

Two Bu' groups in each of the two independent molecules occupy equatorial positions [groups attached to S(1), S(2) and S(4), S(5)]. The third Bu' group in each of the two molecules occupies an axial position [on S(3) and S(6)]. The orientation of these groups is depicted in Fig. 2. This arrangement of the Bu' substituents apparently is a solid-state effect. In solution and at room temperature the Bu' groups are indistinguishable and only a single <sup>1</sup>H NMR resonance is observed in CH<sub>2</sub>Cl<sub>2</sub> solution with a  $\delta$  value of 2.01.

The B—S—B angles range from 103.3 (4) to 110.9 (4)°. The S—B—S angles range from 102.6 (5) to 111.1 (5)°. The disposition of the Bu' groups (axial *vs* equatorial, Fig. 2) seems to affect the magnitude of the B—S—B and S—B—S angles in a systematic fashion. The B—S—B angles adjacent to the axially-disposed Bu' groups in each of the two independent molecules [at 110.9 (4) and 109.4 (5)° respectively for B(2)—S(3)—B(3) and B(4)—S(6)—B(5)] are significantly larger than the B—S—B angles associated with the equatorial Bu' groups. The latter are found at 103.3 (4) and 104.3 (4)° and at 104.4 (5) and 105.4 (4)° in the two independent molecules.

In a similar systematic fashion, the S—B—S angles opposite to the S atoms with axial Bu' groups [S(1)—B(1)—S(2) and S(4)—B(6)—S(5), Fig. 2] are small [103.0 (5) and 102.6 (5)°]. In contrast, the remaining S—B—S angles are larger with values of

110.8 (5), 111.1 (5), 109.0 (5) and 109.0 (5)° (Table 2).

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## 1,6-Dimethyl-1 $\alpha$ ,4 $\alpha$ ,4 $\alpha$ ,5 $\alpha$ ,8 $\beta$ ,8 $\alpha\alpha$ -hexahydro-1,4-methanonaphthalene-5,8-diol

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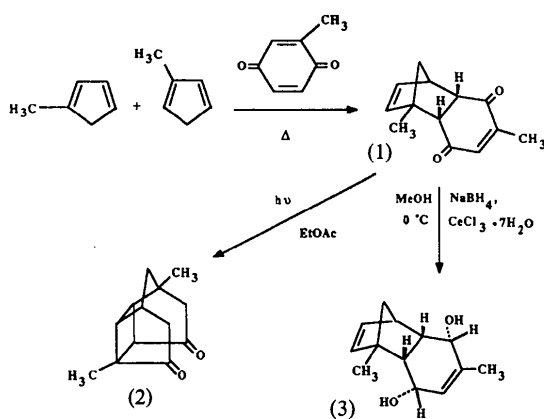
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**Abstract.** C<sub>13</sub>H<sub>18</sub>O<sub>2</sub>,  $M_r = 206.26$ , monoclinic,  $P2_1/c$ ,  $a = 9.830$  (2),  $b = 9.618$  (3),  $c = 12.584$  (4) Å,  $\beta = 111.29$  (2)°,  $V = 1108.5$  (6) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.24$  Mg m<sup>-3</sup>,  $D_m$  not measured,  $\lambda(\text{Cu K}\alpha) = 1.54178$  Å,  $\mu = 0.61$  mm<sup>-1</sup>,  $F(000) = 448$ ,  $T = 295$  K,  $R = 0.077$  for 1252 unique observed data. The X-ray study showed that the hydroxyl groups are on the same side of the six-membered ring and also showed the relative positions of the two methyl groups. There is a *cis* junction between the two six-membered rings, both of which are in a boat conformation. There is one intramolecular OH...O hydrogen bond (O...O =

2.82 Å) and one intermolecular OH...O hydrogen bond (O...O = 2.80 Å).

**Introduction.** A study of the Diels–Alder reaction of substituted cyclopentadienes with substituted *p*-benzoquinones has been undertaken as part of a program that involves the synthesis of novel substituted polycyclic 'cage' molecules (Marchand, Suri, Earlywine, Powell & van der Helm, 1984; Marchand, 1987). Thermolysis of methylcyclopentadiene dimer affords a mixture of 1- and 2-methylcyclopentadienes (Csicsery, 1960). Diels–Alder cycloaddition of this diene mixture to 2-methyl-

*p*-benzoquinone afforded a mixture of isomeric adducts from which a single isomer (1) could be isolated by careful elution chromatography. That this adduct possesses the *endo* configuration was shown by its facile intramolecular photocyclization to afford the corresponding dimethylpentacyclo[5.4.0.0<sup>2,6</sup>.0<sup>3,10</sup>.0<sup>5,9</sup>]-undecane-8,11-dione (2). Reduction of (1) with sodium borohydride in the presence of cerous chloride heptahydrate (Marchand, LaRoe, Sharma, Suri & Reddy, 1986) proceeded stereospecifically to afford a single diol, (3). In order to resolve ambiguities regarding (i) the relative positions of the two methyl groups and (ii) the relative stereochemistry of the two CHOH centers in (3), its structure was elucidated by X-ray diffraction. A suitable crystal, m.p. 402–403 K, was obtained *via* recrystallization from acetone. Once the structure of (3) had been determined, the structures of (1) and (2) could be deduced in accordance with the reaction sequence shown below.



**Experimental.** Crystals grown by evaporation from acetone, unit-cell parameters from 25 reflections ( $50 < 2\theta < 80^\circ$ ),  $P2_1/c$  derived from symmetry and systematic absences, 1846 independent reflections with  $2\theta_{\max} = 115^\circ$ , range of  $hkl$   $-10 \leq h \leq 0 \leq k \leq 10$ ,  $-12 \leq l \leq 12$ , three standard reflections (204, 040, 302) measured after every 60 new reflections showed an average random variation of 2%. Crystal size  $0.40 \times 0.25 \times 0.15$  mm. Nicolet R3M diffractometer, graphite monochromator in incident beam.  $\theta$ - $2\theta$  scan technique with variable scan speed between  $14$  and  $30^\circ \text{ min}^{-1}$ . 1846 reflections measured, 1542 unique, 1252 observed,  $R_{\text{int}} = 0.023$ . Lorentz and polarization corrections but not absorption corrections. Structure solved by direct methods. Full-matrix least squares, H atoms from difference maps,  $\sum w(|F_o| - |F_c|)^2$  minimized where  $w = 1/[\sigma^2(|F_o|) + g(|F_o|)^2]$  and  $g(F_o)^2$  is included to account for random instrumental error ( $g$  estimated to be 0.00023). Secondary-extinction parameter  $P = 0.016$  (3) in  $F_c^* = F_c/[1.0 + 0.002(P)F_o^2/\sin^2\theta]^{0.25}$ . 147 parameters refined, atomic coordinates, anisotropic temperature factors for non-H atoms. H coordinates

(from difference maps) were idealized (C–H distance set at  $0.96 \text{ \AA}$ , CH angles set to trigonal or tetrahedral values, thermal parameter set at  $1.2 \times$  equivalent isotropic value of bonded atom), then allowed to ride on covalently bonded neighbors. Hydroxyl H coordinates refined. The H atoms on C(10) were found to be disordered. One set was refined then held constant along with positions for second set of H atoms as found in difference map. Occupancy refinement for the two methyl positions indicated a ratio of approximately 2:1.  $R = 0.077$ ,  $wR = 0.086$ ,  $S = 2.71$ ,  $(\Delta/\sigma)_{\max} = 0.022$  for 1252 observed reflections [ $F_o > 3\sigma(F_o)$ ], final difference Fourier excursions  $0.24$  and  $-0.32 \text{ e \AA}^{-3}$ . All calculations performed using the *SHELXTL* system of programs (Sheldrick, 1980). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ )

	x	y	z	$U_{\text{eq}}^*$
O1	6023 (4)	1169 (3)	2218 (3)	50 (1)
O2	5280 (3)	-1196 (3)	3224 (3)	50 (1)
C1	7980 (5)	-2463 (4)	2907 (4)	49 (2)
C2	6726 (5)	-2215 (4)	1805 (4)	48 (2)
C3	7018 (5)	-1078 (4)	1319 (4)	50 (2)
C4	8484 (5)	-561 (4)	2086 (4)	51 (2)
C4a	8365 (5)	46 (4)	3186 (3)	45 (2)
C5	7401 (5)	1304 (4)	3137 (3)	43 (2)
C6	7170 (5)	1440 (4)	4263 (4)	48 (2)
C7	6829 (5)	307 (4)	4711 (4)	52 (2)
C8	6685 (5)	-1090 (4)	4128 (4)	47 (2)
C8a	7986 (5)	-1274 (4)	3743 (4)	45 (2)
C9	9229 (5)	-1935 (4)	2537 (5)	60 (2)
C(10)	7229 (6)	2883 (5)	4744 (4)	61 (2)
C11	8087 (6)	-3916 (4)	3405 (5)	66 (2)

\* Equivalent isotropic  $U$  defined as one-third of the trace of the orthogonalized  $U_{ij}$  tensor.

Table 2. Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

O1–C5	1.432 (5)	O2–C8	1.438 (5)
C1–C2	1.502 (6)	C1–C8a	1.551 (5)
C1–C9	1.548 (6)	C1–C11	1.519 (5)
C2–C3	1.334 (6)	C3–C4	1.498 (6)
C4–C4a	1.545 (5)	C4–C9	1.517 (6)
C4a–C5	1.524 (5)	C4a–C8a	1.559 (5)
C5–C6	1.519 (6)	C6–C7	1.324 (5)
C6–C10	1.507 (5)	C7–C8	1.513 (5)
C8–C8a	1.533 (6)		
C8a–C1–C2	108.0 (3)	C9–C1–C2	98.3 (4)
C9–C1–C8a	98.8 (3)	C11–C1–C2	116.0 (4)
C11–C1–C8a	114.6 (4)	C11–C1–C9	118.8 (4)
C3–C2–C1	108.2 (4)	C4–C3–C2	107.0 (4)
C4a–C4–C3	109.6 (3)	C9–C4–C3	100.0 (4)
C9–C4–C4a	100.2 (3)	C5–C4a–C4	120.8 (3)
C8a–C4a–C4	101.7 (3)	C8a–C4a–C5	114.7 (3)
C4a–C5–O1	110.6 (3)	C6–C5–O1	110.1 (4)
C6–C5–C4a	109.4 (3)	C7–C6–C5	118.2 (4)
C10–C6–C5	117.2 (4)	C10–C6–C7	124.4 (4)
C8–C7–C6	121.2 (4)	C7–C8–O2	109.9 (3)
C8a–C8–O2	114.4 (3)	C8a–C8–C7	108.3 (4)
C4a–C8a–C1	103.8 (3)	C8–C8a–C1	120.0 (4)
C8–C8a–C4a	114.2 (3)	C4–C9–C1	94.0 (3)

**Discussion.** Table 1 lists the coordinates and  $U_{eq}$  values for the non-H atoms of (3).<sup>\*</sup> Fig. 1 shows the results of the X-ray analysis and the numbering scheme. There is a *cis* junction between the two six-membered rings (H8a—C8a—C4a—H4a = 0.5°). The bridged six-membered ring is in a normal boat conformation (average absolute value of the four non-planar torsions is 65.2°) while the hydroxylated six-membered ring has a much flatter boat conformation (average absolute value for non-planar torsions is 44.4°). This may be due, in part, to the presence of an intramolecular hydrogen bond with O2 as the donor and O1 as the acceptor (O...O 2.82, H...O 1.89 Å, O—H...O 154.9°). Strain in the molecule is evidenced by the smaller than normal internal ring angles (see Table 2) in the bridged ring system. This is especially true for all the angles in the five-membered ring involving C(9). Packing in this crystal is influenced by the presence of an intermolecular hydrogen bond with O1 as the donor and O2 as the acceptor (O...O 2.80, H...O 1.96 Å, O—H...O 171.8°).

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<sup>\*</sup> Lists of structure factors, H-atom coordinates and anisotropic thermal parameters for non-H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44175 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

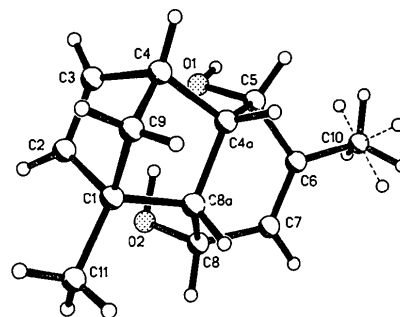


Fig. 1. Results of the X-ray study on (3).

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### Structure of a 7 $\alpha$ -Methoxy-1-oxacephem: Dichloromethane Solvated (–)-(6*R*,7*R*)-7-{2-[(Difluoromethyl)thio]acetamido}-3-([1-(2-hydroxyethyl)-1*H*-tetrazol-5-yl]thio)methyl)-7-methoxy-8-oxo-5-oxa-1-azabicyclo[4.2.0]oct-2-ene-2-carboxylic Acid

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**Abstract.** C<sub>15</sub>H<sub>18</sub>F<sub>2</sub>N<sub>6</sub>O<sub>7</sub>S<sub>2</sub>.CH<sub>2</sub>Cl<sub>2</sub>,  $M_r = 581.39$ , monoclinic,  $P2_1$ ,  $a = 11.435$  (3),  $b = 11.275$  (2),  $c = 10.178$  (2) Å,  $\beta = 113.52$  (1)°,  $V = 1203.2$  (5) Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.605$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7107$  Å,  $\mu(\text{Mo } K\alpha) = 0.51$  mm<sup>-1</sup>,  $F(000) = 596$ ,  $T = 295$  K,  $R = 0.028$  for 2580 reflections. The N—C and C=O bonds in the  $\beta$ -lactam amide group are 1.392 (3) and 1.192 (3) Å, respectively. The N atom is displaced by

0.290 (2) Å from the plane of the three attached C atoms.

**Introduction.** 1-Oxacephems possessing the 1-oxa-1-dethia-3-cephem skeleton are antibiotics which compare favorably with penicillins and cephalosporins. Especially of interest are their 7 $\alpha$ -methoxy derivatives which are stable to  $\beta$ -lactamases. One of them,