organic compounds

anti-Tricyclo[4.2.1.1^{2,5}]deca-3,7-diene-9,10-dione

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The title compound, $C_{10}H_8O_2$, is a precursor to an unusual bis-homoaromatic dication and to heterodiamantanes and other oxa-cage compounds. Two independent molecules, each of which is situated on a center of symmetry, comprise the unit cell. Both molecules are in nearly identical chair conformations.

Related literature

For related structures, see: Eaton *et al.* (2002); Harris *et al.* (2008); Masters *et al.* (1994). For the synthesis and related details, see: Hafner & Goliasch (1961); Weiss *et al.* (1960); Dilthey & Quint (1930); Garbisch & Sprecher (1966); Saito & Ito (2008); Baggiolini *et al.* (1967); Klinsmann *et al.* (1972); Amman *et al.* (1980); Amman & Ganter (1977, 1981); Prakash *et al.* (1987); Harris *et al.* (2008).
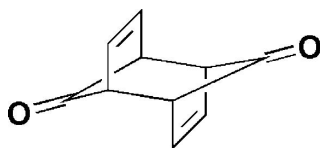
Experimental

Crystal data

$C_{10}H_8O_2$	α = 81.671 (8)°
M_r = 160.16	β = 79.176 (10)°
Triclinic, $P\bar{1}$	γ = 84.745 (8)°
a = 6.4458 (7) Å	V = 370.96 (6) Å^3
b = 6.6120 (6) Å	Z = 2
c = 8.9758 (6) Å	Cu $K\alpha$ radiation

μ = 0.82 mm^{-1}	0.3 × 0.2 × 0.2 mm
T = 295 K	

Data collection

Enraf–Nonius CAD-4 diffractometer	1179 reflections with $I > 2\sigma(I)$
Absorption correction: none	R_{int} = 0.045
2624 measured reflections	3 standard reflections
1329 independent reflections	every 82 reflections
	intensity decay: 1%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037	110 parameters
$wR(F^2)$ = 0.092	H-atom parameters constrained
S = 1.12	$\Delta\rho_{max}$ = 0.2 e Å^{-3}
1329 reflections	$\Delta\rho_{min}$ = −0.15 e Å^{-3}

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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supporting information

anti-Tricyclo[4.2.1.1^{2,5}]deca-3,7-diene-9,10-dione

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S1. Comment

The polycyclic title compound, dione **4**, is formally a dimer of the elusive cyclopentadienone **1**. The latter compound has only a fleeting existence and could be trapped in the form of its Diels-Alder adduct **3** (Hafner & Goliasch, 1961) or stabilized as an iron pentacarbonyl complex (Weiss *et al.*, 1960), although derivatives with bulky substituents have been prepared as stable monomers (Dilthey & Quint, 1930; Garbisch & Sprecher, 1966; Saito & Ito, 2008). The title compound **4** is accessible through photoisomerization of Diels-Alder adduct **3**, a transformation that has been thoroughly studied (Baggiolini *et al.*, 1967; Klinsmann *et al.*, 1972) since dione **4** – *via* diol **5** (Amman *et al.*, 1980; Amman & Ganter, 1977; Amman & Ganter, 1981) - is a valuable precursor to an unusual bishomoaromatic dication (Prakash *et al.*, 1987) and to heterodiamantanes and other oxa-cage compounds (Amman *et al.*, 1980; Amman & Ganter, 1977; Amman & Ganter, 1981). We have recently reported the structure of diol derivative **5** (Harris *et al.*, 2008) and herein report the structure of the parent dione **4**.

Two independent molecules, each of which is situated on a center of symmetry, comprise the unit cell. Both molecules are in nearly identical "chair" conformations, with a maximum deviation between corresponding bond lengths of 0.01 Å. The molecular packing exhibits several short intermolecular contacts, with the shortest being 0.15 Å less than the sum of the van der Waals radii.

Two related structures have been reported. The first (Eaton *et al.*, 2002) has a chlorine atom in place of each hydrogen atom of the title compound, while the second (Masters *et al.*, 1994) lacks the double bonds of the title compound and has methyl groups on each of the four bridgehead carbon atoms.

S2. Experimental

The synthesis of the title compound, **4**, is described in our previous structure report (Harris *et al.*, 2008). Crystals for data collection were obtained from a chloroform solution.

S3. Refinement

H atoms were constrained using a riding model. The olefinic C—H bond lengths were fixed at 0.93 Å and the methine C—H bond lengths at 0.98 Å, with $U_{\text{iso}}(\text{H}) = 1.2\ U_{\text{eq.}}$ (C).
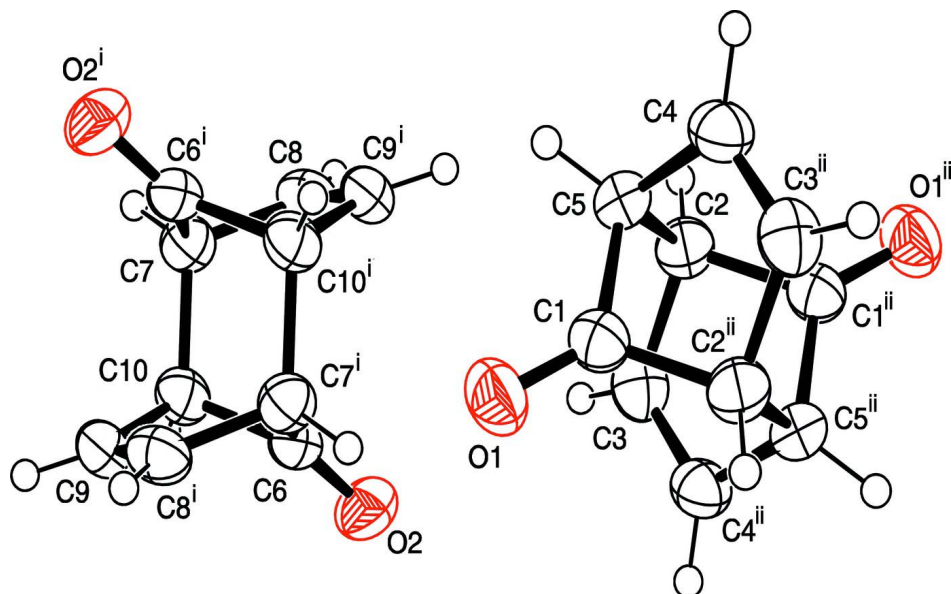
Figure 1

View of the two independent molecules of the title compound, **4**, with 50% probability displacement ellipsoids.

[Symmetry codes: (i) -x, -y + 1, -z + 2; (ii) -x + 1, -y + 2, -z + 1]
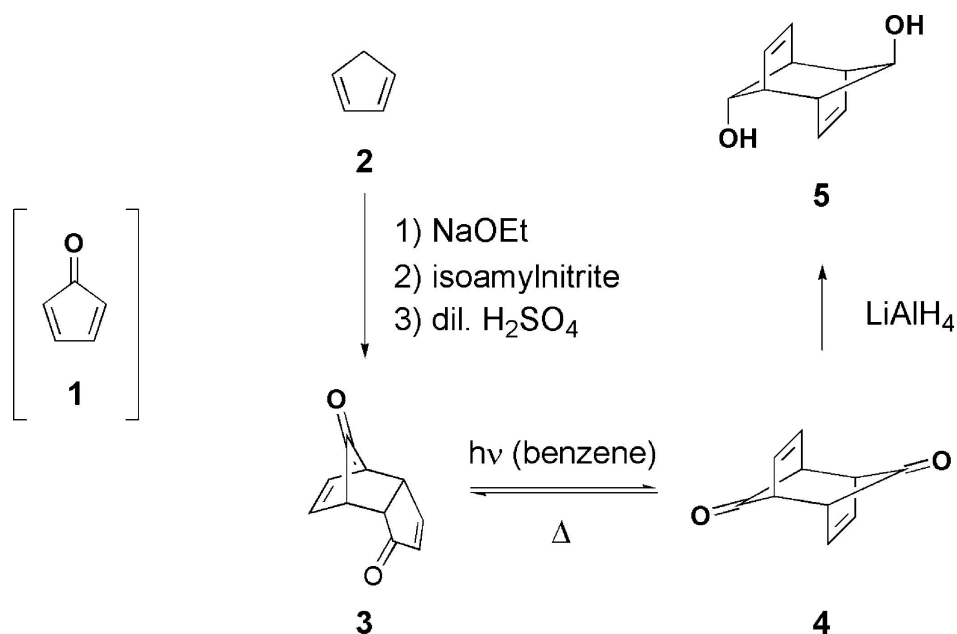
Figure 2

The formation of the title compound.

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Crystal data

$C_{10}H_8O_2$	Hall symbol: -P 1
$M_r = 160.16$	$a = 6.4458$ (7) Å
Triclinic, $P\overline{1}$	$b = 6.6120$ (6) Å

$c = 8.9758$ (6) Å	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$\alpha = 81.671$ (8)°	Cell parameters from 24 reflections
$\beta = 79.176$ (10)°	$\theta = 10.1–44.8°$
$\gamma = 84.745$ (8)°	$\mu = 0.82$ mm^{-1}
$V = 370.96$ (6) Å^3	$T = 295$ K
$Z = 2$	Prism, yellow
$F(000) = 168$	$0.3 \times 0.2 \times 0.2$ mm
$D_x = 1.434$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{max} = 67.4°$, $\theta_{min} = 5.1°$
Non–profiled $\omega/2\theta$ scans	$h = -7\rightarrow7$
2624 measured reflections	$k = -7\rightarrow7$
1329 independent reflections	$l = -10\rightarrow10$
1179 reflections with $I > 2\sigma(I)$	3 standard reflections every 82 reflections
$R_{int} = 0.045$	intensity decay: 1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0242P)^2 + 0.0776P]$
Least-squares matrix: full	where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.092$	$\Delta\rho_{max} = 0.2$ e Å^{-3}
$S = 1.12$	$\Delta\rho_{min} = -0.15$ e Å^{-3}
1329 reflections	Extinction correction: *SHELXL97* (Sheldrick,
110 parameters	2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
0 restraints	Extinction coefficient: 0.115 (5)
H-atom parameters constrained	

Special details

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

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

	x	y	z	$U_{iso}*/U_{eq}$
O1	0.30420 (16)	0.67650 (15)	0.48107 (14)	0.0495 (3)
O2	−0.21014 (18)	0.85668 (16)	0.94715 (16)	0.0593 (4)
C5	0.5818 (2)	0.8181 (2)	0.58171 (17)	0.0369 (4)
H5	0.5912	0.6967	0.6575	0.044*
C10	−0.2032 (2)	0.5136 (2)	1.09484 (17)	0.0392 (4)
H10	−0.3204	0.556	1.173	0.047*
C8	0.1509 (2)	0.6126 (2)	1.13965 (18)	0.0438 (4)
H8	0.1613	0.6898	1.2164	0.053*
C7	0.0067 (2)	0.4394 (2)	1.15786 (17)	0.0409 (4)
H7	−0.0169	0.3633	1.2611	0.049*
C3	0.2728 (2)	1.0665 (2)	0.67086 (18)	0.0423 (4)
H3	0.1766	1.0349	0.7606	0.051*
C2	0.5100 (2)	1.0222 (2)	0.65388 (17)	0.0381 (4)
H2	0.566	1.0299	0.747	0.046*
C9	−0.2602 (2)	0.3614 (2)	1.00162 (19)	0.0427 (4)

H9	−0.3583	0.2631	1.0381	0.051*
C1	0.4297 (2)	0.8034 (2)	0.47378 (17)	0.0362 (4)
C6	−0.1443 (2)	0.6803 (2)	0.96120 (18)	0.0395 (4)
C4	0.7783 (2)	0.8433 (2)	0.46039 (19)	0.0420 (4)
H4	0.9153	0.8016	0.4756	0.05*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0444 (6)	0.0450 (6)	0.0619 (8)	−0.0112 (5)	−0.0102 (5)	−0.0107 (5)
O2	0.0608 (7)	0.0390 (6)	0.0810 (9)	0.0080 (5)	−0.0283 (6)	−0.0043 (6)
C5	0.0368 (7)	0.0364 (7)	0.0373 (8)	0.0005 (5)	−0.0110 (6)	−0.0003 (6)
C10	0.0323 (6)	0.0466 (8)	0.0378 (8)	−0.0031 (6)	−0.0034 (5)	−0.0066 (6)
C8	0.0398 (7)	0.0495 (8)	0.0480 (9)	0.0004 (6)	−0.0172 (7)	−0.0161 (7)
C7	0.0418 (7)	0.0494 (8)	0.0317 (7)	−0.0050 (6)	−0.0099 (6)	0.0005 (6)
C3	0.0413 (7)	0.0427 (8)	0.0405 (8)	−0.0024 (6)	0.0024 (6)	−0.0102 (6)
C2	0.0421 (7)	0.0429 (8)	0.0312 (7)	−0.0024 (6)	−0.0106 (6)	−0.0060 (6)
C9	0.0335 (7)	0.0417 (8)	0.0554 (10)	−0.0060 (6)	−0.0128 (6)	−0.0057 (7)
C1	0.0331 (6)	0.0369 (7)	0.0395 (8)	0.0010 (5)	−0.0063 (6)	−0.0102 (6)
C6	0.0351 (7)	0.0397 (8)	0.0468 (9)	−0.0015 (6)	−0.0169 (6)	−0.0041 (6)
C4	0.0317 (7)	0.0420 (8)	0.0523 (9)	0.0026 (6)	−0.0083 (6)	−0.0086 (7)

Geometric parameters (Å, º)

O1—C1	1.2049 (16)	C8—H8	0.93
O2—C6	1.2012 (17)	C7—C6^i	1.522 (2)
C5—C4	1.5116 (19)	C7—H7	0.98
C5—C1	1.5202 (19)	C3—C4^{ii}	1.326 (2)
C5—C2	1.575 (2)	C3—C2	1.5129 (19)
C5—H5	0.98	C3—H3	0.93
C10—C9	1.509 (2)	C2—H2	0.98
C10—C6	1.5232 (19)	C9—H9	0.93
C10—C7	1.5741 (19)	C1—C2^{ii}	1.5248 (18)
C10—H10	0.98	C6—C7^i	1.522 (2)
C8—C9^i	1.326 (2)	C4—H4	0.93
C8—C7	1.512 (2)		
C4—C5—C1	96.67 (11)	C4^{ii}—C3—C2	110.37 (12)
C4—C5—C2	111.33 (11)	C4^{ii}—C3—H3	124.8
C1—C5—C2	105.88 (10)	C2—C3—H3	124.8
C4—C5—H5	113.8	C3—C2—C1^{ii}	96.61 (10)
C1—C5—H5	113.8	C3—C2—C5	111.11 (11)
C2—C5—H5	113.8	C1^{ii}—C2—C5	106.04 (11)
C9—C10—C6	96.32 (12)	C3—C2—H2	113.9
C9—C10—C7	111.22 (12)	C1^{ii}—C2—H2	113.9
C6—C10—C7	106.35 (11)	C5—C2—H2	113.9
C9—C10—H10	113.8	C8^i—C9—C10	110.46 (13)
C6—C10—H10	113.8	C8^i—C9—H9	124.8

C7—C10—H10	113.8	C10—C9—H9	124.8
C9^{i}—C8—C7	110.14 (14)	O1—C1—C5	128.74 (13)
C9^{i}—C8—H8	124.9	O1—C1—C2^{ii}	128.48 (14)
C7—C8—H8	124.9	C5—C1—C2^{ii}	102.57 (11)
C8—C7—C6^{i}	96.36 (11)	O2—C6—C7^{i}	128.63 (14)
C8—C7—C10	111.33 (11)	O2—C6—C10	128.41 (15)
C6^{i}—C7—C10	106.49 (12)	C7^{i}—C6—C10	102.44 (11)
C8—C7—H7	113.7	C3^{ii}—C4—C5	110.25 (12)
C6^{i}—C7—H7	113.7	C3^{ii}—C4—H4	124.9
C10—C7—H7	113.7	C5—C4—H4	124.9

Symmetry codes: (i) −*x*, −*y*+1, −*z*+2; (ii) −*x*+1, −*y*+2, −*z*+1.