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2,2′-Methylenebis(3-hydroxy-2-cyclohexen-1-one)

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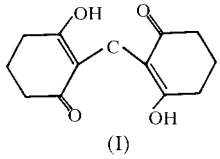
In the title compound, $C_{13}H_{16}O_4$, the cyclohexene rings adopt a sofa conformation. Adjacent molecules are connected by C—H···O intermolecular interactions. Each molecule is characterized by O—H···O intramolecular hydrogen bonds. The *anti* arrangement of the enolic OH group and the carbonyl O atom in the solid state is similar to the *anti* arrangement of the NH and carbonyl groups in indigo.

Comment

The bond lengths and angles of the two cyclohexene rings in the title compound, (I), conform to expectations (Peter *et al.*, 1992; Lalancette *et al.*, 1997; Govindasamy & Subramanian, 1997).



(I)

Rings 1 (C1–C6) and 2 (C1′–C6′) have a sofa conformation. The asymmetry parameters [ΔC_s(C1) = 0.026 (1) and ΔC_s(C1′) = 0.017 (1); Nardelli, 1995] satisfy the condition for the sofa conformation. The values of the total puckering amplitudes [Q_T = 0.476 (2) and 0.477 (3) Å for rings 1 and 2, respectively; Cremer & Pople, 1975] indicate that the two rings have the same conformation. Atoms O2 and O4 deviate from ring 2 by 0.134 (2) and 0.062 (2) Å, respectively. Atoms O1 and O3 deviate from ring 1 by 0.097 (2) and 0.066 (2) Å, respectively. Atom C7 deviates from rings 1 and 2 by −0.460 (2) and −0.394 (2) Å, respectively. The deviations of atoms C4 and C4′ are −0.295 (2) and −0.364 (3) Å with respect to rings 1 and 2.

The two cyclohexene rings are attracted towards each other by O—H···O intramolecular hydrogen bonds. Atoms O2 and O3 act as donors, whereas O4 and O1 act as acceptors. The O···O distance agrees well with earlier reported values (Li *et al.*, 1999; Steiner, 1997; Paixao *et al.*, 1999; Komen *et al.*, 1999; Parvez *et al.*, 1999). The average O···O distance observed in the present structure is 2.615 Å. The sequences of the bond distances along the O1—C2—C1—C6—O3 and O4—C6′—C1′—C2′—O2 systems are indicative of some π conjugation, enhancing the polarization of charge that produces the two O—H···O hydrogen bonds. These are rather strong, as indicated by the short values (1.78 and 1.84 Å) of the H···O distances. The C1—C7—C1′ angle is 117.0 (2)°. The conformation of the two halves of the molecule is determined by the two O—H···O hydrogen bonds.

The packing is stabilized by intermolecular C—H···O interactions. Atoms C5 and C5′ act as donors to form intermolecular interactions with the symmetry-related atoms O1 and O2.

Experimental

The title compound was prepared by the addition of a 40% aqueous solution of formalin (6 ml) to a solution of cyclohexane-1,3-dione (15 g, 0.13 mol) in water (200 ml) and warming until the solution became cloudy. The 2,2′-methylenebis(cyclohexane-1,3-dione) started to separate out. The reaction mixture was allowed to stand overnight and the ketone was collected by filtration and dried. Yield 8.0 g (50.6%), m.p. 403–405 K (Setter, 1995).

Crystal data

$C_{13}H_{16}O_4$
M_r = 236.26
Orthorhombic, *Pbca*
a = 9.9313 (18) Å
b = 10.3818 (14) Å
c = 23.253 (2) Å
V = 2397.5 (6) Å^3
Z = 8
D_x = 1.309 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 15 reflections
θ = 2–28°
μ = 0.799 mm^{-1}
T = 293 (2) K
Rectangular, yellow
0.20 × 0.15 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
2264 measured reflections
2264 independent reflections
1829 reflections with $I > 2\sigma(I)$
θ_{max} = 69.83°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 28$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.176
S = 1.311
2264 reflections
157 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.14 e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0075 (10)

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.271 (2)	O3—C6	1.307 (2)
O2—C2′	1.304 (3)	O4—C6′	1.256 (2)
O4—C6′—C1′	122.41 (19)	O1—C2—C1	121.52 (18)
O4—C6′—C5′	117.72 (19)	O1—C2—C3	117.49 (18)
O3—C6—C1	123.34 (18)	O2—C2′—C1′	123.59 (19)
O3—C6—C5	114.17 (17)	O2—C2′—C3′	114.12 (19)

C2′—C1′—C6′—O4	−170.41 (18)	C7—C1′—C2′—O2	−7.4 (3)
C7—C1′—C6′—O4	7.8 (3)	O1—C2—C3—C4	−156.59 (18)
C2—C1—C6—O3	169.67 (17)	C1—C2—C3—C4	25.9 (3)
C7—C1—C6—O3	−8.6 (3)	O3—C6—C5—C4	161.36 (17)
C6—C1—C2—O1	−171.40 (17)	O4—C6′—C5′—C4′	−157.6 (2)
C7—C1—C2—O1	6.9 (3)	O2—C2′—C3′—C4′	159.6 (2)
C6′—C1′—C2′—O2	170.75 (18)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3*B*···O1^{i}	0.97	2.57	3.522 (3)	168
C5—H5*A*···O1^{ii}	0.97	2.56	3.371 (3)	141
C5′—H5′1···O2^{iii}	0.97	2.65	3.525 (3)	150
C5′—H5′2···O2^{iv}	0.97	2.71	3.477 (3)	136
O2—H2···O1	0.82	1.78	2.581 (2)	165
O3—H3···O4	0.82	1.84	2.649 (2)	171

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $x-\frac{1}{2}, \frac{1}{2}-y, -z$; (iii) $\frac{1}{2}-x, y-\frac{1}{2}, z$; (iv) $-x, y-\frac{1}{2}, \frac{1}{2}-z$.

The H atoms are fixed geometrically and allowed to refine riding on the corresponding non-H atoms (O—H = 0.82 Å and C—H = 0.97 Å).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *SDP* (Frenz, 1978); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1995).

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