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2,3-Dihydro-5,6-dimethyl-1,4-dithiin 1,1,4,4-Tetroxide

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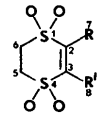
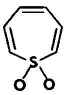
Abstract. $C_6H_{10}O_4S_2$, $M_r = 210{\cdot}28$, monoclinic, $P2_1/c$ (systematic absences $h0l$, l odd; $0k0$, k odd), $a = 11{\cdot}285\ (6)$, $b = 5{\cdot}746\ (2)$, $c = 14{\cdot}22\ (2)$ Å, $\beta = 103{\cdot}69\ (8)°$, $Z = 4$, $D_c = 1{\cdot}56$, $D_m = 1{\cdot}54$ g cm^{-3} (flotation in aqueous KI). The structure was refined to a final R of 0·042 for 1340 reflections. The vinyl-to-sulfone C—S bonds were unexpectedly long [1·778 (3) and 1·779 (4) Å], presumably for steric reasons.

Introduction. Certain 2,3-dihydro-1,4-dithiin 1,1,4,4-tetroxides (I) have powerful herbicidal (Brewer, Neidermyer & McIntyre, 1975, 1976, 1977) and microbiocidal (Brewer & Davis, 1977) properties, and it seemed desirable to obtain molecular parameters for a member of this class. We now report the results of an X-ray study of a crystal of 2,3-dihydro-5,6-dimethyl-1,4-dithiin 1,1,4,4-tetroxide (Harvade®, I*a*), a very effective plant-growth regulator, which in very small doses causes defoliation or desiccation of crops like cotton (Neidermyer, Brewer & Judge, 1974; McIntyre, Lambert & Brewer, 1977) and potatoes (Murphy, 1975).

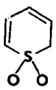


(I)

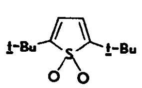
(I*a*): R = R′ = Me



(II)



(III)



(IV)

A crystal 0·5 × 0·5 × 0·1 mm grown from ethanol was used. A Syntex $P2_1$ diffractometer with a graphite monochromator (Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å) and pulse-height analyzer was used for preliminary pictures and intensities. Systematic absences defined the space group $P2_1/c$, with cell constants (see *Abstract*) determined by least-squares treatment of 12 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 1·0. 1826 independent reflections with $2\theta < 50°$ were measured, of which 1340 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 the nonhydrogen atoms. Full-matrix least-squares refinement in which positional and isotropic thermal parameters were varied reduced R to 0·089. Anisotropic refinement brought R to 0·059. All the H atoms were located on difference maps, and their inclusion with isotropic temperature factors in further refinement cycles reduced R to 0·042. Refinement was terminated at this stage since the ratios of shifts in parameters to estimated standard deviations were

Table 1. *Final positional parameters* (×10^4; *for* H ×10^3) *of* (I*a*) *with estimated standard deviations in parentheses*

	x	y	z
S(1)	7348 (1)	−178 (1)	5168 (1)
S(4)	6603 (1)	2225 (1)	2951 (1)
O(1)S(1)	8279 (2)	478 (5)	5994 (2)
O(2)S(1)	6608 (2)	−2164 (4)	5252 (2)
O(1)S(4)	7110 (2)	4530 (4)	3052 (2)
O(2)S(4)	5943 (2)	1515 (4)	2009 (2)
C(2)	8082 (2)	−773 (5)	4216 (2)
C(3)	7812 (2)	206 (5)	3351 (2)
C(5)	5655 (3)	1871 (5)	3764 (2)
C(6)	6378 (3)	2228 (5)	4784 (2)
C(7)	9062 (3)	−2566 (6)	4539 (3)
C(8)	8491 (3)	−291 (7)	2570 (3)
H(1)C(5)	505 (2)	295 (6)	354 (2)
H(2)C(5)	535 (2)	47 (5)	365 (2)
H(1)C(6)	591 (3)	232 (5)	524 (2)
H(2)C(6)	690 (3)	347 (5)	486 (2)
H(1)C(7)	972 (4)	−233 (7)	437 (3)
H(2)C(7)	921 (5)	−285 (9)	516 (4)
H(3)C(7)	892 (4)	−368 (10)	421 (4)
H(1)C(8)	947 (4)	−24 (8)	290 (3)
H(2)C(8)	812 (4)	−150 (8)	223 (3)
H(3)C(8)	840 (3)	90 (8)	217 (3)

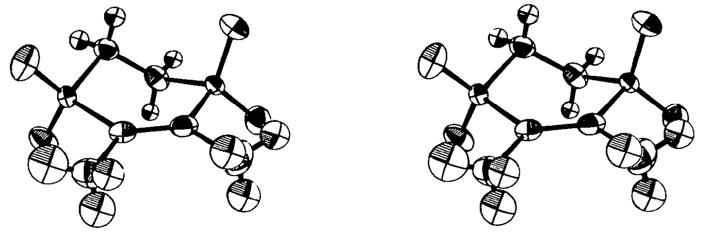


Fig. 1. Stereoscopic view of a molecule of (I*a*), with 50% probability thermal ellipsoids for non-hydrogen atoms and 10% ellipsoids for H atoms.

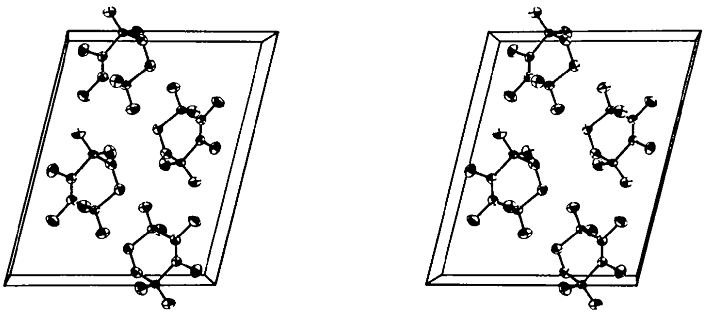


Fig. 2. Stereoscopic view of a unit cell (*b*-axis projection, *a* axis horizontal).

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

O(1)S(1)–S(1)	1·429 (3)	C(5)–H(1)C(5)	0·92 (3)
O(2)S(1)–S(1)	1·436 (2)	C(5)–H(2)C(5)	0·88 (3)
O(1)S(4)–S(4)	1·436 (2)	C(6)–H(1)C(6)	0·94 (4)
O(2)S(4)–S(4)	1·429 (3)	C(6)–H(2)C(6)	0·92 (3)
C(2)–S(1)	1·779 (4)	C(7)–H(1)C(7)	0·84 (5)
C(3)–S(4)	1·778 (3)	C(7)–H(2)C(7)	0·87 (6)
C(6)–S(1)	1·768 (3)	C(7)–H(3)C(7)	0·79 (5)
C(5)–S(4)	1·763 (4)	C(8)–H(1)C(8)	1·09 (4)
C(2)–C(3)	1·320 (4)	C(8)–H(2)C(8)	0·89 (4)
C(2)–C(7)	1·502 (4)	C(8)–H(3)C(8)	0·88 (4)
C(3)–C(8)	1·518 (5)		
C(5)–C(6)	1·501 (4)		

<0·3. 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 factors used were those of Hanson, Herman, Lea & Skillman (1964).*

Discussion. The final atomic coordinates are given in Table 1, with standard deviations taken from the least-squares matrix. Table 2 gives bond lengths and Table 3 bond angles. Fig. 1 depicts a molecule with thermal ellipsoids and Fig. 2 shows the molecular packing. The six-membered ring approaches a cyclohexene half-chair conformation (but lacks the twofold axis through the double bond and the opposite ring bond characteristic of a perfect half-chair), as indicated by the torsion angles, starting from S(1)–C(2)–C(3)–S(4) and proceeding around the ring toward higher numbers: −3·1, −17·3, 56·1, −73·3, 46·9, −8·4° (Bucourt, 1974). A −2·7° twist from coplanarity about the double bond is further revealed by the torsion angles S(1)–C(2)–C(3)–C(8) (177·8°), S(4)–C(3)–C(2)–C(7) (176·8°), and C(7)–C(2)–C(3)–C(8) (−2·3°). The methyl groups are rotated as in duroquinone (Rabinovich, Schmidt & Ubell, 1967).

The most surprising structural feature is the long S–C$_{sp^2}$ bonds: S(1)–C(2) at 1·779 (4) Å and S(4)–C(3) at 1·778 (3) Å. Most other substances with vinyl–sulfone bonds have significantly shorter bonds: (II) [1·730 (3) Å; Boelema, Visser & Vos, 1967] and (III) [1·716 (3) and 1·723 (3) Å; Ammon, Watts, Stewart & Mock, 1968]. (IV), on the other hand, has bond lengths of 1·79 (2) Å (Vorontsova, 1966), comparable to those of (I*a*). In the absence of (I*a*) and (III), it would be tempting to attribute the long bonds of (IV) to a weak anti-aromaticity and the short bonds of (II) to a corresponding weak aromaticity, but if this were the sole factor, (I*a*) and (III), with virtually no contribution from cyclic conjugation, would fall in between. An alternative factor, which accounts for long bonds in (I*a*) and (IV), is steric hindrance; this is analogous to

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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 33611 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

O(1)S(1)–S(1)–O(2)S(1)	118·1 (5)	C(3)–C(2)–C(7)	124·6 (4)	C(5)–C(6)–H(2)C(6)	114 (1)
O(1)S(1)–S(1)–C(2)	107·0 (4)	S(4)–C(3)–C(2)	124·5 (4)	H(1)C(6)–C(6)–H(2)C(6)	109 (1)
O(2)S(1)–S(1)–C(2)	107·1 (4)	S(4)–C(3)–C(8)	111·7 (4)	C(2)–C(7)–H(1)C(7)	116 (2)
O(1)S(1)–S(1)–C(6)	109·2 (5)	C(2)–C(3)–C(8)	123·8 (4)	C(2)–C(7)–H(2)C(7)	113 (2)
O(2)S(1)–S(1)–C(6)	108·5 (4)	S(4)–C(5)–C(6)	110·1 (4)	C(2)–C(7)–H(3)C(7)	110 (2)
C(2)–S(1)–C(6)	106·3 (4)	S(4)–C(5)–H(1)C(5)	102 (1)	H(1)C(7)–C(7)–H(2)C(7)	110 (2)
O(1)S(4)–S(4)–O(2)S(4)	117·7 (3)	S(4)–C(5)–H(2)C(5)	105 (1)	H(1)C(7)–C(7)–H(3)C(7)	92 (2)
O(1)S(4)–S(4)–C(3)	108·2 (3)	C(6)–C(5)–H(1)C(5)	116 (1)	H(2)C(7)–C(7)–H(3)C(7)	114 (2)
O(2)S(4)–S(4)–C(3)	107·7 (3)	C(6)–C(5)–H(2)C(5)	114 (1)	C(3)–C(8)–H(1)C(8)	109 (2)
O(1)S(4)–S(4)–C(5)	109·3 (3)	H(1)C(5)–C(5)–H(2)C(5)	109 (1)	C(3)–C(8)–H(2)C(8)	106 (2)
O(2)S(4)–S(4)–C(5)	108·6 (3)	S(1)–C(6)–C(5)	110·3 (4)	C(3)–C(8)–H(3)C(8)	109 (2)
C(3)–S(4)–C(5)	104·7 (3)	S(1)–C(6)–H(1)C(6)	104 (1)	H(1)C(8)–C(8)–H(2)C(8)	123 (2)
S(1)–C(2)–C(3)	125·5 (4)	S(1)–C(6)–H(2)C(6)	104 (1)	H(1)C(8)–C(8)–H(3)C(8)	102 (2)
S(1)–C(2)–C(7)	109·9 (4)	C(5)–C(6)–H(1)C(6)	114 (1)	H(2)C(8)–C(8)–H(3)C(8)	107 (2)

the somewhat smaller lengthening (0·02 Å) which has been observed for vinyl–carbonyl bonds in *p*-benzoquinones when a H atom is replaced by a methyl group (Rabinovich, Schmidt & Ubell, 1967).

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5,6,7,8-Tetrafluoro-1,2,3,4-tetrahydro-9-isopropyl-1,4-methanonaphthalene

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Abstract. $C_{14}H_{14}F_4$, $M_r = 258·14$, monoclinic, $P2_1/c$ (absent reflections: $h0l$ when l odd, $0k0$ when k odd), $a = 8·56\,(1)$, $b = 9·26\,(2)$, $c = 15·72\,(2)$ Å, $\beta = 96·6\,(5)°$, $U = 1244·53$ Å^3, $Z = 4$, $D_x = 1·383$ g cm^{-3}, $F(000) = 536$. The structure was solved by direct methods and refined to $R = 0·060$ for the 806 observed reflections. The molecular configuration provides an explanation of an unexpected feature in the proton NMR spectrum.

Introduction. During a detailed study of the chemistry of arynes the reaction between tetrafluorobenzyne (I) and 6,6-dimethylfulvene (II) was studied (Hankinson, Heaney, Price & Sharma, 1973) whence the expected