Fig. 3. Stereoscopic illustration of the crystal packing. The thermal ellipsoids are scaled to enclose 20% probability.

which explains the large thermal motion of the rigid molecule in the crystal, even at 153 K. The packing is, however, rather efficient, a fact which is borne out by the surprisingly high density ($1 \cdot 74$ Mg m^{-3}) and melting point (439 K).

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zation of the crystal structure are the contacts made by O(1) and O(3) with C(1) and C(2). The two C=O groups approach other molecules almost perpendicular to the plane of the ring from opposite sides. The negative parts of the C=O dipoles evidently are directed towards the more positive C(1)–C(2) fragments of adjacent molecules. These contacts are all very similar in length, ranging from $2 \cdot 73$ (2) to $2 \cdot 80$ (2) Å. The crystal-packing forces are obviously rather weak,

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2,3-Dihydro-5-methyl-1,4-dithiin 1,1,4,4-Tetroxide

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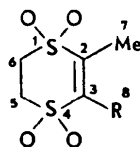
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Abstract. $C_5H_8O_4S_2$, $M_r = 196 \cdot 24$, monoclinic, $P2_1/a$ (systematic absences $h0l$, h odd; $0k0$, k odd), $a = 10 \cdot 613$ (8), $b = 6 \cdot 067$ (5), $c = 12 \cdot 732$ (7) Å, $\beta = 103 \cdot 61$ (5)°, $Z = 4$, $D_c = D_m = 1 \cdot 64$ Mg m^{-3} (flotation in aqueous KI). The structure was refined to a final R of $0 \cdot 068$ for 1081 reflections. Structural comparisons to the 5,6-dimethyl compound are made.

Introduction. Certain 2,3-dihydro-1,4-dithiin 1,1,4,4-tetroxides (I) have biological activity: (Ia) is a very effective plant-growth regulator and defoliant (Neidermyer, Brewer & Judge, 1974; McIntyre, Lambert & Brewer, 1977; Murphy, 1975), while (Ib) has micro-

biocidal activity (Brewer & Davis, 1977). The X-ray study of a crystal of (Ia) has been reported (Arora, Bates, Kriek & Brewer, 1978) and showed unexpectedly long vinyl-to-sulfone bonds, presumably for steric reasons. We now report the structure of (Ib), which provides a test of the idea that the bonds are long for steric reasons, as it contains one methyl group on the double bond to provide hindrance and one hydrogen to exemplify an unhindered situation.

(Ia)   R = Me
(Ib)   R = H

A crystal $0.3 \times 0.2 \times 0.1$ mm grown from ethanol was used. A Syntex $P2_1$ diffractometer with a graphite monochromator (Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å) and pulse-height analyzer was used for preliminary examination and data collection. Systematic absences defined the space group $P2_1/a$ (an alternate setting of $P2_1/c$). Cell constants (see *Abstract*) were determined by least-squares treatment of 18 reflections. Intensities were collected using $2°$ θ–2θ scans with a variable scan rate of 2.0 to $29.3°$ min^{-1} in 2θ and a background-to-scan time ratio of 0.5. 1559 independent reflections with $2\theta < 50°$ were measured, of which 1081 with $I > 3\sigma(I)$ were considered observed. There were no significant variations in the intensities of three check reflections monitored every 100 reflections. Lorentz and polarization corrections were applied but no correction was made for absorption.

The crystal structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971). The E map revealed all nonhydrogen atoms. Full-matrix least-squares refinement in which positional and isotropic thermal parameters were varied reduced R to 0.111. Anisotropic refinement brought R to 0.074. The positions of all H atoms were calculated and were included in least-squares calculations with the last isotropic thermal parameter of the carbon to which they were attached. Refinement of nonhydrogen atoms reduced R to 0.068 where refinement was terminated since the ratios of shifts in parameters to estimated standard deviations were <0.1 and many of the hydrogens did not refine satisfactorily. The refinement was based on F_o, the quantity minimized being $\sum w(F_o - F_c)^2$. The weighting scheme used was based on counter statistics as defined by Corfield, Doedens & Ibers (1967); the value of p was 0.03. The scattering

Table 1. *Final positional parameters* $(\times 10^4)$ *of* (I*b*)
with estimated standard deviations in parentheses

	x	y	z
S(1)	7214 (1)	1382 (2)	2031 (1)
S(4)	5438 (1)	−1420 (3)	3482 (1)
O(1)S(1)	8521 (4)	1076 (7)	1926 (4)
O(2)S(1)	6503 (4)	3138 (7)	1444 (4)
O(1)S(4)	4087 (4)	−1231 (8)	3458 (4)
O(2)S(4)	6172 (5)	−2971 (10)	4223 (3)
C(2)	6350 (5)	−1075 (9)	1602 (4)
C(3)	5621 (5)	−2082 (9)	2184 (4)
C(5)	6049 (7)	1326 (12)	3707 (5)
C(6)	7293 (7)	1582 (12)	3446 (5)
C(7)	6472 (6)	−1840 (10)	510 (5)
HC(3)	5231	−3340	1953
H(1)C(5)	5398	2259	3186
H(2)C(5)	5998	1764	4453
H(1)C(6)	7938	506	3876
H(2)C(6)	7642	3303	3658
H(1)C(7)	6622	−3480	532
H(2)C(7)	5624	−1471	−56
H(3)C(7)	7228	−1092	321

Table 2. *Bond lengths* (Å) *with estimated standard deviations in parentheses*

	(I*b*)	(I*a*)
O(1)S(1)–S(1)	1.437 (5)	1.429 (3)
O(2)S(1)–S(1)	1.414 (4)	1.436 (2)
O(1)S(4)–S(4)	1.432 (5)	1.436 (2)
O(2)S(4)–S(4)	1.427 (6)	1.429 (3)
C(2)–S(1)	1.768 (5)	1.779 (3)
C(3)–S(4)	1.755 (6)	1.778 (3)
C(6)–S(1)	1.788 (7)	1.768 (3)
C(5)–S(4)	1.786 (7)	1.763 (4)
C(2)–C(3)	1.338 (8)	1.320 (4)
C(2)–C(7)	1.500 (8)	1.502 (4)
C(3)–C(8)	–	1.518 (5)
C(5)–C(6)	1.444 (11)	1.501 (4)

Table 3. *Bond angles* (°) *with estimated standard deviations in parentheses*

	(I*b*)	(I*a*)
O(1)S(1)–S(1)–O(2)S(1)	117.1 (3)	118.1 (5)
O(1)S(1)–S(1)–C(2)	107.7 (3)	107.4 (4)
O(2)S(1)–S(1)–C(2)	107.4 (3)	107.1 (4)
O(1)S(1)–S(1)–C(6)	106.6 (4)	109.2 (5)
O(2)S(1)–S(1)–C(6)	112.0 (4)	108.5 (4)
C(2)–S(1)–C(6)	105.5 (4)	106.3 (4)
O(1)S(4)–S(4)–O(2)S(4)	117.0 (3)	117.7 (3)
O(1)S(4)–S(4)–C(3)	109.3 (3)	108.2 (3)
O(2)S(4)–S(4)–C(3)	107.9 (4)	107.7 (3)
O(1)S(4)–S(4)–C(5)	104.6 (4)	109.3 (3)
O(2)S(4)–S(4)–C(5)	112.8 (4)	108.6 (3)
C(3)–S(4)–C(5)	104.4 (4)	104.7 (3)
S(1)–C(2)–C(3)	122.6 (4)	125.5 (4)
S(1)–C(2)–C(7)	113.4 (4)	109.9 (4)
C(3)–C(2)–C(7)	124.0 (5)	124.6 (4)
S(4)–C(3)–C(2)	128.6 (4)	124.5 (4)
S(4)–C(3)–C(8)	–	111.7 (4)
C(2)–C(3)–C(8)	–	123.8 (4)
S(4)–C(5)–C(6)	112.3 (6)	110.1 (4)
S(1)–C(6)–C(5)	113.3 (6)	110.3 (4)

factors used were those of Hanson, Herman, Lea & Skillman (1964).*

Discussion. The final atomic coordinates of (I*b*) are given in Table 1, with standard deviations taken from the least-squares matrix. Table 2 gives bond lengths and Table 3 bond angles of the nonhydrogen atoms of (I*a*) and (I*b*). Fig. 1 depicts the molecular packing of (I*b*) while Fig. 2 shows (I*a*) and (I*b*) superimposed after best-fit least-squares treatment of the positions of the six ring atoms, using the program *BMFIT* (Nyburg, 1974). While both molecules approach a cyclohexene
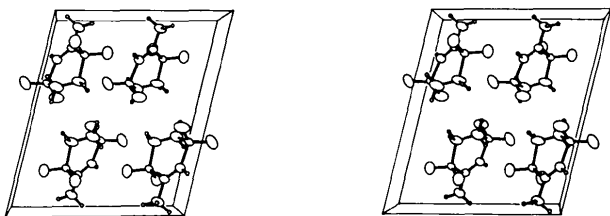
Fig. 1. Stereoscopic view of a unit cell, b-axis projection, a axis horizontal, with 50% probability thermal ellipsoids for non-hydrogens and spheres for hydrogens.

Fig. 2. Stereoscopic view of superimposed molecules of (Ia) (larger spheres) and (Ib).

half-chair conformation, (Ib) surprisingly more nearly has the twofold axis through the double bond and opposite ring bond, characteristic of a perfect half-chair. This is shown by the torsion angles, starting from S(1)—C(2)—C(3)—S(4) and proceeding towards higher numbers, in (Ia) −3·1, −17·3, 56·1, −73·3, 46·9, −8·4°, and in (Ib) 5·3, −16·3, 48·3, −69·0, 50·7, −17·4°.

The vinyl-to-sulfone bonds of (Ib) both have lengths intermediate between the long bonds of (Ia) [1·778 (3) and 1·779 (3) Å] and the short bonds of other cyclic vinyl sulfones [1·730 (3) Å (Boelema, Visser & Vos, 1967); 1·716 (3) and 1·723 (3) Å (Ammon, Watts, Stewart & Mock, 1968)]. The bond to the methyl-bearing carbon in (Ib) [1·768 (5) Å] is somewhat longer than that to the other carbon [1·755 (6) Å], supporting our earlier contention that the overly long S—C$_{sp^2}$ bonds of (Ia) are due to steric crowding when a methyl group is present on the adjacent double-bond C atom.

The very small value [1·444 (11) Å] for the C(5)—C(6) bond length in (Ib) was unexpected, but is consistent with values for other bonds between CH_2 groups attached to two sulfurs or oxygens in a six-membered ring: 1·44 Å [trans-2,3-dibromo-1,4-dioxin (Altona, Knobler & Romers, 1963)], 1·47 Å [trans-2,3-dichloro-1,4-dithiin (Kalff & Romers, 1965); 1,4-dithiin 1,4-dioxide (Montgomery, 1960)], 1·50–1·51 Å [cis- and trans-2,3-dichloro-1,4-dioxin (Altona & Romers, 1963)].

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