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4,4′-(4,5-Dimethyl-1,2-phenylene)-bis(2-methylbut-3-yn-2-ol): structural variation in vicinal dialkynols

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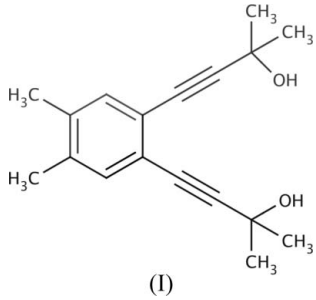
The structure of the title compound, $C_{18}H_{22}O_2$, contains two non-equivalent molecules which differ primarily in the location of the –OH groups on opposite sides or on the same side of the molecular plane. Inversion-symmetric pairs of molecules form intermolecular O—H···O hydrogen-bonded tetrameric synthons that link non-equivalent molecules into an approximately square double layer parallel to ($\bar{1}$02). Recently reported fluorinated analogues [Kane, Meyers, Yu, Gerken & Etzkorn (2011). *Eur. J. Org. Chem.* pp. 2969–2980] have significantly different structures of varying complexity that incorporate intramolecular hydrogen bonding and suggest that further study of structure *versus* substituents in vicinal dialkynols could be fruitful.

Comment

Dialkynols have been extensively studied as part of a broader survey of *gem*-alkynol structures (Madhavi, Desiraju *et al.*, 2000*a*; Nangia, 2010). Since the *gem*-alkynol moiety provides two functional groups, *viz.* –OH and –C≡CH, there are several competing ways in which groups on neighboring molecules can interact which, in turn, lead to a wide variety of synthons and structures (Madhavi, Bilton *et al.*, 2000; Banerjee *et al.*, 2006). One recurring structural motif is a tetrameric synthon of functional groups that are linked by hydrogen bonds in a square arrangement (Madhavi, Desiraju *et al.*, 2000*b*; Bilton *et al.*, 2001). The di-*gem*-alkynols studied often place the alkynol groups on opposite sides of an organic ring, so intramolecular interactions are inhibited. Vicinal dialkynol structures have recently been reported in which the alkynol groups are *ortho*, but with –C≡CH groups absent, so the –OH groups are positioned to act as molecular tweezers in which intramolecular hydrogen bonding is now possible (Kane *et al.*, 2011). We report here the structure of the title new vicinal dialkynol compound, (I), an intermediate obtained in an effort to prepare cyclic diacetylenes (Zhou *et al.*, 1994), which was synthesized by the treatment of 1,2-diiodo-4,5-dimethylbenzene (Hathaway *et al.*, 2009) with excess 2-methyl-3-butyn-2-ol in the presence of copper(I) and palladium catalysts (Melissaris & Litt, 1994).



(I)

The two non-equivalent molecules in the asymmetric unit of (I) (the first digit of the atom label denotes assignment to molecule 0 or 1) are each quasi-planar for the core atoms, *i.e.* those that are, or are bound to atoms that are, *sp*- or sp^2-hybridized. Bond lengths and angles within each molecule conform to expected values (Ladd & Palmer, 1994). The molecules have no formal site symmetry, although each approximates *mm*2 symmetry for the core atoms, with half of the nominally equivalent bond lengths agreeing within 1 s.u. and all within 2 s.u. Nominally equivalent bond angles for the ring atoms agree within 3 s.u. [with one slight exception, for C06—C01—C011 = 120.46 (10)° and C03—C02—C021 = 120.15 (9)°], but the angles in the alkynol groups disagree by more. Similar bond lengths between non-equivalent molecules agree [with one slight exception, for the C*x*1—C*x*11 and C*x*2—C*x*21 bonds which are in the range 1.4353 (15)–1.4400 (15) Å] within 3 s.u. for C*sp*, Csp^2 or O atoms, while the Csp^3—Csp^3 bonds agree within 4 s.u. The differences in similar bond angles between non-equivalent molecules are larger and agree within 3–5 s.u. in the ring, with even greater disagreement in the alkynol groups. Bonds in the ring between substituents are elongated compared with the others, with the C*x*1—C*x*2 bond between alkynol groups being the longest. The substituents are scissored outward, as shown by bond angles at the substituted ring atoms of <120° for aromatic ring atoms only and interior angles of >120° involving the substituent. Angles

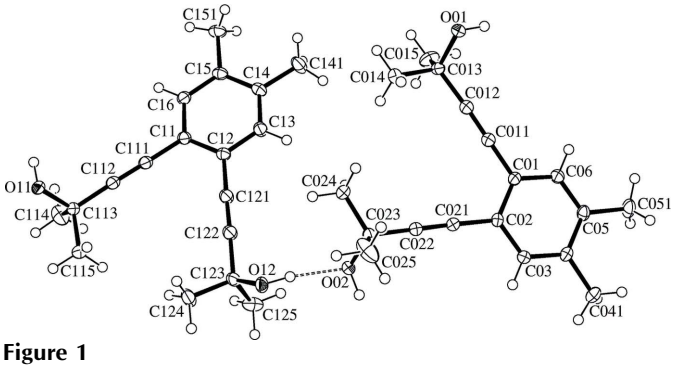


Figure 1
The asymmetric unit of (I), showing the two non-equivalent molecules with atom labels. Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates the hydrogen bond between non-equivalent molecules.

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about the unsubstituted ring atoms of ~122° indicate a slight scissoring inward of these atoms with the outward scissoring of the substituents. The main geometric difference between the non-equivalent molecules is the –OH group location on opposite sides of the molecular plane (molecule 0) or on the same side (molecule 1), which reduces the approximate point-group symmetry of molecule 0 to 2, and of molecule 1 to *m*. A displacement ellipsoid plot of the asymmetric unit of (I) is presented in Fig. 1.

Inversion-related molecular pairs are formed, with interplanar spacings of 3.486 (1) and 3.717 (1) Å for molecules 0 and 1, respectively. The aromatic rings within each pair are offset away from each other, principally along a line parallel to the alkynol arms of O1 or O11, with distances between the ring-atom centroids (measured perpendicular to the mean-plane normal) of 1.394 (2) and 1.547 (2) Å for molecules 0 and 1, respectively. Since the interplanar spacings are greater than the sum of the van der Waals radii (Bondi, 1964) and the large ring displacements lead to only minor (30–35%) overlap, it is unlikely that there is a significant attractive interaction between the molecules of each pair. The long axes of the non-equivalent molecules are almost perpendicular [angle of 86.17 (7)° between the least-squares lines formed by the core atoms], with that of molecule 0 parallel to [201] and that of molecule 1 almost parallel to *b*. These vectors demarcate axes for an approximately square grid [23.0784 (3) Å along [201] *versus* 22.7966 (3) Å along *b*] of inversion-related pairs of molecules linked by hydrogen bonds to form a double layer in ($\bar{1}02$). Different types of molecule pairs alternate along each repeat axis, with a given molecule forming hydrogen bonds to molecules of the other type on each side. This results in O—H···O hydrogen bonds arranged in square tetrameric synthons between rows of molecules. Deviations from a true square within the synthon are small, *e.g.* neighboring O···O distances are in close agreement and the O···O···O angles are ~90°, with the largest due to O—H···O angles of 164–171° that place H atoms outside the square. The mean plane of molecule 1 is closer to ($\bar{1}02$), with both –OH groups directed into the double layer and with the C114 and C125 methyl groups directed outward. The mean-plane normal of molecule 0 forms an angle of 24.86 (2)° to that of molecule 1, with the –OH groups hydrogen bonded to molecules 1 on opposite sides of the double layer. The differences in geometric parameters between the alkynol groups (see above) can thus be ascribed to strains imposed to accommodate hydrogen bonding. The double layer is scored by grooves parallel to [201], generated by the offset of molecules 1, with the tetrameric O—H···O synthons at the floor (or ceiling) of each groove. A diagram of the quasi-square layer is presented in Fig. 2 and hydrogen-bonding parameters are presented in Table 1.

The structure is completed by stacking the double layers so molecule 0 pairs stack along *a* at the lines of inversion centers passing halfway through the *b* and *c* edges, while molecule 1 pairs stack similarly but along the *a* edges or passing through the center of the *bc* face. The mean planes within the stacks are tilted relative to *a*, with the normals forming angles of 60.80 (1) and 36.22 (1)° for molecules 0 and 1, respectively. The stacks of inversion-related molecular pairs are readily observed when the structure is viewed down *a*, as shown in the packing diagram in Fig. 3. However, the double layers are less obvious from a cursory examination, since the methyl groups projecting away from the layer are nested into the grooves of neighboring layers so as to obscure the boundaries between layers.

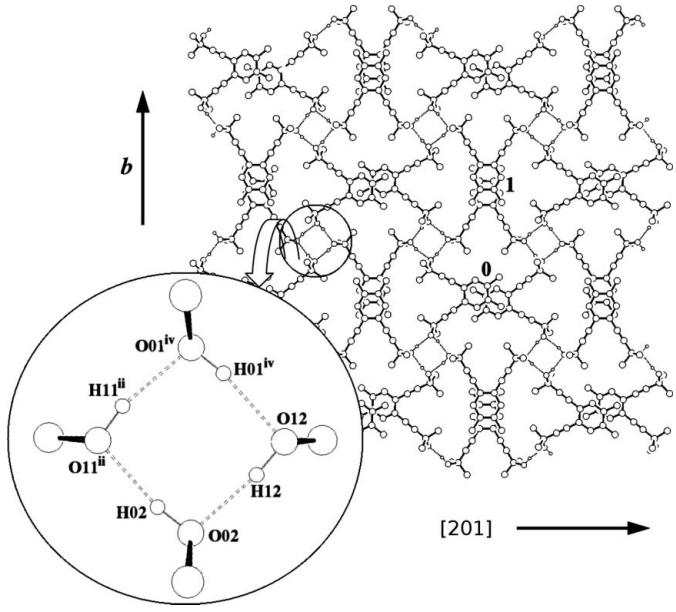

Figure 2
A plot of a portion of the quasi-square layer in (I) (with *b* vertical and [201] horizontal) formed by hydrogen bonding between inversion-related pairs of molecules. Atoms are represented by circles of arbitrary radii and H atoms have been omitted for clarity, except for those bound to oxygen. Pairs of type 0 and 1 molecules are identified in the diagram and the inset shows the detail of the square tetrameric hydrogen-bonded synthon. [Symmetry codes: (ii) $x-1, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$.]

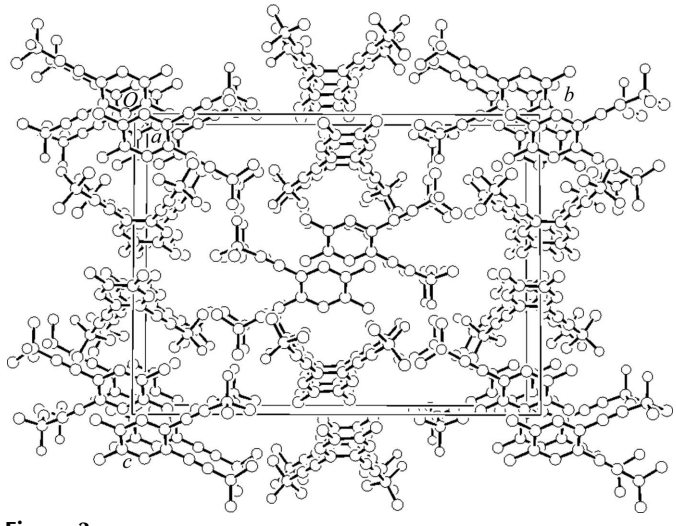

Figure 3
A unit-cell packing diagram for (I), viewed along *a*, showing the stacks of inversion–related pairs of molecules. Atoms are drawn as circles of arbitrary radii and H atoms have been omitted for clarity.

The few known vicinal dialkynols exhibit a variety in their structures that is sensitive to molecular geometry and composition, as is already well known among the much larger *gem*-alkynol family. The structure of (I) is, perhaps, the most conventional, since it contains the recurring tetrameric O—H···O synthon, yet at the same time shows no intramolecular interactions that might be expected for the tweezer-like *ortho* arrangement of the alkynol groups. In contrast, the difluoro analog [Cambridge Structural Database (Version 5.32; Allen, 2002) refcode OQAZUC (Kane *et al.*, 2011)], in which F replaces the ring CH_3 groups, has quite a complex structure (Z' = 9) in which intramolecular O—H···O interactions are also found. This striking difference in complexity between the dimethyl and difluoro analogs raises the question of what other structures might be observed by replacing substituents in these positions. Meanwhile, the tetrafluoro analog (OQEBOC; Kane *et al.*, 2011), in which F replaces the ring CH_3 groups and H atoms, has a simpler structure (Z' = 1) and only localized intra- and intermolecular O—H···O hydrogen bonding between two molecules in the tetrameric synthon, although with a more distorted square than in (I). In contrast, in OQEBIW (Z' = 1; Kane *et al.*, 2011), the analog to OQEBOC with alkynol CH_3 groups replaced by H, a strictly intermolecular O—H···O hydrogen-bonding network of zigzag chains is found. Thus, a two-dimensional hydrogen-bonding network with no intramolecular hydrogen bonding is found in (I), in spite of the presence of alkynol CH_3 groups, the presence of which allows for intramolecular hydrogen bonding in OQAZUC and OQEBIW and localized interactions only in OQEBIW. [Note that the carboxylic acid analog of (I) contains both intra- and intermolecular bonding to form zigzag O—H···O hydrogen-bonded chains (Saravanakumar *et al.*, 2009).] Two other vicinal dialkynols, octa-2,4,6-triyne-1,8-diol (LILHUJ, Z' = 0.5; Enkelmann, 1994) and 2,9-dimethyldeca-3,5,7-triyne-2,9-diol (LILJAR, Z' = 1; Enkelmann, 1994), contain a –C≡C– core that dictates a linear geometry, so the –OH groups are at opposite ends (and intramolecular hydrogen bonding is impossible) and O—H···O hydrogen-bonded networks are present as zigzag single or double layers, respectively. This variation of structure within the vicinal dialkynols (in particular *ortho*-dialkynols), where small variations in ring or alkynol substituents lead to large changes in structure from competition between intra- and intermolecular hydrogen bonding, seems a fruitful area for further investigation.

Experimental

Nitrogen (N_2) was bubbled through triethylamine (75 ml) for 15 min to remove dissolved oxygen, with the N_2 atmosphere maintained throughout the subsequent reaction. 1,2-Diiodo-4,5-dimethylbenzene (5.0 g, 0.014 mol), 2-methyl-3-butyn-2-ol (5.88 g, 0.070 mol), triphenylphosphane (0.10 g) and copper(I) iodide (0.03 g) were added, and the mixture was stirred for 10 min. Dichloridobis(triphenylphosphane)palladium (0.030 g) was added, and the reaction was heated to ~330 K overnight. The resulting green solution was diluted with diethyl ether and filtered. The filtrate was evaporated to yield a green–brown solid that was then redissolved in hot toluene on a steam bath. Crystals of (I) formed as a sand-colored solid upon slow cooling of this solution, first to ambient temperature and then to 273 K in an ice bath (yield: 2.67 g, 70.6%; m.p. 414 K). Single crystals of this sample appeared colorless under microscopic examination and were suitable for X-ray diffraction.

Crystal data

$C_{18}H_{22}O_2$
M_r = 270.37
Monoclinic, $P2_1/c$
a = 8.4720 (1) Å
b = 22.7966 (3) Å
c = 16.8592 (2) Å
β = 93.886 (1)°
V = 3248.58 (7) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.07 mm^{-1}
T = 100 K
0.36 × 0.32 × 0.28 mm

Data collection

Nonius KappaCCD area-detector diffractometer
18231 measured reflections
9466 independent reflections
7185 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.122
S = 1.01
9466 reflections
389 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Solution and refinement of the structure were straightforward; all non-H atoms were found in the initial electron-density map and their anisotropic displacement parameters were refined. All H atoms were visible in subsequent electron-density difference maps, and the positions and isotropic displacement parameters of those bound to O atoms were refined freely. Other H-atom positions were calculated to give an idealized geometry, with C—H = 0.96 or 0.93 Å and U_{iso}(H) = 1.5 or 1.2U_{eq}(C) for CH_3 or aromatic H atoms, respectively. The CH_3 torsion angle was refined to match the electron density. 11 low-angle reflections obscured by the beam stop (as indicated by $F_o^2 << F_c^2$) were omitted from the refinement.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PARST* (Nardelli, 1995).

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Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O01—H01···O12^{i}	0.886 (18)	1.901 (17)	2.773 (1)	167.5 (16)
O02—H02···O11^{ii}	0.886 (19)	1.876 (19)	2.752 (1)	169.8 (18)
O11—H11···O01^{iii}	0.886 (19)	1.892 (19)	2.756 (1)	164.3 (18)
O12—H12···O02	0.904 (18)	1.847 (17)	2.744 (1)	170.7 (17)

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KU3064). Services for accessing these data are described at the back of the journal.

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