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(*Z*)-3,6-Diethynyl-3,6-dihydroxycyclohexa-1,4-diene

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In the title compound, $C_{10}H_8O_2$, the four symmetry-related molecules are connected to each other through O—H···O hydrogen bonds to form a helical chain along the *b* axis. The interconnected system is further extended along the *c* axis through O—H···O hydrogen bonds to form a two-dimensional network. Unlike its *trans* isomer, no C—H···O or C—H···π interactions are observed in the crystal structure.

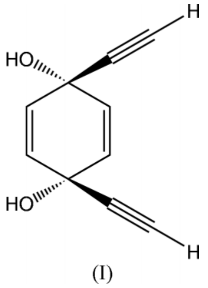
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.059
wR factor = 0.154
Data-to-parameter ratio = 12.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound, (I), which is a *cis* isomer, is a building block for acetylenic macrocycles. In the crystal structure of the *trans* isomer, (II), the molecule has a center of inversion with half the molecule forming the asymmetric unit and the cyclohexadiene ring ideally planar (Madhavi *et al.*, 2000). In (I), the cyclohexadiene ring is not planar (Fig. 1 and Table 1); it assumes a flattened boat conformation, with atoms C2 and C5 0.146 (5) and 0.079 (5) Å, respectively, out the plane defined by atoms C1/C6/C3/C4.



(I)

The packing of molecules shows interesting intermolecular hydrogen-bonding patterns (Fig. 2 and Table 2). The hydrogen bond O1—H1′···O2(x, $\frac{1}{2} - y$, $z - \frac{1}{2}$) is between glide-related molecules and O2—H2′···O1($1 - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$) is between molecules related by a 2_1 screw axis. These pairs with their inversion-related counterparts form hydrogen-bonded helical chains along the *b* axis. These chains are further linked *via* hydrogen bonds, forming a two-dimensional network parallel to (100). In (II), intermolecular C—H···O and C—H···π interactions were observed. However, the structure of (I) does not show any C—H···O or C—H···π interactions. Crystals of (I) cleave easily about the (100) plane, which may result from the lack of hydrogen bonding along the *a* axis.

Experimental

Although the synthesis of the diol has been reported in 30–45% yield (Ried & Schmidt, 1957), we adopted a two-step strategy reported by Srinivasan *et al.* (2003) with 85–90% overall yield starting from *p*-benzoquinone. Addition of two equivalents of lithium trimethylsilyl acetylide in dry tetrahydrofuran to *p*-benzoquinone at 195 K and subsequent warming of the reaction mixture to room temperature furnished the diol as a mixture of *Z* and *E* isomers in the ratio 1:2. The isomers were separated by column chromatography. Deprotection of the TMS groups proceeded smoothly when the *Z*-diol was treated with K_2CO_3 in degassed MeOH to give a pale-yellow solid, which was washed 3–4 times with $CHCl_3$. The residue was dissolved in EtOAc and a few drops of hexane were added until the solution became turbid. Slow evaporation of this solution in an NMR tube yielded colourless crystals of (I).

Crystal data

$C_{10}H_8O_2$
$M_r = 160.16$
Monoclinic, $P2_1/c$
$a = 10.598$ (2) Å
$b = 6.2646$ (10) Å
$c = 14.153$ (3) Å
$\beta = 102.06$ (2)°
$V = 918.9$ (3) Å^3
$Z = 4$

$D_x = 1.158$ Mg m$^{-3$}
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 10$–15°
$\mu = 0.08$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.3 × 0.2 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.941$, $T_{\max} = 0.989$
1712 measured reflections
1617 independent reflections
730 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.048$
$\theta_{\max} = 25.0$°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 7$
$l = -16 \rightarrow 16$
2 standard reflections frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.154$
$S = 1.00$
1617 reflections
127 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0602P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}

Table 1
Selected torsion angles (°).

C6—C1—C2—C3	11.4 (5)	C3—C4—C5—C6	5.9 (5)
C1—C2—C3—C4	−12.7 (5)	C2—C1—C6—C5	−1.8 (6)
C2—C3—C4—C5	4.4 (6)	C4—C5—C6—C1	−7.2 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1′···O2^{i}	0.82	1.93	2.708 (3)	159
O2—H2′···O1^{ii}	0.82	1.93	2.699 (4)	157

Symmetry codes: (i) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (ii) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$.

All the H atoms were located in difference Fourier maps. The acetylenic C—H (0.93 Å) and hydroxy O—H (0.82 Å) distances were idealized and refined using a riding model, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$ or $1.5U_{\rm eq}({\rm O})$. Since the six-membered ring is not planar, appropriate constraints are not obvious, and the four ring H atoms were refined isotropically, with a C—H distance restraint of 0.96 (1) Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 Software; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97 and *WinGX* (Farrugia, 1999).

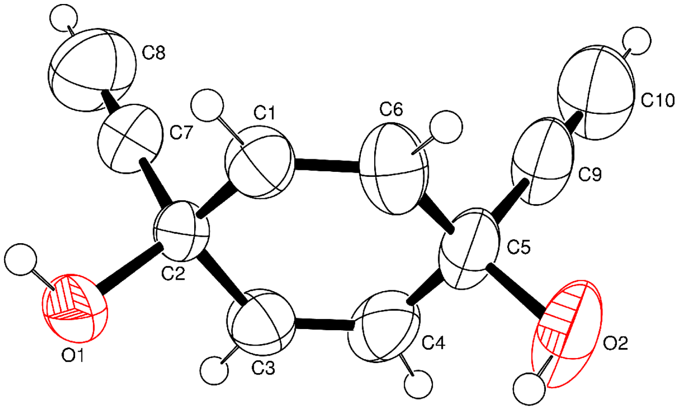


Figure 1
The molecular structure of (I), showing the atomic numbering scheme and 50% probability displacement ellipsoids.

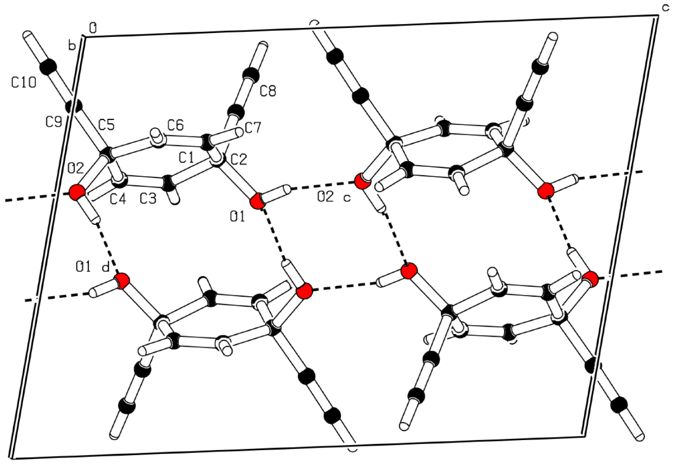


Figure 2
The crystal structure of (I), projected down the *b* axis. Dashed lines indicate hydrogen bonds. [Symmetry codes: (*c*) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (d) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$.]

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