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4-Ethynyl-4-hydroxycyclohexan-1-one and 4-ethynyl-4-hydroxy-2,3,5,6-tetramethylcyclohexa-2,5-dien-1-one

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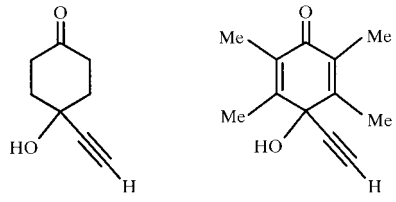
The title compounds, $C_8H_{10}O_2$, (I), and $C_{12}H_{14}O_2$, (II), occurred as by-products in the controlled synthesis of a series of bis(*gem*-alkynols), prepared as part of an extensive study of synthon formation in simple *gem*-alkynol derivatives. The two 4-(*gem*-alkynol)-1-ones crystallize in space group $P2_1/c$, (I) with $Z' = 1$ and (II) with $Z' = 2$. Both structures are dominated by O—H···O═C hydrogen bonds, which form simple chains in the cyclohexane derivative, (I), and centrosymmetric dimers, of both symmetry-independent molecules, in the cyclohexa-2,5-diene, (II). These strong synthons are further stabilized by C≡C—H···O═C, $C_{methylene}$—H···O(H) and C_{methyl}—H···O(H) interactions. The direct intermolecular interactions between donors and acceptors in the *gem*-alkynol group, which characterize the bis(*gem*-alkynol) analogues of (I) and (II), are not present in the ketone derivatives studied here.

Comment

The structures of the title compounds, (I) and (II), have been determined as part of a detailed study of the intermolecular interaction patterns, or synthons (Desiraju, 1995), formed by a series of *gem*-alkynols in which additional substitution has been carefully controlled by novel syntheses. The aim has been to establish the synthons formed by the *gem*-alkynol group alone attached to hydrocarbon skeletons (Bilton *et al.*, 1999; Madhavi, Bilton *et al.*, 2000) and to see how the resulting patterns, arising from a delicate balance between strong and weak interactions, are either maintained or altered by controlled substitution of these skeletons by other functional groups, particularly halogens (Madhavi, Desiraju *et al.*, 2000) and substituted phenyl rings (Bilton *et al.*, 2000). The overall goal has been to determine the robustness of the various synthons formed so as to develop their use in crystal engineering applications. We have been able to study the effects of interaction interference caused by the additional weaker interactions possible in the substituted compounds, and to identify cases of synthon repetitivity and topological similarity within the series.



Compounds (I) and (II) were isolated as by-products in the syntheses of 1,4-diethynylcyclohexane-1,4-diol [(III); Bilton *et al.*, 1999] and 1,4-diethynylcyclohexa-2,5-diene-1,4-diol [(IV); Madhavi, Bilton *et al.*, 2000], respectively. The compounds are clearly similar at the molecular level and it is of interest to see if this molecular similarity is reflected in similarities in their crystal structures, and also how these crystal structures relate to those of the respective bis(*gem*-alkynol) analogues, (III) and (IV), *i.e.* how these structures will react to replacement of one *gem*-alkynol group by the strong keto-O acceptor.

In compound (I) (Fig. 1; $P2_1/c$, $Z = 4$), molecules related by translation along **c** form chains *via* strong O—H···O═C

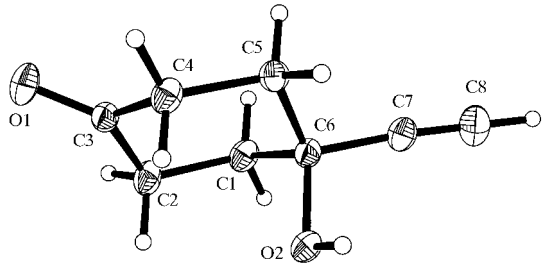


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atomic numbering scheme. H atoms are drawn as small spheres of arbitrary radii.

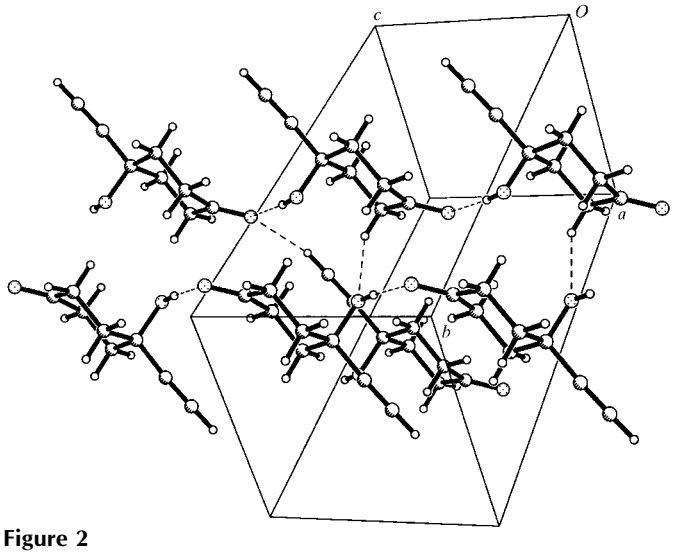


Figure 2
The packing diagram of (I) illustrating the close intermolecular contacts (indicated by the dotted lines).

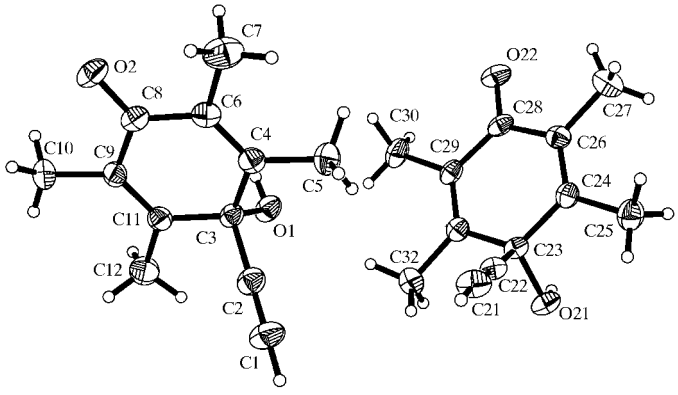


Figure 3
The molecular structure of (II), showing the two independent molecules, 50% probability displacement ellipsoids and the atomic numbering scheme. H atoms are drawn as small spheres of arbitrary radii.

hydrogen bonds. These chains are linked in the *a* direction by pairs of symmetry-related $C_{methylene}$—H···O(H) interactions and along **b** by somewhat weaker C≡C—H···O=C interactions (Fig. 2). Relevant hydrogen-bond geometry is given in Table 2. It would be surprising if the strong keto-O acceptor were not used in hydrogen-bond formation and the relatively simple structure of (I) differs markedly from that of the analogous bis(*gem*-alkynol), (III), which forms robust helical trimeric synthons *via* strong O—H···O(H) bonds in two polymorphs and one pseudo-polymorphic hydrate.

Compound (II) (Fig. 3; $P2_1/c$, $Z = 8$) has two independent molecules in the asymmetric unit and some disorder in two of the methyl groups in each molecule (see *Experimental*). Each symmetry-independent molecule forms an inversion-related dimer *via* O—H···O=C bonds, and these dimers are linked by C≡C—H···O=C bonds to form layers. The overall packing therefore consists of two alternating layers, formed by each symmetry-independent molecule, that are connected only by C_{methyl}—H···O(H) interactions. Geometrical details of the hydrogen bonds are given in Table 4. Structure (II) again differs markedly from that of its close bis(*gem*-alkynol) analogue, (IV), which forms strong co-operative O—H···O(H) chains linked by C≡C—H···O(H) bonds.

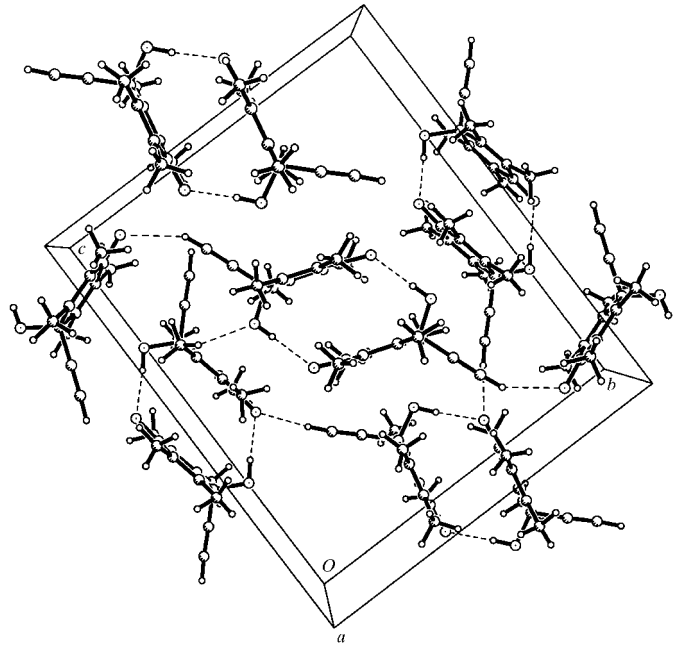


Figure 4
The packing diagram of (II) illustrating the close intermolecular contacts (indicated by the dotted lines).

Clearly, the strong acceptor ability of the carbonyl O atom dominates the packing of (I) and (II). Both structures contain O—H···O=C and C≡C—H···O=C bonds, together with interactions involving the OH acceptor and either $C_{methylene}$—H [in (I)] or C_{methyl}—H [in (II)]. There are no direct intermolecular interactions involving the atoms of the *gem*-alkynol group. These results are not unexpected as our previous analysis of 94 existing *gem*-alkynol structures (Madhavi, Bilton *et al.*, 2000) retrieved from the Cambridge Structural Database (Allen & Kennard, 1993) contained 39 examples which also contained carbonyl acceptors, and in 34 of these cases, the alkynol OH group is hydrogen bonded to the carbonyl-O atom rather than to itself.

Experimental

Compounds (I) and (II) were by-products in the syntheses described by Madhavi, Desiraju *et al.* (2000) and Bilton *et al.* (2000), and were isolated using column chromatography and recrystallized from ethyl acetate.

Compound (I)

Crystal data

$C_8H_{10}O_2$
$M_r = 138.16$
Monoclinic, $P2_1/c$
$a = 6.550$ (1) Å
$b = 16.931$ (3) Å
$c = 6.493$ (1) Å
$\beta = 95.42$ (3)°
$V = 716.9$ (2) Å^3
$Z = 4$
$D_x = 1.280$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 508 reflections
$\theta = 6.71$–$21.21°$
$\mu = 0.091$ mm^{-1}
$T = 150$ K
Plate, colourless
0.40 × 0.10 × 0.05 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
5018 measured reflections
1657 independent reflections
1074 reflections with $I > 2\sigma(I)$
$R_{int} = 0.060$
$\theta_{max} = 27.49°$
$h = -8 \rightarrow 8$
$k = -21 \rightarrow 16$
$l = -8 \rightarrow 8$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.122$
$S = 1.07$
1657 reflections
131 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0376P)^2 + 0.2197P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.24$ e Å^{-3}

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

O1—C3	1.231 (2)	C8—H8	0.97 (3)
C6—C7	1.490 (3)		
C6—O2—H*A*	105 (2)	C8—C7—C6	175.7 (2)
O2—C6—C7	108.69 (16)	C7—C8—H8	179.2 (18)

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—HA···O1^{i}	0.84 (3)	1.99 (3)	2.820 (2)	175 (3)
C1—H1A···O2^{ii}	0.98 (2)	2.51 (2)	3.482 (3)	175.4 (18)
C8—H8···O1^{iii}	0.97 (3)	2.65 (3)	3.373 (3)	132 (2)

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

Compound (II)

Crystal data

$C_{12}H_{14}O_2$
$M_r = 190.23$
Monoclinic, $P2_1/c$
$a = 9.020$ (2) Å
$b = 14.010$ (3) Å
$c = 16.612$ (3) Å
$\beta = 93.56$ (3)°
$V = 2095.2$ (7) Å^3
$Z = 8$
$D_x = 1.206$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 999 reflections
$\theta = 5.13$–$24.00°$
$\mu = 0.081$ mm^{-1}
$T = 150$ K
Block, colourless
0.35 × 0.25 × 0.20 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.802$, $T_{max} = 1.000$
14 728 measured reflections
4796 independent reflections
3037 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
$\theta_{max} = 27.49°$
$h = -11 \rightarrow 11$
$k = -18 \rightarrow 17$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.145$
$S = 1.01$
4796 reflections
329 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0752P)^2 + 0.3548P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

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

C1—C2	1.173 (3)	C21—C22	1.181 (3)
C4—C5	1.505 (3)	C24—C25	1.507 (3)
C8—O2	1.236 (2)	C28—O22	1.241 (2)
C2—C1—H1	176.5 (19)	C22—C21—H21	174.5 (15)
C1—C2—C3	178.7 (2)	C21—C22—C23	177.7 (2)
O1—C3—C2	105.69 (14)	O21—C23—C22	106.64 (14)
C3—O1—H1A	108 (2)	C23—O21—H21A	103.4 (18)
C5—C4—C3	114.84 (18)	C25—C24—C23	115.01 (17)

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O2^{i}	0.82 (3)	1.96 (3)	2.786 (2)	179 (3)
O21—H21A···O22^{ii}	0.89 (3)	1.94 (3)	2.826 (2)	172 (2)
C1—H1···O2^{iii}	0.93 (3)	2.44 (3)	3.271 (3)	149 (2)
C21—H21···O22^{iv}	0.96 (3)	2.21 (3)	3.151 (3)	168 (2)
C12—H12C···O21^{v}	0.96	2.68	3.634 (3)	171
C32—H32B···O1	0.96	2.55	3.447 (3)	155

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

All H atoms were located in (I) and refined freely. H atoms were also located and refined freely in (II), with the exception of four methyl groups (C7, C12, C27 and C32), which were refined as idealized groups.

For both compounds, data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97; software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1109). Services for accessing these data are described at the back of the journal.

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