

## Racemic 1,2-diphenylbut-3-yn-2-ol

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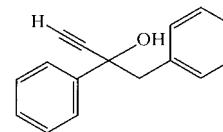
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Molecules of the title compound, C<sub>16</sub>H<sub>14</sub>O, are chiral and crystallize in space group  $P\bar{4}$  with  $Z' = 2$ , and with one *R* and one *S* molecule in the asymmetric unit. The conformations of the phenyl rings in the two independent molecules differ slightly. Supramolecular organization in the crystal is *via* tetrameric O—H···O(H) hydrogen-bonded synthons formed separately by each conformer. These tetrameric synthons stack along the *c* axis *via* C≡C—H···O(H) hydrogen bonds. The only link between the conformer stacks is provided by weaker C<sub>methylene</sub>—H and C<sub>phenyl</sub>—H interactions with  $\pi_{\text{arene}}$  density.

## Comment

The crystal structure of the title compound, (I), was determined as part of a systematic study of synthon formation (Desiraju, 1995) in *gem*-alkynols. This combination of functional groups attached to the same C atom, both of which can act as donors and acceptors of very different potency, provides for a variety of hydrogen-bonding possibilities (Bilton *et al.*, 1999; Madhavi, Bilton *et al.*, 2000). These interaction possibilities are further extended by the controlled inclusion of other functional groups, such as halogens (Madhavi, Desiraju *et al.*, 2000), substituted phenyl groups (Bilton, Howard, Madhavi, Nangia *et al.*, 2000) and keto groups (Bilton, Howard, Madhavi, Desiraju & Allen, 2000). The principal feature of many of these structures is an O—H···O(H) hydrogen bond between the alkynol group moieties, giving rise to synthons such as co-operative chains, helical trimers or cyclic hexamers and tetramers. These major synthons are supported by a variety of weaker interactions involving halogens, C—H donors and oxygen or  $\pi$  acceptors. The O—H···O(H) hydrogen bonding is replaced by the stronger O—H···O=C bonds in the keto series and, surprisingly, is eliminated altogether in the substituted phenyl series, where structural organization relies entirely on the weaker interactions in five related compounds. This unusual observation is ascribed (Bilton, Howard, Madhavi, Nangia *et al.*, 2000) to steric hindrance of the O—H donor/acceptor by the proximity

of two large phenyl substituents on the alkynol C atom. Compound (I) has been synthesized such that one of the phenyl substituents is now separated from the alkynol C atom by an additional methylene group, in order to see if hindrance to O—H···O(H) bond formation still persists.

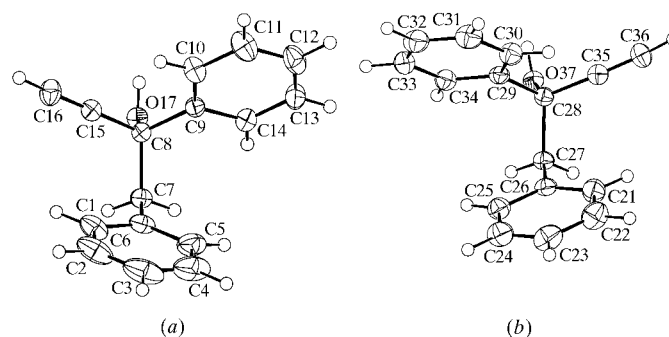


(I)

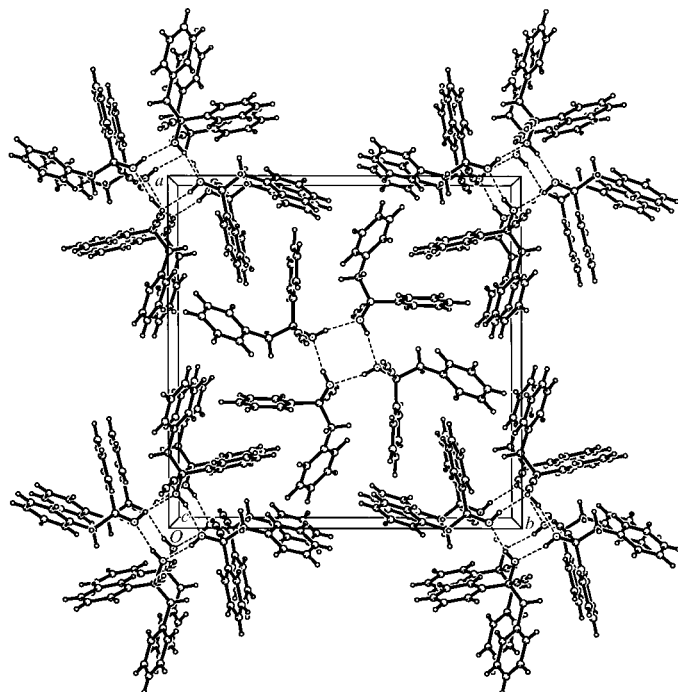
Compound (I) crystallizes in the polar space group  $P\bar{4}$  with  $Z' = 2$ . The compound is racemic and the asymmetric unit was chosen so as to contain one *R* and one *S* molecule (Figs. 1*a* and 1*b*, respectively). As may be seen in Fig. 1, the two independent molecules differ slightly in their conformations. The differences can be easily quantified by comparing relevant torsion angles (which have opposite signs in the *R* and *S* molecules); these angles are: C1—C6—C7—C8 79.25 (15)° and C21—C26—C27—C28 −78.31 (15)°; C7—C8—C9—C10 −121.86 (12)° and C27—C28—C29—C30 104.71 (12)°; and C6—C7—C8—O17 182.92 (9)° and C26—C27—C28—O37 −171.58 (10)°.

Supramolecular organization in the crystal is dominated by O—H···O(H) hydrogen bonds (see Table 2 and Fig. 2). Each independent molecule forms a tetramer about a 4 axis, *i.e.* there is a tetramer (two *R* and two *S* forms) of conformer 1*A* molecules and separate independent tetramer (also two *R* and two *S* forms) of 1*B* molecules. Each separate tetramer forms stacks *via* C≡C—H···O(H) bonds (Table 2), but conformer 1 and conformer 2 stacks only interact *via* weak C<sub>methylene</sub>—H··· $\pi_{\text{arene}}$  and C<sub>phenyl</sub>—H··· $\pi_{\text{arene}}$  interactions (Table 2). This combination of O—H···O(H) tetrameric synthons and C≡C—H···O(H) bonds is also observed in another *gem*-alkynol, 3-phenylpenta-1,4-diyne-3-ol (Steiner *et al.*, 1996), a non-chiral molecule which also crystallizes in a tetragonal space group ( $I\bar{4}$ ), but with  $Z' = 1$ .

By comparison with our series of phenyl-substituted *gem*-alkynols (Bilton, Howard, Madhavi, Nangia *et al.*, 2000), the addition of a methylene spacer in (I) frees up the OH group to form the O—H···O(H) bonds expected from our earlier studies. In particular, the hydrogen-bonded synthon formed



**Figure 1**  
Views of (a) the *R* molecule and (b) the *S* molecule of (I) oriented to allow easy comparison of their conformations. Ellipsoids are drawn at the 50% probability level.


**Figure 2**

A packing diagram for (I) illustrating the close intermolecular contacts (indicated by the dotted lines).

here now repeats the tetrameric pattern observed in the chloro and bromo compounds of our halogen series (Madhavi, Desiraju *et al.*, 2000).

## Experimental

Compound (I), synthesized using the general scheme described by Madhavi, Desiraju *et al.* (2000), was isolated using column chromatography and was recrystallized from ethyl acetate.

### Crystal data

|                                   |                                      |
|-----------------------------------|--------------------------------------|
| $C_{16}H_{14}O$                   | Mo $K\alpha$ radiation               |
| $M_r = 222.27$                    | Cell parameters from 999 reflections |
| Tetragonal, $P4_1$                | $\theta = 10.21$ – $22.42^\circ$     |
| $a = 19.8403$ (4) Å               | $\mu = 0.070$ mm <sup>-1</sup>       |
| $c = 6.5068$ (2) Å                | $T = 150$ K                          |
| $V = 2561.32$ (11) Å <sup>3</sup> | Block, colourless                    |
| $Z = 8$                           | $0.4 \times 0.3 \times 0.3$ mm       |
| $D_x = 1.153$ Mg m <sup>-3</sup>  |                                      |

### Data collection

|   |  |
|---|--|
| Bruker SMART CCD diffractometer   | 7018 independent reflections           |
| $\omega$ scans  | 6166 reflections with $I > 2\sigma(I)$ |
| Absorption correction: empirical ( <i>XPREP</i> in <i>SHELXL97</i> ; Sheldrick, 1997) | $R_{int} = 0.024$                      |
| $T_{min} = 0.907$ , $T_{max} = 0.979$   | $\theta_{max} = 30.35^\circ$           |
| 20 665 measured reflections   | $h = -27 \rightarrow 23$               |
|   | $k = -27 \rightarrow 25$               |
|   | $l = -9 \rightarrow 8$                 |

### Refinement

|                                 |   |
|---------------------------------|---|
| Refinement on $F^2$             | $w = 1/[\sigma^2(F_o^2) + (0.0570P)^2 + 0.1122P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.037$ | where $P = (F_o^2 + 2F_c^2)/3$                    |
| $wR(F^2) = 0.092$               | $(\Delta/\sigma)_{max} = 0.010$                   |
| $S = 1.024$                     | $\Delta\rho_{max} = 0.24$ e Å <sup>-3</sup>       |
| 7018 reflections                | $\Delta\rho_{min} = -0.20$ e Å <sup>-3</sup>      |
| 419 parameters                  |   |
| All H-atom parameters refined   |   |

**Table 1**

Selected geometric parameters (Å, °).

|            |             |             |             |
|------------|-------------|-------------|-------------|
| C7—C8      | 1.5539 (16) | C27—C28     | 1.5564 (16) |
| C8—C15     | 1.4812 (16) | C28—C35     | 1.4856 (17) |
| C15—C16    | 1.1828 (18) | C35—C36     | 1.1893 (18) |
| C6—C7—C8   | 114.50 (10) | C26—C27—C28 | 114.42 (9)  |
| O17—C8—C15 | 108.16 (9)  | O37—C28—C35 | 107.30 (9)  |
| C16—C15—C8 | 177.64 (13) | C36—C35—C28 | 173.46 (13) |

**Table 2**

Hydrogen-bonding geometry (Å, °).

| $D-H\cdots A$                       | $D-H$    | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------------------|----------|-------------|-------------|---------------|
| C16—H16 $\cdots$ O17 <sup>i</sup>   | 0.93 (2) | 2.31 (2)    | 3.181 (2)   | 156 (1)       |
| C36—H36 $\cdots$ O37 <sup>iii</sup> | 0.90 (2) | 2.44 (2)    | 3.2862 (16) | 156 (2)       |
| O37—H37 $\cdots$ O37 <sup>iii</sup> | 0.82 (2) | 2.05 (2)    | 2.852 (1)   | 166 (2)       |
| O17—H17 $\cdots$ O17 <sup>iv</sup>  | 0.83 (2) | 2.00 (2)    | 2.8200 (12) | 169 (2)       |

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

All H atoms were located and refined freely with isotropic displacement parameters.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1108). Services for accessing these data are described at the back of the journal.

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