organic compounds

C≡C—H systems as hydrogen-bond donors and acceptors: *trans*-1,2-diethynylcyclohexane-1,2-diol and *trans*-1,4-diprop-2-ynylcyclohexane-1,4-diol monohydrate

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The title 1,2-diol derivative, $C_{10}H_{12}O_2$, crystallizes with two independent but closely similar molecules in the asymmetric unit. Only two of the four OH groups are involved in classical hydrogen bonding; the molecules thereby associate to form chains parallel to the short *c* axis. The other two OH groups are involved in O—H···(C≡C) systems. Additionally, three of the four C≡C—H groups act as donors in C—H···O interactions. The 1,4-diol derivative crystallizes with two independent half-molecules of the diol (each associated with an inversion centre) and one water molecule in the asymmetric unit, $C_{12}H_{16}O_2$·H_2O. Both OH groups and one water H atom act as classical hydrogen-bond donors, leading to layers parallel to the *ac* plane. The second water H atom is involved in a three-centre contact to two C≡C bonds. One acetylenic H atom makes a very short 'weak' hydrogen bond to a hydroxy O atom, and the other is part of a three-centre system in which the acceptors are a hydroxy O atom and a C≡C bond.

Comment

The title compounds, *trans*-1,2-diethynylcyclohexane-1,2-diol, (II), and *trans*-1,4-diprop-2-ynylcyclohexane-1,4-diol monohydrate, (IV), are related *trans*-cyclohexanediols that we have used as synthetic intermediates. Compound (II) is a long-known (Ried & Schmidt, 1957) bis-propargylic diol which we used in our studies (Eshdat *et al.*, 2002) of novel cross-conjugated enynes. Similarly, compound (IV) is a known (Cognacq *et al.*, 1967) compound that we used in our studies of semicyclic olefins and allenes (Hopf *et al.*, 2002). The structures of both compounds were confirmed by X-ray crystal structure determination and proved to display a variety of

secondary contacts, not only the expected classical hydrogen bonds but also interactions involving the C≡C—H moieties.

Compound (II) crystallizes with two independent molecules in the asymmetric unit, which are closely similar (a least-squares fit of all non-H atoms gives an r.m.s. deviation of
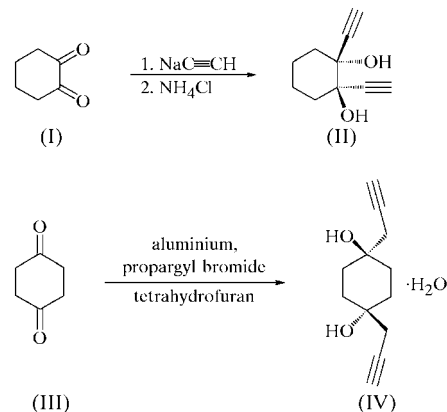
0.044 Å). The hydroxy groups occupy the equatorial and the ethynyl groups the axial positions of the cyclohexyl rings (Fig. 1). Primes indicate atoms of the second molecule, which is inverted with respect to the first in the coordinates chosen for the asymmetric unit [to give a hydrogen bond (see below) between both independent molecules without transformation]. The one major difference lies in the configuration of the OH groups, whereby C1′—C2′—O2′—H02′ is a *trans*-periplanar group [the O—H bond is parallel to the C1′—C2′ ring bond; torsion angle −177 (2)°] and all other analogous groups are *gauche*; the corresponding torsion angles (all involving the ring bonds C1—C2 or C1′—C2′) involving atoms H01, H01′ and H02 are 72 (2), −77 (2) and 76 (2)°, respectively. The molecular dimensions may be regarded as normal. The rings display the usual chair form [absolute torsion angles 54.4 (2)–57.8 (2)°].

The molecular packing of (II) is puzzling at first sight. The molecules associate *via* two classical hydrogen bonds (Table 2)
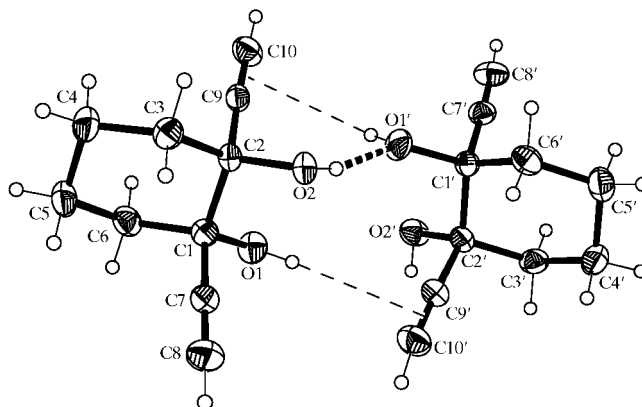

Figure 1
The two independent molecules of compound (II) in the crystal. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Heavy dashed lines indicate classical hydrogen bonds within the asymmetric unit, and thin dashed lines indicate 'weak' O—H···(C≡C) interactions (see *Comment*).

involving O2—H02 and O2′—H02′ as donors, to form chains of graph set $C_2^2(7)$ (Etter, 1990) parallel to the short c axis (Fig. 2; neighbouring chains define layers parallel to the ac plane). However, O1—H01 and O1′—H01′ do not take part in such interactions. Closer inspection shows that these OH groups form 'weak' intermolecular hydrogen bonds (Desiraju & Steiner, 1999) to the alkyne triple bonds, with both interactions being within the asymmetric unit: O1—H01···mid-point(C9′≡C10′), with H···acceptor = 2.60 Å and angle = 162°; O1′—H01′···mid-point(C9≡C10), with H···acceptor = 2.71 Å and angle = 111°. The latter interaction is admittedly a borderline case in view of its narrow angle.

Acetylenic H atoms represent a fairly acidic form of CH group and can also act as hydrogen-bond donors (Desiraju & Steiner, 1999); as a concrete example, we have drawn attention to C≡C—H···Cl—Au interactions (Bardají *et al.*, 2002). In the current structure, three of the four C≡C—H groups act in this way (Table 2) to connect the classical hydrogen-bonded layers in the third dimension parallel to the long b axis (Fig. 3).

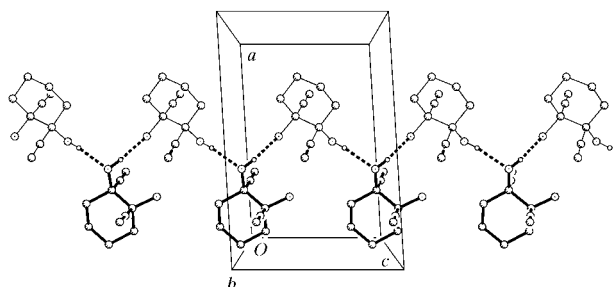All four O atoms are thus topologically different as regards their hydrogen-bonding behaviour, which may be summarized as follows (D = donor, A = acceptor, C = classical and W = 'weak'): O1 WD,WA; O2 CD,CA,WA; O3 CA,WD; O4 CD,WA. One might speculate that the 'extra' interaction for atom O2 is connected with its different C—C—O—H torsion angle (see above).

Compound (IV) also crystallizes with two symmetry-independent molecules, which, however, display inversion symmetry [molecule 1 about $(1, \frac{1}{2}, 1)$ and molecule 2 about $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$] (Fig. 4). A least-squares fit of the ring atoms of the asymmetric unit gives an r.m.s. deviation of 0.07 Å. As in (II), the OH groups of the two molecules are oriented differently; in molecule 2, the C2′—C1′—O1′—H01′ torsion angle is 42 (1)° and the OH group is very approximately parallel to the propargyl group (see Fig. 4, bottom left), whereas in molecule 1 the corresponding angle is 171 (1)° and the corresponding groups point in widely disparate directions. The asymmetric unit also contains a molecule of water, which was presumably absorbed from the atmosphere during the slow crystallization of the oily product. In contrast with (II), the hydroxy groups are axial and the propynyl groups equatorial.

The contribution of classical hydrogen bonds to the packing of (IV) is shown in Fig. 5. Both independent OH groups and one water H atom, H03, act as hydrogen-bond donors (Table 4; for a discussion of atom H04, see below) and the overall effect is to form a layer structure parallel to the ac plane. The two independent rings thus formed are both of graph set $R_6^6(22)$.

The second water H atom, H04, appears at first sight to make no significant contacts at all. However, it projects away from the layer shown in Fig. 5 and makes contacts of 3.03 and 3.04 Å (angles at H04: 114 and 157°, respectively) to the mid-points of the triple bonds C5≡C6 and C5′≡C6′ in the neighbouring layer at $(x, 1 + y, z)$ (Fig. 6a). For a three-centre contact, these very long distances may still indicate a significant interaction.

Figure 2
A packing diagram for compound (II), viewed parallel to the b axis, showing the classical hydrogen bonds forming chains of molecules parallel to the c axis in the region $b \simeq \frac{1}{8}$. Bonds of the second independent molecule are thinner. H atoms other than those of hydroxy groups have been omitted.
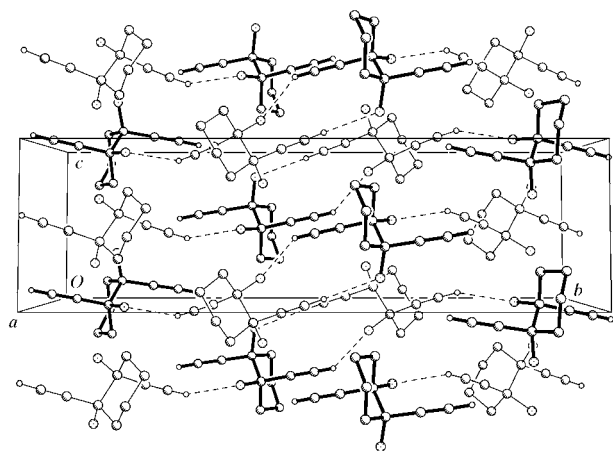

Figure 3
A packing diagram for compound (II), viewed parallel to the a axis, showing the 'weak' hydrogen bonds (dashed lines) between the molecular chains. Bonds of the second independent molecule are thinner.
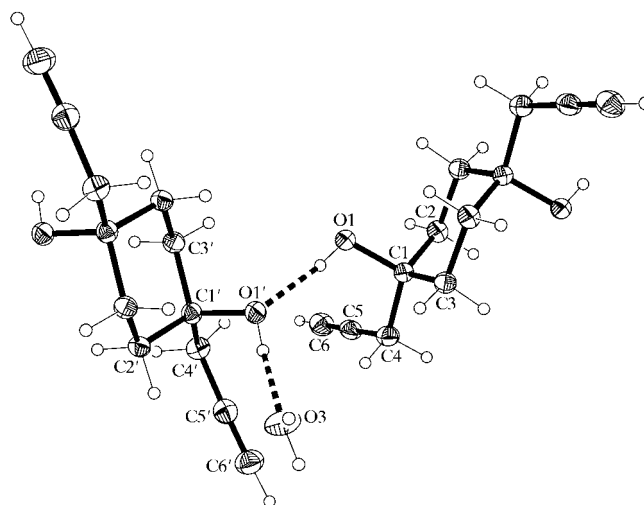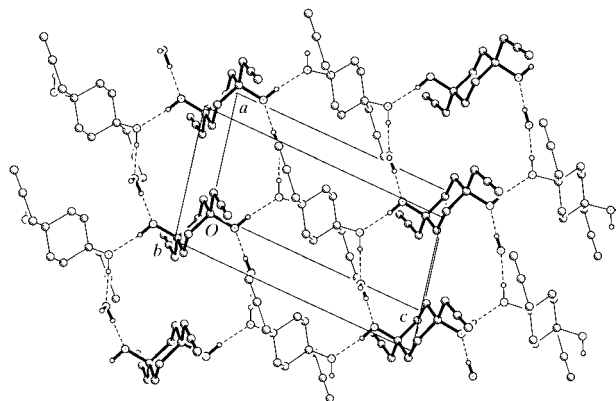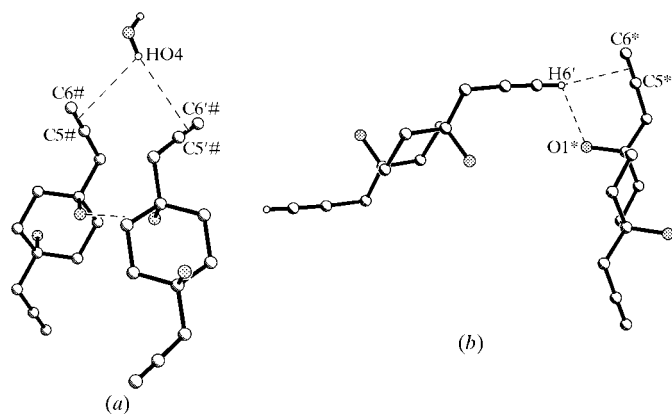

Figure 4
The structure of compound (IV) in the crystal. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Only the asymmetric unit is numbered. Heavy dashed lines represent classical hydrogen bonds within the asymmetric unit.

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Figure 5
A packing diagram of compound (IV). Classical hydrogen bonds are indicated by thin dashed lines. Bonds of the second independent molecule are thinner. H atoms other than those of hydroxy groups and water have been omitted.

Figure 6
The packing of compound (IV), showing (*a*) the environment of water atom H04 and (*b*) the environment of acetylenic atom H6′; for details see *Comment*. [Symmetry codes: (#) $x, 1 + y, z$; (*) $-1 + x, y, z$.]

The acetylenic H atom, H6, of (IV) makes a short (2.37 Å) 'weak' hydrogen bond with atom O1′ in the neighbouring layer at $(x, -1 + y, z)$. The corresponding contact from atom H6′ to atom O1 is, however, very long and bent (Table 4); again, the explanation may be sought in a three-centre interaction, the other branch of which is a C—H···π interaction to the mid-point of C5≡C6 (2.74 Å and 166°). The symmetry code is $(-1 + x, y, z)$ for both branches, so that the system forms part of the layer structure, but this is not easy to recognize in Fig. 5; it is depicted for clarity in Fig. 6(*b*).

Experimental

The diol (II) was prepared from cyclohexane-1,2-dione (I) by reaction with sodium acetylide, as described by Ried & Schmidt (1957). The spectroscopic data (Hamann, 1992) were consistent with literature values. Single crystals were obtained from benzene–petroleum ether. Diol (IV) was prepared from cyclohexane-1,4-dione (III) and propargyl bromide, as described by Cognacq *et al.* (1967). It formed an oil that crystallized slowly. Analytical and spectroscopic data agree with those of the original report.

Diol (II)

Crystal data

$C_{10}H_{12}O_2$	$D_x = 1.235$ Mg m^{-3}
$M_r = 164.20$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 46
$a = 10.563$ (3) Å	reflections
$b = 23.839$ (6) Å	$\theta = 8.5$–11.5°
$c = 7.025$ (2) Å	$\mu = 0.09$ mm^{-1}
$\beta = 93.46$ (2)°	$T = 153$ (2) K
$V = 1765.8$ (8) Å^3	Prism, colourless
$Z = 8$	$0.45 \times 0.40 \times 0.40$ mm

Data collection

Stoe Stadi-4 diffractometer	$h = -12 \rightarrow 11$
ω/θ scans	$k = -28 \rightarrow 9$
4400 measured reflections	$l = -8 \rightarrow 8$
3131 independent reflections	3 standard reflections
2380 reflections with $I > 2\sigma(I)$	frequency: 60 min
$R_{int} = 0.028$	intensity decay: none
$\theta_{max} = 25.0°$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0332P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$+ 0.7551P]$
$wR(F^2) = 0.103$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} < 0.001$
3131 reflections	$\Delta\rho_{max} = 0.18$ e Å^{-3}
250 parameters	$\Delta\rho_{min} = -0.18$ e Å^{-3}
H atoms treated by a mixture of	Extinction correction: *SHELXL97*
independent and constrained	(Sheldrick, 1997)
refinement	Extinction coefficient: 0.0080 (10)

Table 1
Selected geometric parameters (Å, °) for (II).

C1—O1	1.430 (2)	C1′—O1′	1.438 (2)
C2—O2	1.439 (2)	C2′—O2′	1.422 (2)
C7—C8	1.178 (3)	C7′—C8′	1.171 (3)
C9—C10	1.183 (3)	C9′—C10′	1.179 (3)
C8—C7—C1	179.5 (2)	C8′—C7′—C1′	177.8 (2)
C10—C9—C2	176.1 (2)	C10′—C9′—C2′	176.7 (2)

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H02···O1′	0.828 (19)	1.976 (19)	2.787 (2)	166 (3)
O2′—H02′···O2^i	0.832 (19)	2.02 (2)	2.837 (2)	165 (3)
C10—H10···O2′^{ii}	0.950 (18)	2.66 (2)	3.495 (3)	147 (2)
C8′—H8′···O1^{ii}	0.940 (17)	2.529 (19)	3.411 (3)	156 (2)
C10′—H10′···O2^{iii}	0.944 (18)	2.46 (2)	3.272 (3)	144 (2)

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

Diol (IV)

Crystal data

$C_{12}H_{16}O_2 \cdot H_2O$	$Z = 2$
$M_r = 210.26$	$D_x = 1.222$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.6112$ (18) Å	Cell parameters from 56
$b = 7.2474$ (19) Å	reflections
$c = 12.577$ (3) Å	$\theta = 10$–11.5°
$\alpha = 93.384$ (16)°	$\mu = 0.09$ mm^{-1}
$\beta = 102.410$ (16)°	$T = 153$ (2) K
$\gamma = 102.309$ (16)°	Prism, yellow
$V = 571.5$ (3) Å^3	$0.70 \times 0.60 \times 0.25$ mm

Data collection

Stoe Stadi-4 diffractometer	$h = -7 \rightarrow 7$
ω/θ scans	$k = -8 \rightarrow 8$
2374 measured reflections	$l = -13 \rightarrow 14$
2022 independent reflections	3 standard reflections
1849 reflections with $I > 2\sigma(I)$	frequency: 60 min
$R_{int} = 0.021$	intensity decay: none
$\theta_{max} = 25.0°$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0362P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.034$	$+ 0.2046P]$
$wR(F^2) = 0.084$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} < 0.001$
2022 reflections	$\Delta\rho_{max} = 0.20$ e Å^{-3}
160 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 3
Selected geometric parameters (Å, °) for (IV).

O1—C1	1.4381 (15)	O1′—C1′	1.4437 (15)
C5—C6	1.182 (2)	C5′—C6′	1.182 (2)
C6—C5—C4	178.75 (14)	C6′—C5′—C4′	176.68 (15)

Table 4
Hydrogen-bond geometry (Å, °) for (IV).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H01···O1′	0.871 (15)	1.882 (15)	2.7470 (14)	172.2 (17)
O1′—H01′···O3	0.867 (15)	1.895 (15)	2.7399 (15)	164.4 (17)
O3—H03···O1^i	0.884 (16)	1.899 (16)	2.7795 (15)	174 (2)
C6—H6···O1′^{ii}	0.939 (16)	2.370 (17)	3.2516 (19)	156.3 (15)
C6′—H6′···O1^i	0.932 (16)	2.825 (18)	3.4004 (19)	121.0 (14)

Symmetry codes: (i) $x - 1, y, z$; (ii) $x, y - 1, z$.

Methylene H atoms were included in calculated positions and refined using a riding model, with fixed C—H bond lengths of 0.99 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$. Other H atoms were located in difference syntheses and refined freely, but with C—H (acetylenic) and O—H bond distances each restrained to be equal within a notional s.u. of 0.02 Å.

For both compounds, data collection: *DIF4* (Stoe & Cie, 1992); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1992); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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