

on ^1H NMR data. The fulvenic skeleton is planar. The cyano and methoxy groups are coplanar with the ring, while the acetoxy group deviates from it. The angle between the mean planes defined by the six fulvenic C atoms and the acetoxy group is $18.6 (3)^\circ$.

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Structure of an Open-Ended Cage Compound

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Abstract. 11-Oxo-8-propionyloxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-9-carboxylic acid (3a), $\text{C}_{15}\text{H}_{16}\text{O}_5$, $M_r = 276.29$, monoclinic, $P2_1/c$, $a = 7.610 (1)$, $b = 7.972 (1)$, $c = 21.329 (2) \text{ \AA}$, $\beta = 93.94 (1)^\circ$, $V = 1291.1 (2) \text{ \AA}^3$, $Z = 4$, $D_x = 1.421 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$, $\mu = 1.00 \text{ cm}^{-1}$, $F(000) = 584$, $T = 299 \text{ K}$, $R = 0.0427$ for 1437 independent reflections. The compound is composed of a norbornane moiety (two fused five-membered rings) fused along each side to five-membered rings which are joined to form a four-membered ring. The molecule is a cage with one side open. The two C atoms of the open end contain a ketone moiety and a planar *endo*-ester side chain. One end of the norbornane moiety, $1.573 (3) \text{ \AA}$, is significantly longer than all other

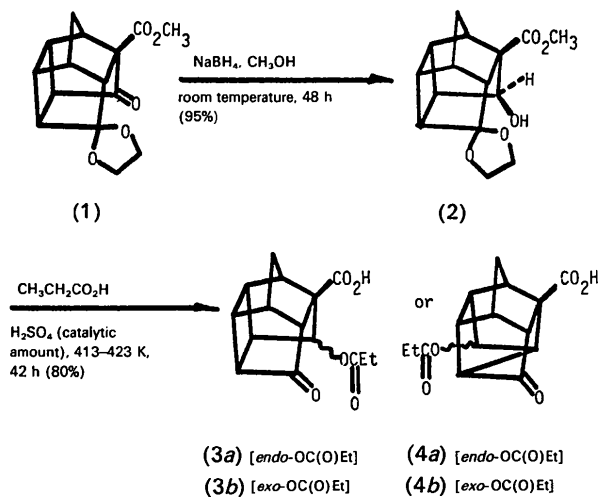
bonds in the structure. The four-membered ring has distances ranging from $1.542 (3)$ to $1.557 (3) \text{ \AA}$ and is planar, r.m.s.d. $\approx 0.002 \text{ \AA}$. The two C atoms at the open end of the cage are separated by $2.665 (3) \text{ \AA}$ with the carbonyl C atom slightly pyramidalized and lying out of the plane of the other three atoms by $0.051 (3) \text{ \AA}$. A hydrogen bond is formed between the acid group of one molecule and the keto of an adjacent molecule.

Introduction. The title reaction was studied as part of a program concerned with the synthesis and chemistry of novel, substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes (Marchand, 1989). The starting material for this study (2) was synthesized by sodium borohydride reduction of the corresponding ketone, (1) (Scheme 1). The synthesis and structure of (1) have been reported previously (Watson, Nagl, Marchand, Reddy & Reddy, 1989). Based upon the

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results of sodium borohydride reductions of ketone carbonyl groups in similar systems (Marchand, LaRoe, Sharma, Suri & Reddy, 1986), it is suggested that the configuration of the C(11)—OH bond in (2) is *endo*. Prolonged treatment of (2) with propionic acid at 413–423 K in the presence of a catalytic amount of concentrated sulfuric acid (Marchand, Sharma, Annapurna & Pednekar, 1987) afforded a single product, C₁₅H₁₆O₅. Analysis of the infrared spectrum and the proton and carbon-13 NMR spectra of this material indicated presence of a CO₂H group, a propionyloxy moiety, and a ketone carbonyl group therein. Attention then became focused upon two points with regard to the structure of the product thereby obtained: (i) Substitution of OH in (2) by OC(O)Et might have occurred either with retention of the pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane skeleton or, alternatively, concomitant Wagner–Meerwein rearrangement to a substituted D₃-trishomocubane might have occurred (Marchand, Sharma, Annapurna & Pednekar, 1987); (ii) In either event, it also would be necessary to establish the configuration of the OC(O)Et group in the product. Four possible structures [*i.e.* (3a), (3b), (4a), and (4b)], all of which are consistent with the infrared and NMR spectral information obtained for the product of reaction of (2) with propionic acid–sulfuric acid] are shown in Scheme 1. The question of the structure of this product has been resolved by single-crystal X-ray structural analysis of compound (3a).



Experimental. A colorless transparent crystal of dimensions 0.25 × 0.38 × 0.40 mm was mounted on a Nicolet R3m/μ update of a P2₁ diffractometer; data collected in ω-scan mode (3 ≤ 2θ ≤ 45°), variable scan rate (4–29.3° min⁻¹), graphite-monochromated Mo Kα radiation; lattice parameters from a least-squares refinement of 25 reflections (25.34 ≤ 2θ ≤ 29.88°), angles measured by a centering routine;

systematic absences (*h*0*l*, *l* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1) and Laue symmetry consistent with space group P2₁/c; monitored reflections (20,10) and (040) showed intensity variations of less than ±2%; 1688 independent reflections measured (−8 ≤ *h* ≤ 8, 0 ≤ *k* ≤ 8, 0 ≤ *l* ≤ 22), 1437 ≥ 3σ(*I*); Lorentz–polarization corrections, ψ-scan-based empirical absorption correction (transmission factors 0.772 to 0.785), equivalent reflections averaged (*R*_{int} = 0.027); structure solved by direct-methods techniques and refined by block-cascade least-squares refinement, all H atoms located in difference maps, H atoms refined with isotropic thermal parameters except for the propionate H atoms which were allowed to ride at fixed distances from the attached C atoms; *R* = 0.0427, *wR* = 0.0528 for 230 parameters and 1437 reflections (*R* = 0.0508 and *wR* = 0.0539 for all 1688 reflections), *S* = 1.670, (Δ/σ)_{max} = 0.009; largest peaks in the final difference map of 0.23 and −0.18 e Å⁻³; Σw(|*F*_o − |*F*_c||)² minimized with *w* = [σ²(*F*_o) + 0.00049*F*_o²]⁻¹. All computer programs supplied by Nicolet (Nicolet Instrument Corporation, 1986) for Desktop 30 Microclipse and Nova 4/C configuration; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Fig. 1 is a drawing of the title compound. Table 1 gives atomic positional parameters while Table 2 gives interatomic distances and valence angles.*

* 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 51968 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

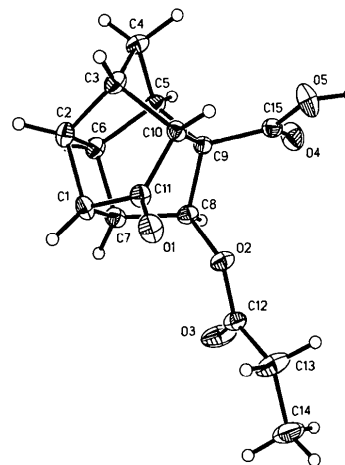


Fig. 1. Drawing of compound (3a) with thermal ellipsoids shown at the 25% probability level. H atoms are represented by spheres of arbitrary size.

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

	x	y	z	U*
C(1)	5955 (3)	-1732 (3)	930 (1)	45 (1)
C(2)	5045 (3)	-110 (3)	1144 (1)	45 (1)
C(3)	5594 (3)	150 (3)	1847 (1)	45 (1)
C(4)	6235 (4)	1941 (3)	1877 (1)	49 (1)
C(5)	7508 (3)	1740 (3)	1365 (1)	42 (1)
C(6)	6383 (3)	974 (3)	814 (1)	43 (1)
C(7)	7311 (3)	-634 (3)	601 (1)	42 (1)
C(8)	9085 (3)	-573 (3)	963 (1)	38 (1)
C(9)	8648 (3)	200 (3)	1586 (1)	34 (1)
C(10)	7290 (3)	-914 (3)	1923 (1)	38 (1)
C(11)	6756 (3)	-2428 (3)	1533 (1)	40 (1)
O(1)	6794 (2)	-3886 (2)	1696 (1)	54 (1)
O(2)	9868 (2)	-2197 (2)	1107 (1)	47 (1)
C(12)	10885 (3)	-2916 (3)	696 (1)	45 (1)
O(3)	11155 (3)	-2295 (3)	209 (1)	80 (1)
C(13)	11542 (5)	-4574 (4)	937 (2)	79 (1)
C(14)	12653 (5)	-5514 (4)	514 (2)	81 (1)
C(15)	10305 (3)	699 (3)	1968 (1)	41 (1)
O(4)	11429 (2)	1535 (3)	1755 (1)	70 (1)
O(5)	10401 (2)	177 (3)	2550 (1)	70 (1)

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

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

C(1)—C(2)	1.551 (4)	C(1)—C(7)	1.557 (3)
C(1)—C(11)	1.491 (3)	C(2)—C(3)	1.543 (3)
C(2)—C(6)	1.542 (3)	C(3)—C(4)	1.508 (4)
C(3)—C(10)	1.544 (3)	C(4)—C(5)	1.517 (4)
C(5)—C(6)	1.533 (3)	C(5)—C(9)	1.557 (3)
C(6)—C(7)	1.547 (3)	C(7)—C(8)	1.509 (3)
C(8)—C(9)	1.523 (3)	C(8)—O(2)	1.450 (3)
C(9)—C(10)	1.573 (3)	C(9)—C(15)	1.507 (3)
C(10)—C(11)	1.506 (3)	C(11)—O(1)	1.213 (3)
O(2)—C(12)	1.337 (3)	C(12)—O(3)	1.182 (3)
C(12)—C(13)	1.492 (4)	C(13)—C(14)	1.481 (5)
C(15)—O(4)	1.199 (3)	C(15)—O(5)	1.305 (3)
C(2)—C(1)—C(7)	89.3 (2)	C(2)—C(1)—C(11)	102.8 (2)
C(7)—C(1)—C(11)	110.7 (2)	C(1)—C(2)—C(3)	107.6 (2)
C(1)—C(2)—C(6)	90.6 (2)	C(3)—C(2)—C(6)	103.0 (2)
C(2)—C(3)—C(4)	103.5 (2)	C(2)—C(3)—C(10)	101.3 (2)
C(4)—C(3)—C(10)	104.5 (2)	C(3)—C(4)—C(5)	95.2 (2)
C(4)—C(5)—C(6)	104.1 (2)	C(4)—C(5)—C(9)	103.6 (2)
C(6)—C(5)—C(9)	100.8 (2)	C(2)—C(6)—C(5)	103.0 (2)
C(2)—C(6)—C(7)	89.9 (2)	C(5)—C(6)—C(7)	108.3 (2)
C(1)—C(7)—C(6)	90.2 (2)	C(1)—C(7)—C(8)	112.6 (2)
C(6)—C(7)—C(8)	103.5 (2)	C(7)—C(8)—C(9)	102.6 (2)
C(7)—C(8)—O(2)	114.8 (2)	C(9)—C(8)—O(2)	106.7 (2)
C(5)—C(9)—C(8)	101.9 (2)	C(5)—C(9)—C(10)	102.3 (2)
C(8)—C(9)—C(10)	111.1 (2)	C(5)—C(9)—C(15)	112.5 (2)
C(8)—C(9)—C(15)	110.7 (2)	C(10)—C(9)—C(15)	117.0 (2)
C(3)—C(10)—C(9)	102.3 (2)	C(3)—C(10)—C(11)	101.0 (2)
C(9)—C(10)—C(11)	111.1 (2)	C(1)—C(11)—C(10)	104.9 (2)
C(1)—C(11)—O(1)	127.1 (2)	C(10)—C(11)—O(1)	127.5 (2)
C(8)—O(2)—C(12)	119.4 (2)	O(2)—C(12)—O(3)	122.7 (2)
O(2)—C(12)—C(13)	110.4 (2)	O(3)—C(12)—C(13)	126.8 (3)
C(12)—C(13)—C(14)	115.5 (3)	C(9)—C(15)—O(4)	122.3 (2)
C(9)—C(15)—O(5)	114.8 (2)	O(4)—C(15)—O(5)	122.9 (2)

Discussion. The molecule (3a) contains four five-membered rings and one four-membered ring. Two five-membered rings are in almost perfect envelope conformations forming a norbornane moiety. A five-membered ring is fused along each side of the norbornane moiety, and these five-membered rings are joined to form a four-membered ring. If C(8) and C(11) were joined, a closed-cage structure would result. Because of the open end the two five-membered rings form distorted envelope conformations with a C(8)⋯C(11) separation of 2.665 (3) Å. Carbon C(11) is slightly pyramidalized lying 0.051 (3) Å out of the plane of C(1)C(10)O(1). The four-membered ring is planar (0.002 Å r.m.s.d.) with distances ranging from 1.542 (3) to 1.557 (3) Å. The ester side chain C(8) to C(18) is planar (0.007 Å r.m.s.d.) and is in an extended conformation. An intermolecular hydrogen bond is formed between the acid group, O(5), and the ketone oxygen O(1) ($2 - x, 0.5 + y, 0.5 - z$): O(5)⋯O(1) = 2.689 (3), O(5)—H(O5) = 0.92 (3), H(O5)⋯O(1) = 1.80 (3) Å, O(5)—H(5)⋯O(1) = 160 (1)°.

The bond-length variations in this cage system have been discussed for the parent diketone (Osawa & Kanematsu, 1986; Marchand, Huang, Kaya, Baker, Jemmis & Dixon, 1987), and crystal structures of a monoketal (Watson, Nagl, Marchand, Reddy & Reddy, 1989), diketones (Marchand, Suri, Earlywine, Powell & van der Helm, 1984) and related structures (Marchand, Annapurna, Reddy, Watson & Nagl, 1989) have been reported. The variation of bond lengths in the current structure, *i.e.* the elongation of C(9)—C(10) and possibly C(1)—C(7), are consistent with the reported data.

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