

Fig. 2. A projection of the structure viewed along *c* (*a* is horizontal).

1.478 (3) Å respectively. The angles at C1 exhibit the usual deviations from 120°.

Both substituents on the lactone ring are in pseudo-equatorial positions *cis* to each other. There are two optically active C atoms in the molecule and the absolute configurations at C2 and C4 were determined as *S* and *R*, respectively.

The six- and five-membered rings of the phthalimido group are planar within 0.018 (3) and 0.003 (3) Å. The dihedral angle between these two rings is 1.82 (8)°. The parameters of the phthalimido group are consistent with those in other phthalimido derivatives (Matijašić *et al.*, 1988; Iwasaki & Masuko, 1986; Bats & Teuber, 1985; Loehlin, 1985; Voliotis, Arrieta & Germain, 1984).

The packing of the molecule in the solid state, illustrated in Fig. 2, is due only to intermolecular van der Waals forces.

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Structure of Diethyl 3,6-Dihydroxy-11,11-dimethoxypentacyclo[6.5.0.0^{4,12}.0^{5,10}.0^{9,13}]-tridecane-2,6-diene-2,7-dicarboxylate

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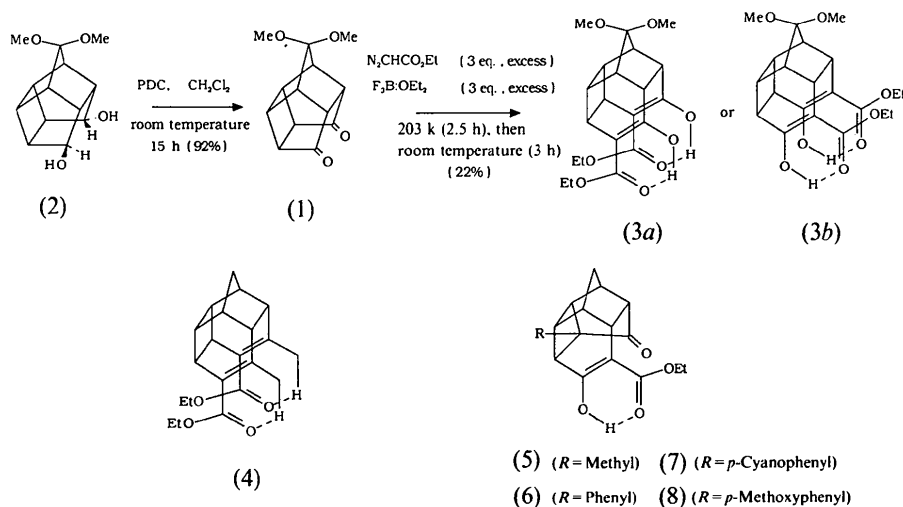
(Received 17 October 1988; accepted 3 February 1989)

Abstract. C₂₁H₂₆O₈, *M_r* = 406.43, orthorhombic, *Pcab* (non-standard setting of *Pbca*), *a* = 8.181 (1), *b* = 18.852 (3), *c* = 25.413 (3) Å, *V* = 3918.1 (8) Å³, *Z* = 8, *D_x* = 1.38 Mg m⁻³, λ(Cu *Kα*) = 1.54178 Å, μ = 0.84 mm⁻¹, *F*(000) = 1728, *T* = 295 K, final *R* = 0.049, *wR* = 0.050 for 2105 observed reflections. Strain is

evidenced in the molecule by the fact that two of the three *sp*³—*sp*³ cross-cage carbon bonds are quite long [1.588 (4) and 1.596 (4) Å] and by the acute internal cage angle of 95.0 (2)° at the C atom which is common to both five-membered rings. Further strain is added to the molecule by the presence of the

four-membered ring. The two six-membered rings forming the sides of the cage bend away from one another and both OH groups form intramolecular hydrogen bonds.

Introduction. As part of a program that involves the synthesis and chemistry of novel, substituted cage compounds (Marchand, 1989), we recently studied the boron-trifluoride-promoted reaction of 4,4-dimethoxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (1) with excess ethyl diazoacetate (EDA). Dione (1) was synthesized by oxidation of *exo*-8,-*exo*-11-dihydropentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecan-4-one dimethyl acetal (2) (Marchand, Sharma, Annapurna & Pednekar, 1987) with pyridinium dichromate (PCD) in methylene chloride solution. A single bishomologation product, (3), was thereby obtained in 22% yield. The reaction sequence by which (3) was synthesized is summarized below.



The ¹³C NMR spectrum of (3) displayed only 12 signals, a result which suggests that this product possesses twofold symmetry. Of the three possible bishomologation products that might have resulted from the reaction of (1) with excess EDA, only two (3a and 3b, scheme) possess the required symmetry. The fact that the material isolated from this reaction is the title compound (3a) and not isomer (3b) was confirmed unambiguously *via* single-crystal X-ray structural analysis. A good quality single crystal of (3a), m.p. 416–417 K, was obtained by careful recrystallization from hexane.

Experimental. Clear, colorless, 0.37 × 0.30 × 0.10 mm crystal. Nicolet R3m/V diffractometer with incident-beam graphite monochromator, 25 centered reflections within 45 < 2θ < 84° used for determining lattice parameters; 2θ_{max} = 115°, range of *hkl*: 0 ≤ *h* ≤ 8, 0 ≤ *k* ≤ 20, -27 ≤ *l* ≤ 27. Standards 200, 060, 008,

monitored every 100 reflections with random variation of ±2.0% over data collection, θ-2θ mode, scan width (2.0 + Δ2θ_{α₁α₂})°, scan rate a function of count rate (10° min⁻¹ minimum, 60° min⁻¹ maximum), 4369 reflections measured, 2673 unique (*R*_{int} = 0.013), 2105 observed [*F*_o > 3σ(*F*_o)]. Data corrected for Lorentz and polarization effects, but not for absorption.

Structure solved by direct methods. Full-matrix least-squares refinement, H atoms from difference maps, Σ*w*(|*F*_o - |*F*_c||² minimized where *w* = 1/[σ²(|*F*_o|| + *g*(|*F*_o||²) and *g*(*F*_o)² is included to account for random instrumental error (*g* estimated to be 0.00025). Secondary-extinction parameter *P* = 0.0038 (3) in *F*_c* = *F*_c/[1.0 + 0.002(*P*)*F*_c²/(sin 2θ)]^{0.25}, 375 parameters refined; atomic coordinates for all non-disordered atoms, anisotropic temperature factors for non-H atoms, isotropic temperature factors

for H atoms except those on disordered atoms. Distances in disordered groups [O(7)—C(20)—C(21) and O(7')—C(20')—C(21')] were constrained [O—C*sp*² = 1.340 (5), O—C*sp*³ = 1.465 (5), C—C = 1.476 (5), C⋯C = 2.380 (8) and C⋯O = 2.370 (8) Å]. Disordered H atoms were included at fixed positions and not allowed to vary. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Final *R* = 0.049, *wR* = 0.050, max. Δ/σ = 0.045, *S* = 1.67. Final difference Fourier excursions 0.43 and -0.38 e Å⁻³.† All calculations were performed using the *SHELXTL* system (Sheldrick, 1980).

† Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51926 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

O(7), C(20), C(21), O(7'), C(20') and C(21') are the atoms involved in the disordered carboxylate group.

	x	y	z	U_{eq} *
O(1)	708 (3)	9449 (1)	3181 (1)	57 (1)
O(2)	4389 (3)	10884 (1)	3361 (1)	61 (1)
O(3)	1073 (3)	11298 (1)	1782 (1)	46 (1)
O(4)	-981 (3)	12082 (1)	2021 (1)	46 (1)
O(5)	-1778 (3)	10328 (1)	4438 (1)	57 (1)
O(6)	-709 (3)	9345 (1)	4079 (1)	61 (1)
O(7)	1991 (9)	11863 (4)	4603 (2)	65 (2)
O(8)	4337 (3)	11356 (1)	4314 (1)	78 (1)
C(1)	402 (4)	11757 (2)	3635 (1)	43 (1)
C(2)	68 (4)	12029 (2)	3066 (1)	39 (1)
C(3)	1292 (4)	11812 (2)	2640 (1)	39 (1)
C(4)	141 (4)	11571 (1)	2200 (1)	41 (1)
C(5)	-763 (4)	11020 (2)	2539 (1)	40 (1)
C(6)	-1332 (4)	11480 (2)	3000 (1)	40 (1)
C(7)	-1032 (4)	11198 (2)	3567 (1)	41 (1)
C(8)	-605 (4)	10426 (1)	3600 (1)	41 (1)
C(9)	230 (4)	10135 (2)	3202 (1)	42 (1)
C(10)	666 (4)	10550 (2)	2723 (1)	41 (1)
C(11)	2115 (4)	11109 (2)	2794 (1)	39 (1)
C(12)	2857 (4)	11159 (2)	3330 (1)	45 (1)
C(13)	2092 (4)	11486 (2)	3733 (1)	43 (1)
C(14)	127 (7)	10963 (3)	1380 (2)	65 (2)
C(15)	-248 (6)	12690 (2)	1777 (2)	63 (1)
C(16)	-1014 (4)	9982 (2)	4049 (1)	47 (1)
C(17)	-2275 (6)	9892 (2)	4887 (1)	62 (1)
C(18)	-2972 (8)	10382 (3)	5286 (2)	78 (2)
C(19)	2933 (5)	11570 (2)	4229 (1)	59 (1)
C(20)	2730 (15)	12002 (3)	5115 (2)	85 (3)
C(21)	2859 (11)	12774 (3)	5181 (3)	97 (3)
O(7')	2265 (20)	12044 (11)	4556 (6)	101 (8)
C(20')	3293 (20)	12267 (12)	4999 (6)	104 (10)
C(21')	2181 (22)	12396 (10)	5446 (4)	92 (7)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_j tensor.

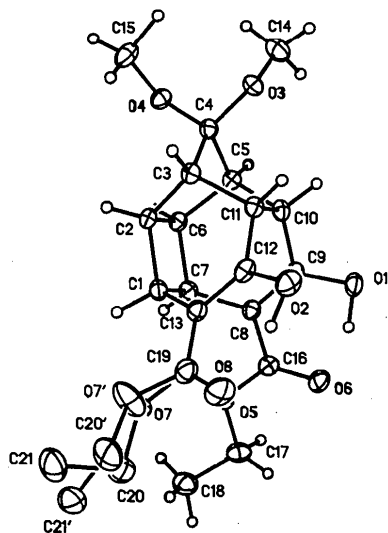


Fig. 1. Perspective view of the molecule showing atom numbering.

Discussion. The numbering in Tables 1 and 2 (coordinates and bond lengths and angles) follows that shown in Fig. 1 which displays the results of the X-ray study on (3a). Bond lengths and angles fall into normal ranges except for the long C(1)—C(7) and C(10)—C(11) bonds [1.588 (4) and 1.596 (4) Å respectively] and the acute C(3)—C(4)—C(5) angle

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

O(1)—C(9)	1.352 (3)	O(2)—C(12)	1.359 (4)
O(3)—C(4)	1.405 (3)	O(3)—C(14)	1.430 (5)
O(4)—C(4)	1.407 (3)	O(4)—C(15)	1.433 (5)
O(5)—C(16)	1.339 (4)	O(5)—C(17)	1.465 (4)
O(6)—C(16)	1.229 (4)	O(7)—C(19)	1.340 (7)
O(7)—C(20)	1.460 (9)	O(8)—C(19)	1.237 (5)
C(1)—C(2)	1.559 (4)	C(1)—C(7)	1.588 (4)
C(1)—C(13)	1.495 (5)	C(2)—C(3)	1.530 (4)
C(2)—C(6)	1.553 (4)	C(3)—C(4)	1.532 (4)
C(3)—C(11)	1.537 (4)	C(4)—C(5)	1.539 (4)
C(5)—C(6)	1.530 (4)	C(5)—C(10)	1.541 (4)
C(6)—C(7)	1.555 (4)	C(7)—C(8)	1.498 (4)
C(8)—C(9)	1.339 (4)	C(8)—C(16)	1.454 (4)
C(9)—C(10)	1.490 (4)	C(10)—C(11)	1.596 (4)
C(11)—C(12)	1.495 (4)	C(12)—C(13)	1.347 (4)
C(13)—C(19)	1.447 (4)	C(17)—C(18)	1.485 (6)
C(19)—O(7')	1.337 (18)	C(20)—C(21)	1.469 (8)
O(7')—C(20')	1.466 (23)	C(20')—C(21')	1.475 (21)
C(4)—O(3)—C(14)	114.1 (3)	C(4)—O(4)—C(15)	114.5 (3)
C(16)—O(5)—C(17)	115.5 (2)	C(19)—O(7)—C(20)	117.9 (4)
C(2)—C(1)—C(7)	89.3 (2)	C(2)—C(1)—C(13)	115.4 (3)
C(7)—C(1)—C(13)	118.3 (2)	C(1)—C(2)—C(3)	117.0 (3)
C(1)—C(2)—C(6)	90.5 (2)	C(3)—C(2)—C(6)	103.2 (2)
C(2)—C(3)—C(4)	101.2 (2)	C(2)—C(3)—C(11)	109.7 (2)
O(4)—C(3)—C(11)	101.5 (2)	O(3)—C(4)—O(4)	111.1 (2)
O(3)—C(4)—C(3)	109.1 (2)	O(4)—C(4)—C(3)	115.7 (2)
O(3)—C(4)—C(5)	116.0 (2)	O(4)—C(4)—C(5)	109.3 (2)
C(3)—C(4)—C(5)	95.0 (2)	C(4)—C(5)—C(6)	101.1 (2)
C(4)—C(5)—C(10)	101.2 (2)	C(6)—C(5)—C(10)	108.9 (2)
C(2)—C(6)—C(5)	103.6 (2)	C(2)—C(6)—C(7)	90.7 (2)
C(5)—C(6)—C(7)	117.8 (2)	C(1)—C(7)—C(6)	89.4 (2)
C(1)—C(7)—C(8)	117.8 (3)	C(6)—C(7)—C(8)	115.0 (2)
C(7)—C(8)—C(16)	118.3 (3)	C(7)—C(8)—C(16)	123.4 (3)
C(9)—C(8)—C(16)	118.3 (3)	O(1)—C(9)—C(8)	124.7 (3)
O(1)—C(9)—C(10)	113.7 (2)	C(8)—C(9)—C(10)	121.6 (3)
C(5)—C(10)—C(9)	111.6 (3)	C(5)—C(10)—C(11)	102.6 (2)
C(9)—C(10)—C(11)	115.7 (2)	C(3)—C(11)—C(10)	102.4 (2)
C(3)—C(11)—C(12)	110.8 (2)	C(10)—C(11)—C(12)	116.4 (2)
O(2)—C(12)—C(11)	113.7 (3)	O(2)—C(12)—C(13)	124.0 (3)
C(11)—C(12)—C(13)	122.2 (3)	C(1)—C(13)—C(12)	117.4 (3)
C(1)—C(13)—C(19)	123.1 (3)	C(12)—C(13)—C(19)	119.4 (3)
O(5)—C(16)—O(6)	121.6 (3)	O(5)—C(16)—C(8)	113.9 (3)
O(6)—C(16)—C(8)	124.4 (3)	O(5)—C(17)—C(18)	106.8 (3)
O(7)—C(19)—O(8)	123.0 (4)	O(7)—C(19)—C(13)	112.9 (4)
O(8)—C(19)—C(13)	123.9 (3)	O(8)—C(19)—O(7')	119.3 (7)
C(13)—C(19)—O(7')	115.0 (7)	O(7)—C(20)—C(21)	108.1 (6)
C(19)—O(7')—C(20')	115.7 (14)	O(7')—C(20')—C(21')	106.5 (14)

[95.0 (2)°]. However, it should be noted that these values are not unusual for this particular class of compound. Repulsive forces between the ketoester moieties cause the six-membered rings forming the sides of the cage to bend away from one another where they are not constrained by cross-cage bonds [i.e. C(1)—C(7), C(2)—C(6) and C(10)—C(11)]. The non-bonded C(9)⋯C(12) contact is only 2.91 Å while the C(8)⋯C(13) contact is 2.99 Å and the C(19)⋯C(16) contact is 4.43 Å. One of the two ketoester moieties is disordered. During refinement distances in the disordered ester were constrained to values close to those found in the second ester group. The ratio of the disordered atoms refined to 60:40. Both hydroxyl groups act as donors in intramolecular hydrogen bonds, O(1)—H⋯O(6) and O(2)—H⋯O(8). In the O(1) bond the O⋯O distance is 2.57 Å, the H⋯O distance 1.58 Å and the O—H⋯O angle 159.9°. In the O(2) bond the O⋯O distance is 2.58 Å, the H⋯O distance 1.65 Å and the O—H⋯O angle 158.6°. We have recently reported the structure of a closely related compound (4) (Marchand, Arney, Gilardi & Flippen-Anderson, 1987), which shows

very similar features. The corresponding structures of several monohomologation products that were synthesized *via* the boron-trifluoride-promoted reaction of EDA (1 equivalent) with several 1-substituted pentacyclo[5.5.0.0^{2,6}.0^{3,11}.0^{5,10}]dodecane-8,12-diones (5–8) have also been reported (Marchand, Annapurna, Reddy, Watson & Nagl, 1989). Interestingly, the regiochemistry of the ring homologation that resulted in the formation of (5–8) is the *opposite* of that observed in the case of (3a) and of (4).

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Structure of 1a,2,2a,3,3a,4,4a,5a,6,6a,7,7a,8,8a-Tetradecahydro-2,8:4,6-dimethanoanthra[2,3-*b*:6,7-*b'*]bisoxirene-3,7-diol Monohydrate

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Abstract. C₁₆H₂₀O₄·H₂O, *M_r* = 294.34, m.p. 422–424 K, monoclinic, *Cc*, *a* = 16.100 (2), *b* = 7.198 (1), *c* = 12.858 (2) Å, β = 105.26 (2)°, *V* = 1437.59 Å³, *Z* = 4, *D_x* = 1.36 Mg m⁻³, λ(Cu Kα) = 1.5418 Å, μ(Cu Kα) = 0.735 mm⁻¹, *F*(000) = 632, *T* = 297 K, *R* = 0.048 and *wR* = 0.054 for 1294 unique reflections. The overall stereochemistry of the title compound is found to be *endo, cis, anti, cis, endo* with the orientation of the epoxy groups being *exo, exo*. All the six-membered rings assume boat conformation with varying degrees of distortion. The crystal packing is stabilized by both hydrogen bonds and van der Waals interactions.

Introduction. Polycyclic polyfunctional molecules are found to have potential use in the polymer industry. They are used as curing agents for polyurethanes containing isocyanates (NCO) as terminal groups. Urethane systems are useful in the fabrication of polymeric materials ranging from elastoplastics to rigid foams. Polyurethanes have the advantage that

no by-products are formed in their production. By the combination of polyaddition followed by polycondensation, polyurethanes can be used to generate thermally stable polymers. Here we report the crystal structure of the title compound, C₁₆H₂₀O₄·H₂O, which belongs to the above class of polycyclic polyfunctional compounds. The synthesis of the title compound was achieved by Ramadas and Bakthavatchalam (Bakthavatchalam, 1987) and will be reported elsewhere.

Experimental. Rectangular plate-like transparent crystals, 0.35 × 0.25 × 0.15 mm, Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Cu Kα radiation, unit-cell parameters by least-squares fit of 25 reflections in the range 30 < θ < 50°, ω/2θ scan technique, 1357 independent reflections in the range 2 < θ < 70°, *hkl* range *h*: 0 → 19, *k*: 0 → 8 and *l*: -15 → 14, 1294 reflections with *I* ≥ 3σ(*I*) considered observed, two standard reflections (206 and 112) measured every hour did not show any signifi-