Fig. 4. Stereoview (*ORTEP*) of the crystal packing. The dimensions of the box of enclosure are: $X = 2a$, $Y = 1b$, and $Z = 2c$.

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The Structures of 2,4,6-Tri-*tert*-butyl-7,8,9-dithiazabicyclo[4.3.0]nona-1(9),2,4-triene and Its 7-Oxide

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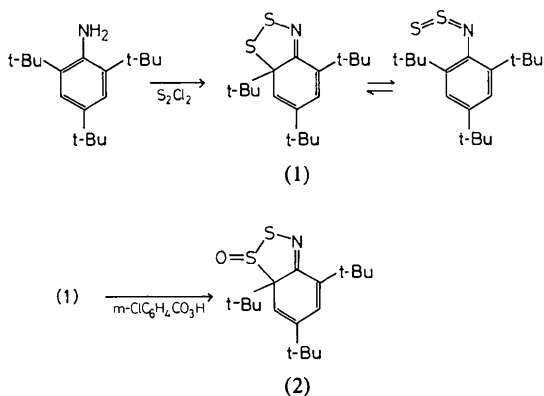
Abstract

The crystal and molecular structures of 2,4,6-tri-*tert*-butyl-7,8,9-dithiazabicyclo[4.3.0]nona-1(9),2,4-triene (1) and its 7-oxide (2) have been determined by X-ray diffraction. Crystals of (1) are monoclinic, space group $P2_1/c$, with cell dimensions: $a = 15.736$ (4), $b = 10.083$ (1), $c = 13.041$ (3) Å, $\beta = 115.31$ (2)° and $Z = 4$. Crystals of (2) are triclinic, $P\bar{1}$, $a = 16.724$ (4), $b = 7.115$ (2), $c = 9.910$ (2) Å, $\alpha = 106.65$ (3), $\beta = 118.45$ (2), $\gamma = 72.53$ (2)° and $Z = 2$. The structures were solved by the heavy-atom method and refined by the block-diagonal least-squares method. The final R values were 0.045 for (1) and 0.039 for (2). The molecular moieties of the oxide and non-oxide are very similar. One of the *tert*-butyl groups is axial to the molecular plane in each molecule. In (2) the sulphinyl oxygen is *trans* to this *tert*-butyl group across the S—C

bond with a torsion angle of 150°. The S—S, S—N and S—C distances are 2·084, 1·656 and 1·843 Å in (1) and 2·119, 1·679 and 1·881 Å in (2), respectively.

Introduction

Reaction of 2,4-di-*tert*-butyl-6-methylaniline with disulphur dichloride gave black-reddish crystals of 2,4-di-*tert*-butyl-6-methyl-*N*-thiosulphinylaniline (Inagaki, Okazaki & Inamoto, 1975), whose structure has recently been reported (Iwasaki, 1979). On the other hand, a similar reaction with 2,4,6-tri-*tert*-butylaniline gave (1), a different type of compound. The compound is yellow in the solid state, but reddish in solution. In solution, this compound is found by NMR to be a tautomeric mixture of a cyclic form (1) and *N*-thiosulphinylaniline (Inagaki *et al.*, 1975). Oxidation of (1) with *m*-chloroperbenzoic acid gave a sulphoxide (2) (Inagaki, Okazaki & Inamoto, 1978). Spectroscopic data and chemical evidence were not sufficient for the elucidation of the structure of this oxidation product. X-ray analyses were carried out on (1) and (2) in order to determine the molecular structures of these new heterocyclic compounds and to facilitate an understanding of their reactions.

(1)

(2)

Experimental

Crystals of (1) were grown from a methanol solution. They are yellow prisms but reddish in solution owing to the formation of a mixture of two tautomeric isomers. Crystals of (2) were also grown from a methanol solution. They are pale-yellow flat plates. Crystal data are listed in Table 1.

Intensity data of each compound were collected on a Rigaku automatic diffractometer using graphite-monochromated Mo $K\alpha$ radiation. Specimens of (1) and (2) with approximate dimensions $0.3 \times 0.2 \times 0.3$ mm and $0.13 \times 0.30 \times 0.35$ mm, respectively, were used. Reflexions within the range $2\theta \le 55°$ were measured by the ω–2θ scan technique with a scanning speed of $4°$ min^{-1} in 2θ and scan widths of $\Delta\omega = 1.2°$ +

Table 1. *Crystal data*

	(1)	(2)
	$C_{18}H_{29}NS_2$	$C_{18}H_{29}NOS_2$
M_r	323·55	339·55
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a	15·736 (4) Å	16·724 (4) Å
b	10·083 (1)	7·115 (2)
c	13·041 (3)	9·910 (2)
α		106·65 (3)°
β	115·31 (2)	118·45 (2)
γ		72·53 (2)
U	1870·5 (6) Å^3	974·4 (3) Å
Z	4	2
D_x	1·149 Mg m^{-3}	1·157 Mg m^{-3}
$F(000)$	704	368
m.p.	371·7–372·7 K	397·9–398·9 K

$0.5°$ tan θ for (1) and $\Delta\omega = 1.3° + 0.5°$ tan θ for (2). At both ends of the scan range 10 s background counts were taken for each reflexion. Three standard reflexions, measured after every 50 reflexions, showed no decrease in intensity during the measurements. For (1), 2814 reflexions had $|F_o| \ge 3\sigma(F_o)$ and were considered as observed. For (2), 3415 reflexions were obtained with $|F_o| \ge 3\sigma(F_o)$. No absorption corrections were applied.

Structure determination

For each compound, a sharpened three-dimensional Patterson synthesis was calculated from which the coordinates of the S atoms could be determined. A sulphur-phased Fourier synthesis then made it possible to locate all the non-hydrogen atoms. The structure was refined using the block-diagonal least-squares method. When the R values were 0·080 and 0·074 for (1) and (2), respectively, difference syntheses were calculated which revealed the positions of all the H atoms. All the atoms were then refined with several cycles of block-diagonal least squares, using anisotropic temperature factors for the non-hydrogen atoms and isotropic ones for the H atoms. The quantity minimized was $\sum w(|F_o| - K^{-1}|F_c|)^2$. For (1), $w = (20/|F_o|)^2/\sigma(F_o)$ if $|F_o| \ge 20$ and $w = 1/\sigma(F_o)$ if $|F_o| < 20$. For (2), $w = 0.7$ if $|F_o| < 4$, $w = 1.0$ if $4 \le |F_o| \le 16$ and $w = (16/|F_o|)^2$ if $|F_o| > 16$. The final R values are 0·045 for (1) and 0·039 for (2). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Final atomic parameters and their estimated standard deviations are given in Tables 2 and 3.*

Table 2. *Atomic parameters for* (1) *with their estimated standard deviations*

Table 3. *Atomic parameters for* (2) *with their estimated standard deviations*

(a) Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters of the non-hydrogen atoms

	x	y	z	B_{eq} (Å^2)
S(1)	1420 (0)	592 (1)	3751 (1)	4·0
S(2)	649 (0)	2348 (1)	3378 (1)	3·4
N	2474 (1)	1270 (2)	4423 (2)	3·2
C(1)	2524 (1)	2544 (2)	4380 (2)	2·5
C(2)	3375 (1)	3257 (2)	5144 (2)	2·7
C(3)	3237 (1)	4489 (3)	5443 (2)	3·0
C(4)	2316 (1)	5142 (2)	5027 (2)	2·8
C(5)	1585 (1)	4610 (3)	4167 (2)	2·9
C(6)	1678 (1)	3374 (2)	3581 (2)	2·6
C(21)	4334 (1)	2569 (3)	5628 (2)	3·3
C(22)	4381 (2)	1487 (3)	6477 (2)	5·1
C(23)	5130 (1)	3551 (3)	6253 (3)	5·6
C(24)	4518 (2)	1964 (3)	4667 (3)	5·3
C(41)	2267 (1)	6456 (3)	5591 (2)	3·6
C(42)	1261 (2)	7005 (3)	5102 (3)	6·2
C(43)	2592 (2)	6249 (3)	6865 (2)	4·9
C(44)	2910 (2)	7474 (3)	5407 (3)	5·7
C(61)	1732 (1)	3696 (3)	2422 (2)	2·9
C(62)	2583 (1)	4565 (3)	2621 (2)	3·9
C(63)	1788 (2)	2428 (3)	1813 (2)	4·4
C(64)	845 (1)	4460 (3)	1648 (2)	4·3

(a) Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters of the non-hydrogen atoms

	x	y	z	B_{eq} (Å^2)
S(1)	1521 (0)	829 (1)	6961 (1)	3·9
S(2)	688 (0)	1096 (1)	4585 (1)	2·9
O	390 (1)	−828 (2)	3713 (2)	4·0
N	2562 (1)	98 (3)	6918 (2)	3·5
C(1)	2586 (1)	141 (3)	5656 (2)	2·6
C(2)	3416 (1)	−904 (3)	5376 (2)	2·7
C(3)	3265 (1)	−1581 (3)	3884 (2)	2·9
C(4)	2353 (1)	−1319 (3)	2546 (2)	2·7
C(5)	1636 (1)	−95 (3)	2787 (2)	2·6
C(6)	1742 (1)	1097 (3)	4357 (2)	2·5
C(21)	4365 (1)	−1285 (3)	6759 (2)	3·3
C(22)	4406 (2)	−2911 (4)	7541 (3)	4·7
C(23)	4549 (2)	654 (4)	7940 (3)	4·7
C(24)	5149 (1)	−2027 (4)	6227 (3)	4·4
C(41)	2277 (1)	−2413 (3)	933 (2)	3·4
C(42)	2560 (3)	−4655 (4)	925 (3)	6·4
C(43)	2910 (2)	−1733 (6)	534 (3)	6·0
C(44)	1296 (2)	−1954 (5)	−330 (3)	5·1
C(61)	1748 (1)	3372 (3)	4445 (2)	3·3
C(62)	903 (2)	4205 (3)	3064 (3)	4·6
C(63)	1736 (2)	4684 (3)	5958 (3)	4·9
C(64)	2621 (2)	3484 (4)	4359 (3)	4·3

(b) Atomic coordinates ($\times 10^3$) and thermal parameters of the hydrogen atoms

	x	y	z	B (Å^2)
H(3)	380 (1)	505 (2)	605 (2)	3·5 (5)
H(5)	93 (1)	500 (2)	383 (2)	4·8 (6)
H(21)	398 (2)	80 (3)	607 (2)	7·1 (7)
H(22)	415 (2)	171 (3)	700 (2)	7·0 (7)
H(23)	500 (1)	106 (3)	682 (2)	5·7 (6)
H(24)	503 (2)	382 (3)	686 (2)	6·9 (7)
H(25)	577 (1)	306 (3)	649 (2)	5·9 (7)
H(26)	512 (1)	442 (3)	585 (2)	6·0 (7)
H(27)	514 (2)	150 (3)	495 (2)	5·1 (6)
H(28)	460 (2)	276 (3)	412 (2)	7·7 (8)
H(29)	409 (1)	129 (3)	426 (2)	5·4 (6)
H(41)	109 (2)	724 (3)	426 (2)	7·7 (8)
H(42)	79 (2)	635 (3)	520 (2)	6·7 (7)
H(43)	133 (2)	786 (3)	538 (2)	6·7 (7)
H(44)	215 (1)	568 (3)	700 (2)	5·4 (6)
H(45)	265 (2)	716 (3)	731 (2)	6·5 (7)
H(46)	330 (1)	591 (3)	732 (2)	5·6 (6)
H(47)	292 (2)	829 (3)	572 (2)	6·8 (7)
H(48)	358 (2)	716 (3)	565 (2)	7·9 (8)
H(49)	267 (2)	759 (3)	456 (2)	6·9 (7)
H(61)	256 (1)	545 (3)	295 (2)	6·3 (7)
H(62)	316 (1)	413 (2)	306 (2)	4·8 (6)
H(63)	264 (1)	479 (3)	197 (2)	5·2 (6)
H(64)	238 (1)	195 (3)	218 (2)	5·1 (6)
H(65)	189 (1)	270 (3)	114 (2)	4·8 (6)
H(66)	121 (2)	184 (3)	157 (2)	7·3 (8)
H(67)	89 (1)	457 (3)	88 (2)	5·0 (6)
H(68)	24 (2)	398 (3)	148 (2)	6·0 (7)
H(69)	86 (1)	533 (3)	196 (2)	5·4 (6)

(b) Atomic coordinates ($\times 10^3$) and thermal parameters of the hydrogen atoms

	x	y	z	B (Å^2)
H(3)	375 (1)	−230 (3)	364 (3)	3·3 (5)
H(5)	104 (1)	13 (3)	198 (2)	3·5 (5)
H(21)	430 (2)	−415 (4)	685 (3)	4·7 (6)
H(22)	394 (2)	−251 (4)	793 (3)	4·8 (6)
H(23)	499 (2)	−311 (4)	841 (3)	5·5 (6)
H(24)	456 (2)	159 (4)	738 (3)	4·9 (6)
H(25)	412 (2)	110 (4)	840 (3)	5·4 (6)
H(26)	515 (2)	38 (4)	876 (3)	4·5 (5)
H(27)	570 (2)	−212 (4)	711 (3)	4·5 (5)
H(28)	510 (2)	−334 (4)	557 (3)	5·4 (6)
H(29)	510 (2)	−106 (4)	567 (3)	6·1 (7)
H(41)	210 (2)	−505 (5)	124 (4)	9·2 (9)
H(42)	312 (2)	−504 (5)	176 (3)	6·9 (7)
H(43)	256 (2)	−541 (4)	−3 (3)	6·5 (7)
H(44)	350 (2)	−208 (5)	122 (4)	7·7 (8)
H(45)	286 (2)	−237 (4)	−48 (3)	6·4 (7)
H(46)	275 (2)	−30 (5)	57 (4)	7·1 (8)
H(47)	126 (2)	−263 (4)	−133 (3)	5·3 (6)
H(48)	91 (2)	−244 (4)	−11 (3)	6·4 (7)
H(49)	109 (2)	−51 (5)	−39 (4)	7·0 (8)
H(61)	96 (2)	351 (5)	210 (4)	6·8 (7)
H(62)	34 (2)	414 (4)	302 (3)	5·8 (6)
H(63)	89 (2)	562 (4)	317 (3)	4·7 (6)
H(64)	114 (2)	481 (4)	604 (3)	6·4 (7)
H(65)	224 (2)	417 (4)	680 (3)	4·5 (5)
H(66)	178 (2)	596 (4)	598 (3)	5·7 (6)
H(67)	318 (2)	315 (4)	526 (3)	5·1 (6)
H(68)	268 (2)	266 (4)	343 (3)	4·8 (6)
H(69)	256 (2)	486 (4)	426 (3)	4·9 (6)

Results and discussion

Fig. 1 shows stereoscopic views of the molecules of (1) and (2). Bond lengths and angles with their estimated standard deviations are listed in Tables 4 and 5, respectively.

It has been revealed that molecules of (1) are in a cyclic form, of $5H$-1,2,3-dithiazole type, formed by

Table 4. *Bond lengths* (Å)

	(1)	(2)		(1)	(2)		(1)	(2)
S(1)–S(2)	2·084 (1)	2·119 (1)	C(41)–C(43)	1·530 (4)	1·525 (5)	C(42)–H(42)	1·04 (3)	0·94 (4)
S(1)–N	1·656 (2)	1·679 (2)	C(41)–C(44)	1·530 (4)	1·523 (4)	C(42)–H(43)	0·93 (3)	0·94 (4)
S(2)–C(6)	1·843 (3)	1·881 (2)	C(61)–C(62)	1·526 (4)	1·530 (4)	C(43)–H(44)	0·98 (3)	0·90 (4)
S(2)–O		1·481 (2)	C(61)–C(63)	1·526 (4)	1·528 (4)	C(43)–H(45)	1·07 (3)	0·96 (3)
N–C(1)	1·290 (3)	1·279 (3)	C(61)–C(64)	1·536 (4)	1·529 (4)	C(43)–H(46)	1·07 (3)	0·97 (4)
C(1)–C(6)	1·540 (3)	1·519 (3)	C(3)–H(3)	1·06 (2)	0·93 (3)	C(44)–H(47)	0·92 (3)	0·95 (3)
C(1)–C(2)	1·470 (3)	1·478 (3)	C(5)–H(5)	1·01 (3)	0·93 (3)	C(44)–H(48)	1·02 (3)	0·95 (3)
C(2)–C(3)	1·348 (4)	1·338 (3)	C(22)–H(21)	0·94 (3)	0·95 (3)	C(44)–H(49)	1·01 (3)	0·99 (4)
C(3)–C(4)	1·468 (4)	1·471 (3)	C(22)–H(22)	0·93 (3)	0·96 (3)	C(62)–H(61)	1·00 (3)	0·98 (4)
C(4)–C(5)	1·329 (3)	1·334 (3)	C(22)–H(23)	0·98 (3)	0·95 (3)	C(62)–H(62)	0·96 (3)	0·94 (3)
C(5)–C(6)	1·502 (3)	1·497 (3)	C(23)–H(24)	0·92 (3)	0·99 (3)	C(62)–H(63)	0·92 (3)	0·97 (3)
C(2)–C(21)	1·530 (4)	1·534 (3)	C(23)–H(25)	1·04 (3)	0·96 (3)	C(63)–H(64)	0·97 (3)	1·00 (3)
C(4)–C(41)	1·533 (4)	1·527 (3)	C(23)–H(26)	1·01 (3)	0·95 (3)	C(63)–H(65)	0·99 (3)	0·92 (3)
C(6)–C(61)	1·583 (4)	1·598 (3)	C(24)–H(27)	1·00 (3)	0·92 (3)	C(63)–H(66)	1·01 (3)	0·93 (3)
C(21)–C(22)	1·534 (4)	1·536 (4)	C(24)–H(28)	1·11 (3)	0·97 (3)	C(64)–H(67)	1·03 (3)	0·96 (3)
C(21)–C(23)	1·530 (5)	1·535 (4)	C(24)–H(29)	0·95 (3)	0·96 (3)	C(64)–H(68)	1·01 (3)	0·97 (3)
C(21)–C(24)	1·530 (4)	1·535 (4)	C(42)–H(41)	1·04 (3)	1·09 (4)	C(64)–H(69)	0·96 (3)	0·98 (3)
C(41)–C(42)	1·535 (5)	1·521 (5)						

Table 5. *Bond angles* (°)

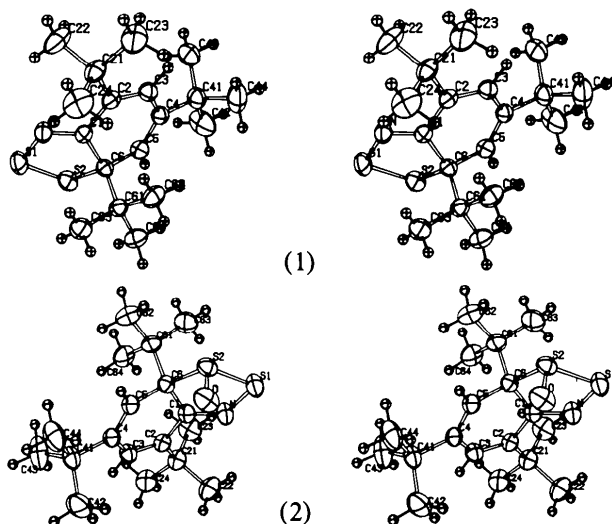|	(1)	(2)		(1)	(2)		(1)	(2)
S(2)S(1)N	97·13 (9)	98·56 (8)	C(3)C(4)C(41)	117·0 (2)	118·3 (2)	C(42)C(41)C(44)	109·1 (3)	108·9 (3)
S(1)S(2)C(6)	93·17 (8)	90·27 (7)	C(5)C(4)C(41)	123·5 (2)	123·0 (2)	C(43)C(41)C(44)	109·0 (2)	107·2 (2)
S(1)NC(1)	117·0 (2)	116·9 (2)	S(2)C(6)C(5)	105·5 (2)	107·0 (1)	C(6)C(61)C(62)	110·9 (2)	109·7 (2)
S(2)C(6)C(1)	104·1 (2)	107·6 (1)	S(2)C(6)C(61)	112·3 (2)	107·2 (1)	C(6)C(61)C(63)	111·3 (2)	111·9 (2)
NC(1)C(6)	121·3 (2)	121·2 (2)	C(1)C(6)C(61)	112·0 (2)	112·6 (2)	C(6)C(61)C(64)	109·0 (2)	109·7 (2)
S(1)S(2)O		108·66 (8)	C(5)C(6)C(61)	111·9 (2)	110·6 (2)	C(62)C(61)C(63)	109·2 (2)	109·0 (2)
C(6)S(2)O		107·2 (1)	C(2)C(21)C(22)	110·8 (2)	110·1 (2)	C(62)C(61)C(64)	108·0 (2)	108·2 (2)
C(2)C(1)C(6)	117·8 (2)	118·3 (2)	C(2)C(21)C(23)	111·5 (2)	110·2 (2)	C(63)C(61)C(64)	108·4 (2)	108·3 (2)
C(1)C(2)C(3)	115·7 (2)	115·9 (2)	C(2)C(21)C(24)	110·0 (2)	111·2 (2)	C(2)C(3)H(3)	121 (1)	120 (2)
C(2)C(3)C(4)	124·2 (2)	124·9 (2)	C(22)C(21)C(23)	107·5 (3)	110·3 (2)	C(4)C(3)H(3)	115 (1)	115 (2)
C(3)C(4)C(5)	119·5 (2)	118·7 (2)	C(22)C(21)C(24)	109·9 (2)	107·3 (2)	C(4)C(5)H(5)	125 (1)	123 (2)
C(4)C(5)C(6)	121·8 (2)	122·1 (2)	C(23)C(21)C(24)	107·2 (3)	107·7 (2)	C(6)C(5)H(5)	114 (1)	115 (2)
C(1)C(6)C(5)	110·6 (2)	111·6 (2)	C(4)C(41)C(42)	111·5 (2)	109·4 (2)			
NC(1)C(2)	120·8 (2)	120·2 (2)	C(4)C(41)C(43)	109·9 (2)	109·3 (2)	Mean values (*tert*-Bu)		
C(1)C(2)C(21)	120·8 (2)	119·9 (2)	C(4)C(41)C(44)	109·4 (2)	112·0 (2)	CCH	111 (2)	110 (2)
C(3)C(2)C(21)	123·4 (2)	124·0 (2)	C(42)C(41)C(43)	107·8 (3)	110·0 (3)	HCH	107 (2)	109 (2)

Fig. 1. Stereoscopic views of (1) and (2). Thermal ellipsoids of the non-hydrogen atoms are at the 50% probability level (*ORTEP*; Johnson, 1965).

cycloaddition of the —N=S=S group to C(6). On the other hand, a similar reaction with 2,4-di-*tert*-butyl-6-methylaniline gave *N*-thiosulphinylaniline, not a cyclic compound. In (1) and (2) S–S and N–S are single bonds and N–C is a double bond, while in 2,4-di-*tert*-butyl-6-methylaniline S=S and N=S have double-bond lengths (1·898 and 1·548 Å, respectively) and C–N is a single bond (1·420 Å) (Iwasaki, 1979). X-ray analysis of (2) shows that the oxidation of (1) occurs at S(2), not at S(1), contrary to the chemical behaviour.

The two molecules (1) and (2) are remarkably similar as far as the molecular moieties are concerned, in spite of the different oxidation state of the S atom. The planarity of the six-membered ring is not maintained when the intramolecular addition occurs. The deviations of atoms from some least-squares planes are shown in Table 6. In the six-membered ring, C(1), C(2), C(3) and C(4) are coplanar but C(5) and C(6) are out of plane of the other four atoms by 0·27 and 0·60 Å for (1) and 0·22 and 0·53 Å for (2), respectively. In both

compounds the five-membered ring is approximately in an envelope conformation. S(2) deviates from the plane of the other four atoms by 0·55 Å for (1) and 0·50 Å for (2). Similar deviations from planarity have been observed for derivatives of 1-oxo-1λ^4,2,4-thiadiazolidin-3-one (Schuckmann, Fuess, Mösinger & Ried, 1978), and for phenanthro[9,10-c][1,2,5]thiadiazol-1-one hydrate (Arora, 1974).

Table 6. Least-squares planes

The equations are of the form $AX + BY + CZ + D = 0$, where X, Y and Z are along a, b and c^* respectively. Atoms which define the planes are marked with asterisks.

Plane (I) C(1)—C(4)

Molecule (1)	$0·502X + 0·364Y - 0·785Z + 2·348 = 0$
Molecule (2)	$0·454X + 0·889Y - 0·488Z + 0·129 = 0$

Plane (II) S(1), N, C(1), C(6)

Molecule (1)	$0·608X - 0·150Y - 0·780Z + 3·435 = 0$
Molecule (2)	$-0·306X - 0·850Y - 0·429Z + 2·004 = 0$

Deviations (Å) of atoms from the planes

Plane	(I)		(II)	
Molecule	(1)	(2)	(1)	(2)
S(1)	−0·834	−0·835	−0·017*	0·017*
S(2)	−0·349	−0·359	−0·550	0·503
O		−1·596		1·976
N	−0·563	−0·540	0·043*	−0·041*
C(1)	−0·004*	−0·002*	−0·048*	0·041*
C(2)	0·009*	0·005*	−0·304	0·315
C(3)	−0·009*	−0·006*	−0·999	0·972
C(4)	0·005*	0·004*	−1·456	1·400
C(5)	0·269	0·224	−0·991	0·957
C(6)	0·596	0·531	0·023*	−0·015*
C(21)	−0·071	−0·078	0·108	−0·060
C(41)	−0·231	−0·194	−2·410	2·298
C(61)	2·152	2·095	1·484	−1·448
E.s.d.'s	0·014	0·009	0·070	0·062

The torsion angles (Fig. 2) again reflect the similarity of the two compounds. The C(6)—C(61) bond is axial to the molecular plane in both molecules. In (2) the sulphinyl oxygen is pseudo-axial to the molecular plane and *trans* to the *tert*-butyl group across the S(2)—C(6) bond, with a torsion angle of 150°.

The lengths of C(2)—C(3) and C(4)—C(5) are 1·348 and 1·329 Å for (1), and 1·338 and 1·334 Å for (2), respectively, which suggest greater double-bond character than is normal for an aromatic C—C bond. C(1)—C(2) and C(3)—C(4) are longer than the usual C—C lengths in benzene rings. The lengths of C(1)—C(6) and C(5)—C(6) are 1·540 and 1·502 Å in (1) and 1·519 and 1·497 Å in (2), respectively. They are close to the normal C_{sp^3}–C_{sp^2} single-bond length. C(5)—C(6) is, however, shorter than C(1)—C(6) in both molecules, indicating at least some conjugation within the —C=C—C=C— group in the six-membered ring. The length of S(1)—S(2) (2·084 Å) in (1) is normal for a single S—S bond. For (2) the corresponding value is 2·119 Å. The S—N distances [1·656 for (1) and 1·679 Å for (2)] are in the range often found for S—N single bonds (1·63 ~ 1·68 Å), although they are shorter than the 1·74 Å calculated theoretically for a S—N single bond from Pauling's (1960) atomic radii. Some $d\pi$–$p\pi$ overlap may therefore be taking place. The S(2)—C(6) lengths are 1·843 and 1·881 Å for (1) and (2), respectively, significantly longer than normal for S—C single bonds (1·80 Å), which may be attributed to the bulky *tert*-butyl group at C(6). The C(6)—C(61) lengths are also significantly longer than normal C—C single bonds at 1·583 and 1·598 Å for (1) and (2), respectively. In both molecules C(2)—C(21) and C(4)—C(41) have normal C_{ar}–$C_{tert\text{-}Bu}$ lengths. In (2) the sulphinyl S—O length is 1·481 Å, which is normal for sulphoxide and agrees closely with the values of 1·473 and 1·468 Å found by Schuckmann *et al.*
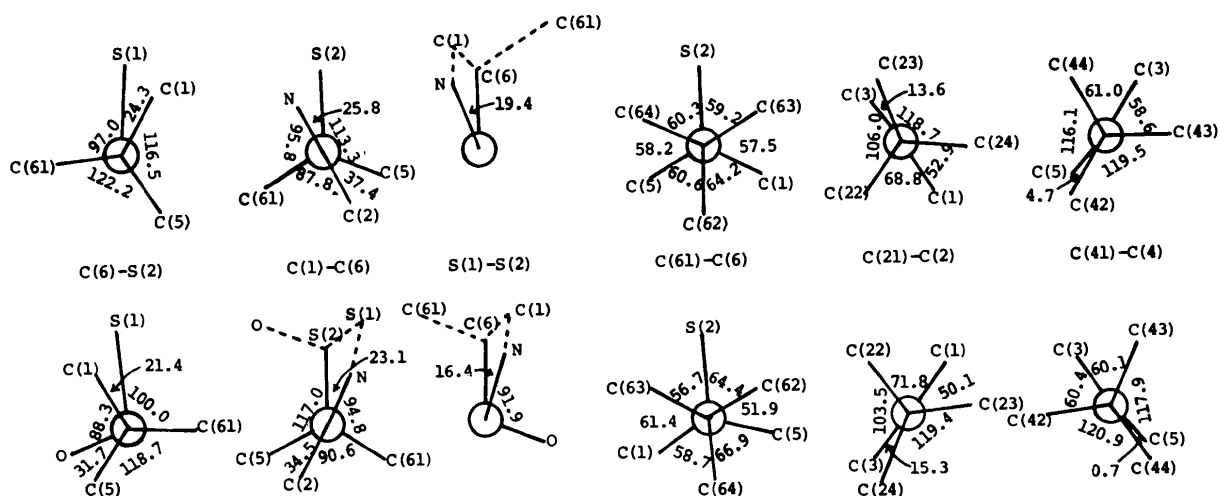

Fig. 2. Torsion angles (°) in the molecules [upper row, (1); lower row, (2)]. The e.s.d.'s are within the range 0·1–0·3° for both molecules.

(1978). The C(1)—N lengths, 1·290 Å for (1) and 1·279 Å for (2), are those of normal non-conjugated C—N double bonds.

Slight differences in the bond lengths between molecules (1) and (2) are noticed. Longer S—C and S—S bonds are observed in (2) than in (1), which is a consequence of the electronic effect of the sulphinyl S atom. Such an increase in the bond lengths in sulphinyl compounds, compared to the non-oxide or sulphonate, has also been observed in 2,2,6,6-tetramethyl-4-piperidone derivatives (Sato, Yoshioka & Tamura, 1975) and cyclooctasulphur oxide (Steudel, Luger, Bradaczek & Rebsch, 1973).

The bond angles around C(6) are tetrahedral. The sums of the three bond angles about C(1) are 359·9° for (1) and 359·7° for (2). The bond angles in the six-membered ring are similar in both molecules. The C(2)C(3)C(4) and C(4)C(5)C(6) angles are larger, and C(2)C(1)C(6), C(1)C(2)C(3) and C(3)C(4)C(5) smaller than 120°. The endocyclic bond angles opposite the alkyl groups have smaller values than those in benzene derivatives. The S(2)S(1)N angles are 97·1 and 98·6° for (1) and (2), respectively. These values are slightly larger than the SSC angles in five-membered rings such as 1,2,4-dithiazole derivatives (Hordvik, 1966). The S(1)S(2)C(6) angle in (1) (93·2°) is a normal value. The corresponding angle in (2) is 90·3°, smaller than that in (1). In some five-membered heterocyclic sulphoxides, angles of 86·9 and 86·3° have been observed for NSC (Schuckmann et al., 1978) and 86·9° for CSC (Thorup, 1971). The other angles related to the sulphinyl group, S(1)S(2)O and C(6)S(2)O, are 108·7 and 107·2°, respectively. These are close to the XSO (X = N or C) angles in the above heterocyclic compounds and normal open-chained sulphoxides (Iwasaki, Mitamura & Tsuchihashi, 1978).

Projections of the crystal structures are shown in Figs. 3 and 4. Intermolecular contacts are all of the van der Waals type.
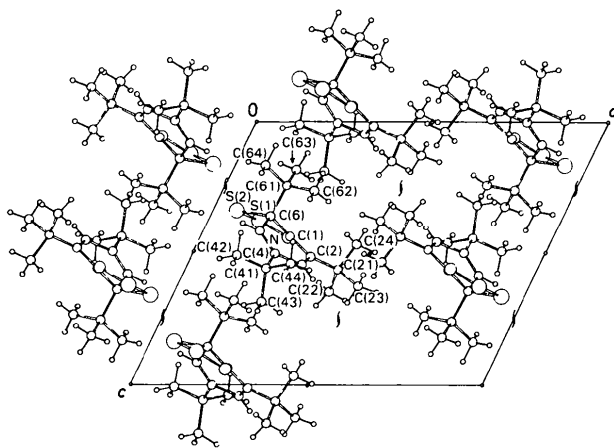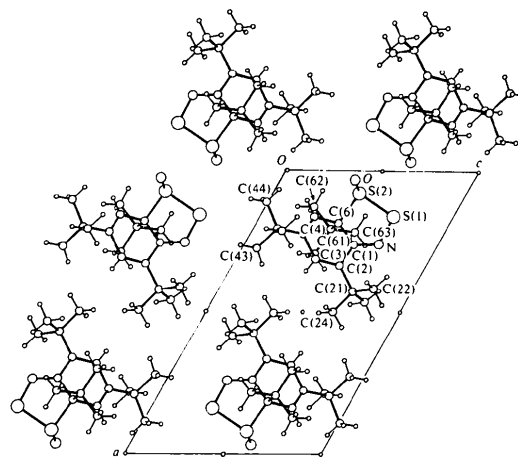

Fig. 4. Projection of the structure of (2) along the b^* axis.

All crystallographic computations were performed on the HITAC 8800/8700 computer of the Computer Center of the University of Tokyo, using the local version of the program system *UNICS* (Crystallographic Society of Japan, 1967; Sakurai, Ito, Iwasaki, Watanabe & Fukuhara, 1967). The author is grateful to Professor Naoki Inamoto and Dr Renji Okazaki of the University of Tokyo for supplying the samples and to Dr Ei-ichi Asada and Mrs Midori Goto of the National Chemical Laboratory for Industry for the use of the X-ray diffractometer.

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Fig. 3. Projection of the structure of (1) along the b axis.