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A Twisted Pentacyclic Ketone Derivative

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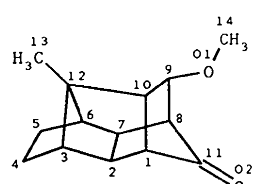
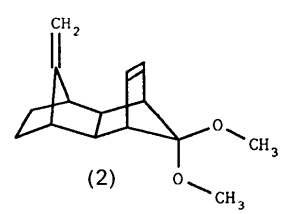
Abstract. *exo*-11-Methoxy-9-methylpentacylco[6.3.1.-$0^{3,10}.0^{4,12}.0^{5,9}$]dodecan-2-one (1), $C_{14}H_{18}O_2$, M_r = 218.30, orthorhombic, *Pbca*, $a = 7.288(1)$, $b = 12.432(3)$, $c = 24.392(2)$ Å, $V = 2209.88$ Å^3, $Z = 8$, $D_x = 1.311$ g cm^{-3}, λ(Cu $K\alpha$) = 1.54056 Å, $\mu = 6.425$ cm^{-1}, $F(000) = 944$, $T = 148$ K, $R = 0.0547$ and $wR = 0.0552$ for 1602 unique reflections. The molecule consists of a 'twisted' pentacyclic hydrocarbon ring system with methyl and methoxy substituents and a ketone functional group.

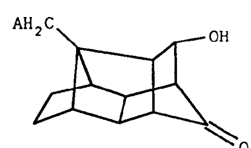
Introduction. The preparation and X-ray crystal structure of diene ketal (2) were recently reported (Lloyd, Arif & Allred, 1992). In an effort to hydrolyze the dimethoxy ketal to the ketone (4), compound (2) was subjected to aqueous acids. Normally ketals can be acid hydrolyzed in the presence of alkene functional groups to unrearranged ketones in high yields (Bertsch, Grimme, Reinhardt, Rose & Warner, 1988; Fessner, Sedelmeier, Spurr, Rihs & Prinsbach, 1987; Gassman & Marshall, 1973). However, chemical behavior is apparently influenced by the π–π interaction in (2). Attempted hydrolysis of (2) with strong aqueous acids yielded mostly the ring-closed 'twisted' products (1) and (3).‡



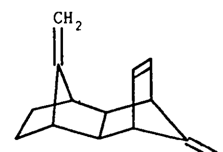
(1)



(2)



(3) A = H
(3-d_1) A = D



(4)

Experimental. Compound (2) was stirred with excess 5% H_2SO_4/H_2O (Gassman & Marshall, 1973) for 18 h at 296 K. After neutralization of the reaction mixture with $NaHCO_3$, ether extraction, drying (Na_2SO_4), and evaporation of the solvent, the

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‡ Nonstandard numbering of atoms was used in structure (1) in order to facilitate comparison with structure (2).

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product mixture contained 60% product (1), 31% product (3) and 10% product (4), where yields were determined from ^{1}H NMR integrations. Products were separated by medium-pressure liquid chromatography (MPLC) on silica (200–400 mesh), eluting with hexanes, ether and tetrahydrofuran. Product (1) (ether fraction) was further purified by double recrystallization from ether/pentane: m.p. 339–341 K; ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.14 (*s*, 3H), 1.22–2.43 (*m*, 11H), 3.28 (*s*, 3H), 3.75 (*d*, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 20 MHz) δ 13.72, 22.48, 25.79, 37.89, 43.57, 45.42, 45.55, 48.99, 50.81, 52.05, 54.10, 55.43, 77.12, 212.77; IR ($CDCl_3$) 3000–2800 (*s*), 1770 (*s*), 1480–1440 (*m*), 1378 (*m*) 1100 (*s*) cm^{-1}; high-resolution mass spectrum, m/z (relative intensity) 218.1310 (3.3, $M^{+\cdot}$) (Lloyd, 1985); exact mass calculated for $^{12}C_{14}{}^{1}H_{18}{}^{16}O_2$ 218.1307; elemental analysis calculated for $C_{14}H_{18}O_2$ gave C 77.03, H 8.31, O 14.66; elemental analysis found C 76.80, H 8.35, O, 14.87.

Product (3), from the tetrahydrofuran MPLC fraction, was identified by the similarity of its spectral data to that of compound (1). ^{1}H NMR ($CDCl_3$, 90 MHz) δ 1.12 (*s*, 3H), 1.18–2.41 (*m*, 11H), 3.20 (*bs*, 1H), 4.23 (*d*, 1H); IR ($CDCl_3$) 3600–3200 (*s*), 3000–2800 (*s*), 1770 (*s*), 1480–1440 (*m*), 1378 (*m*), 1150–1050 (*s*) cm^{-1}. ^{1}H NMR splitting patterns for (3) were very similar to those of (1). High-resolution mass spectral data were obtained for the monodeuterated compound (3-d_1), from hydrolysis of (2) in D_2SO_4/D_2O; m/z (relative intensity) 205.1209 (2.6, $M^{+\cdot}$) (Lloyd, 1985). Exact mass calculated for $^{12}C_{13}{}^{1}H_{15}{}^{2}H^{16}O_2$: 205.1213. Peaks at m/z (relative intensity) 188.1086 (0.6), 177.1284 (3.4) and 160.1144 (2.0) correspond to loss of $OH^{\cdot}$, CO and both, respectively. A peak at m/z 134.1065 (13.1) corresponds to $^{12}C_{10}{}^{1}H_{12}{}^{2}H^{+}$ (loss of $C_3H_3O_2^{\cdot}$) and is consistent with two O atoms bonded within three C atoms of each other. A similar, though less intense, peak exists at m/z 133.1006 (2.9) for (nondeuterated) compound (1).

A crystal of (1) suitable for X-ray structure analysis was obtained by vacuum sublimation in an 11 mm × 0.5 m Pyrex tube in a temperature gradient (298–353 K) tube heater (10 Pa). Crystal dimensions were 0.22 × 0.21 × 0.18 mm. Intensity measurements were collected at 148 K on an Enraf–Nonius CAD-4 diffractometer using $\theta/2\theta$ scans (4 to 130°). Lattice parameters were calculated from least-squares refinement of 25 reflections in the range $16 \leq 2\theta \leq 32°$. An empirical absorption correction was applied (minimum transmission 93.9, maximum 99.9%). The maximum value of $\sin\theta/\lambda$ was 0.588 $Å^{-1}$; $0 \leq h \leq 8$, $0 \leq k \leq 14$, $0 \leq l \leq 28$. Standard reflections $31\bar{4}$ and 437 showed variations in intensity of less than 2%. A total of 2206 unique reflections were measured with 1602 having $I \geq 3\sigma(I)$ in the final cycle of refinement.

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* ($Å^2$)

$$B_{eq} = (1/3)\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
O(1)	0.0889 (3)	0.8823 (1)	0.17110 (7)	2.18 (3)
O(2)	0.3653 (3)	1.0213 (2)	0.17681 (8)	2.70 (4)
C(1)	0.2494 (4)	1.0609 (2)	0.1002 (1)	1.82 (5)
C(2)	0.1997 (3)	1.1810 (2)	0.1016 (1)	1.93 (5)
C(3)	0.0534 (4)	1.1919 (2)	0.0571 (1)	1.83 (5)
C(4)	−0.0437 (4)	1.3006 (2)	0.0594 (1)	2.31 (5)
C(5)	−0.1636 (4)	1.2909 (2)	0.1116 (1)	2.38 (5)
C(6)	−0.1128 (4)	1.1808 (2)	0.1351 (1)	1.87 (5)
C(7)	0.0843 (4)	1.1830 (2)	0.1576 (1)	1.88 (5)
C(8)	0.1341 (4)	1.0757 (2)	0.1875 (1)	2.03 (5)
C(9)	0.0167 (4)	0.9866 (2)	0.1607 (1)	1.85 (5)
C(10)	0.0495 (4)	1.0137 (2)	0.0998 (1)	1.75 (5)
C(11)	0.3145 (4)	1.0482 (2)	0.1591 (1)	2.02 (5)
C(12)	−0.0775 (3)	1.1092 (2)	0.0834 (1)	1.73 (5)
C(13)	−0.2477 (4)	1.0763 (2)	0.0520 (1)	2.36 (5)
C(14)	0.0270 (4)	0.8390 (2)	0.2218 (1)	2.47 (5)

Table 2. *Bond distances* (Å) *and bond angles* (°)

C(1)—C(2)	1.536 (3)	C(1)—C(10)	1.571 (3)
C(1)—C(11)	1.522 (3)	C(2)—C(3)	1.528 (3)
C(2)—C(7)	1.604 (3)	C(3)—C(4)	1.527 (3)
C(3)—C(12)	1.542 (3)	C(4)—C(5)	1.549 (4)
C(5)—C(6)	1.529 (3)	C(6)—C(7)	1.538 (3)
C(5)—C(12)	1.565 (3)	C(7)—C(8)	1.562 (3)
C(8)—C(9)	1.545 (3)	C(8)—C(11)	1.525 (3)
C(9)—C(10)	1.540 (3)	C(10)—C(12)	1.558 (3)
C(12)—C(13)	1.514 (3)	C(9)—O(1)	1.422 (3)
C(11)—O(2)	1.199 (3)	C(14)—O(1)	1.423 (3)

C(9)—O(1)—C(14)	112.5 (2)	C(2)—C(1)—C(10)	98.3 (2)
C(2)—C(1)—C(11)	98.8 (2)	C(10)—C(1)—C(11)	104.8 (2)
C(1)—C(2)—C(3)	103.6 (2)	C(1)—C(2)—C(7)	99.1 (2)
C(3)—C(2)—C(7)	103.8 (2)	C(2)—C(3)—C(4)	112.0 (2)
C(2)—C(3)—C(12)	94.4 (2)	C(4)—C(3)—C(12)	106.7 (2)
C(3)—C(4)—C(5)	102.9 (2)	C(4)—C(5)—C(6)	103.9 (2)
C(5)—C(6)—C(7)	110.1 (2)	C(5)—C(6)—C(12)	104.3 (2)
C(7)—C(6)—C(12)	98.4 (2)	C(2)—C(7)—C(6)	100.6 (2)
C(2)—C(7)—C(8)	105.2 (2)	C(6)—C(7)—C(8)	111.7 (2)
C(7)—C(8)—C(9)	106.6 (2)	C(7)—C(8)—C(11)	100.3 (2)
C(9)—C(8)—C(11)	97.1 (2)	O(1)—C(9)—C(8)	111.9 (2)
O(1)—C(9)—C(10)	108.3 (2)	C(8)—C(9)—C(10)	99.6 (2)
C(1)—C(10)—C(9)	102.7 (2)	C(1)—C(10)—C(12)	105.5 (2)
C(9)—C(10)—C(12)	108.8 (2)	O(2)—C(11)—C(1)	130.1 (2)
O(2)—C(11)—C(8)	131.7 (2)	C(1)—C(11)—C(8)	97.9 (2)
C(3)—C(12)—C(6)	93.3 (2)	C(3)—C(12)—C(10)	104.3 (2)
C(3)—C(12)—C(13)	118.5 (2)	C(6)—C(12)—C(10)	108.9 (2)
C(6)—C(12)—C(13)	115.3 (2)	C(10)—C(12)—C(13)	114.3 (2)

The structure was solved and refined using the direct-methods *SDP* package (Frenz, 1978). *F* magnitudes were used in the least-squares refinement. H atoms were located and refined with fixed isotropic thermal parameters. The number of parameters refined in the final cycle was 199 (C and O anisotropic, non-Poisson contribution weighting) yielding $R = 0.0547$, $wR = 0.0552$, $S = 1.2206$, $(\Delta/\sigma)_{max} = 0.007$. The highest peak in the final difference map was 0.365 e $Å^{-3}$. Primary- and secondary-extinction values were used, and atomic scattering factors f' and f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Table 1 lists the atomic positional parameters while Table 2 gives bond lengths and bond angles for structure (1).*

Discussion. The 'twisted' hydrocarbon ring skeleton is known (Malojcic, Borcic & Sunko, 1977; Winstein & Hansen, 1960) and the X-ray crystal structures of polyfunctional derivatives have been determined (Astin, Fletcher, Mackenzie, Miller, Ratcliffe, Frew & Muir, 1982; Khan, Bauer & Khan, 1972).

An *ORTEP*II (Johnson, 1976) drawing of one of the enantiomers of (1) is shown in Fig. 1, and a cell-packing diagram is shown in Fig. 2. There are only three intermolecular contacts ≤3.5 Å, all involving O atoms. The shortest of these is O(1)···C(2)′ [3.392 (3) Å].

* Lists of H-atom coordinates, least-squares planes, torsion angles, thermal parameters, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55545 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1006]

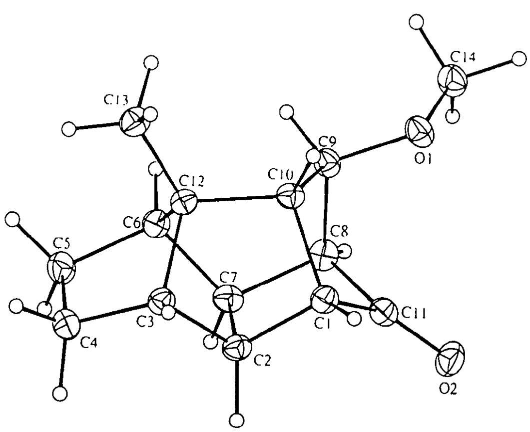

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of one of the enantiomers of (1) with thermal ellipsoids at the 30% probability level and spherical H atoms of arbitrary size.

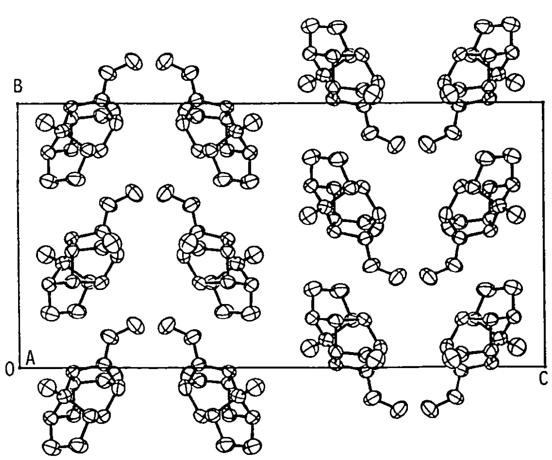

Fig. 2. Cell-packing diagram of (1).

Considerable ring strain is indicated by deviations of various bond lengths and bond angles from the usual values. The two longest bonds, C(2)—C(7) and C(1)—C(10), are consistent with those of literature structures (Astin, Fletcher, Mackenzie, Miller, Ratcliffe, Frew & Muir, 1982; Khan, Bauer & Khan, 1972), but the C(1)—C(2) bond is not as short as those reported.

Pyramidalization at C(11) as a result of nucleophilic intramolecular $CH_3O\cdots C{=}O$ interaction (Cossu, Bachmann, N'Guessan, Viani, Lapasset, Aycard & Bodot, 1987; Bürgi & Dunitz, 1983) is expected because the O(1)···C(11) intramolecular distance [2.654 (3) Å] is less than the sum of the nonbonded (van der Waals) radii, 3.2 Å (Bondi, 1964), and is in the usual range for this effect (Schweizer, Procter, Kaftory & Dunitz, 1978). The perpendicular distance of C(11) from the C(1)—C(8)—O(2) plane (Δ_c) is 0.042 (3) Å, and the angle between O(1) and the C(11)—O(2) bond (α) is 113.0 (2)°. From a different viewpoint, O(2) is 0.092 (2) Å out of the C(1)—C(8)—C(11) plane and the C(11)—O(2) bond makes an angle of 4.39° with respect to this plane. These data are consistent with those of literature structures.

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