

7-Methoxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione

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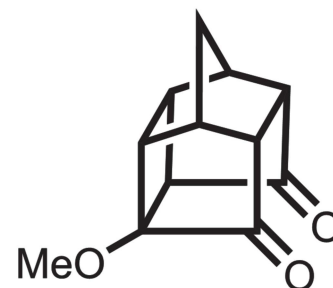
Structural data: full structural data are available from iucrdata.iucr.org

The structure of 7-methoxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione, C₁₂H₁₂O₃, at 150 K has monoclinic (*P*2₁/*c*) symmetry. The pentacycloundecane cage compound is composed of four five-membered rings, a planar four-membered ring and a six-membered ring in a boat conformation fused into a closed strained-cage framework. All of the five-membered rings adopt an envelope conformation.

3D view



Chemical scheme



Structure description

Polycyclic cage hydrocarbons act as valuable synthons in pharmaceutical and medicinal chemistry (Bisetty *et al.*, 2006; Geldenhuys, *et al.*, 2005). They are also useful candidates in energetic materials (Zhang *et al.*, 2018). Most of the cage systems display functions in supramolecular chemistry and asymmetric catalysis (Gharpure *et al.*, 2013). Oxygenated cage compounds show significant biological activity (Oliver *et al.*, 1991; van Dijk *et al.*, 2008). In addition, various rearrangement approaches in pentacycloundecane-containing cage frameworks provide an alternative route for the synthesis of biologically relevant frameworks such as *D*₃-trishomocubane derivatives that are not available by conventional multi-step synthetic routes (Liu *et al.*, 2001; Sklyarova *et al.*, 2013).

The bond angle C1–O1–C2 is 113.86°(16). Notably, the distance between the methoxy-substituted carbon atom, C2, and C3 is 1.521 (3) Å while the C8–C9 distance is 1.516 (3) Å. The methoxy substitution (presence of electron-donating group) has led to an elongation of the C2–C3 bond. Additionally, all bonds of the cyclobutane ring are not equal, the observed range being 1.552 (3)–1.579 (3) Å. Thus, a slight distortion is observed after substitution with a methoxy group (Fig. 1) compared to Cookson's dione skeleton (Linden *et al.*, 2005).

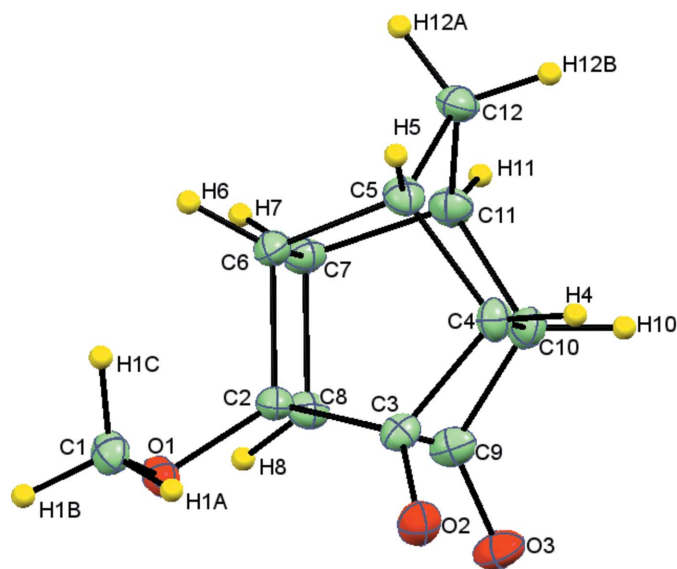


Figure 1
Perspective view of the title compound. Displacement parameters are drawn at the 50% probability level.

Synthesis and crystallization

The title compound **1** was prepared (Fig. 2) from quinone **3**, which was derived from the commercially available starting materials 4-hydroxy-3-methoxybenzaldehyde **2** (vanillin) and cyclopentadiene **4** using the reported method (Pratt *et al.*, 1987) *via* a Diels–Alder reaction and [2 + 2] photocycloaddition as key steps (Mehta *et al.*, 1984). The Diels–Alder adduct **5** (100 mg, 0.40 mmol, synthesized from quinone **3** *via* Diels–Alder reaction with freshly cracked cyclopentadiene **4**) was dissolved in anhydrous ethyl acetate (300 ml) and irradiated in a Pyrex immersion well using a 125 W medium-pressure UV mercury-vapour lamp for 30 min under nitrogen at room temperature. After conclusion of the reaction as monitored by TLC, the solvent was evaporated under reduced pressure and the crude reaction mixture was purified by silica gel column chromatography using 40% ethyl acetate/petroleum ether as an eluent, which furnished **1** as a colourless solid. The resulting isolated compound was crystallized from petroleum ether and CHCl₃ (4:1) in a refrigerator by slow evaporation (83 mg, 83%). Colourless crystalline solid, m.p. 89–91 °C; (lit. reported m.p. 85 °C); ¹H NMR (500 MHz, CDCl₃): δ = 3.40 (s, 3H), 3.24–3.20 (m, 1H), 3.08–3.05 (m, 1H), 2.93 (s, 1H), 2.89 (s, 1H), 2.83 (d, *J* = 6.4 Hz, 1H), 2.68–2.58 (m, 2H), 2.00 (d, *J* = 11.4 Hz, 1H), 1.9 (d, *J* = 11.4 Hz, 1H) p.p.m. ¹³C NMR (125 MHz, CDCl₃): δ = 210.8, 209.9, 82.1, 54.7, 53.5, 50.8, 48.5, 43.9, 43.2, 41.9, 36.4 p.p.m. HRMS (ESI): *m/z* calculated for C₁₂H₁₂NaO₃ [*M* + *K*]⁺: 243.418; found: 243.415.

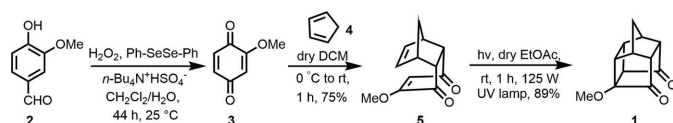


Figure 2
Reaction scheme for the synthesis of the title compound.

Table 1
Experimental details.

Crystal data	
Chemical formula	C ₁₂ H ₁₂ O ₃
<i>M_r</i>	204.22
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.3136 (2), 11.6138 (5), 12.6330 (5)
β (°)	95.292 (3)
<i>V</i> (Å ³)	922.37 (6)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.11
Crystal size (mm)	0.34 × 0.28 × 0.23
Data collection	
Diffractometer	Oxford Diffraction Xcalibur-S
Absorption correction	Multi-scan (<i>CrysAlis RED</i> ; Oxford Diffraction, 2008)
<i>T_{min}</i> , <i>T_{max}</i>	0.965, 0.976
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	4686, 1620, 1432
<i>R_{int}</i>	0.020
(sin θ/λ) _{max} (Å ⁻¹)	0.594
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.048, 0.111, 1.10
No. of reflections	1620
No. of parameters	137
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.31, −0.19

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2008), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

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full crystallographic data

IUCrData (2020). 5, x201380 [https://doi.org/10.1107/S2414314620013802]

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7-Methoxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione*Crystal data*

$C_{12}H_{12}O_3$	$F(000) = 432$
$M_r = 204.22$	$D_x = 1.471 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
$a = 6.3136 (2) \text{ \AA}$	Cell parameters from 1649 reflections
$b = 11.6138 (5) \text{ \AA}$	$\theta = 3.3\text{--}32.8^\circ$
$c = 12.6330 (5) \text{ \AA}$	$\mu = 0.11 \text{ mm}^{-1}$
$\beta = 95.292 (3)^\circ$	$T = 150 \text{ K}$
$V = 922.37 (6) \text{ \AA}^3$	Block, colourless
$Z = 4$	$0.34 \times 0.28 \times 0.23 \text{ mm}$

Data collection

Oxford Diffraction Xcalibur-S diffractometer	1620 independent reflections
Detector resolution: 15.9948 pixels mm^{-1}	1432 reflections with $I > 2\sigma(I)$
ω/q -scan	$R_{\text{int}} = 0.020$
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2008)	$\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 3.7^\circ$
$T_{\text{min}} = 0.965$, $T_{\text{max}} = 0.976$	$h = -7 \rightarrow 4$
4686 measured reflections	$k = -13 \rightarrow 13$
	$l = -13 \rightarrow 15$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.048$	$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2 + 1.1811P]$
$wR(F^2) = 0.111$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.10$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1620 reflections	$\Delta\rho_{\text{max}} = 0.31 \text{ e \AA}^{-3}$
137 parameters	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
0 restraints	
Primary atom site location: dual	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The H atoms were found in a difference map but refined using a riding model with C—H ranging from 0.98 Å to 1.00 Å and $U(\text{H})$ set to 1.2 $U_{\text{eq}}(\text{C})$ or 1.5 $U_{\text{eq}}(\text{C}_{\text{methyl}})$.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.5101 (2)	0.05611 (13)	0.88757 (12)	0.0213 (4)
O2	0.7295 (2)	0.00528 (14)	0.69852 (12)	0.0252 (4)
O3	0.1795 (2)	-0.10734 (14)	0.62216 (13)	0.0281 (4)
C1	0.7014 (4)	0.1112 (2)	0.93007 (18)	0.0231 (5)
H1A	0.8199	0.0856	0.8910	0.035*
H1B	0.7304	0.0910	1.0053	0.035*
H1C	0.6852	0.1949	0.9231	0.035*
C2	0.4378 (3)	0.09282 (18)	0.78544 (17)	0.0183 (5)
C3	0.5748 (3)	0.06703 (18)	0.69536 (17)	0.0186 (5)
C4	0.4765 (3)	0.13774 (19)	0.60217 (17)	0.0205 (5)
H4	0.5664	0.1421	0.5411	0.025*
C5	0.4380 (3)	0.25570 (19)	0.65426 (17)	0.0219 (5)
H5	0.5615	0.3100	0.6586	0.026*
C6	0.3617 (3)	0.21926 (19)	0.76243 (17)	0.0204 (5)
H6	0.3814	0.2757	0.8223	0.024*
C7	0.1322 (3)	0.17496 (19)	0.73067 (17)	0.0201 (5)
H7	0.0168	0.2055	0.7720	0.024*
C8	0.2040 (3)	0.04885 (19)	0.75312 (17)	0.0202 (5)
H8	0.1322	0.0060	0.8084	0.024*
C9	0.2003 (3)	-0.00636 (19)	0.64421 (18)	0.0211 (5)
C10	0.2401 (3)	0.0924 (2)	0.57020 (18)	0.0225 (5)
H10	0.2100	0.0735	0.4931	0.027*
C11	0.1045 (4)	0.1921 (2)	0.60828 (18)	0.0232 (5)
H11	-0.0461	0.1944	0.5759	0.028*
C12	0.2344 (4)	0.30022 (19)	0.59218 (18)	0.0239 (5)
H12A	0.1760	0.3693	0.6250	0.029*
H12B	0.2528	0.3151	0.5164	0.029*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0240 (8)	0.0213 (8)	0.0187 (8)	-0.0036 (7)	0.0019 (6)	0.0028 (6)
O2	0.0209 (8)	0.0287 (9)	0.0265 (9)	0.0030 (7)	0.0040 (6)	-0.0010 (7)
O3	0.0281 (9)	0.0185 (9)	0.0369 (10)	-0.0011 (7)	-0.0014 (7)	-0.0055 (7)
C1	0.0258 (12)	0.0230 (12)	0.0200 (11)	-0.0045 (10)	-0.0006 (9)	-0.0018 (9)
C2	0.0223 (11)	0.0147 (11)	0.0178 (11)	0.0000 (9)	0.0015 (9)	0.0009 (8)
C3	0.0167 (11)	0.0172 (11)	0.0223 (11)	-0.0036 (9)	0.0032 (8)	-0.0021 (9)
C4	0.0188 (10)	0.0250 (12)	0.0182 (11)	-0.0013 (9)	0.0045 (8)	-0.0004 (9)
C5	0.0237 (11)	0.0199 (12)	0.0222 (12)	-0.0044 (9)	0.0026 (9)	0.0015 (9)
C6	0.0260 (11)	0.0162 (11)	0.0194 (11)	-0.0004 (9)	0.0042 (9)	-0.0011 (9)
C7	0.0186 (11)	0.0176 (11)	0.0249 (12)	0.0029 (9)	0.0060 (9)	0.0000 (9)
C8	0.0181 (11)	0.0190 (11)	0.0243 (12)	-0.0009 (9)	0.0065 (8)	0.0031 (9)
C9	0.0130 (10)	0.0202 (12)	0.0292 (12)	0.0001 (9)	-0.0034 (8)	-0.0024 (9)
C10	0.0235 (12)	0.0234 (12)	0.0201 (12)	0.0013 (9)	-0.0009 (9)	-0.0034 (9)
C11	0.0209 (11)	0.0234 (12)	0.0249 (12)	0.0030 (9)	0.0001 (9)	0.0015 (10)

C12	0.0286 (12)	0.0187 (11)	0.0248 (12)	0.0024 (10)	0.0047 (9)	0.0048 (9)
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Geometric parameters (Å, °)

O1—C1	1.427 (3)	C5—C12	1.533 (3)
O1—C2	1.395 (3)	C6—H6	1.0000
O2—C3	1.209 (3)	C6—C7	1.555 (3)
O3—C9	1.210 (3)	C7—H7	1.0000
C1—H1A	0.9800	C7—C8	1.552 (3)
C1—H1B	0.9800	C7—C11	1.553 (3)
C1—H1C	0.9800	C8—H8	1.0000
C2—C3	1.521 (3)	C8—C9	1.516 (3)
C2—C6	1.564 (3)	C9—C10	1.516 (3)
C2—C8	1.579 (3)	C10—H10	1.0000
C3—C4	1.520 (3)	C10—C11	1.543 (3)
C4—H4	1.0000	C11—H11	1.0000
C4—C5	1.549 (3)	C11—C12	1.523 (3)
C4—C10	1.599 (3)	C12—H12A	0.9900
C5—H5	1.0000	C12—H12B	0.9900
C5—C6	1.549 (3)		
C2—O1—C1	113.86 (16)	C6—C7—H7	117.0
O1—C1—H1A	109.5	C8—C7—C6	90.88 (16)
O1—C1—H1B	109.5	C8—C7—H7	117.0
O1—C1—H1C	109.5	C8—C7—C11	107.91 (17)
H1A—C1—H1B	109.5	C11—C7—C6	103.36 (17)
H1A—C1—H1C	109.5	C11—C7—H7	117.0
H1B—C1—H1C	109.5	C2—C8—H8	117.0
O1—C2—C3	118.11 (17)	C7—C8—C2	89.57 (16)
O1—C2—C6	121.84 (18)	C7—C8—H8	117.0
O1—C2—C8	111.03 (17)	C9—C8—C2	107.88 (17)
C3—C2—C6	103.41 (17)	C9—C8—C7	104.69 (18)
C3—C2—C8	108.99 (17)	C9—C8—H8	117.0
C6—C2—C8	89.53 (15)	O3—C9—C8	127.7 (2)
O2—C3—C2	127.2 (2)	O3—C9—C10	127.8 (2)
O2—C3—C4	128.1 (2)	C10—C9—C8	104.48 (18)
C4—C3—C2	104.68 (17)	C4—C10—H10	114.1
C3—C4—H4	113.9	C9—C10—C4	107.28 (17)
C3—C4—C5	102.57 (17)	C9—C10—H10	114.1
C3—C4—C10	108.83 (17)	C9—C10—C11	104.33 (18)
C5—C4—H4	113.9	C11—C10—C4	101.91 (17)
C5—C4—C10	102.63 (17)	C11—C10—H10	114.1
C10—C4—H4	113.9	C7—C11—H11	115.2
C4—C5—H5	115.4	C10—C11—C7	101.50 (17)
C4—C5—C6	101.95 (17)	C10—C11—H11	115.2
C6—C5—H5	115.4	C12—C11—C7	103.08 (18)
C12—C5—C4	103.79 (17)	C12—C11—C10	104.82 (18)
C12—C5—H5	115.4	C12—C11—H11	115.2

C12—C5—C6	103.25 (17)	C5—C12—H12A	112.7
C2—C6—H6	117.4	C5—C12—H12B	112.7
C5—C6—C2	107.77 (17)	C11—C12—C5	95.17 (17)
C5—C6—H6	117.4	C11—C12—H12A	112.7
C5—C6—C7	102.77 (17)	C11—C12—H12B	112.7
C7—C6—C2	90.01 (16)	H12A—C12—H12B	110.2
C7—C6—H6	117.4		
O1—C2—C3—O2	10.0 (3)	C5—C4—C10—C11	0.4 (2)
O1—C2—C3—C4	-168.95 (17)	C5—C6—C7—C8	108.30 (17)
O1—C2—C6—C5	141.85 (19)	C5—C6—C7—C11	-0.3 (2)
O1—C2—C6—C7	-114.7 (2)	C6—C2—C3—O2	147.9 (2)
O1—C2—C8—C7	124.27 (18)	C6—C2—C3—C4	-31.0 (2)
O1—C2—C8—C9	-130.43 (18)	C6—C2—C8—C7	0.06 (16)
O2—C3—C4—C5	-134.1 (2)	C6—C2—C8—C9	105.37 (18)
O2—C3—C4—C10	117.7 (2)	C6—C5—C12—C11	-53.4 (2)
O3—C9—C10—C4	-111.3 (2)	C6—C7—C8—C2	-0.06 (16)
O3—C9—C10—C11	141.1 (2)	C6—C7—C8—C9	-108.45 (17)
C1—O1—C2—C3	65.0 (2)	C6—C7—C11—C10	74.92 (19)
C1—O1—C2—C6	-64.9 (2)	C6—C7—C11—C12	-33.4 (2)
C1—O1—C2—C8	-168.08 (17)	C7—C8—C9—O3	-155.1 (2)
C2—C3—C4—C5	44.8 (2)	C7—C8—C9—C10	27.8 (2)
C2—C3—C4—C10	-63.4 (2)	C7—C11—C12—C5	52.89 (19)
C2—C6—C7—C8	0.06 (16)	C8—C2—C3—O2	-117.9 (2)
C2—C6—C7—C11	-108.58 (17)	C8—C2—C3—C4	63.2 (2)
C2—C8—C9—O3	110.5 (2)	C8—C2—C6—C5	-103.48 (18)
C2—C8—C9—C10	-66.6 (2)	C8—C2—C6—C7	-0.06 (16)
C3—C2—C6—C5	5.9 (2)	C8—C7—C11—C10	-20.4 (2)
C3—C2—C6—C7	109.36 (17)	C8—C7—C11—C12	-128.80 (18)
C3—C2—C8—C7	-103.97 (18)	C8—C9—C10—C4	65.8 (2)
C3—C2—C8—C9	1.3 (2)	C8—C9—C10—C11	-41.8 (2)
C3—C4—C5—C6	-39.4 (2)	C9—C10—C11—C7	37.7 (2)
C3—C4—C5—C12	-146.43 (17)	C9—C10—C11—C12	144.74 (18)
C3—C4—C10—C9	-0.7 (2)	C10—C4—C5—C6	73.49 (19)
C3—C4—C10—C11	108.63 (19)	C10—C4—C5—C12	-33.6 (2)
C4—C5—C6—C2	20.5 (2)	C10—C11—C12—C5	-53.0 (2)
C4—C5—C6—C7	-73.64 (19)	C11—C7—C8—C2	104.29 (18)
C4—C5—C12—C11	52.71 (19)	C11—C7—C8—C9	-4.1 (2)
C4—C10—C11—C7	-73.82 (19)	C12—C5—C6—C2	128.00 (18)
C4—C10—C11—C12	33.2 (2)	C12—C5—C6—C7	33.8 (2)
C5—C4—C10—C9	-108.86 (19)		
