—O(19)		114·6 (5)	112·2 (4)
N(8)—S(1)—O(20)			107·9 (3)
O(19)-S(1)—O(20)			117·6 (3)
S(1)—C(2)—C(3)	116·1 (5)	119·2 (6)	118·3 (5)
S(1)—C(2)—C(7)	124·8 (8)	118·5 (7)	119·2 (4)
C(3)—C(2)—C(7)	119·1 (10)	121·5 (9)	122·4 (6)
C(2)—C(3)—C(4)	120·7 (6)	119·0 (8)	118·9 (6)
C(3)—C(4)—C(5)	120·6 (10)	120·8 (9)	120·3 (6)
C(4)—C(5)—C(6)	118·8 (13)	120·1 (10)	119·9 (7)
C(5)—C(6)—C(7)	122·1 (7)	120·2 (8)	120·7 (7)
C(2)—C(7)—C(6)	118·6 (8)	118·3 (8)	117·8 (5)
S(1)—N(8)—C(9)	113·2 (5)	113·3 (5)	119·4 (5)
S(1)—N(8)—C(13)	113·7 (5)	122·8 (5)	117·9 (4)
C(9)—N(8)—C(13)	118·9 (8)	121·4 (8)	118·9 (6)
N(8)—C(9)—C(10)	110·3 (8)	109·5 (4)	110·2 (7)
N(8)—C(9)—C(14)	109·2 (10)	111·0 (9)	109·0 (6)
N(8)—C(9)—C(15)	113·2 (6)	110·8 (7)	112·3 (4)
C(10)-C(9)—C(14)	107·2 (6)	102·8 (8)	106·9 (6)
C(10)-C(9)—C(15)	108·6 (9)	112·7 (10)	106·0 (7)
C(14)-C(9)—C(15)	108·2 (8)	109·9 (8)	112·4 (8)
C(9)—C(10)-C(11)	110·9 (7)	113·5 (8)	113·7 (6)
C(10)-C(11)-C(12)	113·9 (10)	116·7 (11)	115·7 (5)
C(10)-C(11)-O(16)	122·3 (13)	122·2 (9)	124·1 (7)
C(12)-C(11)-O(16)	123·9 (10)	120·9 (11)	120·2 (8)
C(11)-C(12)-C(13)	110·7 (9)	113·4 (11)	116·0 (6)
N(8)—C(13)-C(12)	110·3 (7)	109·1 (6)	106·2 (6)
N(8)—C(13)-C(17)	115·3 (8)	108·0 (8)	111·4 (6)
N(8)—C(13)-C(18)	108·9 (8)	108·0 (8)	113·6 (7)
C(12)-C(13)-C(17)	107·9 (9)	110·5 (10)	114·6 (7)
C(12)-C(13)-C(18)	108·0 (9)	110·6 (9)	105·2 (5)
C(17)-C(13)-C(18)	106·2 (9)	103·6 (7)	105·9 (7)

Barens & Sundaralingam, 1973). In TMPSO, the bond angles C(2)-S(1)-O(19) and N(8)-S(1)-O(19), 104·2 and 114·6°, are not equivalent. This difference is probably due to the steric hindrance between the oxygen atom and the methyl group on the piperidine ring. The atomic configuration of sulphur in TMPSO has a pyramidal structure and the deviation from the C(2)–N(8)–O(19) plane is 0·610 Å.

Atomic configuration of nitrogen

The spatial arrangement about the nitrogen atom in each piperidine ring is significantly different. In TMPS, TMPSO and TMPSO2, the sums of the three bond angles about each nitrogen are 345·8, 357·5 and 356·2°, and the deviations of the nitrogen atom from the S(1)-C(9)-C(13) plane are 0·343, 0·144 and 0·175 Å. These results mean that the deviation of the nitrogen atomic configuration from a pure sp^2 hybrid is largest in TMPS. Combined with the S–N bond lengths and the above results, it can be said that the nitrogen atoms in TMPSO and TMPSO2 have more contribution from an sp^2 hybridized configuration than an sp^3, as compared with the nitrogen in TMPS. This may allow the remaining filled *p* orbital to participate more effectively in *d-p* π bonding with the sulphur atom. However, it appears that the difference in the nitrogen atomic configuration is not reflected in the N–C bond. The average N–C bond lengths for TMPS, TMPSO and TMPSO2 are 1·495, 1·501 and 1·512 Å; these values do not significantly differ from each other.

It is interesting to see that in the TMPSO molecule two of the S–N–C bond angles (113·3 and 122·8°) differ significantly. This may result from the O(19) atom of the asymmetric sulphoxide group being at a closer distance to the methyl carbon C(17) attached to C(13) than that the methyl C(15) attached to C(9) (Table 5). In the other two molecules, these angles are normal.

Table 5. *Selected intramolecular non-bonded distances* (Å)

TMPS			
S(1)···C(14)	3·04	C(9)···C(13)	2·58
C(7)···C(18)	3·59	C(7)···C(14)	3·74
S(1)···C(18)	3·05	C(15)···C(17)	3·30
TMPSO			
S(1)···C(14)	3·02	C(9)···O(19)	3·66
C(3)···O(19)	3·92	C(15)···C(17)	4·39
C(9)···C(13)	2·62	C(3)···C(18)	3·35
C(14)···C(18)	4·34	C(7)···O(19)	2·89
C(17)···O(19)	2·92	C(13)···O(19)	3·27
S(1)···C(17)	3·05	C(15)···O(19)	3·67
C(7)···C(17)	3·52		
TMPSO2			
S(1)···C(15)	3·16	C(14)···O(20)	2·99
C(3)···O(19)	2·89	C(17)···O(19)	3·22
C(9)···C(13)	2·60	C(3)···C(18)	3·53
C(15)···O(20)	2·90	C(7)···O(20)	3·21
S(1)···C(18)	2·99	C(15)···C(17)	3·63
C(7)···C(18)	3·49	C(18)···O(19)	3·02

Conformation of the tetramethylpiperidine ring

Of special interest are the conformations of the piperidine rings, which take three different types; a chair form in TMPS, a twisted form in TMPSO and a boat form in TMPSO2. In Table 6, the deviations from the best least-squares planes which consist of four relevant atoms in each of the piperidine ring systems are shown. The best four-atom planes are defined by the atoms C(9), C(10), C(12) and C(13) in TMPS, N(8), C(10), C(11) and C(13) in TMPSO, and N(8), C(9), C(11) and C(12) in TMPSO2, respectively. As discerned from Table 6, their signs indicate that the piperidine ring in TMPS takes a chair form, and those in TMPSO and in TMPSO2 a boat form. In TMPSO, however, the atoms N(8), C(10), C(11) and C(13) of the best four-atom plane deviate 0·128, −0·106, 0·111 and −0·123 Å from the best least-squares plane, which indicates that in this conformation the ring is considerably distorted.

Table 7. *Torsional angles* (°) *in the piperidine ring and ideal cyclohexane ring*

	TMPS	TMPSO	TMPSO2
C(13)-N(8)—C(9)—C(10)	46·9	31·9	−10·9
N(8)—C(9)—C(10)-C(11)	−48·3	−50·7	−41·1
C(9)—C(10)-C(11)-C(12)	56·2	18·3	47·1
C(10)-C(11)-C(12)-C(13)	−57·9	36·0	0·0
C(11)-C(12)-C(13)-N(8)	50·4	−53·8	−48·2
C(12)-C(13)-N(8)—C(9)	−47·1	19·2	54·1
Ideal cyclohexane ring	Chair	Twist	Boat
	60·0	33·2	0·0
	−60·0	−70·6	−60·0
	60·0	33·2	60·0
	−60·0	33·2	0·0
	60·0	−70·6	−60·0
	−60·0	33·2	60·0

An alternative description of the ring conformations can be made by calculating the torsional angles. In Table 7, these angles for each ring are listed together with those for an ideal cyclohexane ring system (Hendrickson, 1964). The torsional angles of the piperidine rings differ remarkably from each other and indicate three characteristic different conformations, a chair, a twisted and a boat form. However, some torsional angles are not strictly in agreement with the values for

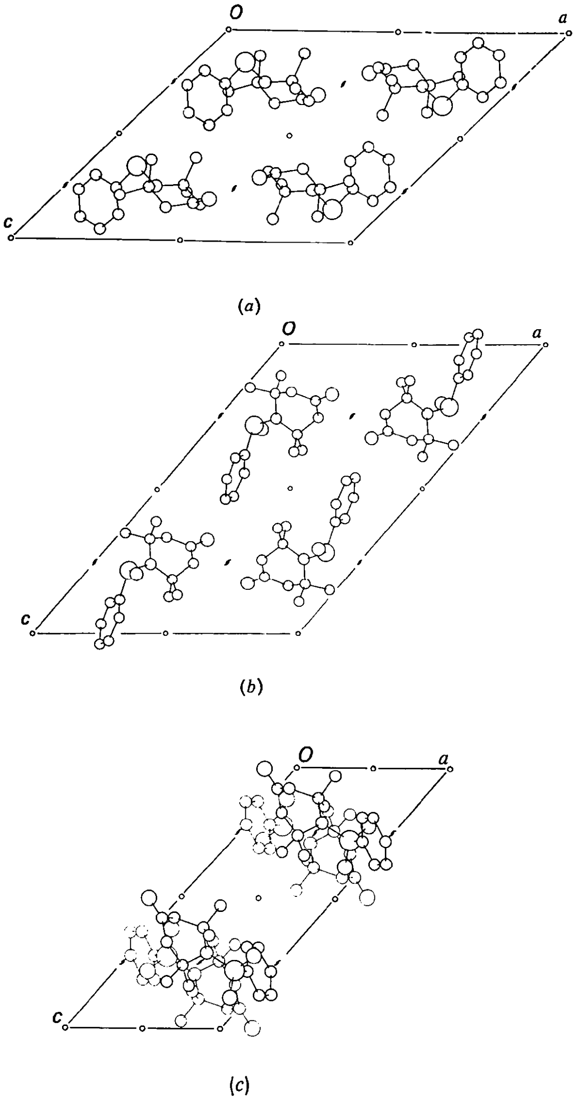
Table 6. *Deviations* (Å) *of the atoms from various least-squares planes*

Atoms denoted by * were not included in the calculations of the planes.

	Piperidine rings			N atoms			S atom
	TMPS	TMPSO	TMPSO2	TMPS	TMPSO	TMPSO2	TMPSO
S(1)				0·000	0·000	0·000	0·613*
C(2)							0·000
C(3)							
C(4)							
C(5)							
C(6)							
C(7)							
N(8)	−0·525*	0·128	−0·021	−0·343*	−0·144*	−0·175*	0·000
C(9)	−0·007	0·538*	0·021	0·000	0·000	0·000	
C(10)	0·007	−0·106	0·526*				
C(11)	0·642*	0·111	−0·021				
C(12)	−0·007	0·528*	0·022				
C(13)	0·007	−0·123	0·627*	0·000	0·000	0·000	
C(14)	−0·947*	−0·057*	−1·367*				
C(15)	1·424*	2·065*	0·988*				
O(16)							
C(17)	1·441*	0·325*	2·146*				
C(18)	−0·930*	+1·723*	0·288*				
O(19)							0·000
O(20)							

the corresponding conformations in the ideal structure. The respective mean bond angles in the piperidine rings of TMPS, TMPSO and TMPSO2 are 112·5, 113·9 and 113·5° which are significantly larger than the ideal tetrahedral angle. This may be caused by the atomic configuration of the C(11) atom which is sp^2 hybridized, and as previously stated, the N(8) atoms have a large endocyclic angle because of the steric hindrance between the methyl groups. In the case of the six-membered ring system, the more the mean bond angle approaches 120°, the more the ring flattens with each torsional angle approaching 0°. Thus, the conformations of these piperidine rings are distorted to some extent from each of the corresponding ideal conformations.

In Fig. 2, the molecular structures and conformational angles viewed down the S(1)–N(8) bond are shown, and the expected directions of lone pairs on the sulphur and nitrogen atoms are also displayed. In TMPS, the conformational angles C(3)–S(1)–N(8)–C(9), 115°, and C(2)–S(1)–N(8)–C(13), 105°, are not so different from each other, and the plane of the phenyl group is approximately coplanar with the C(2)–S(1)–N(8) plane (dihedral angle; 7·7°) and almost perpendicular to the C(9)–S(1)–C(13) plane (dihedral angle; 87·0°). These facts indicate that the steric interactions between the phenyl group and other functional groups may be at a minimum. Furthermore, the lone pairs on the sulphur and nitrogen atoms are oriented to minimize electronic repulsive forces. Consequently the direction of the lone pairs and the substituents at sulphur and nitrogen are in a *cis* conformation. In TMPSO and TMPSO2, there are oxygen atom(s) attached to the sulphur atom; their conformational angles and the direction with respect to the phenyl plane differ from those in TMPS. Thus if the TMPSO2 molecule takes the same conformation as TMPS, the intramolecular atomic repulsion between the oxygen atoms and methyl groups may be considerable. It would not be possible to relieve this steric hindrance by simple rotation around the S–N bond, because this results in the approach of the more bulky phenyl group to the neighbouring tetramethyl group. Therefore under such circumstances the conformation of the piperidine ring may be required to change to a form in which these steric hindrances are substantially reduced such that the ring should take a flexible conformation. The piperidine ring of TMPSO2 has a boat form in which the bow and stern atoms are C(9) and C(12). Why the TMPSO molecule takes the twisted form is still not clear. However, we may say here that the functional group of the non-symmetrically arranged sulphoxide in the molecule does affect the overall conformation. Furthermore, the differences in the atomic configuration of the nitrogen atom may also be related to the ring conformation. As already mentioned, the atomic configuration assumed by nitrogen in TMPS is sp^3 hybridized, but TMPSO and TMPSO2 have a somewhat greater contribution from the sp^2 hybridized configuration. Consequently, this suggests that the bond nature of the piperidine ring system in TMPSO and TMPSO2 is analogous to that of a ring system having two sp^2 hybridized atoms at the 1,4 positions. In the literature, most of the six-membered ring systems containing one sp^2 hybridized atom usually take a chair form in the crystalline state. However, cyclohexane-1,4-dione (Groth & Hassel, 1964*a*; Mossel & Romers, 1964) involving two sp^2 hybridized atoms, and its complex with mercuric chloride (Groth & Hassel, 1964*b*) were observed to take a twisted conformation. On the other hand, the complex cyclohexane-1,4-dione diiodoacetylene (Groth & Hassel, 1965) maintained a chair form.



(*a*)

(*b*)

(*c*)

Fig. 3. Molecular packing viewed along the *b* axis. (*a*) TMPS. (*b*) TMPSO. (*c*) TMPSO2.

From simple geometrical considerations, it should be mentioned that the intramolecular non-bonded distance between the substituted atoms in the 1,3-diaxial configuration should be equal in either the chair or the boat forms. Table 5 shows the shortest intramolecular non-bonded distances between the methyl carbons attached to C(9) and C(13). The distances are 3·296, 4·391 and 3·632 Å for TMPS, TMPSO and TMPSO2, respectively. The distance in TMPS is completely analogous to those found in the related compound in a chair form, *i.e.* (IV): 3·28 Å (Tamura *et al.*, 1969), (V): 3·30 Å (Goaman & Grant, 1964), (VI): 3·37 Å (Goaman & Grant, 1964) and (VII): 3·196 Å (Rees & Weiss, 1971). The only exception is compound (VIII): 3·64 Å (Lajzérowicz-Bonneteau, 1968; Berliner, 1970), since it contains a nitroxide group which shows an extremely large endocyclic angle about the nitrogen atom. In the TMPSO2 molecule in the boat form, the bow and the stern do not consist of the N(8) and C(11) atoms, but the C(10) and C(13) atoms. Thus, the 1,3-diaxial configuration of the methyl groups on the six-membered ring system is not retained. The atomic distance between these methyl groups is longer than that found in TMPS in the chair form, and the twisted TMPSO molecule has an even greater separation.

Table 8. *Intermolecular contacts* (Å) *within* 3·7 Å

TMPS			
C(4) ···C(18^{i})	3·67	C(14)···O(16^{i})	3·45
C(15)···O(16^{ii})	3·56		
TMPSO			
C(2) ···C(14^{iii})	3·45	C(4) ···O(16^{iv})	3·68
C(5) ···O(16^{iv})	3·43	C(6) ···O(6^{v})	3·62
C(7) ···C(14^{vi})	3·47	C(10)···O(19^{i})	3·42
C(12)···O(16^{vii})	3·59	C(18)···O(10^{i})	3·33
TMPSO2			
C(5) ···O(20^{viii})	3·37	C(6) ···C(14^{ix})	3·61
C(6) ···O(16^{x})	3·40	C(7) ···O(16^{x})	3·20
C(10)···O(19^{xi})	3·46	C(14)···O(19^{xi})	3·57
C(15)···O(19^{xi})	3·60	C(17)···O(20^{xii})	3·57

i	x,	$1+y$,	z	ii	$1-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
iii	$-x$,	$\frac{3}{2}+y$,	$\frac{1}{2}-z$	iv	x,	$\frac{3}{2}-y$,	$\frac{1}{2}+z$
v	x,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$	vi	$-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$
vii	$1-x$,	$-\frac{1}{2}+y$,	$\frac{1}{2}-z$	viii	$-x$,	$\frac{1}{2}+y$,	$\frac{1}{2}-z$
ix	$1-x$,	$1-y$,	$1-z$	x	$2-x$,	$1-y$,	$1-z$
xi	$1+x$,	$\frac{1}{2}-y$,	$\frac{1}{2}+z$	xii	$1+x$,	y,	z

Molecular packing

The molecular packings and intermolecular atomic distances within 3·7 Å in the three compounds are shown in Fig. 3 and Table 8.

Short intermolecular atomic distances less than 3·4 Å are C(18)···O(19) (3·33 Å) in TMPSO, C(17)···O(16) (3·20 Å) and C(5)···O(20) (3·37 Å) in TMPSO2; no such short distance is observed in TMPS.

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