

membered ring the angle at the  $sp^2$ -hybridized C(5) atom is  $87.1(9)^\circ$ , and at the other three atoms  $82.1-85.0(8)^\circ$ . Intermolecular distances correspond to van der Waals interactions; the shortest contacts are O(3) $\cdots$ C(13)  $3.38(1)$ , O(1) $\cdots$ O(3)  $3.61(1)$ , Br $\cdots$ C(7)  $3.72(1)$  Å.

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## Structure of 2-Methyl-4-phenyl-3-butyn-2-ol

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**Abstract.**  $C_{11}H_{12}O$ ,  $M_r = 160.22$ , orthorhombic,  $Pca2_1$ ,  $a = 35.454(8)$ ,  $b = 6.024(1)$ ,  $c = 13.606(1)$  Å,  $V = 2905.9(8)$  Å<sup>3</sup>,  $Z = 12$ ,  $D_x = 1.099$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $\mu = 0.6$  cm<sup>-1</sup>,  $F(000) = 1032$ , room temperature,  $R = 0.0486$  for 2183 unique reflections. The asymmetric unit contains three molecules which exhibit almost identical shapes and sizes. They only differ in the orientation of the phenyl ring relative to the C-O axis. A hydrogen-bonding system connects the O atoms and produces spirals parallel to the **b** direction that are held together solely by van der Waals forces. The position of the ethynyl group is in accordance with IR measurements, where an intramolecular OH $\cdots\pi$  hydrogen-bond interaction has been suggested.

**Introduction.** Visser & Van der Maas (1983) have studied  $\alpha$ -ethynyl alcohols in solution by means of IR spectroscopy. From this study it follows that the hydroxyl-H atom is involved in an OH $\cdots\pi$  interaction. Lin, Okaya, Chiou & le Noble (1982) have reported a similar hydrogen bond in 2-ethynyladamantan-2-ol, which is structurally related to the title compound. The presence of an electron-withdrawing phenyl ring in 2-methyl-4-phenyl-3-butyn-2-ol influences the charge on the C atoms of the ethynyl group and weakens the OH $\cdots\pi$  interaction (Visser & Van der Maas, 1984). However, the IR measurements indicated that in solution only the OH-*gauche* conformation is present. The X-ray analysis was undertaken to compare this finding with the molecular stereochemistry in the crystalline state.

**Experimental.** The compound was kindly donated by Professor L. Brandsma. Data were obtained on an Enraf-Nonius CAD-4F diffractometer with Zr-filtered Mo  $K\alpha$  radiation. Lattice constants from 16 reflections in the range of  $22 < 2\theta < 26^\circ$ ;  $\omega$ - $2\theta$  mode,  $\Delta\omega = (0.60 + 0.35\tan\theta)^\circ$ . Reflections were measured up to  $2\theta = 50^\circ$ . The crystal is orthorhombic with space group  $Pca2_1$ , with three independent molecules in the asymmetric unit. On the exposure to X-rays the crystal (initial dimensions  $1.0 \times 0.5 \times 0.5$  mm) started to decay and disappeared gradually; however, the reflections maintained their relative intensities. Four periodically measured standard reflections (125,  $1\bar{2}5$ ,  $1\bar{2}\bar{5}$ ,  $1\bar{2}\bar{5}$ ) showed relative intensity variations less than 10%. Two crystals were used to collect the full data set. The first crystal disappeared completely, whereas the data collection from the second one was continued until the intensities reached about 15% of their original values. The intensities were corrected for this decrease as well as for Lorentz and polarization effects, but not for absorption. Variance  $\sigma^2(I)$  calculated based on counting statistics plus a term  $(PI)^2$  where  $P (= 0.073)$  is the instability constant (McCandlish, Stout & Andrews, 1975). First crystal: 1690 reflections,  $-42 \leq h \leq -12$ ; second crystal: 2992 reflections,  $0 \leq h \leq 29$ ; both crystals:  $0 \leq k \leq 16$ ,  $0 \leq l \leq 7$ . The data sets were merged using the common reference transitions and with averaging over Friedel pairs (internal consistency index 0.16, based on intensity values); 2664 independent reflections were left.

2183 reflections with  $I > 1.5\sigma(I)$  were considered observed and used in the calculations. The structure was solved with *SHELXS84* (Sheldrick, 1984); the best *E* map gave all non-H atoms. To specify the origin an

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arbitrary value was assigned to one O-atom  $z$  coordinate. H atoms were placed on calculated positions except the hydroxyl-H atoms which were located on a difference map. The temperature parameters of the H atoms were set equal to the equivalent isotropic temperature factor of the carrier atoms. All refinements were by blocked full-matrix least squares using *SHELX76* (Sheldrick, 1976). H-atom parameters were

Table 1. Positional and equivalent isotropic thermal parameters ( $\text{\AA}^2$ ) for non-H atoms and hydroxyl-H atoms with *e.s.d.'s* in parentheses, for the three independent molecules in the asymmetric unit

$$U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3.$$

Molecule (I)	$x$	$y$	$z$	$U_{\text{eq}}$
O	0.0799 (1)	0.6198 (4)	0.0902	0.059 (1)
H	0.091 (1)	0.510 (7)	0.092 (3)	0.054
C(1)	0.0409 (1)	0.8279 (7)	-0.0158 (3)	0.068 (1)
C(2)	0.0734 (1)	0.6640 (6)	-0.0126 (3)	0.051 (1)
C(3)	0.1074 (1)	0.7715 (6)	-0.0560 (3)	0.052 (1)
C(4)	0.1333 (1)	0.8641 (6)	-0.0935 (3)	0.053 (1)
C(5)	0.1639 (1)	0.9896 (6)	-0.1349 (3)	0.051 (1)
C(6)	0.2011 (1)	0.9192 (7)	-0.1225 (3)	0.061 (1)
C(7)	0.2304 (1)	1.0496 (8)	-0.1574 (3)	0.072 (1)
C(8)	0.2232 (1)	1.2460 (7)	-0.2049 (3)	0.068 (1)
C(9)	0.1866 (1)	1.3143 (7)	-0.2192 (3)	0.066 (1)
C(10)	0.1571 (1)	1.1867 (6)	-0.1850 (3)	0.057 (1)
C(11)	0.0644 (1)	0.4473 (7)	-0.0659 (3)	0.069 (1)
Molecule (II)				
O	0.1239 (1)	0.2614 (4)	0.1407 (2)	0.0577 (8)
H	0.110 (1)	0.165 (6)	0.170 (3)	0.052
C(1)	0.1803 (1)	0.4038 (7)	0.0760 (3)	0.071 (1)
C(2)	0.1638 (1)	0.2650 (6)	0.1585 (3)	0.047 (1)
C(3)	0.1714 (1)	0.3748 (6)	0.2537 (3)	0.051 (1)
C(4)	0.1781 (1)	0.4753 (6)	0.3271 (3)	0.055 (1)
C(5)	0.1859 (1)	0.6095 (6)	0.4120 (3)	0.050 (1)
C(6)	0.1675 (1)	0.8114 (6)	0.4223 (3)	0.059 (1)
C(7)	0.1752 (1)	0.9483 (7)	0.5013 (3)	0.070 (2)
C(8)	0.2006 (1)	0.8854 (8)	0.5713 (3)	0.075 (2)
C(9)	0.2191 (1)	0.6837 (8)	0.5624 (3)	0.076 (2)
C(10)	0.2116 (1)	0.5451 (7)	0.4826 (3)	0.065 (1)
C(11)	0.1792 (1)	0.0302 (6)	0.1574 (3)	0.061 (1)
Molecule (III)				
O	0.0903 (1)	0.9118 (4)	0.2439 (2)	0.0580 (8)
H	0.086 (1)	0.811 (6)	0.198 (3)	0.055
C(1)	0.0678 (1)	1.0329 (9)	0.3990 (3)	0.086 (2)
C(2)	0.0580 (1)	0.9010 (7)	0.3072 (3)	0.060 (1)
C(3)	0.0261 (1)	1.0046 (7)	0.2582 (3)	0.061 (1)
C(4)	-0.0010 (1)	1.0979 (6)	0.2231 (3)	0.062 (1)
C(5)	-0.0330 (1)	1.2162 (6)	0.1838 (3)	0.054 (1)
C(6)	-0.0689 (1)	1.1325 (8)	0.1951 (3)	0.070 (1)
C(7)	-0.0994 (1)	1.254 (1)	0.1604 (4)	0.087 (2)
C(8)	-0.0944 (2)	1.452 (1)	0.1160 (3)	0.096 (2)
C(9)	-0.0589 (2)	1.5390 (9)	0.1054 (4)	0.091 (2)
C(10)	-0.0282 (1)	1.4217 (8)	0.1396 (3)	0.077 (2)
C(11)	0.0503 (1)	0.6618 (8)	0.3326 (4)	0.082 (2)

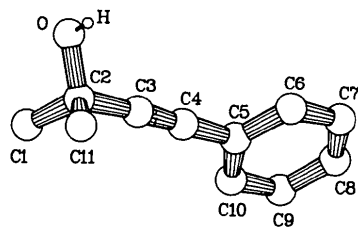


Fig. 1. Molecular structure with atom numbering of 2-methyl-4-phenyl-3-butyn-2-ol.

kept fixed except for the coordinates of the hydroxyl-H atom. The reflection 800 was omitted [ $\Delta F/\sigma(F) = 10.63$ ] and the refinement on  $F$  converged at  $R = 0.0486$ ,  $wR = 0.0599$ , where  $w = 1/\sigma^2(F)$ , and  $S = 4.3$ .  $|\Delta/\sigma| = 0.12$  (av.) and 0.48 (max.) for non-H-atom parameters; final difference electron density showed a maximum and a minimum of 0.14 and  $-0.21 \text{ e \AA}^{-3}$ . Scattering factors were taken from Cromer & Mann (1968) for C and O atoms and from Stewart, Davidson & Simpson (1965) for H atoms. Calculations were carried out on the Cyber 180-855 of the University of Utrecht Computer Center. The program package *EUCLID* (Spek, 1982) was used for the calculation of geometric data and preparation of illustrations.

**Discussion.** The final atomic parameters are given in Table 1.\* The conformation of the molecule and atom numbering is illustrated in Fig. 1. Bond distances and angles are listed in Table 2. This shows that the three molecules in the asymmetric unit exhibit similar bond

\* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43575 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) for non-H atoms and hydroxyl-H atoms with *e.s.d.'s* in parentheses, for the three independent molecules in the asymmetric unit

	(I)	(II)	(III)
O—H	0.77 (4)	0.86 (4)	0.88 (4)
O—C(2)	1.442 (4)	1.435 (5)	1.434 (5)
C(1)—C(2)	1.516 (5)	1.516 (6)	1.519 (6)
C(2)—C(11)	1.525 (6)	1.514 (5)	1.504 (6)
C(2)—C(3)	1.489 (5)	1.478 (6)	1.453 (5)
C(3)—C(4)	1.189 (5)	1.191 (6)	1.210 (5)
C(4)—C(5)	1.436 (5)	1.436 (6)	1.441 (5)
C(5)—C(10)	1.388 (5)	1.379 (5)	1.385 (6)
C(5)—C(6)	1.395 (5)	1.385 (5)	1.377 (5)
C(6)—C(7)	1.385 (6)	1.381 (6)	1.387 (6)
C(7)—C(8)	1.370 (6)	1.364 (6)	1.347 (8)
C(8)—C(9)	1.374 (5)	1.384 (6)	1.37 (1)
C(9)—C(10)	1.378 (5)	1.394 (6)	1.377 (8)
O—O'	2.751 (4)	2.797 (4)	2.757 (3)
C(2)—O—H	106 (3)	120 (2)	105 (2)
O—C(2)—C(1)	105.6 (3)	105.3 (3)	106.7 (3)
O—C(2)—C(3)	109.6 (3)	109.5 (3)	109.0 (3)
O—C(2)—C(11)	109.7 (3)	109.9 (3)	109.0 (3)
C(1)—C(2)—C(3)	108.7 (3)	109.4 (3)	109.3 (3)
C(1)—C(2)—C(11)	112.5 (3)	111.5 (3)	110.6 (4)
C(3)—C(2)—C(11)	110.6 (3)	111.1 (3)	112.0 (3)
C(2)—C(3)—C(4)	176.6 (4)	175.8 (4)	175.7 (4)
C(3)—C(4)—C(5)	176.0 (4)	176.3 (4)	177.8 (4)
C(4)—C(5)—C(10)	120.7 (3)	122.0 (3)	120.3 (3)
C(6)—C(5)—C(10)	118.9 (3)	119.1 (4)	119.2 (4)
C(4)—C(5)—C(6)	120.4 (3)	118.9 (3)	120.3 (4)
C(5)—C(6)—C(7)	119.7 (4)	120.5 (4)	119.3 (4)
C(6)—C(7)—C(8)	120.7 (3)	120.6 (4)	121.0 (5)
C(7)—C(8)—C(9)	120.0 (4)	119.6 (4)	120.4 (6)
C(8)—C(9)—C(10)	120.1 (4)	120.1 (4)	119.6 (5)
C(5)—C(10)—C(9)	120.6 (4)	120.0 (4)	120.4 (6)
H—O—C(2)—C(11)	39 (3)	43 (3)	48 (3)
O—H...O'	160 (4)	168 (4)	173 (4)
O—C(2)— $\phi$ -plane	49.4 (3)	39.7 (3)	35.3 (3)

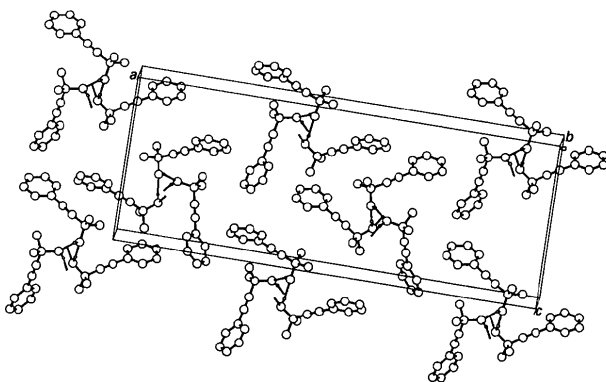


Fig. 2. Packing diagram viewed down **b**.

distances and angles which are within normal ranges, except the angle O—C(2)—C(1). In all molecules this angle [mean value 105.8 (1)°] deviates from the regular tetrahedral value. The only difference between the three molecules is the orientation of the phenyl ring relative to the C—O axis.

The molecular packing is illustrated in Fig. 2. This shows that the O atoms of the three molecules in the asymmetric unit are linked by hydrogen bonds producing spirals parallel to the **b** direction; molecule (II) is linked with a molecule (III) from a unit cell translated over **b**. The distances between O atoms involved in a hydrogen bond are similar with a mean value of

2.767 (2) Å; the angles are also within normal ranges. There are no intermolecular C—C distances less than 3.6 Å and the shortest H—H contact is 2.21 (4) Å. In each molecule the hydroxyl-H atom is positioned between C(3) and C(11), which results in a mean distance H(OH)—C(3) of 2.64 (4) Å. The position of the hydroxyl-H atoms is the same as that found in IR studies (Visser & Van der Maas, 1983).

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## Structure of a Chloral–Benzamidoxime Adduct

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**Abstract.** *O*-(2,2,2-Trichloro-1-hydroxyethyl)-benzamidoxime, C<sub>9</sub>H<sub>9</sub>Cl<sub>3</sub>N<sub>2</sub>O<sub>2</sub>, *M<sub>r</sub>* = 283.5, monoclinic, *P*2<sub>1</sub>/*a*, *a* = 11.881 (7), *b* = 9.338 (4), *c* = 12.098 (5) Å, β = 118.01 (4)°, *V* = 1185 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.59 g cm<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 7.6 cm<sup>-1</sup>, *F*(000) = 576, *T* ~ 173 K, *R* = 0.028 for 1537 unique observed reflections with *I* > σ(*I*). The molecule has the expected hemiacetal structure. It is nearly planar and the bond lengths and angles are normal. The trichloromethyl group is nearly tetra-

hedral. The molecules form dimers through O—H...N hydrogen bonds.

**Introduction.** A variety of evidence (Srivastava, Freire, Chaves, Beltrão & Carpenter, 1986, references therein) suggests that the reaction of an arylamidoxime with an aldehyde proceeds by attack of the acetaldehyde at the O atom to form an O-hemiacetal intermediate, rather than by attack at the amide N atom to form an N-hemiacetal. The postulated hemiacetal intermediates