organic papers

2,3-Dihydro-5,6-dimethyl-1,4-dithiine 1,1,4-trioxide

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The title compound, $C_6H_{10}O_3S_2$, has twofold imposed crystallographic symmetry in the solid state, with concomitant disorder of the three unique O atoms, so that in this trioxide, each S atom is effectively bonded to a unit-occupancy O atom and to a half-occupancy O atom. The six-membered 2,3-dihydro-5,6-dimethyl-1,4-dithiine ring has a half-chair conformation, with the twofold axis passing through the mid-points of the C=C and C—C bonds.

Comment

Dihydro-1,4-dithiine tetroxides are a class of compounds with diverse biological activities. Depending on their substitution patterns, they can have bactericidal, fungicidal and viricidal properties (Brewer & Davis, 1977, 1978) or herbicidal and plant growth-regulant properties (Brewer *et al.*, 1975, 1976). Crystallographic data have been published on a number of compounds in this series (Arora *et al.*, 1978; Bates *et al.*, 1980; Ferguson *et al.*, 1990). By contrast, the corresponding dihydro-1,4-dithiine trioxides have been little studied; synthetic details of only one simple alkyl-substituted example, *viz.* 2,3-dihydro-5,6-dimethyl-1,4-dithiine 1,1,4-trioxide, (I), have ever been published (CAS number 131459-41-1) and no data are available on crystal structures of this type of compound. Consequently, it seemed worthwhile to investigate this unique compound since it was available in suitable crystalline form.

(I)
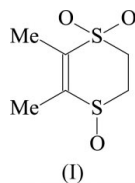
A displacement ellipsoid plot of (I) is shown in Fig. 1. The six-membered 2,3-dihydro-5,6-dimethyl-1,4-dithiine ring has a half-chair conformation very similar to that found in the
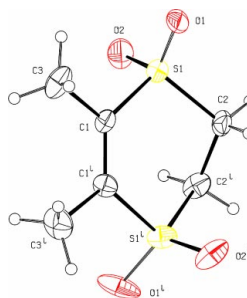
Figure 1
A view of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry code: (i) $1 - x$, $1 - y$, z.]

corresponding tetroxide (Arora *et al.*, 1978). With $Z = 2$ in space group $P2_12_12$, the molecule has imposed twofold symmetry, with the twofold axis passing through the midpoints of the C1—C1^i and C2—C2^i bonds (Fig. 1) [symmetry code: (i) $1 - x, 1 - y, z$]. There is then concomitant disorder of the three O atoms of (I) over four sites (see *Experimental*).

Principal dimensions are in Table 1 and are not unusual. In the crystal structure, the shortest intermolecular contacts are of the C—H···O type between methylene H atoms and adjacent O atoms; details are in Table 2. The shortest separation between half-occupancy O1 atoms is 2.519 (14) Å between O1 and O1($2 - x, 1 - y, z$).

Experimental

2,3-Dihydro-5,6-dimethyl-1,4-dithiine (Massingill *et al.*, 1970) (30 g) was dissolved in methanol (1.0 l). To the solution, stirred in an ice-bath, was added a solution of oxone ($2 KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) (189 g) in water (1.0 l) with stirring over a period of 6 h. The reaction mixture was allowed to come to room temperature, was stirred overnight, then filtered, giving a two-phase liquid. The aqueous layer was extracted with dichloromethane and added to the organic layer from which the solvent had been removed under vacuum. The combined solution was dried over magnesium sulfate and reduced under vacuum to an amber oil (25.5 g), which contained both the trioxide and tetroxide of the starting material. The trioxide was isolated by preparative-scale chromatography on silica gel, followed by recrystallization from toluene of the solid obtained by evaporating the eluate, giving white needles (m.p. 355–357 K). ^{1}H NMR (CDCl$_3$): 2.169–2.173 (complex singlet, 3H), 2.271–2.275 (complex singlet, 3H), 3.341–3.418 (complex quartet, 1H), 3.549–3.631 (complex quartet, 1H), 3.677–3.769 (complex quartet, 1H), 3.917–4.010 (complex quartet, 1H). ^{13}C NMR (CDCl$_3$): 11.377,17.308, 41.444, 43.371, 137.677, 141.725.

Crystal data

$C_6H_{10}O_3S_2$	Mo $K\alpha$ radiation
$M_r = 194.28$	Cell parameters from 761
Orthorhombic, $P2_12_12$	reflections
$a = 5.5919 (5)$ Å	$\theta = 2.6$–$25.5°$
$b = 9.2507 (10)$ Å	$\mu = 0.60$ mm^{-1}
$c = 7.9146 (9)$ Å	$T = 150 (1)$ K
$V = 409.41 (7)$ Å^3	Block, white block
$Z = 2$	$0.12 \times 0.12 \times 0.10$ mm
$D_x = 1.576$ Mg m^{-3}	

Data collection

Nonius KappaCCD diffractometer	$R_{int} = 0.076$
φ scans, and ω scans with κ offsets	$\theta_{max} = 25.5°$
Absorption correction: none	$h = -6 \rightarrow 6$
3121 measured reflections	$k = -11 \rightarrow 11$
761 independent reflections	$l = -9 \rightarrow 9$
672 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.002$
$R[F^2 > 2\sigma(F^2)] = 0.056$	$\Delta\rho_{max} = 0.27$ e Å^{-3}
$wR(F^2) = 0.143$	$\Delta\rho_{min} = -0.29$ e Å^{-3}
$S = 1.16$	Extinction correction: *SHELXL*97
761 reflections	Extinction coefficient: 0.09 (2)
58 parameters	Absolute structure: Flack (1983),
H-atom parameters constrained	287 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2$	Flack parameter = 0.4 (3)
$+ 0.467P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

S1—O1	1.464 (8)	C1—C1^i	1.330 (10)
S1—O2	1.451 (5)	C1—C3	1.482 (7)
S1—C1	1.797 (5)	C2—C2^i	1.509 (11)
S1—C2	1.772 (5)		
O1—S1—O2	120.8 (5)	C1—S1—C2	104.1 (2)
O1—S1—C1	101.8 (4)	C1^i—C1—S1	125.70 (16)
O1—S1—C2	113.0 (4)	C1^i—C1—C3	122.2 (4)
O2—S1—C1	106.6 (3)	C3—C1—S1	112.1 (4)
O2—S1—C2	108.8 (3)	C2^i—C2—S1	111.8 (4)

Symmetry code: (i) $1 - x, 1 - y, z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2B···O1^{ii}	0.99	2.40	3.120 (10)	130
C2—H2B···O2^{iii}	0.99	2.50	3.241 (7)	131
C3—H3A···O1^{iv}	0.98	2.44	3.183 (11)	133

Symmetry codes: (ii) $2 - x, 1 - y, z$; (iii) $\frac{3}{2} - x, \frac{1}{2} + y, 2 - z$; (iv) $x - \frac{1}{2}, \frac{1}{2} - y, 1 - z$.

The crystal showed no signs of twinning and, with $Z = 2$, the compound has to have twofold symmetry with O-atom disorder. In electron-density maps, the peak corresponding to O1 was half the height of that of O2. Tied-occupancy refinement confirmed that this was indeed the case and in the final cycles the occupancies of O1 and O2 were fixed at 0.5 and 1, respectively. All H atoms were clearly visible in difference maps and were subsequently treated as riding atoms with C—H = 0.99 (CH$_2$) and 0.98 Å (CH$_3$), and with U_{iso}(CH$_2$) = $1.2U_{eq}$(C) and U_{iso}(CH$_3$) = $1.5U_{eq}$(C)).

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *WordPerfect* macro *PRPKAPPA* (Ferguson, 1999).

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