

–0.080 (2) Å. This difference in planarity also results in generally smaller angles within the pyrrolidino ring in (2) compared with (1). The dihedral angle between the pyrrolidino group and ring γ in the benzo[c]cinnoline skeleton is 5.43 (5) in (1) and 6.80 (5)° in (2).

Back donation of the lone pair of electrons of the N15 atom affects the bond lengths and angles of ring γ in the benzo[c]cinnoline skeleton. The hybridization of N15 is close to $sp^2 + p$ which results in short bonds C2–N15 = 1.363 (3) in (1) and C4–N15 = 1.358 (3) Å in (2). In 1- and 3-piperidinobenzo[c]cinnoline (Hökelek, Kılıç & Tüzün, 1991) the corresponding distances are C1–N15 = 1.382 (5) (molecule A) and 1.388 (5) Å (molecule B) which might be ascribed to a hybridization intermediate between sp^3 and $sp^2 + p$. The type and position of the substituent determine the shape of the benzo[c]cinnoline skeleton as well as the overall shape of the molecule.

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Formation of Methyl 11-Hydroxy-8-oxopentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanecarboxylate by a Regiospecific and Stereospecific Reduction

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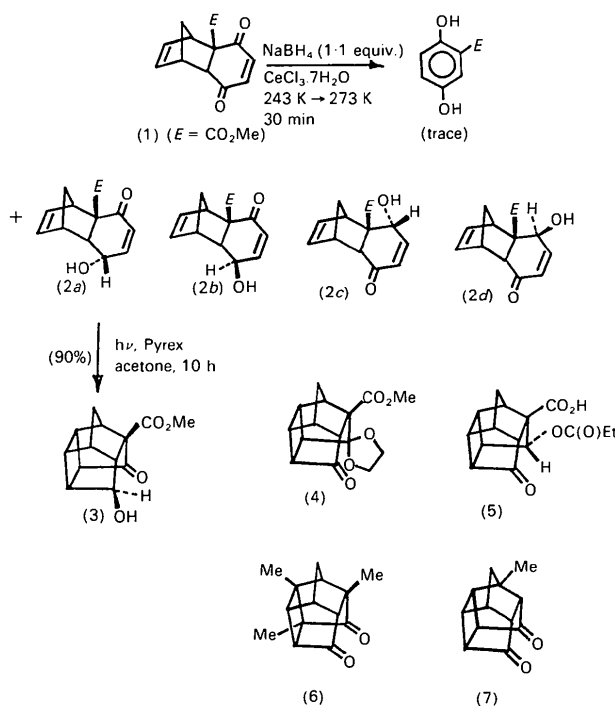
Abstract. Methyl 11-hydroxy-8-oxopentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanecarboxylate (3), C₁₃H₁₄O₄, $M_r = 234.26$, triclinic, $P\bar{1}$, $a = 7.291$ (1), $b = 7.441$ (1), $c = 10.414$ (1) Å, $\alpha = 104.56$ (1), $\beta = 90.41$ (1), $\gamma = 99.07$ (1)°, $V = 539.3$ (1) Å³, $Z = 2$, $D_x = 1.442$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 1.00$ cm⁻¹, $F(000) = 248$, $T = 295$ K, $R = 0.0487$ for 2138 reflections. Compound (3) contains four five-membered rings and a four-membered ring fused to form an open-ended cage structure. The through-bond interaction of the π systems in the parent

diketone is absent in compound (3), which is reflected in the reduction of bond lengths. Although one C–C bond is 1.579 (2) Å, it has been shortened significantly. A hydrogen bond is formed between the hydroxyl group and the carbonyl O atom of the ester.

Introduction. In connection with an ongoing study of the synthesis and chemistry of novel substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes (PCU's; Marchand, 1989), sodium borohydride reduction of compound (1) (Watson, Nagl, Marchand, Reddy & Reddy, 1989) has been investigated. Highly stereo-

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and regioselective reductions of ketone C=O groups to secondary alcohols frequently can be performed by using sodium borohydride in the presence of added cerium(III) chloride (Luhe, Rodriguez-Hahn & Crabbe, 1978; Marchand, LaRoe, Sharma, Suri & Reddy, 1986; Flippen-Anderson, Gilardi, George, Marchand & Jin, 1987). The NaBH₄-CeCl₃-promoted reduction of a substituted 1,4-cyclohexanedione containing non-equivalent carbonyl groups led exclusively to the stereospecific reduction of the less sterically hindered C=O group (Srivastava, Marchand, Vidyasagar, Flippen-Anderson, Gilardi, George, Zachwieja & le Noble, 1989). Analogous reduction of only one of the two non-equivalent enedione C=O groups in (1) conceivably could afford any (or all) of four hydroxyketones, *i.e.* (2a)–(2d). In our hands, reduction of (1) with NaBH₄-CeCl₃ produced a single hydroxyketone in 90% yield. The structure of this PCU derivative, *i.e.* (3), was established unequivocally *via* single-crystal X-ray structural analysis. On the basis of this result, we conclude that the NaBH₄-CeCl₃-promoted reduction of (1) occurs stereo- and regiospecifically at the less sterically hindered C=O group, thereby affording (2a).



Experimental. A colorless crystal of dimensions 0.48 × 0.38 × 0.25 mm was mounted on a Nicolet R3m/μ update of a P2₁ diffractometer; data collected in the ω-scan mode (3 ≤ 2θ ≤ 55°), variable scan rate of 4 to 29.5° min⁻¹, graphite-monochromated Mo Kα radiation; lattice parameters from a least-squares

refinement of 25 reflections (23.58 ≤ 2θ ≤ 29.23°); monitored reflections (126) and (106) showed less than a 2% variation in intensities (linear correction). Intensity statistics consistent with space group P1̄; 2719 reflections measured (−9 ≤ h ≤ 9; −9 ≤ k ≤ 9; 0 ≤ l ≤ 13), equivalent reflections averaged (R_{merge} = 0.007), 2496 independent reflections of which 2138 had I ≥ 3σ(I); Lorentz-polarization correction and ψ-scan-based absorption correction applied (transmission factors 0.919 to 0.966); structure solved by direct methods and refined by a block-cascade least-squares technique, all H atoms located in a difference map and refined with isotropic thermal parameters; R = 0.0486 (R_{all} = 0.0556), wR = 0.0685 (wR_{all} = 0.0695) for 211 parameters and 2138 reflections, S = 2.091, (Δ/σ)_{max} = 0.016, largest peaks in the final difference map of −0.18 and 0.29 e Å⁻³; Σw(|F_o| − |F_c|)² minimized with w = [σ²(F_o) + 0.00054F_o²]⁻¹; isotropic extinction correction F = F_c[1.0 + 1.3 (4) × 10⁻⁵F_c²/sin(2θ)]^{0.25}. SHELXTL computer programs for Desktop 30 Microclipse and Nova 4/C configuration supplied by Nicolet (Nicolet Instrument Corporation, 1986); atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974, Vol. IV). Table 1 lists atomic positional parameters while Table 2 gives interatomic distances and valence angles.*

Discussion. Fig. 1 is a drawing of compound (3). The molecule is composed of four five-membered rings in envelope conformations and a planar (0.002 Å r.m.s. deviation) four-membered ring fused to form an open-ended cage. The ester side chain is planar (0.02 Å r.m.s. deviation) and in an extended conformation. Unlike related compounds (Flippen-Anderson, Gilardi, George, Marchand & Jin, 1987; Watson, Nagl, Marchand & Reddy, 1989) the C(8) atom is not pyramidalized but lies out of the plane of the three attached atoms by only 0.006 Å. In compounds (6) (Watson, Nagl, Kashyap, Marchand & Zhao, 1989), (7) (Marchand, Suri, Earlywine, Powell & van der Helm, 1984), and a related derivative with an exocyclic methylene replacing O(8) (Watson, Kashyap, Marchand & Vidyasagar, 1990) there are two long bonds with average values for C(1)—C(7) of 1.590 (5) and C(9)—C(10) of 1.589 (3) Å. The lengthening of these bonds has been attributed to a through-bond interaction of the π systems (Osawa & Kanematsu, 1986; Marchand, Huang, Kaya, Baker, Jemmis & Dixon, 1987). In compounds (4) (Watson,

* Lists of H-atom coordinates, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53225 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	7839 (2)	15309 (2)	1444 (2)	41 (1)
C(2)	9384 (2)	14165 (2)	1606 (2)	39 (1)
C(3)	9283 (2)	13821 (2)	2993 (2)	42 (1)
C(4)	9190 (2)	11708 (3)	2726 (2)	51 (1)
C(5)	7548 (2)	11194 (2)	1733 (2)	39 (1)
C(6)	8185 (2)	12364 (2)	726 (2)	41 (1)
C(7)	6642 (2)	13497 (3)	553 (2)	45 (1)
C(8)	5091 (2)	12780 (2)	1328 (2)	39 (1)
O(8)	3440 (2)	12599 (2)	1113 (1)	63 (1)
C(9)	6065 (2)	12288 (2)	2460 (1)	31 (1)
C(10)	7282 (2)	14145 (2)	3334 (1)	34 (1)
C(11)	7054 (3)	15839 (2)	2811 (2)	44 (1)
O(11)	8179 (2)	17500 (2)	3563 (1)	66 (1)
C(12)	4690 (2)	11319 (2)	3238 (1)	34 (1)
O(12A)	4145 (2)	12066 (2)	4277 (1)	71 (1)
O(12B)	4109 (2)	9542 (2)	2624 (1)	49 (1)
C(13)	2702 (3)	8513 (3)	3258 (2)	53 (1)

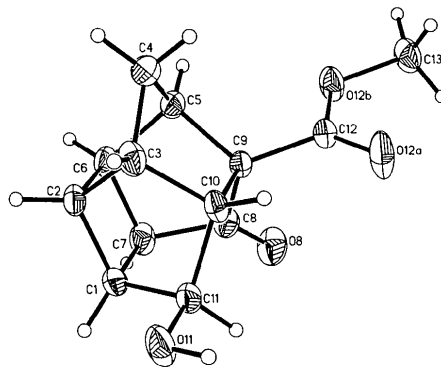


Fig. 1. Drawing of compound (3) with thermal ellipsoids at the 35% probability level. H atoms are represented by spheres of arbitrary size.

O(11), O(12A)···H(11O)(1 - x, 3 - y, 1 - z) = 1.94 (5), O(12A)···O(11) = 2.809 (2), O(11)—H(11O) = 0.95 (2) Å and O(12A)···H(11O)—O(11) = 149.7 (8)°.

Table 2. Bond lengths (Å) and angles (°) for compound (3)

C(1)—C(2)	1.547 (3)	C(1)—C(7)	1.558 (2)
C(1)—C(11)	1.518 (2)	C(2)—C(3)	1.528 (2)
C(2)—C(6)	1.550 (2)	C(3)—C(4)	1.516 (3)
C(3)—C(10)	1.545 (2)	C(4)—C(5)	1.513 (2)
C(5)—C(6)	1.551 (3)	C(5)—C(9)	1.544 (2)
C(6)—C(7)	1.544 (3)	C(7)—C(8)	1.500 (2)
C(8)—O(8)	1.203 (2)	C(8)—C(9)	1.521 (2)
C(9)—C(10)	1.579 (2)	C(9)—C(12)	1.502 (2)
C(10)—C(11)	1.523 (2)	C(11)—O(11)	1.413 (2)
C(12)—O(12A)	1.186 (2)	C(12)—O(12B)	1.315 (2)
O(12B)—C(13)	1.444 (2)		
C(2)—C(1)—C(7)	90.1 (1)	C(2)—C(1)—C(11)	105.1 (1)
C(7)—C(1)—C(11)	110.8 (1)	C(1)—C(2)—C(3)	107.8 (1)
C(1)—C(2)—C(6)	89.8 (1)	C(3)—C(2)—C(6)	102.9 (1)
C(2)—C(3)—C(4)	103.4 (1)	C(2)—C(3)—C(10)	100.9 (1)
C(4)—C(3)—C(10)	104.5 (1)	C(3)—C(4)—C(5)	95.8 (1)
C(4)—C(5)—C(6)	102.5 (1)	C(4)—C(5)—C(9)	104.3 (1)
C(6)—C(5)—C(9)	101.0 (1)	C(2)—C(6)—C(5)	103.2 (1)
C(2)—C(6)—C(7)	90.6 (1)	C(5)—C(6)—C(7)	108.2 (1)
C(1)—C(7)—C(6)	89.6 (1)	C(1)—C(7)—C(8)	109.8 (1)
C(6)—C(7)—C(8)	103.5 (2)	C(7)—C(8)—O(8)	128.7 (2)
C(7)—C(8)—C(9)	104.5 (1)	O(8)—C(8)—C(9)	126.7 (2)
C(5)—C(9)—C(8)	102.2 (1)	C(5)—C(9)—C(10)	102.5 (1)
C(8)—C(9)—C(10)	108.3 (1)	C(5)—C(9)—C(12)	118.2 (1)
C(8)—C(9)—C(12)	111.0 (1)	C(10)—C(9)—C(12)	113.5 (1)
C(3)—C(10)—C(9)	102.5 (1)	C(3)—C(10)—C(11)	104.0 (1)
C(9)—C(10)—C(11)	111.0 (1)	C(1)—C(11)—C(10)	101.3 (1)
C(1)—C(11)—O(11)	108.1 (1)	C(10)—C(11)—O(11)	111.5 (1)
C(9)—C(12)—O(12A)	124.4 (1)	C(9)—C(12)—O(12B)	112.4 (1)
O(12A)—C(12)—O(12B)	123.1 (1)	C(12)—O(12B)—C(13)	116.7 (1)

Nagl, Marchand, Reddy & Reddy, 1989), (5) (Watson, Nagl, Marchand & Reddy, 1989) and related structures, the C(1)—C(7) distance is reduced significantly to 1.558 (3) and C(9)—C(10) to 1.573 (4) Å. In compound (3) the C(1)—C(7) and C(9)—C(10) bond distances of 1.558 (2) and 1.579 (2) and the C(8)···C(11) intramolecular distance of 2.605 (2) Å are consistent with this trend. There is a hydrogen bond between O(12A) and

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