

Fig. 2. A perspective view of the unit cell of (3).

found in 2,6-dimethylpyran-4-one (Brown, Norment & Levy, 1957).

The shortest intermolecular contact is between O(3) and C(12) at 3.203 (5) Å.

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## 7-Hydroxy-1,2,3,5,6,8-hexamethyltetracyclo[4.2.1.1<sup>2,5</sup>.0<sup>3,7</sup>]dec-4-yl Methanesulphonate, C<sub>17</sub>H<sub>28</sub>O<sub>4</sub>S

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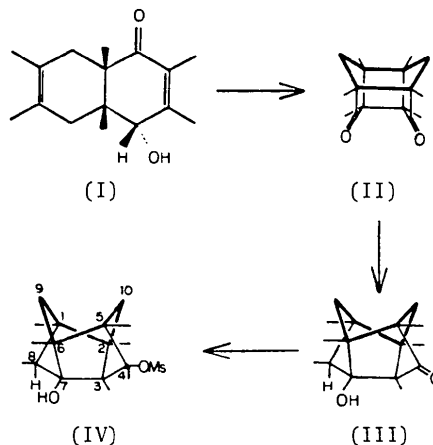
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**Abstract.**  $M_r = 328.48$ ,  $F(000) = 712$ , monoclinic,  $P2_1/c$ ,  $a = 9.246$  (2),  $b = 10.938$  (1),  $c = 17.335$  (4) Å,  $\beta = 102.11$  (1)°,  $V = 1714.1$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.273$  g cm<sup>-3</sup>,  $\mu(\text{Mo } K\alpha) = 1.94$  cm<sup>-1</sup>,  $\lambda = 0.71073$  Å,  $T = 294$  K,  $R = 0.042$  for 2997 reflexions. The ring skeleton has approximate 2 ( $C_2$ ) symmetry, with a twist-boat six-membered ring and envelope five-membered rings. Steric strain is evident in an intramolecular H...H distance of 2.03 Å, long C—C bonds (1.584–1.614 Å), and deviations from tetrahedral angles. Molecules are linked by an O—H...O hydrogen bond, H...O = 2.07 Å, O—H...O = 177°.

**Introduction.** Photoirradiation of the hexamethyl-tetrahydronaphthoquinol (I), followed by oxidation of the resulting photoproduct, produces the diketone (II) (Appel, Greenhough, Scheffer, Trotter & Walsh, 1980). An attempted intramolecular pinacolization of (II) resulted in formation of an unexpected product (Herbert, Scheffer, Secco & Trotter, 1981); crystals suitable for X-ray analysis could not be obtained. Sodium borohydride reduction of the product, followed by treatment of one of the resultant diols with methanesulphonyl chloride yielded a crystalline meth-

anesulphonate. Crystal structure analysis of this derivative now shows it to have structure (IV), containing a tetracyclo[4.2.1.1<sup>2,5</sup>.0<sup>3,7</sup>]decane ring system; the unexpected precursor is therefore (III).



**Experimental.** After several attempts at recrystallization of (IV), a crystal of fair quality was obtained from a hexane–acetone solution; 0.45 × 0.43 × 1.03 mm, not

cut to a smaller size for fear of shattering. CAD-4 diffractometer, monochromatized  $\text{Mo K}\alpha$ ,  $0 < \theta \leq 27.5^\circ$ ,  $\omega - (\frac{2}{3})\theta$  scans,  $\omega$  scan angle  $(0.90 + 0.35 \times \tan\theta)^\circ$ , scan speeds 1.44 to 10.06 deg min $^{-1}$ . The large mosaic spread and the size of the crystal necessitated the use of horizontal aperture widths between 3.00 and 3.52 mm, derived from the expression  $(3.00 + \tan\theta)$  mm; vertical aperture 4 mm. Three reflections checked to ensure proper crystal orientation; three additional reflections ( $\bar{4}85$ ;  $\bar{6},0,10$ ;  $5,0,10$ ) as intensity controls. Lorentz and polarization corrections, isotropic decay correction (3%), 3911 unique data measured, 2997 (76.6%) with  $I \geq 3\sigma(I)$ ,  $\sigma^2(I) = S + 2B + [0.040(S - B)]^2$ ;  $S$  is the scan count and  $B$  the time-averaged background. *MULTAN* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), full-matrix least squares,\* finally with anisotropic thermal parameters and with anomalous-dispersion correction for the S atom (Cromer & Liberman, 1970). H atoms from a difference map included with isotropic temperature factors. Final weighting scheme  $w = (A + B|F_o| + C|F_o|^2 + D|F_o|^3)^{-1}$ , with the parameters adjusted to give uniform averages of  $w\Delta^2$  ( $\Delta = |F_o| - k|F_c|$ ) over ranges of  $F_o$ ; 102 reflection given zero weight, since its high intensity overloaded the detection system. Atomic scattering factors from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965). Final  $R = 0.042$  and  $R_w = 0.058$  for the 2997 reflections with  $I \geq 3\sigma(I)$ , 311 parameters, mean and maximum shifts on final cycle 0.22 and 0.98 $\sigma$ , respectively, final values for the polynomial weighting scheme parameters  $A = 0.1986$ ,  $B = 0.01147$ ,  $C = -0.000743$ , and  $D = 0.000075$ . A difference-Fourier map had a peak of 0.48 e  $\text{\AA}^{-3}$ , midway between S and C(1S), other peaks ranging from  $-0.34$  to 0.36 e  $\text{\AA}^{-3}$ .

\* The computer programs used include locally written programs for data processing and locally modified versions of the following: *MULTAN* 78, multiresolution program (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); *ORFLS*, full-matrix least squares, and *ORFFE*, function and errors (Busing, Martin & Levy, 1962, 1964); *FORDAP*, Patterson and Fourier syntheses, by A. Zalkin (unpublished); *ORTEP* II, illustrations, by Johnson (1971).

Table 1. Final positional (fractional  $\times 10^5$ , H  $\times 10^3$ ) and isotropic thermal parameters ( $U \times 10^3 \text{\AA}^2$ ) with estimated standard deviations in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}/U_{iso}$
S	83184 (5)	52807 (4)	89249 (3)	43
O(1)	84901 (14)	38764 (10)	90544 (8)	41
O(2)	72994 (19)	55187 (13)	82021 (10)	64
O(3)	97730 (16)	57429 (14)	90274 (10)	59
O(4)	50043 (17)	21623 (13)	74732 (9)	53
C(1S)	75588 (39)	57845 (30)	97079 (21)	73
C(1)	76462 (19)	-1049 (16)	83729 (11)	39
C(11)	84945 (30)	-12879 (20)	83556 (21)	65
C(2)	86229 (18)	11101 (15)	85669 (11)	38
C(21)	101656 (25)	10284 (25)	83793 (22)	66
C(3)	76017 (18)	21744 (14)	81113 (9)	32
C(31)	80665 (31)	28463 (22)	74364 (13)	55
C(4)	72686 (18)	30234 (15)	87511 (10)	33
C(5)	71416 (21)	20454 (16)	93569 (10)	39

Table 1 (cont.)

	x	y	z	$U_{eq}/U_{iso}$
C(51)	68076 (40)	24510 (29)	101354 (15)	69
C(6)	59675 (19)	11802 (16)	88225 (11)	37
C(61)	43891 (27)	13283 (26)	89295 (19)	62
C(7)	61455 (18)	14684 (14)	79342 (10)	33
C(8)	65000 (21)	2214 (16)	76188 (11)	39
C(81)	69640 (40)	1689 (26)	68292 (15)	65
C(9)	65705 (23)	-1238 (17)	89386 (12)	42
C(10)	86609 (22)	14523 (17)	94287 (11)	44
H(O4)	435 (3)	173 (3)	730 (2)	78 (9)
H1(1S)	738 (4)	660 (4)	962 (2)	114 (13)
H2(1S)	816 (4)	554 (3)	1022 (2)	93 (10)
H3(1S)	664 (4)	542 (3)	968 (2)	87 (10)
H1(11)	908 (4)	-120 (3)	789 (2)	97 (11)
H2(11)	781 (3)	-195 (3)	825 (2)	72 (8)
H3(11)	920 (4)	-144 (3)	887 (2)	101 (11)
H1(21)	1064 (3)	190 (3)	846 (2)	83 (9)
H2(21)	1005 (4)	74 (3)	777 (2)	97 (11)
H3(21)	1076 (3)	46 (3)	869 (2)	83 (10)
H1(31)	841 (3)	232 (3)	705 (2)	94 (9)
H2(31)	881 (3)	341 (3)	765 (2)	67 (7)
H3(31)	724 (3)	337 (3)	716 (2)	81 (9)
H(4)	643 (2)	343 (2)	856 (1)	46 (6)
H1(51)	592 (4)	296 (3)	1006 (2)	101 (11)
H2(51)	654 (3)	177 (3)	1045 (2)	97 (10)
H3(51)	763 (4)	301 (4)	1043 (2)	109 (12)
H1(61)	411 (3)	219 (3)	889 (2)	69 (8)
H2(61)	370 (3)	80 (3)	855 (2)	83 (9)
H3(61)	427 (3)	107 (3)	948 (2)	87 (9)
H(8)	569 (2)	-32 (2)	758 (1)	42 (6)
H1(81)	788 (3)	42 (3)	684 (2)	64 (8)
H2(81)	693 (3)	-69 (3)	665 (2)	85 (9)
H3(81)	630 (4)	67 (4)	644 (2)	111 (12)
H1(9)	705 (3)	-33 (2)	947 (2)	60 (7)
H2(9)	579 (3)	-71 (2)	878 (1)	59 (6)
H1(10)	945 (2)	202 (2)	960 (1)	48 (6)
H2(10)	889 (3)	69 (3)	981 (2)	72 (8)

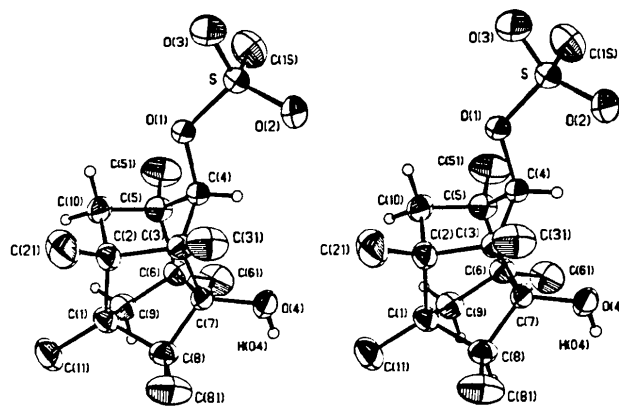


Fig. 1. Stereodiagram of the title compound.

**Discussion.** Atomic coordinates and isotropic thermal parameters are listed in Table 1.\*

The tetracyclo[4.2.1.1 $^{2,5}$ .0 $^{3,7}$ ]decane ring skeleton (Fig. 1) has approximate 2 ( $C_2$ ) symmetry, the pseudo-rotation axis passing through the centre of the lone six-membered ring, C(1,2,10,5,6,9), and the midpoint of the C(3)–C(7) bond. The six-membered ring has a

\* Anisotropic thermal parameters, torsion angles, bond lengths and angles involving H atoms, packing diagram, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38394 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

twist-boat conformation, with some distortion from the ideal twist-boat arrangement (Bucourt & Hainaut, 1965). The torsion angles\* are:

C(9)–C(1)–C(2)–C(10)	25.9 (2)°	C(10)–C(5)–C(6)–C(9)	28.9 (2)°
C(1)–C(2)–C(10)–C(5)	–78.2 (2)	C(5)–C(6)–C(9)–C(1)	81.4 (2)
C(2)–C(10)–C(5)–C(6)	46.4 (2)	C(6)–C(9)–C(1)–C(2)	48.8 (2)

The CH<sub>3</sub>–C(1)–C(2)–CH<sub>3</sub> and CH<sub>3</sub>–C(5)–C(6)–CH<sub>3</sub> torsion angles are 23.9 and 27.9° ( $\sigma = 0.3^\circ$ ), respectively. All four five-membered rings have approximate envelope conformations, with one atom deviating markedly from the plane through the remaining four atoms.

The ring system produces considerable steric compression of the inner H atoms of C(9) and C(10) [see formula (IV)], with H1(9)···H2(10) = 2.02 (3) Å, considerably below the van der Waals radii sum of 2.40 Å. Some bond lengths in the ring system (Table 2) are considerably lengthened as a result of strain, in particular C(1)–C(2) = 1.602, C(5)–C(6) = 1.584, C(2)–C(3) = 1.599, and C(6)–C(7) = 1.614 (2) Å [formula (IV) indicates the disposition of these bonds]. Many bond angles (Table 2) also differ considerably from the ideal tetrahedral angle, with values in the range 94–120° ( $\sigma = 0.1$ – $0.2^\circ$ ); these deviations are not surprising for such a caged ring system.

The geometry of the methylsulphonyl group is similar to that observed in other structures (Daly, 1961; Attig & Mootz, 1975). S–OC = 1.556 (1), S–O(terminal) = 1.425 (2) (involved in hydrogen bonding), 1.413 (2), S–C = 1.743 (3) Å; O(2)–S–O(3) is the largest angle (as expected) at 118.8 (1)°. The C–CH<sub>3</sub> bond distances, 1.513–1.531 (3) Å, are generally slightly smaller than normal C(sp<sup>3</sup>)–C(sp<sup>3</sup>) lengths, but the observed lengths may be affected by thermal libration.

The structure contains chains of molecules along **b**,\* linked by O(2)···H–O(4)(1–*x*,  $\frac{1}{2}+y$ ,  $\frac{3}{2}-z$ ) hydrogen bonds, O···O = 2.845 (2), O···H = 2.07 (3) Å, O···H–O = 177 (3)°.

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Table 2. Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses

S–O(1)	1.5556 (12)	C(3)–C(31)	1.518 (2)
S–O(2)	1.4248 (15)	C(3)–C(4)	1.527 (2)
S–O(3)	1.4128 (15)	C(3)–C(7)	1.526 (2)
S–C(1S)	1.743 (3)	C(4)–C(5)	1.521 (2)
O(1)–C(4)	1.474 (2)	C(5)–C(51)	1.513 (3)
O(4)–C(7)	1.405 (2)	C(5)–C(6)	1.584 (2)
C(1)–C(11)	1.517 (3)	C(5)–C(10)	1.529 (3)
C(1)–C(2)	1.602 (2)	C(6)–C(61)	1.518 (3)
C(1)–C(8)	1.542 (2)	C(6)–C(7)	1.614 (2)
C(1)–C(9)	1.536 (3)	C(6)–C(9)	1.529 (2)
C(2)–C(21)	1.531 (3)	C(7)–C(8)	1.530 (2)
C(2)–C(3)	1.599 (2)	C(8)–C(81)	1.519 (3)
C(2)–C(10)	1.533 (3)		
O(1)–S–O(2)	109.64 (8)	O(1)–C(4)–C(5)	111.30 (13)
O(1)–S–O(3)	105.64 (8)	C(3)–C(4)–C(5)	97.49 (13)
O(1)–S–C(1S)	104.20 (13)	C(4)–C(5)–C(51)	118.0 (2)
O(2)–S–O(3)	118.79 (11)	C(4)–C(5)–C(6)	99.16 (13)
O(2)–S–C(1S)	109.08 (15)	C(4)–C(5)–C(10)	98.75 (14)
O(3)–S–C(1S)	108.50 (15)	C(51)–C(5)–C(6)	117.0 (2)
S–O(1)–C(4)	121.74 (10)	C(51)–C(5)–C(10)	114.1 (2)
C(11)–C(1)–C(2)	116.1 (2)	C(6)–C(5)–C(10)	107.42 (14)
C(11)–C(1)–C(8)	116.6 (2)	C(5)–C(6)–C(61)	115.0 (2)
C(11)–C(1)–C(9)	114.1 (2)	C(5)–C(6)–C(7)	104.28 (12)
C(2)–C(1)–C(8)	104.05 (13)	C(5)–C(6)–C(9)	107.10 (15)
C(2)–C(1)–C(9)	106.80 (15)	C(61)–C(6)–C(7)	112.9 (2)
C(8)–C(1)–C(9)	97.03 (14)	C(61)–C(6)–C(9)	114.6 (2)
C(1)–C(2)–C(21)	114.6 (2)	C(7)–C(6)–C(9)	101.56 (14)
C(1)–C(2)–C(3)	104.58 (13)	O(4)–C(7)–C(3)	111.50 (13)
C(1)–C(2)–C(10)	107.68 (15)	O(4)–C(7)–C(6)	115.69 (14)
C(21)–C(2)–C(3)	114.7 (2)	O(4)–C(7)–C(8)	118.02 (14)
C(21)–C(2)–C(10)	112.9 (2)	C(3)–C(6)–C(9)	99.74 (12)
C(3)–C(2)–C(10)	101.18 (13)	C(3)–C(7)–C(8)	106.07 (14)
C(2)–C(3)–C(31)	120.0 (2)	C(6)–C(7)–C(8)	103.84 (13)
C(1)–C(3)–C(4)	105.80 (13)	C(1)–C(8)–C(7)	93.67 (13)
C(2)–C(3)–C(7)	97.79 (12)	C(1)–C(8)–C(81)	118.8 (2)
C(31)–C(3)–C(4)	113.47 (15)	C(7)–C(8)–C(81)	118.5 (2)
C(31)–C(3)–C(7)	118.05 (15)	C(1)–C(9)–C(6)	99.82 (13)
C(4)–C(3)–C(7)	98.63 (13)	C(2)–C(10)–C(5)	101.03 (13)
O(1)–C(4)–C(3)	112.82 (14)		

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\* See deposition footnote.