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Structure of an Unusual Octacyclic Cage Compound

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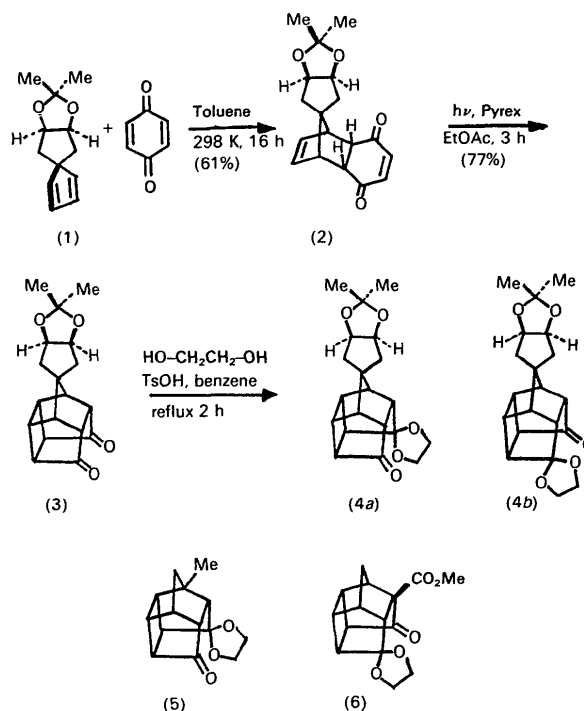
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Abstract. 11,11-Ethylenedioxy-pentacyclo[5.4.0.0^{2,6}.-0^{3,10}.0^{5,9}]undecane-4-spiro-7'-(*syn*-3',3'-dimethyl-2',4'-dioxabicyclo[3.3.0]octan-8-one (4a), C₂₀H₂₄O₅, M_r = 344.45, monoclinic, P₂₁/c, a = 11.466 (2), b = 7.744 (1), c = 19.249 (2) Å, β = 98.85 (1)°, V = 1688.8 (3) Å³, Z = 4, D_x = 1.360 g cm⁻³, λ(Mo Kα) = 0.71073 Å, μ = 1.00 cm⁻¹, F(000) = 736, T = 295 K, R = 0.0615 for 2472 reflections. The molecule consists of a cage containing four five-membered rings and a four-membered ring. The cage is spiro fused to a *cis*-fused dioxabicyclooctane ring and to an ethylenedioxy moiety. One bond in the cage is lengthened to 1.568 (3) Å.

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 (PCUs; Marchand, 1989), the Diels–Alder cycloaddition of spirocyclic diene (1) (Semmelhack, Foos & Katz, 1973) to *p*-benzoquinone has been investigated. Thus, when an equimolar toluene solution of the diene and dienophile was stirred at ambient temperature for 16 h, the corresponding cycloadduct (2) was produced in 61% yield. The fact that this adduct possesses the *endo* configuration was demonstrated by its facile intramolecular [2 + 2] photocyclization to the corresponding substituted PCU, (3), in 77% yield. When a benzene solution of (3) and ethylene glycol (1 equivalent) containing a catalytic amount of *p*-toluenesulfonic acid was refluxed for 2 h (Eaton,

Cassar, Hudson & Hwang, 1976), a mixture of products was formed. Careful fractional recrystallization of the mixture from ethyl acetate afforded a single monoethylene ketal, C₂₀H₂₄O₅, m.p. 467–468 K. The structure of this compound is shown to be (4a) [rather than (4b)] via single-crystal X-ray structural analysis.



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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)	2143 (2)	2194 (3)	1591 (1)	36 (1)
C(2)	1967 (2)	4138 (3)	1426 (1)	42 (1)
C(3)	1099 (2)	4875 (3)	1898 (1)	45 (1)
C(4)	994 (2)	3377 (3)	2381 (1)	42 (1)
O(3)	1056 (2)	3401 (3)	3013 (1)	63 (1)
C(5)	1026 (2)	1800 (3)	1926 (1)	36 (1)
C(6)	25 (2)	1822 (3)	1271 (1)	38 (1)
C(7)	-755 (2)	3387 (3)	1288 (1)	41 (1)
C(8)	101 (2)	4862 (3)	1249 (1)	44 (1)
C(9)	979 (2)	4150 (3)	782 (1)	43 (1)
C(10)	708 (2)	2216 (3)	663 (1)	39 (1)
C(11)	1893 (2)	1316 (3)	869 (1)	37 (1)
C(12)	1849 (2)	-661 (3)	890 (1)	48 (1)
C(13)	3094 (2)	-1262 (3)	864 (1)	48 (1)
C(14)	3697 (2)	186 (4)	510 (1)	51 (1)
C(15)	2809 (2)	1647 (4)	379 (1)	49 (1)
C(16)	4893 (2)	-714 (4)	1509 (1)	52 (1)
O(4)	3758 (2)	-1370 (2)	1553 (1)	51 (1)
O(5)	4679 (2)	672 (3)	1019 (1)	59 (1)
C(17)	5425 (3)	-16 (5)	2210 (2)	75 (1)
C(18)	5660 (3)	-2073 (5)	1241 (2)	78 (1)
C(19)	-2735 (3)	3743 (7)	916 (2)	95 (2)
C(20)	-2483 (3)	3997 (7)	1673 (2)	96 (2)
O(1)	-1665 (1)	3395 (3)	692 (1)	54 (1)
O(2)	-1334 (1)	3428 (2)	1887 (1)	48 (1)

Table 2. Bond lengths (\AA) and angles ($^\circ$) for compound (4a)

C(1)—C(2)	1.545 (3)	C(1)—C(5)	1.550 (3)
C(1)—C(11)	1.535 (3)	C(2)—C(3)	1.556 (4)
C(2)—C(9)	1.546 (3)	C(3)—C(4)	1.504 (3)
C(3)—C(8)	1.559 (3)	C(4)—O(3)	1.207 (3)
C(4)—C(5)	1.507 (3)	C(5)—C(6)	1.568 (3)
C(6)—C(7)	1.509 (3)	C(6)—C(10)	1.536 (3)
C(7)—C(8)	1.515 (3)	C(7)—O(1)	1.427 (2)
C(7)—O(2)	1.417 (3)	C(8)—C(9)	1.551 (4)
C(9)—C(10)	1.540 (4)	C(10)—C(11)	1.524 (3)
C(11)—C(12)	1.532 (4)	C(11)—C(15)	1.538 (3)
C(12)—C(13)	1.509 (4)	C(13)—C(14)	1.532 (4)
C(13)—O(4)	1.426 (3)	C(14)—C(15)	1.517 (4)
C(14)—O(5)	1.425 (3)	C(14)—O(4)	1.412 (3)
C(16)—O(5)	1.425 (3)	C(16)—C(17)	1.494 (4)
C(16)—C(18)	1.512 (5)	C(19)—C(20)	1.455 (5)
C(19)—O(1)	1.388 (4)	C(20)—O(2)	1.389 (3)
C(2)—C(1)—C(5)	100.8 (2)	C(2)—C(1)—C(11)	104.2 (2)
C(5)—C(1)—C(11)	103.8 (2)	C(1)—C(2)—C(3)	108.2 (2)
C(1)—C(2)—C(9)	103.1 (2)	C(3)—C(2)—C(9)	90.6 (2)
C(2)—C(3)—C(4)	101.4 (2)	C(2)—C(3)—C(8)	89.2 (2)
C(4)—C(3)—C(8)	111.8 (2)	C(3)—C(4)—O(3)	127.8 (2)
C(3)—C(4)—C(5)	104.7 (2)	O(3)—C(4)—C(5)	126.6 (2)
C(1)—C(5)—C(4)	100.3 (2)	C(1)—C(5)—C(6)	102.3 (2)
C(4)—C(5)—C(6)	112.2 (2)	C(5)—C(6)—C(7)	110.8 (2)
C(5)—C(6)—C(10)	102.6 (2)	C(7)—C(6)—C(10)	103.3 (2)
C(6)—C(7)—C(8)	102.4 (2)	C(6)—C(7)—O(1)	110.4 (2)
C(8)—C(7)—O(1)	110.9 (2)	C(6)—C(7)—O(2)	112.9 (2)
C(8)—C(7)—O(2)	114.3 (2)	O(1)—C(7)—O(2)	106.1 (2)
C(3)—C(8)—C(7)	111.5 (2)	C(3)—C(8)—C(9)	90.3 (2)
C(7)—C(8)—C(9)	104.1 (2)	C(2)—C(9)—C(8)	89.9 (2)
C(2)—C(9)—C(10)	102.7 (2)	C(8)—C(9)—C(10)	107.3 (2)
C(6)—C(10)—C(9)	101.2 (2)	C(6)—C(10)—C(11)	104.5 (2)
C(9)—C(10)—C(11)	104.8 (2)	C(1)—C(11)—C(10)	93.9 (2)
C(1)—C(11)—C(12)	114.8 (2)	C(10)—C(11)—C(12)	115.6 (2)
C(1)—C(11)—C(15)	115.6 (2)	C(10)—C(11)—C(15)	115.5 (2)
C(12)—C(11)—C(15)	102.2 (2)	C(11)—C(12)—C(13)	105.8 (2)
C(12)—C(13)—C(14)	106.5 (2)	C(12)—C(13)—O(4)	111.1 (2)
C(14)—C(13)—O(4)	104.1 (2)	C(13)—C(14)—C(15)	106.4 (2)
C(13)—C(14)—O(5)	104.5 (2)	C(15)—C(14)—O(5)	110.9 (2)
C(11)—C(15)—C(14)	106.1 (2)	O(4)—C(16)—O(5)	104.1 (2)
O(4)—C(16)—C(17)	109.1 (2)	O(5)—C(16)—C(17)	109.3 (2)
O(4)—C(16)—C(18)	111.1 (2)	O(5)—C(16)—C(18)	110.4 (2)
C(17)—C(16)—C(18)	112.5 (2)	C(13)—O(4)—C(16)	106.8 (2)
C(14)—O(5)—C(16)	107.1 (2)	C(20)—C(19)—O(1)	106.7 (2)
C(19)—C(20)—O(2)	106.7 (3)	C(7)—O(1)—C(19)	108.9 (2)
C(7)—O(2)—C(20)	107.9 (2)		

Experimental. A colorless crystal of dimensions 0.48 \times 0.25 \times 0.13 mm was mounted on a Nicolet R3M/ μ update of a $P2_1$ diffractometer; data collected in the ω -scan mode ($3 \leq 2\theta \leq 55^\circ$), variable scan rate of 4 to 29.5° min⁻¹, graphite-monochromated Mo $K\alpha$ radiation; lattice parameters from a least-squares refinement of 25 reflections ($22.97 \leq 2\theta \leq 29.30^\circ$); monitored reflections (131) and (414) showed less than a 2% variation in intensity (linear correction). Systematic absences ($h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$) consistent with space group $P2_1/c$; 4339 reflections measured ($-14 \leq h \leq 14$; $0 \leq k \leq 10$; $0 \leq l \leq 24$), 3850 independent ($R_{merge} = 0.007$), 2472 with $I \geq 3\sigma(I)$; Lorentz-polarization correction and ψ -scan-based empirical absorption correction applied (transmission factors 0.909 to 0.944); structure solved by direct methods and refined by a block-cascade least-squares technique, all cage H atoms and H(13) and H(14) refined with isotropic thermal parameters, the remaining H atoms were allowed to ride on the attached heavy atom but isotropic thermal parameters refined; final $R = 0.0615$ ($R_{all} = 0.0966$), $wR = 0.0563$ ($wR_{all} = 0.0699$) for 281 parameters and 2472 reflections, $S = 1.642$, $(\Delta/\sigma)_{max} = 0.025$; largest peaks in the final difference map -0.24 and 0.30 e \AA^{-3} ; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma^2(F_o) + 0.00028F_o^2]^{-1}$; isotropic extinction correction $F = F_c/[1.0 + 3.5(4) \times 10^{-6}F_c^2/\sin(2\theta)]^{0.25}$. Computer programs for Desktop 30 Microclipse and Nova 4/C configuration supplied by Nicolet (Nicolet Instrument Corporation, 1986);

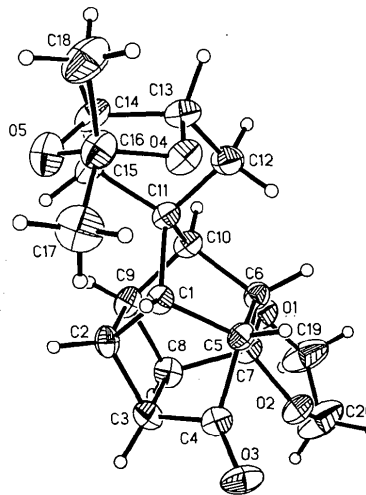


Fig. 1. Compound (4a) drawn at the 30% probability level. H atoms are represented by spheres of arbitrary size.

atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974). Table 1 contains a list of atomic positional parameters while Table 2 gives interatomic distances and bond angles.*

Discussion. Fig. 1 is a drawing of compound (4a). The molecule consists of a cage containing four five-membered rings in envelope conformations and a planar (0.005 Å r.m.s. deviation) four-membered ring. The cage is spiro fused to a *cis*-bicyclooctane ring and to an ethylenedioxy moiety. The bond lengths around the cage are statistically equivalent to the average values for compounds (5) (Flippin-Anderson, Gilardi, George, Marchand & Reddy, 1989) and (6) (Watson, Nagl, Marchand, Reddy & Reddy, 1989) except for the lengthening of C(1)—C(11) and C(10)—C(11) from an average of 1.515 (3) Å in (5) and (6) to 1.530 (5) Å in (4a) owing to the spiro fusion at C(11). The long bond at C(5)—C(6) of 1.568 (3) Å is consistent with the average value of 1.575 (2) Å observed in the reference compounds. C(4) is slightly pyramidalized, lying 0.075 (3) Å out of the plane of C(3)C(5)O(3).

* 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 53030 (26 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Molecular-mechanics calculations (*PCMODEL*, 1989) indicate the molecule has 267.3 kJ mol⁻¹ of strain energy distributed primarily between angle and torsional contributions.

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Structure of a Bromonitro-Substituted 2-Oxapentacyclo[7.3.0.0^{3,7}.0^{4,12}.0^{6,10}]dodecane

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Abstract. 5-Bromo-11-ethylenedioxy-5-nitro-2-oxapentacyclo[7.3.0.0^{3,7}.0^{4,12}.0^{6,10}]dodecane, (4a), C₁₃H₁₄BrNO₅, *M_r* = 344.17, monoclinic, *P*2₁/*a*, *a* = 9.296 (1), *b* = 10.664 (2), *c* = 12.508 (1) Å, β = 93.41°, *V* = 1237.7 (2) Å³, *Z* = 4, *D_x* = 1.847 g cm⁻³, λ(Mo Kα) = 0.71073 Å, μ = 33.0 cm⁻¹, *F*(000) = 696, *T* = 295 K, *R* = 0.0470 for 2270 reflections. The

compound is an open-ended cage containing four five-membered rings in envelope conformations and a six-membered heterocyclic ring in a boat conformation. Steric crowding may have a greater effect upon bond lengths than the bromonitro substitution at C(8).

Introduction. As part of a program that is concerned with the synthesis and chemistry of novel, substi-

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