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The *meso* and (±) Isomers of 1,4-Dimesityl-1,4-dithiabutane 1,4-Dioxide

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1,4-Dimesityl-1,4-dithiabutane 1,4-dioxide, $C_{20}H_{26}O_2S_2$, exists as two isomers. The *meso* isomer [monoclinic, $P2_1/n$, $a = 15\cdot851$ (6), $b = 11\cdot565$ (5), $c = 5\cdot157$ (1) Å, $\beta = 91\cdot32$ (2)°] possesses a center of symmetry. Both halves of the (±) isomer [triclinic, $P1$, $a = 13\cdot056$ (5), $b = 7\cdot860$ (2), $c = 4\cdot812$ (1) Å, $\alpha = 75\cdot57$ (2), $\beta = 94\cdot00$ (2), $\gamma = 85\cdot19$ (2)°] have the same conformation with both oxygen atoms having disordered positions. The conformations of the two isomers are different.

Experimental

Samples of the *meso* and (±) isomers of 1,4-dimesityl-1,4-dithiabutane 1,4-dioxides were obtained through the courtesy of Dr A. L. Ternay Jr of the Department of Chemistry of the University of Texas at Arlington. Single crystals in the form of clear prisms were grown from ethanol solution. The unit-cell parameters and the intensity data were measured on a Syntex $P2_1$ diffractometer. A $\theta/2\theta$ scanning mode was used in the intensity measurements. A reflection was considered as observed by the criterion $I > 3\cdot0\sigma(I)$, where $\sigma(I)$ was determined from counting statistics. The intensity data were reduced to structure amplitudes by the application of Lorentz and polarization factors; no absorption corrections were applied. The crystal and experimental data are given in Table 1.

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Structure determination and refinement

Both structures were determined by the heavy-atom method. The refinement was carried out by the full-matrix least-squares method (Busing, Martin & Levy, 1962) with isotropic temperature factors and the block-diagonal least-squares method (Shiono, 1971) with anisotropic temperature factors. Only some H positions were located on difference Fourier syntheses, and the others were calculated on the basis that they make reasonable bond lengths and bond angles with the bonded atoms. In the refinements, isotropic temperature factors were used for the *meso* isomer. For the (±) isomer, the positional and thermal parameters of the H atoms were not refined, and their isotropic thermal parameters were made the same as those of the atoms to which they are bonded. Cruickshank's (1965) weighting scheme was used in order to make $[\Sigma \, w(F_o - F)^2/(\text{number of reflections} - \text{number of parameters})]^{1/2}$ approximately equal to unity, and the average $w(F_o - F_c)^2$ is approximately constant for different magnitudes

Table 1. *Crystal data of* 1,4-*dimesityl*-1,4-*dithiabutane* 1,4-*dioxide*

Chemical formula: $C_{20}H_{26}O_2S_2$, FW 362·56

	meso Isomer	(±) Isomer
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$	$P1$
Unit-cell dimensions	$a = 15\cdot851$ (6) Å	$a = 13\cdot056$ (5) Å
	$b = 11\cdot565$ (5)	$b = 7\cdot860$ (2)
	$c = 5\cdot157$ (1)	$c = 4\cdot812$ (1)
	$\beta = 91\cdot32$ (2)°	$\alpha = 75\cdot57$ (2)°
		$\beta = 94\cdot00$ (2)
		$\gamma = 85\cdot19$ (2)
V	945·2 Å³	474·3 Å³
D_c	1·274 g cm⁻³	1·269 g cm⁻³
D_m (flotation)	1·26	1·26
Number of molecules per unit cell, Z	2	1
X-radiation used for data collection	λ(Mo $K\alpha$) = 0·7107 Å	λ(Cu $K\alpha$) = 1·5418 Å
Linear absorption coefficient	μ(Mo $K\alpha$) = 2·858 cm⁻¹	μ(Cu $K\alpha$) = 25·5 cm⁻¹
Total number of reflections	1661 ($2\theta_{max} = 50°$)	1826 ($2\theta_{max} = 140°$)
Number of reflections with $I > 3\sigma(I)$	1368	1726
Goodness of fit	0·86	0·81
Maximum residual electron density	0·34 e Å⁻³	0·58 e Å⁻³
Disagreement index, R	0·063	0·051
Crystal size	0·12 × 0·27 × 0·54 mm	0·12 × 0·21 × 0·48 mm

of F_o and sin θ. The final R indices $(\Sigma ||F_o| - |F_c||/\Sigma |F_o|)$ were 0·063 and 0·051 for the *meso* and (±) isomers respectively.[*] The atomic scattering factors used for S, O, and C atoms were those from *International Tables for X-ray Crystallography* (1962) and, for H, the values given by Stewart, Davidson & Simpson (1965) were used. The final positional parameters are given in Table 2.

Discussion

1,4-Diaryl-1,4-dithiabutane 1,4-dioxides (I) exist as two isomers, *meso* and (±), and each *meso* isomer possesses a center of symmetry. The crystal structures of the *meso* and (±) isomers of the phenyl derivative of (I) have been determined in this laboratory (Ternay, Lin, Sutliff, Chu & Chung, 1977). In this work, the crystal structures of the mesityl derivatives of (I) have been determined in order to correlate their molecular structures in the solid state with the proton magnetic resonance data in solution (Ternay, 1968; Ternay, Lin, Sutliff, Chu & Chung, 1977).

$$\text{Ar}-\underset{\underset{O}{|}}{S}-\text{CH}_2-\text{CH}_2-\underset{\underset{O}{|}}{S}-\text{Ar}$$

(I)

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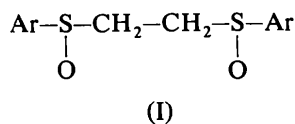
* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33120 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The configurations of the two isomers are shown in the *ORTEP* drawings (Johnson, 1965) in Fig. 1. The *meso* isomer possesses a center of symmetry, and both halves of the (±) isomer have the same conformation with both O atoms having disordered positions. The occupancy factors of these O atoms are shown in Fig. 2.
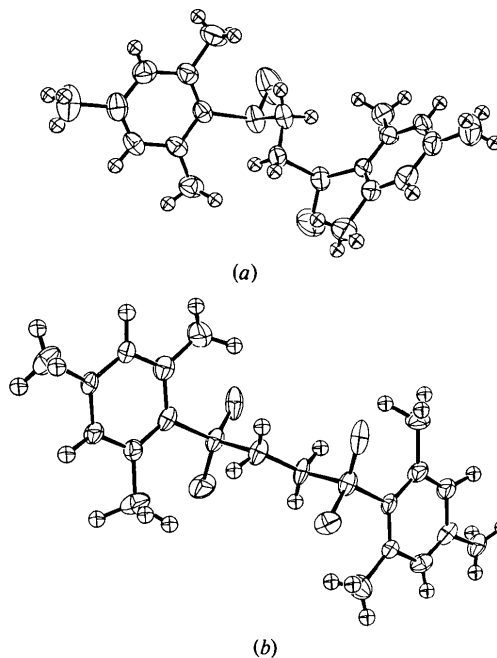

(a)

(b)

Fig. 1. *ORTEP* drawings of 1,4-dimesityl-1,4-dithiabutane 1,4-dioxide: (a) *meso* isomer, (b) (±) isomer.

Table 2. *Fractional atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$)

The estimated standard deviations are given in parentheses and refer to the last positions of respective values.

	x	y	z
meso Isomer			
S	5106 (0)	3680 (1)	3090 (1)
O	5908 (2)	3205 (4)	4046 (8)
C(1)	4496 (2)	2673 (2)	1165 (5)
C(2)	3617 (2)	2727 (2)	1459 (5)
C(3)	3116 (2)	1998 (3)	−76 (6)
C(4)	3447 (2)	1241 (3)	−1803 (6)
C(5)	4318 (2)	1186 (3)	−1977 (7)
C(6)	4861 (2)	1885 (2)	−518 (9)
C(7)	3201 (2)	3522 (3)	3354 (7)
C(8)	2894 (3)	479 (4)	−3498 (8)
C(9)	5803 (2)	1760 (4)	−782 (11)
C(19)	5378 (2)	4678 (2)	512 (5)
H(3)	255 (2)	201 (3)	0 (6)
H(5)	455 (2)	69 (3)	−298 (7)
H(7)1	332 (3)	340 (4)	516 (9)
H(7)2	264 (3)	333 (4)	332 (9)
H(7)3	327 (3)	434 (3)	310 (7)
H(8)1	280 (3)	−21 (4)	−301 (8)
H(8)2	291 (4)	57 (5)	−503 (12)
H(8)3	244 (4)	57 (5)	−305 (11)
H(9)1	600 (3)	239 (4)	−169 (9)
H(9)2	614 (4)	176 (5)	105 (11)
H(9)3	588 (3)	119 (4)	−165 (9)
H(19)1	570 (2)	430 (3)	−72 (6)
H(19)2	574 (2)	516 (3)	138 (6)
(±) Isomer			
S(1)	0 (0)	0 (0)	0 (0)
S(2)	2667 (1)	2053 (2)	3472 (3)
O(1)	604 (6)	−1439 (9)	−957 (15)
O(2)	3122 (5)	358 (7)	−4252 (11)
O*(1)	−371 (10)	1606 (20)	−2166 (24)
O*(2)	2098 (10)	3528 (23)	4515 (28)
C(1)	−893 (4)	−803 (7)	2564 (11)
C(2)	−1693 (4)	366 (7)	2949 (12)
C(3)	−2358 (4)	−291 (8)	4998 (14)
C(4)	−2251 (5)	−2059 (8)	6626 (12)
C(5)	−1488 (5)	−3165 (7)	6049 (11)
C(6)	−778 (4)	−2543 (7)	4147 (12)
C(7)	−1854 (5)	2328 (8)	1415 (16)
C(8)	−3004 (5)	−2602 (9)	8857 (12)
C(9)	60 (5)	−3896 (9)	3628 (15)
C(10)	3605 (4)	2811 (7)	968 (11)
C(11)	4417 (4)	1674 (7)	522 (12)
C(12)	5119 (4)	2277 (7)	−1423 (11)
C(13)	5011 (4)	4008 (7)	−3013 (11)
C(14)	4181 (4)	5144 (7)	−2605 (13)
C(15)	3489 (4)	4655 (8)	−497 (12)
C(16)	4580 (7)	−266 (9)	2197 (19)
C(17)	5713 (6)	4709 (9)	−5250 (14)
C(18)	2611 (6)	5929 (10)	−334 (18)
C(19)	894 (4)	616 (8)	2552 (12)
C(20)	1774 (4)	1384 (8)	963 (11)
H(3)	−309	26	553
H(5)	−150	−425	655
H(7)1	−121	305	153
H(7)2	−187	260	−78
H(7)3	−215	337	194
H(8)1	−288	−371	978
H(8)2	−365	−192	802

Table 2 (*cont.*)

	x	y	z
H(8)3	−303	−208	1024
H(9)1	66	−362	414
H(9)2	27	−373	161
H(9)3	2	−505	463
H(12)	570	150	−230
H(14)	403	652	−369
H(16)1	543	−77	225
H(16)2	436	−75	24
H(16)3	394	−110	303
H(17)1	579	584	−572
H(17)2	548	434	−655
H(17)3	637	389	−427
H(18)1	272	610	187
H(18)2	191	538	−79
H(18)3	258	685	−206
H(19)1	37	152	324
H(19)2	113	−49	391
H(20)1	161	227	−39
H(20)2	236	72	71

The identification of the atoms and the bond lengths and bond angles, with their standard deviations, are shown in Fig. 2. Except for the large O—S—C(sp^2) bond angle with a mean value of 113·3 ± 0·4°, all other bond lengths and bond angles involving the S atom are in agreement with other sulfoxide structures (Chu, 1975). There exist close non-bonded intramolecular contacts between the O and the methyl group in the mesityl substituent which are listed in Table 3. These close contacts also exist in the structures of both isomers of the phenyl derivative of (I) (Ternay, Lin, Sutliff, Chu & Chung, 1977). These are presumably due to the weak hydrogen bonding from the lone-pair electrons on O atoms. However, the H positions, especially those on the methyl groups, were not determined with enough accuracy to make a definite conclusion.

The conformation of both isomers can be illustrated from the torsion angles about the S—C bonds, as shown in Table 3. The torsion angles about the S—C(ethano) bonds (Ar—S—C—C fragment) indicated that the *meso* isomer has the *anti–gauche* conformation and both halves of the (±) isomer have the *gauche–anti* conformation. However, in the phenyl derivative of (I), the two halves of the molecule of the (±) isomer have different conformations, *gauche–gauche* and *gauche–anti*, and the *meso* isomer has the *gauche–gauche* conformation (Ternay, Lin, Sutliff, Chu & Chung, 1977). The crystal structure of the *meso* isomer of the methyl derivative of (I) was also studied (Svinning, Mo & Bruun, 1976); the CH_3—S—CH_2—CH_2 fragment has the *gauche–anti* conformation. The torsion angles about the S and C(aryl) bonds indicated that the mesityl ring has a partial-eclipse conformation with respect to the S—O bond. This partial-eclipse conformation was also observed in the phenyl derivative of

(I); however, the methyl derivative of (I) has the staggered conformation about the S—C(methyl) bond (Svinning, Mo & Bruun, 1976). The partial-eclipse conformation, which was preferred in the aryl derivatives of (I), is apparently due to the interactions between O atoms and C(aryl) as indicated by the close non-bonded intramolecular contacts.

The least-squares planes of the mesityl groups calculated from the six-membered benzene rings indicated that they deviated slightly from the planar configuration. The deviations range from 0·003 to 0·04 Å. The methyl C atoms are out of the plane of the benzene rings by the order of 0·02 to 0·08 Å. The packing of the molecules in the crystal is determined
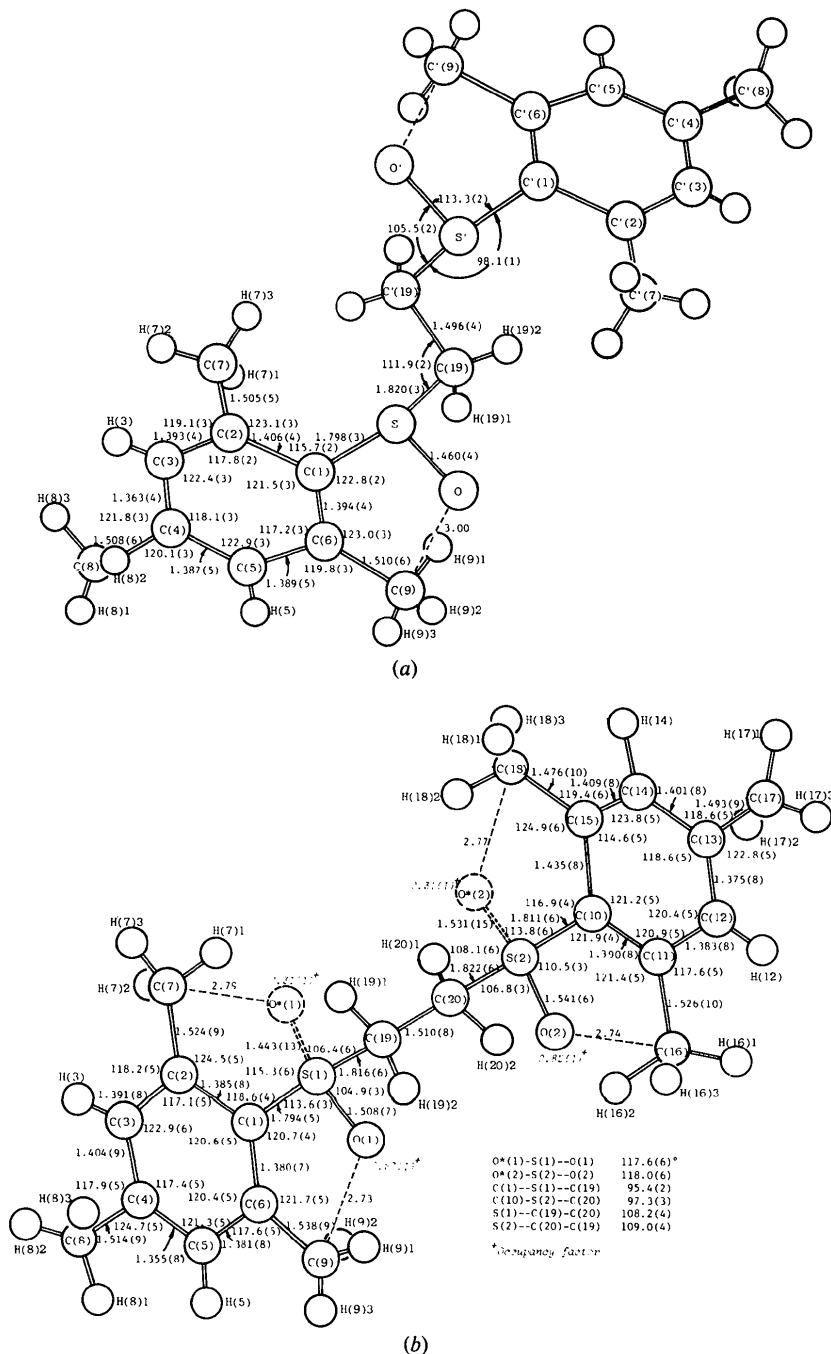

(a)

O*(1)-S(1)--O(1)	117.6(6)*
O*(2)-S(2)--O(2)	118.0(6)
C(1)--S(1)--C(19)	95.4(2)
C(10)-S(2)--C(20)	97.3(3)
S(1)--C(19)-C(20)	108.2(4)
S(2)--C(20)-C(19)	109.0(4)

*Occupancy factor

(b)

Fig. 2. Bond lengths (Å) and bond angles (°) of 1,4-dimesityl-1,4-dithiabutane 1,4-dioxide with e.s.d.'s in parentheses: (a) *meso* isomer, (b) (±) isomer.

Table 3. *Torsion angles* (°) *about the* S—C *bonds*

The angle is positive if measured clockwise.

meso Isomer

O–S–C(1)–C(2)	143·5	O···S–C(19)–C(1)	117·0
O–S–C(1)–C(6)	–36·5	C'(19)–S–C(19)–C(1)	–68·2 ·
C(19)–S–C(1)–C(2)	–105·7		
C(19)–S–C(1)–C(6)	74·3		

(±) Isomer

O(1)–S(1)–C(1)–C(2)	–160·7	O(2)···S(2)–C(10)–C(15)	–155·5
O(1)–S(1)–C(1)–C(6)	20·1	O(2)···S(2)–C(10)–C(11)	23·0
O*(1)–S(1)–C(1)–C(2)	–20·9	O*(2)···S(2)–C(10)–C(15)	–20·3
C(19)–S(1)–C(1)–C(2)	90·9	C(20)···S(2)–C(10)–C(15)	92·7
C(19)–S(1)–C(1)–C(6)	–88·3	C(20)···S(2)–C(10)–C(11)	–88·8
O(1)–S(1)–C(19)–C(20)	64·6	O(2)···S(2)–C(20)–C(19)	64·3
O*(1)–S(1)–C(19)–C(20)	–61·4	O*(2)···S(2)–C(20)–C(19)	–64·3
C(1)–S(1)–C(19)–C(20)	180·3	C(10)···S(2)–C(20)–C(19)	178·2

Table 4. *Non-bonded intra- and intermolecular distances* (Å)

Intramolecular distances		Intermolecular distances	
meso Isomer			
O···C(9)	3·00	O···C(9)^a	3·15
(±) Isomer			
O(1)···C(9)	2·73	O(1)···C(6)^b	3·20
O(2)···C(16)	2·74	O(1)···C(19)^b	3·20
O*(1)···C(7)	2·79	O(2)···C(11)^a	3·19
O*(2)···C(18)	2·77	O(2)···C(20)^a	3·38
		O*(1)···C(2)^b	3·21
		O*(1)···C(19)^b	3·34
		O*(2)···C(15)^a	3·25
		O*(2)···C(20)^a	3·22

Symmetry code

(a) x, y, $1 + z$
(b) x, y, $-1 + z$

mainly by van der Waals interactions; however, there are some close intermolecular contacts between the O atoms and the mesityl C atoms, as shown in Table 4.

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