the counting errors (Grant, Killean & Lawrence, 1969).*

Discussion. Final positional parameters are listed in Table 1. Bond distances and angles are given in Figs. 1 and 2, respectively. The mean estimated standard deviations are 0·006 Å for bond lengths and 0·3° for angles. A perspective view of the molecule is shown in Fig. 3. Some of the bond lengths, especially those related by C(9), deviate significantly from their standard values.

The ring conformations are as follows:

	Ring	Conformation
A:	C(1), C(2), C(3), C(4), C(5), C(10)	chair
B:	C(5), C(6), C(7), C(8), C(9), C(10)	chair
C:	C(8), C(9), C(11), C(12), O(25), C(15), C(14)	boat
D:	C(13), C(14), C(15), C(16), C(17)	envelope
E:	C(4), C(5), C(6), O(27), C(30)	envelope.

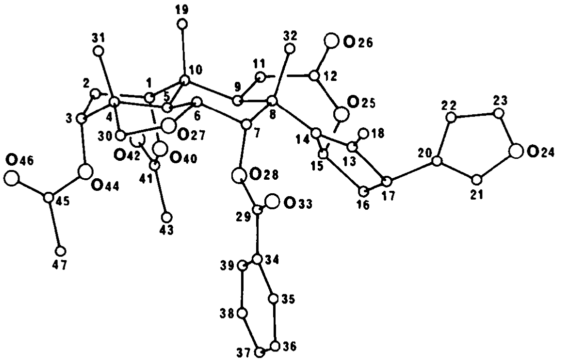

Fig. 3. Perspective view of the molecule with the atom-numbering system.

Rings *A*, *B*, *C* and *E* are fused with *trans* ring junctions. The seven-membered ring may be described as consisting of the three planes C(14)—C(15)—O(25), C(8)—C(12)—O(25)—C(14), and C(8)—C(9)—C(11)—C(12). The bonds C(15)—O(25) and C(17)—C(20) are *cis* in relation to each other.

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* Lists of structure factors, anisotropic thermal parameters and H-atom positional parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35163 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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The Structure of 2,4,6-Tri-*tert*-butyl-*N*-sulphinylaniline

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(*Received 19 December 1979; accepted 29 February 1980*)

Abstract. $C_{18}H_{29}NOS$, $M_r = 307{\cdot}49$, monoclinic, $P2_1/n$, $a = 15{\cdot}871\ (2)$, $b = 11{\cdot}584\ (2)$, $c = 10{\cdot}062\ (2)$ Å, $\beta = 90{\cdot}12\ (1)°$, $U = 1849{\cdot}8\ (5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}104$ Mg m^{-3}, $F(000) = 672$. The final R value is 0·051 for 2491 observed reflexions. The S=O and N=S lengths are 1·436 and 1·494 Å, respectively, and the OSN and SNC angles are 121·9 and 131·7°, respectively. The terminal O atom is *cis* to the C atom across the N=S bond with a torsion angle of 0·6°. The molecule has approximate mirror symmetry, apart from the methyl groups in the 4-*tert*-butyl group.

Introduction. Reaction of 2,4,6-tri-*tert*-butylaniline with disulphur dichloride gave a heterocyclic compound, 2,4,6-tri-*tert*-butyl-7,8,9-dithiazabicyclo[4.3.0]-nona-1(9),2,4-triene (1). Treatment of (1) with Ph_3P in

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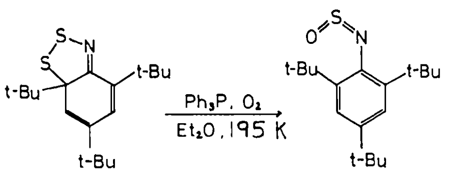
the presence of O_2 gave an aromatic compound 2,4,6-tri-*tert*-butyl-*N*-sulphinylaniline (2) (Inagaki, Hosogai, Okazaki & Inamoto, 1980). The determination of the crystal structure of this compound was carried out in order to reveal the nature of the *N*-sulphinyl group.



(1) (2)

The crystals were grown from an ethanol solution. They are orange prisms. Intensity data were collected on a Rigaku automatic diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. A crystal with approximate dimensions $0{\cdot}5 \times 0{\cdot}3 \times 0{\cdot}3$ mm was used. Reflexions within the range $2\theta \leq 55°$ were measured by the ω–2θ scan technique with a scan width of $\Delta\omega = 1{\cdot}1° + 0{\cdot}5° \tan\theta$ and a scanning speed of 4° min^{-1} in 2θ. At both ends of the scan range 10s background counts were taken for each reflexion. 2491 reflexions had $|F_o| \geq 3\sigma(F_o)$ and were considered as observed. No absorption corrections were applied.

The position of the S atom was determined from a sharpened three-dimensional Patterson map. A 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 value was 0·095, a difference synthesis was calculated, which revealed the positions of all the H atoms. All atoms were refined with the block-diagonal least-squares method using anisotropic temperature factors for the non-hydrogen atoms and isotropic for H. The quantity minimized was $\sum w(|F_o| - k^{-1}|F_c|)^2$ where $w = 0{\cdot}5$ if $|F_o| < 5$, $w = 1{\cdot}0$ if $5 \leq |F_o| \leq 20$ and $w = (20/|F_o|)^2$ if $|F_o| > 20$. The final R value was 0·051 for all the observed reflexions. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). All crystallographic computations were performed on the HITAC 8800/8700 computer of the Computer Center of the University of Tokyo, using a local version of the program system *UNICS* (1967). The final atomic parameters and their estimated standard deviations are given in Table 1.*

Table 1. *Atomic parameters with their estimated standard deviations*

(a) Atomic coordinates ($\times 10^4$) of the non-hydrogen atoms (the B_{eq} values are the equivalent isotropic temperature factors)

	x	y	z	B_{eq} (Å^2)
S	2747 (1)	5707 (1)	4560 (1)	6·0
O	3424 (2)	6508 (2)	4768 (3)	8·6
N	2744 (1)	4537 (2)	5186 (2)	4·2
C(1)	3341 (1)	3968 (2)	6040 (2)	3·1
C(2)	3248 (1)	4062 (2)	7430 (2)	3·2
C(3)	3848 (1)	3509 (2)	8199 (2)	3·4
C(4)	4501 (1)	2856 (2)	7676 (2)	3·2
C(5)	4536 (1)	2745 (2)	6317 (2)	3·4
C(6)	3961 (1)	3271 (2)	5457 (2)	3·3
C(21)	2512 (2)	4701 (2)	8112 (3)	4·0
C(22)	1667 (2)	4260 (3)	7592 (3)	5·7
C(23)	2517 (2)	4500 (3)	9620 (3)	5·8
C(24)	2589 (2)	6017 (2)	7913 (3)	5·5
C(41)	5143 (2)	2283 (2)	8606 (2)	4·1
C(42)	4688 (2)	1626 (3)	9708 (3)	6·0
C(43)	5700 (2)	3209 (3)	9219 (4)	7·7
C(44)	5704 (2)	1416 (3)	7879 (3)	6·5
C(61)	4054 (2)	3044 (2)	3946 (2)	4·2
C(62)	4646 (2)	2033 (4)	3683 (3)	7·2
C(63)	4426 (2)	4105 (3)	3263 (3)	6·7
C(64)	3210 (2)	2703 (3)	3316 (3)	6·6

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

	x	y	z	B (Å^2)
H(3)	380 (2)	357 (2)	915 (2)	4·4 (5)
H(5)	500 (1)	227 (2)	594 (2)	4·3 (5)
H(21)	156 (2)	436 (3)	665 (3)	6·6 (7)
H(22)	123 (2)	468 (3)	798 (3)	6·8 (7)
H(23)	160 (2)	336 (3)	781 (3)	7·3 (8)
H(24)	205 (2)	485 (2)	999 (3)	5·5 (6)
H(25)	306 (2)	482 (3)	1010 (3)	7·6 (8)
H(26)	245 (2)	367 (2)	983 (3)	5·9 (7)
H(27)	248 (2)	626 (3)	701 (3)	7·4 (8)
H(28)	216 (2)	642 (3)	846 (3)	6·4 (7)
H(29)	313 (2)	629 (3)	814 (3)	7·5 (8)
H(41)	429 (2)	100 (3)	931 (4)	9·4 (9)
H(42)	432 (2)	217 (3)	1025 (3)	7·1 (7)
H(43)	510 (2)	122 (3)	1026 (3)	5·9 (6)
H(44)	532 (2)	380 (3)	974 (3)	7·9 (8)
H(45)	612 (2)	287 (3)	986 (3)	7·7 (8)
H(46)	603 (2)	362 (3)	848 (3)	8·8 (9)
H(47)	608 (2)	103 (3)	852 (3)	7·1 (8)
H(48)	605 (2)	174 (3)	716 (3)	8·5 (9)
H(49)	532 (2)	78 (3)	744 (3)	7·6 (8)
H(61)	445 (2)	132 (3)	421 (3)	7·5 (8)
H(62)	525 (2)	222 (3)	400 (3)	7·4 (8)
H(63)	470 (2)	190 (3)	275 (3)	8·2 (8)
H(64)	503 (2)	419 (3)	363 (3)	7·9 (8)
H(65)	454 (2)	397 (3)	231 (3)	7·7 (8)
H(66)	416 (2)	482 (3)	347 (3)	9·3 (9)
H(67)	329 (2)	249 (3)	238 (3)	7·4 (8)
H(68)	276 (2)	325 (3)	342 (3)	8·5 (8)
H(69)	295 (2)	205 (3)	384 (4)	10·9 (10)

Discussion. Fig. 1 shows a stereoscopic view of the molecule. The bond lengths and angles with their estimated standard deviations are listed in Table 2. Newman projections of the molecule are shown in Fig.

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* Lists of the structure factors and anisotropic temperature factors for non-hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35175 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å) *and angles* (°) *with their estimated standard deviations*

S–O	1·436 (3)	C(21)–C(24)	1·542 (4)
S–N	1·494 (2)	C(4)–C(41)	1·534 (3)
N–C(1)	1·437 (3)	C(41)–C(42)	1·528 (4)
C(1)–C(2)	1·410 (3)	C(41)–C(43)	1·520 (5)
C(2)–C(3)	1·384 (3)	C(41)–C(44)	1·528 (4)
C(3)–C(4)	1·387 (3)	C(6)–C(61)	1·550 (4)
C(4)–C(5)	1·375 (3)	C(61)–C(62)	1·525 (5)
C(5)–C(6)	1·397 (3)	C(61)–C(63)	1·528 (5)
C(1)–C(6)	1·403 (3)	C(61)–C(64)	1·533 (5)
C(2)–C(21)	1·544 (3)	C(3)–H(3)	0·96 (3)
C(21)–C(22)	1·527 (4)	C(5)–H(5)	0·99 (2)
C(21)–C(23)	1·535 (4)	$C_{tert\text{-}Bu}$–H (mean)	1·00 (3)
OSN	121·9 (2)	C(22)C(21)C(23)	110·9 (2)
SNC(1)	131·7 (2)	C(23)C(21)C(24)	106·2 (2)
NC(1)C(2)	119·2 (2)	C(4)C(41)C(42)	110·1 (2)
NC(1)C(6)	118·4 (2)	C(4)C(41)C(43)	109·1 (2)
C(2)C(1)C(6)	122·3 (2)	C(4)C(41)C(44)	112·3 (2)
C(1)C(2)C(3)	116·5 (2)	C(42)C(41)C(43)	109·5 (3)
C(2)C(3)C(4)	123·7 (2)	C(42)C(41)C(44)	107·3 (2)
C(3)C(4)C(5)	117·4 (2)	C(43)C(41)C(44)	108·7 (3)
C(4)C(5)C(6)	123·2 (2)	C(6)C(61)C(62)	111·1 (3)
C(1)C(6)C(5)	116·8 (2)	C(6)C(61)C(63)	110·0 (2)
C(1)C(2)C(21)	123·9 (2)	C(6)C(61)C(64)	111·4 (2)
C(3)C(2)C(21)	119·6 (2)	C(62)C(61)C(63)	107·5 (3)
C(3)C(4)C(41)	120·0 (2)	C(62)C(61)C(64)	105·6 (3)
C(5)C(4)C(41)	122·6 (2)	C(63)C(61)C(64)	111·1 (3)
C(1)C(6)C(61)	125·2 (2)	C(2)C(3)H(3)	118 (2)
C(5)C(6)C(61)	118·0 (2)	C(4)C(3)H(3)	119 (2)
C(2)C(21)C(22)	110·6 (2)	C(4)C(5)H(5)	118 (1)
C(2)C(21)C(23)	111·4 (2)	C(6)C(5)H(5)	119 (1)
C(2)C(21)C(24)	110·9 (2)	CCH (*tert*-Bu, mean)	111 (2)
C(22)C(21)C(23)	106·9 (2)	HCH (*tert*-Bu, mean)	108 (3)

2. The molecule has approximate mirror symmetry, apart from the methyl groups in the 4-*tert*-butyl group. The sulphinyl oxygen is *cis* to C(1) across the S=N bond. In 2,4-di-*tert*-butyl-6-methyl-*N*-thiosulphinylaniline the terminal sulphur is also *cis* to the C atom across the S=N bond (Iwasaki, 1979). A comparison of the distances and angles of the N=S=O group in several related compounds is given in Table 3. The S=O length in the present molecule is 1·436 Å. This value is shorter than the normal S^{IV}=O lengths (1·47–1·50 Å) found in trivalent sulphoxides, but is nearly equal to those of divalent sulphoxides, such as HNSO (1·451 Å) and S_2O (1·459 Å; Tiemann, Hoeft, Lovas & Johnson, 1974). The S=N bond length is 1·494 Å, which is significantly shorter than the S=N double-bond lengths reported previously. As shown in Fig. 1, the thermal motions of the S and O atoms are considerable. Correction of the bond lengths due to riding motion (Busing & Levy, 1964) gave values of 1·447 Å for S=O and 1·502 Å for N=S.

The N=S length in *N*-thiosulphinylaniline is 1·548 Å. The shortening of the N=S bond in the *N*-sulphinyl group compared with that in the N=S=S group may be due to the greater electronegativity of oxygen compared with sulphur. In the case of *N*-phenyl-*N*′-sulphinylhydrazine, the distances and angles in the N=S=O group are rather different and the electronegativity of the O atom is changed because of the formation of a NH···OS hydrogen bond. The C–N distance in (2) is 1·437 Å, which is longer than that

Table 3. *Comparison of N-sulphinyl groups*

	N=S (Å)	S=O (Å)	NSO (°)	Reference
Present compound	1·494	1·436	121·9	
$PhSO_2NSO$	1·512	1·434	119·6	*a*
PhNHNSO	1·560	1·474	113·6	*b*
HNSO	1·512	1·451	120·4	*c*
(*tert*-Bu)$_2$(Me)PhNSS	1·548		119·9 (NSS)	*d*

References: (*a*) Déléris, Courseille, Kowalski & Dunoguès (1979). (*b*) Gieren & Dederer (1977). (*c*) Kirchhoff (1969). (*d*) Iwasaki (1979).

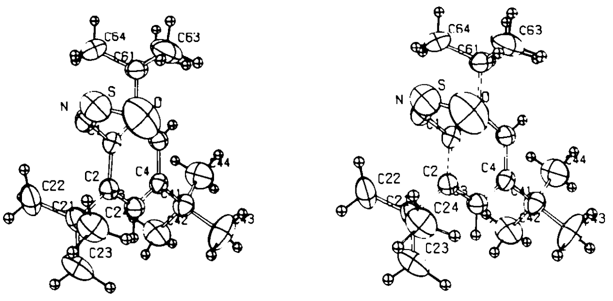

Fig. 1. Stereoscopic view of the molecule. Thermal ellipsoids of the non-hydrogen atoms are at the 50% probability level (*ORTEP*; Johnson, 1965).

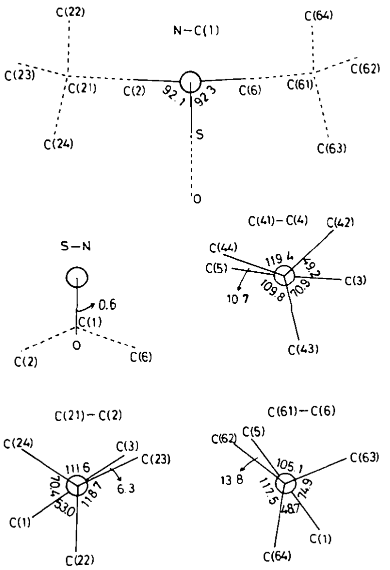

Fig. 2. Torsion angles (°). The e.s.d.'s are within the range 0·2–0·3°.

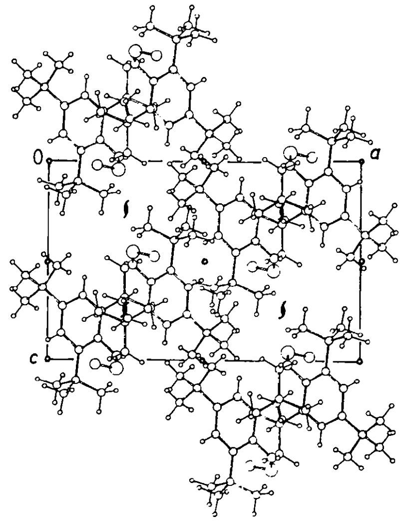

Fig. 3. Projection of the structure along the *b* axis.

(1·290 Å) in (1) (Iwasaki, 1980). The NSO angle is 121·9°, which is comparable to the values listed in Table 3 except for that of *N*-phenyl-*N'*-sulphinylhydrazine. The CNS angle is 131·7°. The corresponding angle for *N*-thiosulphinylaniline is 126·4°.

The C(1)—C(2) and C(1)—C(6) lengths are longer than the other C—C distances in the phenyl ring and the C(1)C(2)C(21) and C(1)C(6)C(61) angles are larger than 120° owing to the bulky *ortho* substituents. The short intramolecular non-bonding distances are S···C(24) 3·402 (3), S···C(63) 3·502 (4), S···H(27) 2·58 (3), S···H(66) 2·71 (4), N···C(21) 2·973 (3), N···C(22) 2·983 (4), N···C(61) 2·980 (3), N···C(64) 2·934 (4), N···H(21) 2·40 (3) and N···H(68) 2·32 (4) Å. The endocyclic bond angles opposite the *tert*-butyl groups are smaller than 120°.

Fig. 3 shows a projection of the structure along the *b* axis. There are no intermolecular contacts shorter than the sums of the van der Waals radii.

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Acta Cryst. (1980). B**36**, 1703–1706

Structure du Méthyl-4 (*N*-Méthyl *N*-phényl-amino)-6 Spiro[4.5]décène-6 Dione-1,8

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(*Reçu le* 10 *décembre* 1979, *accepté le* 10 *mars* 1980)

Abstract. $C_{18}H_{21}NO_2$, orthorhombic, $P2_12_12_1$, a = 11·679 (3), b = 15·007 (7), c = 8·879 (1) Å, V = 1557 ± 4 Å^3, ρ_o = 1·21, ρ_c = 1·21 Mg m^{-3} (for Z = 4). The structure was solved by the direct method and refined by full-matrix least squares to a final R = 0·056 for 1632 observed data recorded with Mo radiation. The compound has a spiran structure which results from the spiro-annelation of enolic lactones; its stereochemical study shows that the predominant diastereoisomer is that expected from chemical considerations.

Introduction. Ficini, Genêt & Revial (1979) ont entrepris l'étude du cours stérique de la spiro-annélation de lactones d'énols bicycliques par action du *N*-méthyl *N*-phényl-aminoacétylène. Ils observent la

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