(Marchand, Suri, Earlywine, Powell & van der Helm, 1984) and a series of monoketone complexes with an unsaturated six-membered-ring alcohol replacing one five-membered-ring ketone (Marchand, Annapurna, Watson & Nagl, 1989), except for the changes associated with the ketal functionality. While the C(1)—C(7) bond [1·560 (2) Å] and the C(9)—C(10) bond [1·572 (2) Å] are the longest bonds in compound (2*a*), they are significantly shorter than the corresponding bonds in diketone (3) and the related series of monoketone complexes. In the unsaturated compounds the π-orbitals on C(8) and C(11) are almost collinear and possibly overlap. The C(1)—C(7) and C(9)—C(10) bonds are parallel to these collinear π-orbitals and are one bond removed from C(8) and C(11). A STO-3G procedure was used to calculate the geometries of compounds (4)–(6) (Marchand, Huang, Kaya, Baker, Jemmis & Dixon, 1987) giving values of 1·572–1·575 and 1·579–1·585 Å for C(1)—C(7) and C(8)—C(9), respectively. Osawa & Kanematsu (1986) discussed various factors which might influence the bond lengths in open-cage structures such as (2). Through-space coupling involving direct interaction of the π-orbitals and through-bond coupling involving interaction of the π-orbitals with the parallel bonds were considered. STO-3G and photoelectron spectroscopy results were considered to be more consistent with through-bond coupling involving a 1,3 interaction pathway. Couplings by either mechanism might be expected to be absent in (2*a*) due to replacement of the π-bond at C(11) by a saturated ketal functionality. The C(1)—C(7) and C(9)—C(10) bonds in (2*a*) are significantly shorter than either those observed or calculated for the diketone; however, they remain the longest bonds in structure (2*a*). Molecular-mechanics calculations (Allinger & Yuh, 1980) do not take into account the π-orbital couplings and C(1)—C(7) and C(9)—C(10) bonds are calculated to be the same length in (2*a*) and (3), 1·522 and 1·555 Å, respectively. The decrease in bond lengths in going from (3) to (2*a*) appears to be related to the loss of coupling rather than to steric effects.

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Structure of a 3-Methylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione Monoethylene Ketal

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Abstract. $C_{14}H_{16}O_3$, $M_r = 232·28$, triclinic, $P\bar{1}$, $a = 6·517$ (1), $b = 7·569$ (2), $c = 11·910$ (3) Å, $\alpha = 103·28$ (2), $\beta = 105·13$ (2), $\gamma = 91·71$ (2)°, $V = 549·5$ (2) Å^3, $Z = 2$, $D_x = 1·40$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 0·75$ mm^{-1}, $F(000) = 248$, $T = 295$ K, final $R = 0·042$, $wR = 0·044$ for 1419 observed

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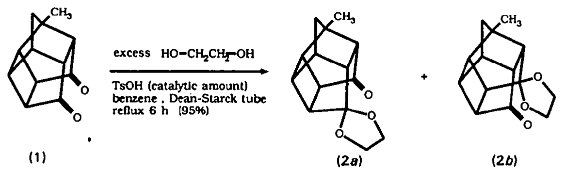
reflections. Unshared C—C (sp^3—sp^3) bonds in the pentacyclo cage system are either short or long [av. of 1·514 (3) Å for the four short bonds and 1·574 (3) Å for the one long bond]. The shared cage sp^3—sp^3 single bonds are in the normal range [av. of 1·550 (3) Å for eight bonds].

Introduction. As part of a program that involves the synthesis and chemistry of novel, substituted pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecanes (Marchand, 1989), we recently studied the acid-catalyzed reaction of 3-methylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione [(1), synthesized *via* the procedure described in Marchand, Suri, Earlywine, Powell & van der Helm (1984)] with excess ethylene glycol. Since the parent pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione is known to react with ethylene glycol under these conditions to afford exclusively the corresponding monoethylene ketal (Eaton, Cassar, Hudson & Hwang, 1976), it was anticipated that (1) might react similarly to afford one (or both) of the two possible monoethylene ketals [(2*a*) and (2*b*)]. Indeed, both isomeric monoethylene ketals, m.p. 349–350 K and m.p. 408–409 K, were obtained from the reaction of (1) with ethylene ketal. The lower-melting isomer predominated: the ratio of major to minor product, determined by integration of the proton NMR spectrum of the product mixture, was *ca* 4:1. The combined yield of (2*a*) and (2*b*) thereby obtained was 95%.

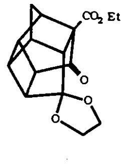


(1)

(2*a*)
(m.p. 349–350 K)

(2*b*)
(m.p. 408–409 K)

product ratio: 4 1



(3)

The mixture of isomeric monoethylene ketals (2*a*) and (2*b*) was separated by fractional recrystallization from hexane. We are unable to assign the structure of each isomer unequivocally on the basis of analysis of their respective proton and carbon-13 NMR spectra. Accordingly unequivocal assignment of one of the two products (2*a*) or (2*b*), was sought *via* single-crystal X-ray structural analysis. The fact that the higher-melting isomer possesses structure (2*b*) [rather than (2*a*)] was established by X-ray analysis.

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic displacement parameters* (Å^2 $\times$ 10^3)

	x	*y*	*z*	U_{eq}*
C(1)	659 (3)	1498 (3)	2129 (2)	41 (1)
C(2)	104 (3)	2822 (3)	1301 (2)	45 (1)
C(3)	−504 (3)	4603 (3)	2022 (2)	44 (1)
C(4)	−2700 (4)	4826 (4)	1229 (3)	54 (1)
C(5)	−3682 (3)	2925 (3)	1090 (2)	47 (1)
C(6)	−2066 (4)	1681 (3)	651 (2)	48 (1)
C(7)	−1515 (3)	342 (3)	1474 (2)	46 (1)
C(8)	−3095 (3)	715 (3)	2201 (2)	44 (1)
C(9)	−3279 (3)	2734 (3)	2394 (2)	43 (1)
C(10)	−1055 (3)	3877 (3)	3042 (2)	40 (1)
C(11)	656 (3)	2634 (3)	3357 (2)	38 (1)
O(12)	2663 (2)	3636 (2)	3977 (1)	50 (1)
C(13)	3797 (4)	2631 (4)	4777 (3)	58 (1)
C(14)	2225 (5)	1210 (5)	4797 (3)	71 (1)
O(15)	220 (2)	1590 (2)	4126 (1)	52 (1)
O(16)	−4199 (3)	−394 (2)	2424 (2)	64 (1)
C(17)	1130 (5)	6249 (4)	2406 (3)	65 (1)

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

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

C(1)—C(2)	1·549 (3)	C(1)—C(7)	1·554 (3)
C(1)—C(11)	1·517 (3)	C(2)—C(3)	1·546 (3)
C(2)—C(6)	1·547 (3)	C(3)—C(4)	1·533 (3)
C(3)—C(10)	1·558 (3)	C(3)—C(17)	1·517 (3)
C(4)—C(5)	1·512 (3)	C(5)—C(6)	1·546 (3)
C(5)—C(9)	1·548 (3)	C(6)—C(7)	1·553 (3)
C(7)—C(8)	1·504 (3)	C(8)—C(9)	1·506 (3)
C(8)—O(16)	1·208 (3)	C(9)—C(10)	1·574 (3)
C(10)—C(11)	1·509 (3)	C(11)—O(12)	1·418 (2)
C(11)—O(15)	1·414 (2)	O(12)—C(13)	1·425 (3)
C(13)—C(14)	1·472 (4)	C(14)—O(15)	1·418 (3)

C(7)—C(1)—C(2)	90·5 (2)	C(11)—C(1)—C(2)	104·2 (2)
C(11)—C(1)—C(7)	111·5 (2)	C(3)—C(2)—C(1)	108·5 (2)
C(6)—C(2)—C(1)	89·7 (2)	C(6)—C(2)—C(3)	103·9 (2)
C(4)—C(3)—C(2)	102·8 (2)	C(10)—C(3)—C(2)	99·4 (2)
C(10)—C(3)—C(4)	103·3 (2)	C(17)—C(3)—C(2)	116·4 (2)
C(17)—C(3)—C(4)	115·8 (2)	C(17)—C(3)—C(10)	116·8 (2)
C(5)—C(4)—C(3)	96·1 (2)	C(6)—C(5)—C(4)	103·4 (2)
C(9)—C(5)—C(4)	104·1 (2)	C(9)—C(5)—C(6)	101·1 (2)
C(5)—C(6)—C(2)	103·0 (2)	C(7)—C(6)—C(2)	90·6 (2)
C(7)—C(6)—C(5)	107·8 (2)	C(6)—C(7)—C(1)	89·3 (2)
C(8)—C(7)—C(1)	111·5 (2)	C(8)—C(7)—C(6)	101·8 (2)
C(9)—C(8)—C(7)	104·6 (2)	O(16)—C(8)—C(7)	127·2 (2)
O(16)—C(8)—C(9)	127·3 (2)	C(8)—C(9)—C(5)	100·2 (2)
C(10)—C(9)—C(5)	102·5 (2)	C(10)—C(9)—C(8)	111·9 (2)
C(9)—C(10)—C(3)	103·1 (2)	C(11)—C(10)—C(3)	104·1 (2)
C(11)—C(10)—C(9)	110·4 (2)	C(10)—C(11)—C(1)	102·0 (2)
O(12)—C(11)—C(1)	111·7 (2)	O(12)—C(11)—C(10)	111·5 (2)
O(15)—C(11)—C(1)	113·7 (2)	O(15)—C(11)—C(10)	112·5 (2)
O(15)—C(11)—O(12)	105·6 (1)	C(13)—O(12)—C(11)	107·3 (2)
C(14)—C(13)—O(12)	105·9 (2)	O(15)—C(14)—C(13)	105·9 (2)
C(14)—O(15)—C(11)	106·5 (2)		

Experimental. Clear, colorless, 0·12 × 0·15 × 0·20 mm crystal. Nicolet *R*3*m*/*V* diffractometer with incident-beam graphite monochromator, 25 centered reflections within $42 < 2\theta < 62°$ used for determining lattice parameters: $2\theta_{max} = 125°$, range of *hkl*: $-7 \leq h \leq 7$, $-8 \leq k \leq 0$, $-12 \leq l \leq 13$. Standards 300, 020, 003, monitored every 100 reflections with random variation of ±2·0% over data collection, $\theta/2\theta$ mode, scan width $(2{\cdot}0 + \Delta 2\theta\alpha_1\alpha_2)°$, scan rate a function of count rate (12° min^{-1} minimum, 30° min^{-1} maximum), 1990 reflections measured, 1774 unique ($R_{int} = 0{\cdot}017$), 1419 observed $[F_o > 3\sigma(F_o)]$. 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, $\sum w(|F_o| - |F_o|)^2$ 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 0·00025). Secondary-extinction parameter $P =$ 0·020 (3) in $F_c^* = F_c/[1{\cdot}0 + 0{\cdot}002(P)F_c^2/\sin 2\theta]^{0\cdot25}$, 214 parameters refined, atomic coordinates for all atoms, anisotropic temperature factors for non-H atoms, isotropic temperature factors for H atoms. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Final $R = 0{\cdot}042$, $wR = 0{\cdot}044$, max. $\Delta/\sigma = 0{\cdot}01$, $S = 1{\cdot}61$. Final difference Fourier excursions 0·16 and −0·14 e Å^{-3}.† All calculations were performed using the *SHELXTL* system (Sheldrick, 1980).

Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 1, bond lengths and angles in Table 2. Fig. 1 shows the atom numbering.

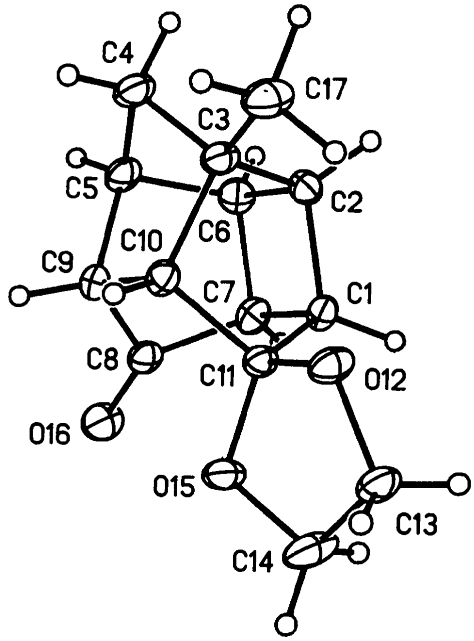


Fig. 1. A view of the molecule showing the atom numbering.

Discussion. In the five-membered rings adjacent to the cyclobutane ring the two sp^3–sp^3 bonds not in common with any other ring are quite short [av. 1·505 (3) Å] while the C—C cage bond across from the cyclobutane ring (C9—C10) is longer than normal [1·574 (3) Å]. In the six-membered boat-shaped ring the two bonds not in common with other rings are also short [av. 1·522 (3) Å]. All the other C—C cage bonds, which are shared by more than one ring, fall in the normal range for C—C single bonds [av. 1·550 (3) Å]. A long cage bond across from the cyclobutane ring was also noted in the X-ray structure of (1) (Marchand, Suri, Earlywine, Powell & van der Helm, 1984). Very similar bonding was also found in a study carried out on a molecule with the same polycyclic system as (*2b*) but with a carboxylate group on C10 instead of the methyl group on C3 (Watson, Nagl, Marchand, Reddy & Reddy, 1989) as well as in several other compounds with the same pentacycloundecane cage moiety and different substituents (Marchand *et al.*, 1984; Coxon, O'Connell & Steele, 1986). In the cage itself the cyclobutane ring is planar (±0·002 Å) and the two adjacent five-membered rings are flattened envelopes (O9 and C10 being the out-of-plane atoms) as is the spiro heterocyclic five-membered ring (C11 out of plane).

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† 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 51561 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.