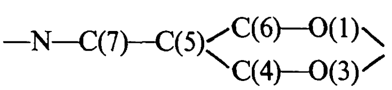
groups. Bond lengths and angles agree well with those reported for analogous compounds (Vickery, Willey & Drew, 1985) and with those containing analogous resonance systems (Diánez, López-Castro & Márquez, 1987). The ethylene group is planar, the C=C bond distance is as long as 1·399 (10) Å and the torsion angles around this bond are 176·8 (10) and 0·5 (17)°. Angles at C(2) are in the range 105·0 (8)–114·4 (8)°, consistent with the expected high degree of tetrahedral character corresponding to the (sp^3) carbon. The asymmetry (Nardelli, 1983) and puckering parameters (Cremer & Pople, 1975) for the atomic sequence O(1), C(2), O(3), C(4), C(5) and C(6), $\theta = 119\,(1)°$, $\varphi = -117\,(1)°$, $Q = 0{\cdot}42\,(1)$ Å and $\Delta C_s[\mathrm{C}(2)] = 0{\cdot}013\,(4)$, show that the molecular conformation of the dioxane ring approximates a 'half-boat' with a mirror plane through the vertex C(2). The substituents O(4), O(2) and C(7) are in equatorial positions. The half-boat conformation of the 1,3-dioxane ring is consistent with the quasi-planarity of resonance systems. The group is



$$-\mathrm{N}-\mathrm{C(7)}-\mathrm{C(5)}\begin{array}{l}\diagup\,\mathrm{C(6)}-\mathrm{O(1)}\,\diagdown\\ \diagdown\,\mathrm{C(4)}-\mathrm{O(3)}\,\diagup\end{array}$$

strictly planar [maximum deviation from the least-squares plane $-0{\cdot}040\,(9)$ Å] and the O(4) and O(6) atoms are at $-0{\cdot}137\,(7)$ and $-0{\cdot}148\,(8)$ Å. The C(8) and C(2) atoms are at 0·016 (12) and 0·597 (9) Å from the same plane.

In addition, the distortion of the dioxane ring from the chair conformation is also due to the O(4) and O(6) substituents in equatorial positions, which agrees with the results of Kok & Romers (1970) and Nader (1975) which showed that equatorial substituents at C(4) and C(6) have a considerable effect on the torsion angles and hence the heterocyclic conformation.

As expected there is an intramolecular H bond between the N atom and a carbonyl oxygen O(4) [N—H···O(4) = 2·811 (12) Å and N—H···O(4) = 127·8 (5)°], showing a chelate structure. There are no intermolecular distances less than the sum of van der Waals radii.

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Structure of 2,6-Dimethoxy-1,4-oxathiane 4,4-Dioxide

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Abstract. $C_6H_{12}O_5S$, $M_r = 196{\cdot}2$, monoclinic, $P2_1/c$, $a = 8{\cdot}473\,(4)$, $b = 7{\cdot}437\,(3)$, $c = 13{\cdot}952\,(2)$ Å, $\beta = 94{\cdot}51\,(2)°$, $V = 876{\cdot}3\,(6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}49$, $D_m = 1{\cdot}48$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}7107$ Å, $\mu = 0{\cdot}03$ mm^{-1}, $F(000) = 416$, $T = 293$ K, $R = 0{\cdot}038$ for 1307 independent reflections. The oxathiane ring is in

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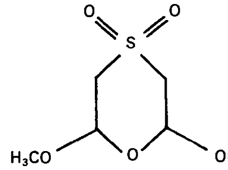
a chair conformation. The two OCH_3 substituents are in *trans* positions. The packing of the molecules is governed by van der Waals contacts.

Introduction. 1,4-Oxathianes are well known synthetic intermediates in organic chemistry, whereas the corresponding dioxides have received relatively little attention. The title compound (1), obtained (Campos, 1989) by oxidative reaction of 2,6-dimethoxy-1,4-oxathiane with *m*-chlorobenzoic acid (proportion 2·5:1), showed an ^1H NMR spectrum with a high degree of second-order coupling and it was difficult to ascertain the configuration (*cis* or *trans*). Accordingly, an X-ray crystallographic study was undertaken to establish the crystal and molecular structure and the stereochemistry of this compound.



(1)

Experimental. Single crystals in the form of prisms elongated along [001] were prepared in the Organic Chemistry Department of the University of Seville and kindly supplied by Professor A. L. Campos; D_m by flotation; crystal size 0·12 × 0·14 × 0·11 mm, unit-cell parameters by least squares from 25 reflections ($5 < \theta < 19°$). Enraf–Nonius CAD-4 diffractometer, graphite monochromator, space group $P2_1/c$, ω–2θ scan. 1572 reflections measured ($2 < \theta < 25°$, $h \leq 11$, $k \leq 10$, $-17 \leq l \leq 17$), two standard reflections ($01\bar{4}$, 122) monitored every 100 reflections, variations less than 10% of mean intensity, 1307 reflections with $I \leq 2\sigma(I)$ observed. Lorentz–polarization corrections but no absorption correction. Structure solved by direct methods with *MULTAN* (Main *et al.*, 1980); anisotropic full-matrix least-squares refinement on *F* for non-H atoms, isotropic for H atoms corresponding to those of carrier atoms. The positional parameters of the H atoms (difference map) were refined. $w = 1/\sigma^2(F_o)$. Refinement produced convergence with $R = 0·038$, $wR = 0·043$; max. Δ/σ (excluding H atoms) = 0·04, $\Delta\rho = \pm 0·3$ e Å^{-3}, $S = 1·22$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculation performed with the *XRAY76* system of crystallographic programs (Stewart, Machin, Dickinson, Amon, Heck & Flack, 1976) and *PARST* (Nardelli, 1983).

Table 1. *Atomic and equivalent isotropic thermal parameters*

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq} (Å^2 × 10^4)
S(1)	0·5149 (1)	0·5363 (2)	0·2311 (1)	357 (3)
O(1)	0·2912 (3)	0·4524 (4)	0·0518 (2)	334 (9)
O(2)	0·6664 (4)	0·6219 (6)	0·2512 (3)	550 (13)
O(3)	0·4381 (4)	0·4645 (5)	0·3104 (2)	491 (12)
O(4)	0·1446 (3)	0·5330 (4)	0·1810 (2)	338 (9)
O(5)	0·4056 (4)	0·1815 (5)	0·0290 (2)	425 (11)
C(1)	0·5354 (5)	0·3658 (7)	0·1442 (3)	382 (14)
C(2)	0·3746 (5)	0·3049 (6)	0·0997 (3)	331 (12)
C(3)	0·2443 (5)	0·5926 (6)	0·1132 (3)	326 (12)
C(4)	0·3870 (5)	0·6873 (7)	0·1643 (3)	352 (13)
C(5)	−0·0106 (6)	0·4881 (9)	0·1397 (4)	524 (19)
C(6)	0·2688 (7)	0·0880 (8)	−0·0111 (4)	497 (18)

Table 2. *Bond distances* (Å) *and angles* (°)

S(1)—O(3)	1·430 (4)	C(4)—C(3)	1·526 (6)
S(1)—C(4)	1·774 (5)	O(1)—C(2)	1·441 (5)
S(1)—C(1)	1·772 (5)	O(1)—C(3)	1·425 (5)
S(1)—O(2)	1·440 (4)	C(1)—C(2)	1·521 (6)
O(4)—C(3)	1·390 (5)	C(2)—O(5)	1·387 (6)
O(4)—C(5)	1·434 (6)	O(5)—C(6)	1·428 (7)
C(1)—S(1)—O(2)	108·4 (2)	S(1)—C(1)—C(2)	111·1 (3)
C(4)—S(1)—O(2)	108·7 (2)	O(1)—C(2)—C(1)	110·7 (4)
C(4)—S(1)—C(1)	100·5 (2)	C(1)—C(2)—O(5)	105·9 (4)
O(3)—S(1)—O(2)	117·9 (2)	O(1)—C(2)—O(5)	106·7 (3)
O(3)—S(1)—C(1)	109·7 (2)	C(2)—O(5)—C(6)	114·1 (4)
O(3)—S(1)—C(4)	110·3 (2)	C(4)—C(3)—O(1)	111·7 (3)
C(3)—O(4)—C(5)	112·8 (4)	O(4)—C(3)—O(1)	112·9 (3)
S(1)—C(4)—C(3)	112·5 (3)	O(4)—C(3)—C(4)	109·3 (3)
C(2)—O(1)—C(3)	115·3 (3)		

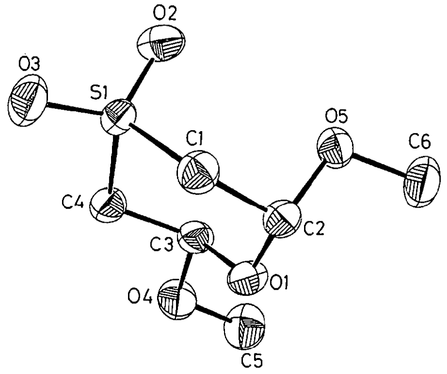


Fig. 1. An *ORTEP* plot of the molecule.

Discussion. Final positional parameters and equivalent values of the anisotropic temperature factors are given in Table 1.* Fig. 1 shows a schematic view of the molecule with the atom numbers, prepared from the output of *ORTEP*II (Johnson, 1976). Table 2 contains bond lengths and bond angles. The endocyclic mean S—C, C—C and C—O bond lengths of 1·774 (5), 1·524 (6) and 1·433 (5) Å and the corresponding bond angles agree with other reported

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53544 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

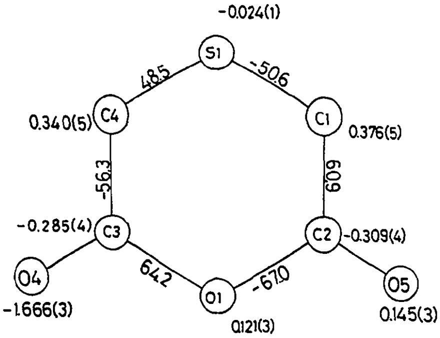

Fig. 2. Endocyclic torsional angles (°) and distances (Å) of the atoms from the mean plane through the ring.

values (Barnes, Paton & McKissock, 1983). The exocyclic mean C_{methyl}—O, C_{ring}—O and S—O bond lengths of 1·431 (7), 1·389 (6) and 1·435 (4) Å agree with the values given for these bond distances (*International Tables for X-ray Crystallography*, 1962, Vol. III). The O—S—O, C—S—O and C—S—C angles are in the range 100·5 (2)–117·8 (2)°, consistent with the expected tetrahedral geometry. The oxathiane ring is in a chair conformation as can be seen from the endocyclic torsional angles given in Fig. 2. However, the C—S—C part is more flattened than the C—O—C part. The mean absolute value of S(1)—C(1)—C(2)—O(1) and S(1)—C(4)—C(3)—O(1) is 58·6°, the mean of C(4)—C(3)—O(1)—C(2) and C(1)—C(2)—O(1)—C(3) is 65·6°, whereas for C(3)—C(4)—S(1)—C(1) and C(2)—C(1)—S(1)—C(4) it is 49·6°. Other numerical values given in Fig. 2 are the distances of the atoms from the mean planes through the ring. Hence we conclude that the O(4) atom is in an axial position and O(5) in an equatorial position, and that the title compound crystallizes in the *trans* configuration. The torsion angles C(5)—O(4)—C(3)—C(4) and C(6)—O(5)—C(2)—C(1) are 163·7 (4) and 170·9 (4)°, respectively.

The crystal packing is determined by van der Waals contacts.

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Functionalized Hydrocarbons with Condensed Ring Skeletons. VI. A Tricyclo[8.4.0.0^{3,8}]tetradec-1-ene and its Parent Fourteen-Membered Dimethyl Macrocycle

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Abstract. $C_{24}H_{34}O_8$, $M_r = 450\cdot52$, $\lambda(\mathrm{Cu}\ K\bar{\alpha}) = 1\cdot54056$ Å, room temperature. (I) Tetramethyl (3*Z*,5*E*,11*E*)-3,11-dimethylcyclotetradeca-3,5,11-triene-1,1,8,8-tetracarboxylate, monoclinic, $P2_1/a$, $a = 13\cdot5494$ (8), $b = 14\cdot739$ (3), $c = 13\cdot6734$ (10) Å, $\beta = 117\cdot340$ (5)°, $V = 2425\cdot6$ (5) Å^3, $Z = 4$, $D_x = 1\cdot234$ Mg m^{-3}, $\mu = 0\cdot72$ mm^{-1}, $F(000) = 967\cdot90$, final $R = 0\cdot045$ for 3780 observed reflections. (II) Tetramethyl 3,8-*cis*-8,9-*transoid*-9,14-*cis*-1,7-di-methyltricyclo[8.4.0.0^{3,8}]tetradec-1-ene-5,5,12,12-tetracarboxylate (alternative name: tetramethyl 3,9-dimethyltricyclo[8.4.0.0^{2,7}]tetradec-8-ene-5,5,12,12-tetracarboxylate), monoclinic, $P2_1/c$, $a = 9\cdot287$ (1), $b = 18\cdot460$ (2), $c = 27\cdot7976$ (9) Å, $\beta = 98\cdot119$ (9)°, $V = 4717\cdot8$ (7) Å^3, $Z = 8$, $D_x = 1\cdot269$ Mg m^{-3}, $\mu = 0\cdot74$ mm^{-1}, $F(000) = 1935\cdot79$, final $R = 0\cdot087$ for

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