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Two Methylated Hexacyclic Cage Diketones

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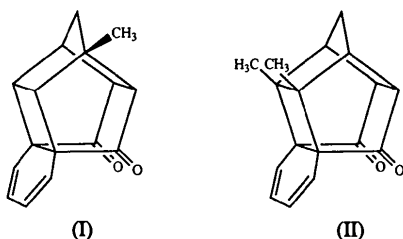
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Abstract

The structures of two methylated hexacyclic cage diketones, 1-methylhexacyclo[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]-pentadeca-5,7-diene-3,10-dione, C₁₆H₁₄O₂, and 13,14-dimethylhexacyclo[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]-pentadeca-5,7-diene-3,10-dione, C₁₇H₁₆O₂, have been determined. All bond lengths and angles are consistent with strained-cage geometry.

Comment

As part of a general investigation of the synthesis and chemistry of novel polycyclic cage systems (Marchand, 1989, 1992), we have recently undertaken a study of the synthesis of novel functionalized hexacyclo[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]-pentadeca-5,7-diene-3,10-diones. The structures of 1-methylhexacyclo[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]-pentadeca-5,7-diene-3,10-dione, (I), and 13,14-dimethylhexacyclo[10.2.1.0^{2,11}.0^{4,9}.0^{4,14}.0^{9,13}]-pentadeca-5,7-diene-3,10-dione, (II), are presented here.



These unusual diene systems are currently of considerable interest as substrates for the study of remote substituent effects on the π -facial selectivities of Diels–Alder reactions (Coxon, O’Connell & Steel, 1987; Coxon, Maclagan, McDonald & Steel, 1991); for the structure of the unmethylated compound, see Dhaneshwar, Tavale, Row, Zope, Pandey & Ayyangar (1988). Several Diels–Alder adducts have been reported (Coxon, O’Connell & Steel, 1986, 1987). Structures similar to the title structures in which one ketone group has been replaced by either an alkoxide or a ketal (Bott, Mar-

chand, Zope, Coxon, Fong & Steel, 1993) and a Diels–Alder adduct of the parent compound (Dhaneshwar, Krishnan, Tavale, Zope, Pandey & Ayyangar, 1991) have also been reported.

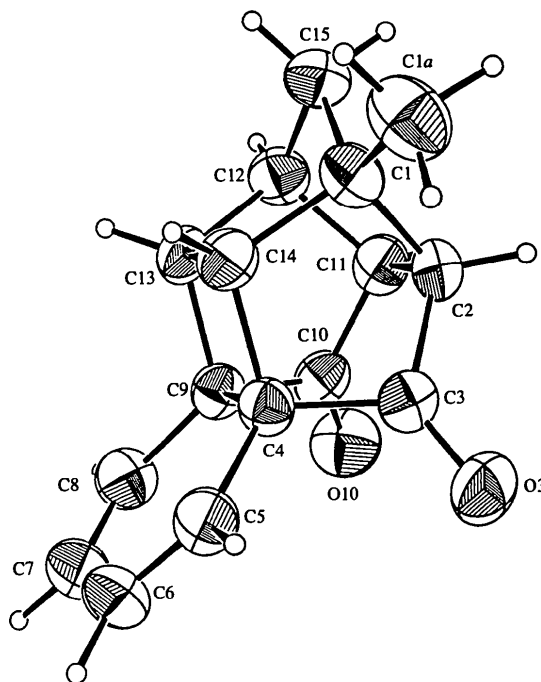


Fig. 1. ORTEPII (Johnson, 1976) drawing of compound (I). H atoms have been assigned arbitrary radii and C and O atoms are shown with 50% probability ellipsoids.

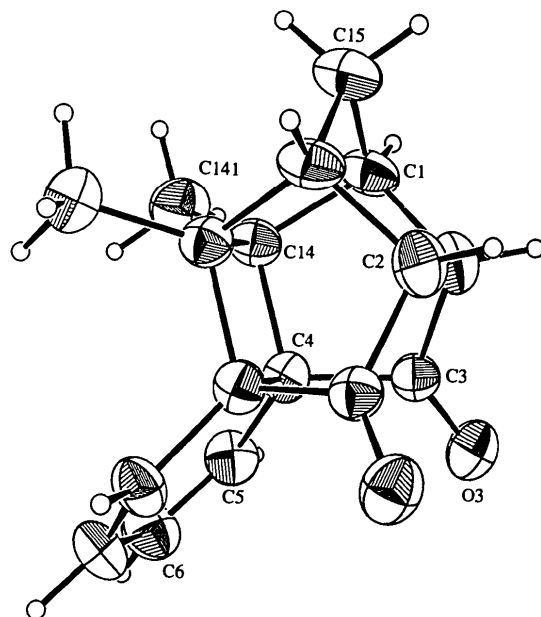


Fig. 2. ORTEPII (Johnson, 1976) drawing of compound (II). H atoms have been assigned arbitrary radii and C and O atoms are shown with 50% probability ellipsoids.

Experimental

The title compounds were prepared according to Coxon, O'Connell & Steel (1987).

Compound (I)

Crystal data

C₁₆H₁₄O₂M_r = 238.29

Monoclinic

P2₁/n

a = 6.7134 (8) Å

b = 9.8931 (9) Å

c = 17.485 (1) Å

β = 92.101 (8)°

V = 1160.5 (6) Å³

Z = 4

D_x = 1.364 Mg m⁻³D_m not measured

Data collection

Enraf-Nonius CAD-4 diffractometer

θ/2θ scans

Absorption correction: none

1662 measured reflections

1524 independent reflections

1072 observed reflections

[I > 3σ(I)]

Refinement

Refinement on F

R = 0.0384

wR = 0.0416

S = 1.36

1072 reflections

163 parameters

H-atom parameters not refined

w = 1/[σ²(F) + 0.04F²]

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 13–20°

μ = 0.083 mm⁻¹

T = 294 K

Block

0.32 × 0.26 × 0.22 mm

Colorless

R_{int} = 0.024θ_{max} = 22°

h = 0 → 7

k = 0 → 10

l = -18 → 18

3 standard reflections

frequency: 60 min

intensity decay: 1%

Table 2. Selected geometric parameters (Å, °) for (I)

O3—C3	1.211 (4)	O10—C10	1.207 (4)
C1—C1a	1.516 (5)	C1—C2	1.539 (5)
C1—C14	1.550 (5)	C1—C15	1.521 (5)
C2—C3	1.507 (5)	C2—C11	1.584 (5)
C3—C4	1.503 (5)	C4—C5	1.484 (5)
C4—C9	1.601 (4)	C4—C14	1.559 (5)
C5—C6	1.320 (5)	C6—C7	1.457 (5)
C7—C8	1.316 (5)	C8—C9	1.479 (5)
C9—C10	1.515 (5)	C9—C13	1.549 (5)
C10—C11	1.503 (5)	C11—C12	1.537 (5)
C12—C13	1.547 (5)	C12—C15	1.511 (5)
C13—C14	1.540 (4)		
C1a—C1—C2	114.4 (3)	C4—C14—C13	91.1 (2)
C1a—C1—C15	118.0 (3)	C1a—C1—C14	115.6 (3)
C2—C1—C15	103.8 (3)	C2—C1—C14	100.6 (3)
C1—C2—C3	102.7 (3)	C14—C1—C15	102.1 (3)
C3—C2—C11	109.0 (3)	C1—C2—C11	102.9 (3)
O3—C3—C4	126.7 (3)	O2—C3—C2	127.8 (3)
C3—C4—C5	115.9 (3)	C2—C3—C4	105.5 (3)
C3—C4—C14	102.6 (3)	C3—C4—C9	109.3 (2)
C5—C4—C14	122.0 (3)	C5—C4—C9	114.8 (3)
C4—C5—C6	122.9 (3)	C9—C4—C14	88.6 (2)
C6—C7—C8	121.5 (3)	C5—C6—C7	122.2 (3)
C4—C9—C8	114.9 (3)	C7—C8—C9	123.6 (3)
C4—C9—C13	89.2 (2)	C4—C9—C10	108.7 (3)
C8—C9—C13	120.0 (3)	C8—C9—C10	117.4 (3)
O10—C10—C9	126.7 (3)	C10—C9—C13	102.6 (3)
C9—C10—C11	105.0 (3)	O10—C10—C11	128.3 (3)
C2—C11—C10	102.5 (3)	C2—C11—C10	109.8 (3)
C11—C12—C13	100.8 (3)	C10—C11—C12	102.9 (3)
C13—C12—C15	103.0 (3)	C1—C14—C13	103.9 (3)
C9—C13—C14	91.2 (2)	C1—C15—C12	96.3 (3)
C1—C14—C4	108.4 (3)		

Compound (II)

Crystal data

C₁₇H₁₆O₂M_r = 252.32

Monoclinic

P2₁/m

a = 7.175 (1) Å

b = 12.0275 (8) Å

c = 7.275 (1) Å

β = 95.510 (9)°

V = 624.9 (5) Å³

Z = 2

D_x = 1.361 Mg m⁻³D_m not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25

reflections

θ = 20–22°

μ = 0.081 mm⁻¹

T = 294 K

Plate

0.18 × 0.12 × 0.05 mm

Colorless

Data collection

Enraf-Nonius CAD-4 diffractometer

θ/2θ scans

Absorption correction: none

884 measured reflections

818 independent reflections

613 observed reflections

[I > 3σ(I)]

Refinement

Refinement on F

R = 0.0676

wR = 0.0805

R_{int} = 0.048θ_{max} = 22°

h = 0 → 7

k = 0 → 12

l = -7 → 7

3 standard reflections

frequency: 60 min

intensity decay: 1%

(Δ/σ)_{max} = 0.01Δρ_{max} = 0.30 e Å⁻³Δρ_{min} = -0.22 e Å⁻³Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (I)

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$			
	x	y	z	B _{eq}
O3	0.9942 (3)	0.0798 (3)	0.7969 (2)	4.61 (6)
O10	0.4589 (4)	0.0658 (3)	0.6986 (1)	4.96 (6)
C1	0.7127 (5)	0.2832 (4)	0.9101 (2)	3.50 (8)
C1a	0.8893 (6)	0.3351 (4)	0.9579 (2)	5.3 (1)
C2	0.7561 (5)	0.2583 (4)	0.8254 (2)	3.23 (7)
C3	0.8444 (5)	0.1182 (4)	0.8268 (2)	3.06 (7)
C4	0.7111 (5)	0.0356 (3)	0.8758 (2)	2.78 (7)
C5	0.7917 (5)	-0.0970 (4)	0.9018 (2)	3.51 (8)
C6	0.6891 (6)	-0.2106 (4)	0.8955 (2)	4.07 (8)
C7	0.4879 (6)	-0.2150 (4)	0.8615 (2)	4.09 (8)
C8	0.3996 (5)	-0.1056 (4)	0.8341 (2)	3.70 (8)
C9	0.4922 (5)	0.0300 (3)	0.8364 (2)	2.85 (7)
C10	0.4923 (5)	0.1091 (4)	0.7623 (2)	3.25 (7)
C11	0.5402 (5)	0.2522 (4)	0.7860 (2)	3.47 (8)
C12	0.4047 (5)	0.2750 (4)	0.8538 (2)	3.66 (8)
C13	0.4230 (5)	0.1366 (4)	0.8946 (2)	3.17 (7)
C14	0.6330 (5)	0.1424 (4)	0.9330 (2)	3.19 (8)
C15	0.5235 (6)	0.3679 (4)	0.9067 (2)	4.22 (9)

$S = 2.10$
 613 reflections
 88 parameters
 H-atom parameters not refined
 $w = 1/[\sigma^2(F) + 0.04F^2]$

Extinction correction: none
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for (II)

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B_{eq}
O3	0.3571 (6)	0.0922 (4)	1.0462 (6)	3.5 (1)
C1	0.8269 (8)	0.1561 (5)	1.0585 (9)	3.1 (1)
C2	0.6496 (9)	0.1830 (5)	1.1518 (8)	3.1 (1)
C3	0.4947 (8)	0.1438 (5)	1.0160 (8)	2.4 (1)
C4	0.5470 (8)	0.1832 (5)	0.8294 (8)	2.4 (1)
C5	0.4433 (9)	0.1307 (5)	0.6637 (9)	2.9 (1)
C6	0.3625 (9)	0.1888 (6)	0.5262 (8)	3.6 (1)
C14	0.7659 (8)	0.1846 (5)	0.8543 (8)	2.5 (1)
C15	0.959 (1)	1/4	1.115 (1)	4.1 (2)
C141	0.8692 (9)	0.1219 (6)	0.7168 (9)	4.0 (2)

Table 4. Selected geometric parameters (\AA , $^\circ$) for (II)

O3—C3	1.204 (7)	C1—C2	1.533 (9)
C1—C14	1.546 (9)	C1—C15	1.505 (9)
C2—C2 ⁱ	1.610 (9)	C2—C3	1.491 (8)
C3—C4	1.519 (9)	C4—C4 ⁱ	1.606 (8)
C4—C5	1.495 (8)	C4—C14	1.564 (8)
C14—C14 ⁱ	1.573 (8)	C5—C6	1.309 (9)
C6—C6 ⁱ	1.472 (9)	C14—C141	1.504 (9)
C2—C1—C14	102.0 (5)	C2—C1—C15	104.3 (6)
C14—C1—C15	102.0 (6)	C1—C2—C3	103.8 (5)
C1—C2—C2 ⁱ	102.2 (5)	C3—C2—C2 ⁱ	108.5 (5)
O3—C3—C2	128.0 (6)	O3—C3—C4	127.0 (5)
C2—C3—C4	105.1 (5)	C3—C4—C4 ⁱ	108.2 (5)
C3—C4—C14	103.4 (4)	C14—C4—C4 ⁱ	89.4 (5)
C3—C4—C5	116.2 (5)	C14—C4—C5	121.0 (5)
C5—C4—C4 ⁱ	115.0 (5)	C1—C14—C4	107.3 (5)
C1—C14—C14 ⁱ	102.8 (5)	C1—C14—C141	114.6 (5)
C4—C14—C141	118.1 (5)	C4—C14—C14 ⁱ	90.6 (5)
C141—C14—C14 ⁱ	120.1 (5)	C1—C15—C1 ⁱ	97.3 (5)
C4—C5—C6	122.7 (6)	C5—C6—C6 ⁱ	122.3 (6)

Symmetry code: (i) $x, \frac{1}{2} - y, z$.

H atoms were located on a difference map. Their geometries were idealized and they were constrained to ride upon their attached non-H atoms, with $U(\text{H}) = 1.3U_{\text{eq}}(\text{attached atom})$. *CAD-4 Software* (Enraf-Nonius, 1989) was used for data collection and cell refinement. The programs used for the structure solution and refinement were *MULTAN80* (Main *et al.*, 1980) and *MolEN* (Fair, 1990), respectively. The figures were drawn using *ORTEPII* (Johnson, 1976). *MolEN* was also used for data reduction.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1064). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two N-Aryl-Substituted Silyl Carbamates

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Abstract

Trimethylsilyl *N*-(4-bromophenyl)carbamate, $\text{C}_{10}\text{H}_{14}\text{BrNO}_2\text{Si}$, and trimethylsilyl *N*-*tert*-butyl-*N*-phenylcarbamate, $\text{C}_{14}\text{H}_{23}\text{NO}_2\text{Si}$, are both important silylating agents. The structures of both molecules are dominated by a plane containing a remarkably large number of atoms. The planes are organized by delocalization around the carbamate moiety. A quasi-pentacoordination of the Si atom in both compounds is also described.