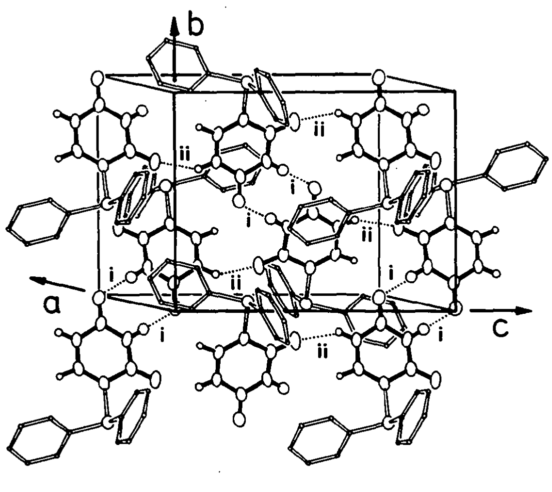

Fig. 2. Molecular packing in the crystal of 5-(diphenylphosphino)uracil; the phenyl rings are symbolized for clarity.

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The Structure of a Five-Membered Cyclic Sultone

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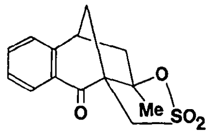
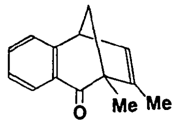
Abstract. 1,5-Dihydro-3a,5-dimethyl-1*H*-1,5-methanonaphtho[2,1-*c*][1,2]oxathiol-4(3a*H*)-one 3,3-dioxide, $C_{14}H_{14}O_4S$, $M_r = 278{\cdot}2$, monoclinic, *Cc*, $a = 7{\cdot}450\,(10)$, $b = 25{\cdot}246\,(10)$, $c = 6{\cdot}980\,(5)$ Å, $\beta = 104{\cdot}6\,(1)°$, $U = 1270{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}455$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0{\cdot}7107$ Å, $\mu = 2{\cdot}5$ cm^{-1}, $F(000) = 584$, $T = 293$ K, $R = 0{\cdot}062$ for 1012 reflexions with $I > 3\sigma(I)$. The structure contains a five- and a seven-membered saturated sultone ring. It is compared with known structures of saturated and partially unsaturated sultone rings. Bond lengths of interest are: mean acyclic S—O 1·415 (5), cyclic S—O 1·58 (1) and S—C 1·78 (1) Å.

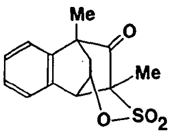
Introduction. In our studies of the rearrangement reactions of 1-methoxy-2,6-dimethylbenzobarrelene derivatives in sulfuric acid we obtained the sultone (1) whose structure was established by X-ray diffraction (Brown, Heaney & Mason, 1984). The product was thought to arise by sulfonation of an olefin (Roberts & Williams, 1987) concurrently with a 1,2-acyl shift. Since the complex formed between dioxan and sulfur trioxide is known to have electrophilic properties (Wolinsky, Dimmel & Gibson, 1967; Dimmel & Fu, 1973) we have studied the reaction of the ketone (2) with that reagent. The sultone (1) was formed but in addition we isolated a second sultone (3) whose X-ray crystal structure is now reported.



(1)



(2)



(3)

Experimental. Preparation by the method of Brown, Heaney, Ley, Mason & Singh (1978); colourless acicular crystals grown from ethanol, crystal (1·0 × 0·1 × 0·2 mm) mounted about **c**; Stoe Weissenberg diffractometer, $(\sin\theta)/\lambda < 0{\cdot}6$ Å^{-1}; lattice parameters from maximizing fit of axial row reflexions $10 < 2\theta < 30°$; 1186 unique reflexions measured, 1012 with

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$I > 3\sigma(I)$; h −8→8, k 0→30, l 0→7; standard check reflexion on each layer; no significant changes; no absorption corrections applied; structure solved by direct methods using *MULTAN* (Germain, Main & Woolfson, 1971), and refined by full-matrix least squares on F to $R = 0{\cdot}062$, $wR = 0{\cdot}062$; non-hydrogen atoms anisotropic, H atoms in calculated positions and not refined; unit weights from weight analysis; max. $\Delta/\sigma = 0{\cdot}9$, $\Delta\rho$ excursions $\pm 0{\cdot}2$ e Å^{-3}. Scattering factors for C, O and S from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). Calculations carried out with *XRAY* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) implemented at the University of Manchester Regional Computer Centre.*

Table 1. *Positional parameters* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å^2)

$$B_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i B_{ii}.$$

	x	y	z	$B_{\rm eq}$
S(1)	5984 (36)	2066 (1)	4986 (39)	4·0 (1)
C(1)	8823 (38)	1263 (3)	9596 (39)	2·8 (4)
C(2)	10593 (39)	1208 (4)	10786 (41)	3·6 (4)
C(3)	11093 (37)	753 (4)	11854 (40)	4·6 (5)
C(4)	9821 (41)	356 (4)	11773 (40)	4·4 (4)
C(5)	8022 (38)	397 (3)	10607 (40)	3·5 (4)
C(6)	7548 (38)	858 (3)	9518 (40)	3·0 (3)
C(7)	5630 (38)	979 (3)	8161 (40)	3·4 (4)
C(8)	6093 (37)	1055 (3)	6160 (39)	2·6 (3)
C(9)	8141 (38)	1720 (3)	8252 (40)	3·1 (3)
O(1)	5580 (37)	775 (2)	4730 (39)	4·1 (3)
C(10)	6368 (39)	8055 (3)	3687 (40)	3·8 (4)
C(11)	5001 (38)	8484 (3)	3842 (38)	3·4 (4)
C(12)	7393 (38)	8477 (3)	1108 (40)	2·9 (3)
C(13)	4204 (39)	9455 (4)	3048 (41)	4·9 (5)
C(14)	8872 (40)	8594 (4)	48 (41)	4·4 (5)
O(2)	5545 (37)	7714 (2)	1928 (39)	4·9 (3)
O(3)	7056 (39)	2444 (3)	4256 (39)	6·6 (5)
O(4)	4305 (40)	1899 (3)	3685 (39)	6·1 (4)

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

C(1)–C(2)	1·38 (4)	C(8)–C(12)	1·53 (3)
C(1)–C(6)	1·39 (3)	C(8)–O(1)	1·20 (3)
C(1)–C(9)	1·49 (2)	C(12)–C(14)	1·50 (4)
C(2)–C(3)	1·37 (2)	C(12)–C(9)	1·54 (4)
C(3)–C(4)	1·37 (3)	C(12)–S(1)	1·78 (2)
C(4)–C(5)	1·39 (4)	C(9)–C(10)	1·55 (4)
C(5)–C(6)	1·39 (2)	C(10)–C(11)	1·51 (3)
C(6)–C(7)	1·53 (3)	C(10)–O(2)	1·50 (3)
C(7)–C(8)	1·53 (4)	S(1)–O(2)	1·57 (4)
C(7)–C(11)	1·55 (2)	S(1)–O(3)	1·42 (3)
C(7)–C(13)	1·51 (3)	S(1)–O(4)	1·41 (3)

C(2)–C(1)–C(6)	119·5 (16)	C(1)–C(9)–C(10)	109·6 (23)
C(2)–C(1)–C(9)	125·5 (19)	C(1)–C(9)–C(12)	110·1 (11)
C(6)–C(1)–C(9)	115·0 (21)	C(10)–C(9)–C(12)	101·0 (20)
C(1)–C(2)–C(3)	120·1 (19)	C(11)–C(10)–O(2)	109·0 (20)
C(2)–C(3)–C(4)	120·0 (23)	C(11)–C(10)–C(9)	112·2 (12)
C(3)–C(4)–C(5)	121·7 (16)	O(2)–C(10)–C(9)	104·2 (23)
C(4)–C(5)–C(6)	117·4 (19)	C(10)–C(11)–C(7)	110·2 (23)
C(5)–C(6)–C(7)	125·1 (19)	C(14)–C(12)–S(1)	111·0 (19)
C(1)–C(6)–C(5)	121·3 (22)	C(14)–C(12)–C(8)	113·9 (15)
C(1)–C(6)–C(7)	113·6 (14)	C(14)–C(12)–C(9)	114·2 (22)
C(6)–C(7)–C(11)	107·0 (16)	S(1)–C(12)–C(8)	107·3 (18)
C(6)–C(7)–C(8)	101·6 (23)	S(1)–C(12)–C(9)	102·0 (13)
C(6)–C(7)–C(13)	114·9 (14)	C(8)–C(12)–C(9)	107·6 (21)
C(8)–C(7)–C(11)	109·0 (14)	C(10)–O(2)–S(1)	111·9 (15)
C(8)–C(7)–C(13)	111·0 (19)	O(3)–S(1)–O(4)	117·2 (22)
C(11)–C(7)–C(13)	112·8 (23)	O(3)–S(1)–C(12)	110·6 (20)
C(7)–C(8)–O(1)	125·8 (20)	O(3)–S(1)–O(2)	109·2 (13)
C(7)–C(8)–C(12)	113·9 (18)	O(4)–S(1)–C(12)	112·4 (8)
O(1)–C(8)–C(12)	120·2 (27)	O(4)–S(1)–O(2)	108·5 (24)
		C(12)–S(1)–O(2)	96·9 (17)

Discussion. The final atomic parameters for non-H atoms are given in Table 1 and a projection of the molecule with atom numbering is shown in Fig. 1. Bond lengths and angles are presented in Table 2.

The structure determination confirms the molecular structure of (3), with the molecule possessing both a five- and a seven-membered saturated sultone ring (with some common atoms). As far as we are aware there are only two other examples of saturated sultone crystal structures reported in the literature (Brown, Heaney & Mason, 1984; Petit, Lenstra, Geise, Hellier & Phillips, 1980). The former reference relates to the structure of (1) which contains a five/eight-membered sultone-ring system and the latter reference reports a single five-membered ring structure. There are also a number of structure reports on sultone rings with some degree of unsaturation (Barnett, Newton & McCormack, 1972; Beetz, Kellogg, Kiers & Piepenbroek, 1975; Brisse, Olivier, Harpp & Steliou, 1983; Fleischer, Kaiser, Langford, Hawkinson, Stone & Dewar, 1967) and an example of a partially unsaturated sultone ring containing nitrogen (Ballé, Born, Dieterich, Petinaux & Reiff, 1982).

The bond lengths and angles in the present structure are all in good accord with previously reported values.

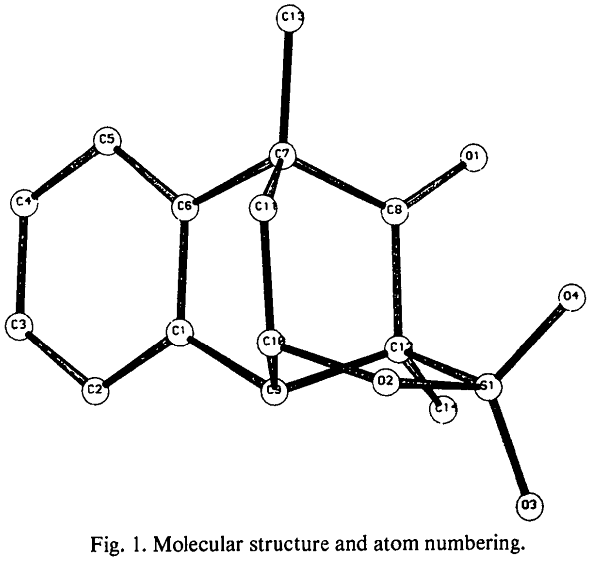

Fig. 1. Molecular structure and atom numbering.

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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 44039 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The acyclic S—O bond lengths of 1·41 (3) and 1·42 (3) Å agree well with reported values in the range 1·41 to 1·44 Å for similar compounds. The cyclic S—O bond length of 1·57 (4) Å compares with values in the range 1·55 to 1·63 Å in both saturated and partially unsaturated sultones. The S—C bond length of 1·78 (2) Å similarly falls in the middle of the range of previously reported values (1·73 to 1·82 Å).

There are no abnormal intermolecular contacts.

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Structure and Absolute Configuration, by Several Methods, of (*S*)-2-*O*-Acetyl-2-demethylthiocolchicine

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Abstract. 7-Acetamido-5,6,7,9-tetrahydro-1,3-dimethoxy-10-methylthio-9-oxobenzo[*a*]heptalen-2-yl acetate, $M_r = 501·59$, monoclinic, *A*2, $a = 13·721$ (2), $b = 10·925$ (1), $c = 16·795$ (1) Å, $\beta = 94·97$ (1)°, $V = 2508·14$ Å^3, $Z = 4$, $D_x = 1·328$ g cm^{-3}, λ(Cu $K\alpha$) $= 1·5418$ Å, $\mu = 14·91$ cm^{-1}, $F(000) = 1064$ [M_r, D_x, μ and $F(000)$ based on the formula $C_{23}H_{25}NO_6S.C_3H_6O$], $T = 293$ K, $R = 0·045$ for 2166 reflections with $I > \sigma(I)$. This colchicine derivative crystallizes as a solvate (possibly but not conclusively of acetone) and the structure reported represents the first X-ray determination of absolute configuration in this series of biologically active compounds. The absolute configuration was determined by several methods; all of which concur. The conformation of this compound resembles that of all previously reported colchicinoid compounds. The structure refinement was used as a test of a new vector processor.

Introduction. Colchicine and its analogs are thought to inhibit biological processes by blocking the polymerization of tubulin. For discussion and investigation of the biological action of colchicinoid compounds, it is important to know both conformation and configuration (Capraro & Brossi, 1983). Although a chemical determination was carried out by Corrodi & Hardegger (1955), no crystallographic determination of absolute configuration in this series has been reported in the literature. This investigation remedies the situation and adds a new colchicinoid crystal structure. In the preliminary stages of this work a large number of previously uninvestigated salts and derivatives of

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