

were fitted to difference electron density maxima (*HFIX* 137). The isotropic displacement parameters of the H atoms of the disordered methylene groups were set equal to  $1.2U_{eq}$  of the parent C atom, while those of the remaining H atoms were refined freely. Two reflections whose intensities were considered to be severe outliers were excluded during the refinement.

Data collection: *P3/F* (Nicolet XRD Corporation, 1987). Cell refinement: *P3/F*. Data reduction: locally modified *XTAPES* from *P3/F*. Program(s) used to solve structure: direct methods *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97*. Molecular graphics: *ORTEPII* (Johnson, 1976). 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: AB1528). Services for accessing these data are described at the back of the journal.

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## *meso*-1-[3-(1-Hydroxy-3-butynyl)phenyl]-3-butyn-1-ol†

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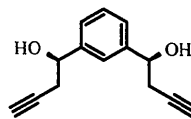
(Received 17 July 1997; accepted 11 November 1997)

## Abstract

The title compound, C<sub>14</sub>H<sub>14</sub>O<sub>2</sub>, crystallizes with two independent molecules which are very similar and differ mainly by their involvement in the hydrogen-bonding system.

## Comment

The title structure, (I), contains two independent molecules which are related by a pseudo-translation about vector  $(\frac{1}{2}, 0, \frac{1}{2})$ , leading to a pseudo-*B*-centered cell. This pseudo-translation is equivalent to a pseudo-inversion centre at  $(\frac{1}{4}, 0, \frac{1}{4})$  (Desiraju *et al.*, 1991). The independent molecules differ mainly in the relative orientation of the hydroxyl groups, which is a result of the different involvement of the molecules in the hydrogen-bonding system.



(I)

† Alternative name: *meso*-1,1'-(*m*-phenylene)bis(but-3-ynol).

The molecules form centrosymmetric dimers connected by O—H...O hydrogen bonds. The dimers are connected by additional O—H...O hydrogen bonds to infinite layers parallel to the crystallographic *ac* plane (Fig. 2).

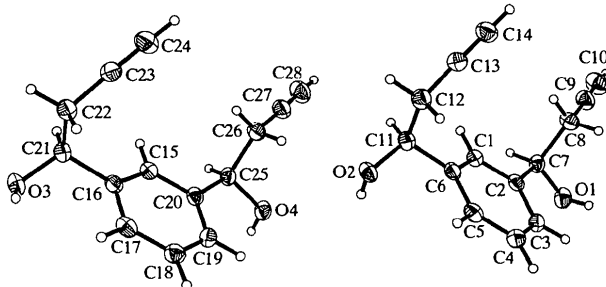


Fig. 1. The structures of the two independent molecules of (I) with 50% probability displacement ellipsoids.

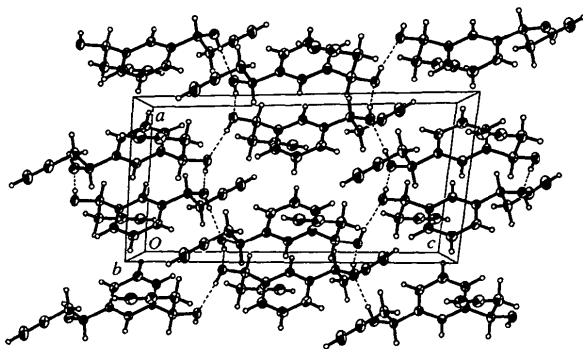


Fig. 2. The crystal packing of (I) showing the hydrogen-bonding system.

The two hydroxybutynyl groups of each molecule adopt different conformations: one C—C≡C group is *trans* oriented with respect to the hydroxyl group, the other is *trans* to the central benzene ring. The distances between the planes of the two benzene rings within the hydrogen-bonded dimers are 3.65 Å for molecule 1 and 3.66 Å for molecule 2, which is too long for any  $\pi$  interactions to be significant. The crystal packing shows no other short intra- or intermolecular contacts besides the observed hydrogen bonds.

## Experimental

Isophthalaldehyde (2.68 g, 20.0 mmol) was added to allenylmagnesium bromide (25.0 ml, 40.0 mmol, 1.60 M) in diethyl ether (25 ml). After the usual workup (Brandsma, 1988), the crude product was purified by column chromatography (hexane–ethyl acetate 1.6:1) and gave 2.96 g (13.8 mmol, 69%) of the title compound and its diastereomer as a highly

viscous oil. From this mixture of diastereomers, only the *C<sub>s</sub>* symmetrical isomer crystallized.

## Crystal data

$C_{14}H_{14}O_2$   
 $M_r = 214.27$   
 Triclinic  
 $P\bar{1}$   
 $a = 8.5162(12)$  Å  
 $b = 8.8856(14)$  Å  
 $c = 16.625(2)$  Å  
 $\alpha = 81.103(11)^\circ$   
 $\beta = 82.321(14)^\circ$   
 $\gamma = 71.925(11)^\circ$   
 $V = 1176.6(3)$  Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.209$  Mg m<sup>-3</sup>  
 $D_m$  not measured

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073$  Å  
 Cell parameters from 186 reflections  
 $\theta = 0-23^\circ$   
 $\mu = 0.074$  mm<sup>-1</sup>  
 $T = 133$  K  
 Prismatic  
 $0.70 \times 0.44 \times 0.24$  mm  
 Colorless

## Data collection

Siemens SMART diffractometer  
 $\omega$  scans  
 Absorption correction: empirical (SADABS; Sheldrick, 1996b)  
 $T_{\min} = 0.823$ ,  $T_{\max} = 1.000$   
 17 357 measured reflections  
 5234 independent reflections

4739 reflections with  $I > 0$   
 $R_{\text{int}} = 0.018$   
 $\theta_{\max} = 28.78^\circ$   
 $h = -11 \rightarrow 11$   
 $k = -11 \rightarrow 11$   
 $l = -20 \rightarrow 21$   
 218 standard reflections  
 frequency: 540 min  
 intensity decay: none

## Refinement

Refinement on  $F$   
 $R = 0.060$   
 $wR = 0.074$   
 $S = 2.585$   
 4739 reflections  
 401 parameters  
 H atoms refined isotropically  
 $w = 4F_o^2/[\sigma^2(F_o^2) + 0.0009F_o^4]$

$(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.56$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.13$  e Å<sup>-3</sup>  
 Extinction correction: none  
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

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

D—H...A	D—H	H...A	D...A	D—H...A
O1—H01...O4 <sup>i</sup>	0.81 (1)	1.85 (1)	2.662 (1)	175 (2)
O2—H02...O1 <sup>ii</sup>	0.82 (2)	1.82 (2)	2.641 (1)	177 (1)
O3—H03...O2	0.81 (1)	1.90 (1)	2.696 (1)	171 (1)
O4—H04...O3 <sup>iii</sup>	0.85 (2)	1.81 (2)	2.659 (1)	170 (1)

Symmetry codes: (i)  $x, y, z-1$ ; (ii)  $1-x, 1-y, -z$ ; (iii)  $2-x, 1-y, 1-z$ .

H atoms were located from a difference synthesis and were refined with isotropic displacement parameters.

Data collection: SMART (Siemens, 1995). Cell refinement: SMART. Data reduction: SAINT (Siemens, 1995). Program(s) used to solve structure: direct methods (SHELXTL; Sheldrick, 1996a). Program(s) used to refine structure: LSFM in MolEN (Fair, 1990). Molecular graphics: XP in SHELXTL. Software used to prepare material for publication: MolEN.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1257). Services for accessing these data are described at the back of the journal.

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## A *gem*-Dichloro[4.3.1]propellane and a *gem*-Dichloro[5.3.1]propellenone

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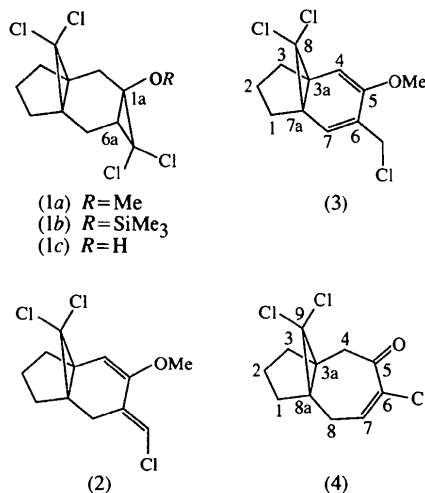
### Abstract

X-ray analyses have established the structures of (3 $\alpha$ ,7 $\alpha$ )-6-chloromethyl-8,8-dichloro-2,3-dihydro-5-methoxy-3 $\alpha$ ,7 $\alpha$ -methano-1*H*-indene, C<sub>12</sub>H<sub>13</sub>Cl<sub>3</sub>O, and (3 $\alpha$ ,8 $\alpha$ )-6,9,9-trichloro-2,3,5,8-tetrahydro-1*H*,4*H*-3 $\alpha$ ,8 $\alpha$ -methanoazulen-5-one, C<sub>11</sub>H<sub>11</sub>Cl<sub>3</sub>O, which have resulted from different modes of cyclopropane ring cleavage within the framework of two closely related *gem*-dichloro[4.3.1]propellanes.

### Comment

We have been developing new methods for the syntheses of *gem*-dihalogen[5.3.1]propellanes because of their utility in the construction of novel analogues of the anti-cancer agent Taxol<sup>TM</sup> (Banwell *et al.*, 1995). In this respect, we have studied the response of compounds (1*a*) and (1*b*) to various reaction conditions which might have been expected to effect the cleavage of the C1 $\alpha$ —C6 $\alpha$  bond, thereby providing the desired propellanes.

However, we have shown (Banwell *et al.*, 1994) that when compound (1*a*) is treated with a dilute solution of potassium *tert*-butoxide in tetrahydrofuran, C1 $\alpha$ —C6 $\alpha$  bond cleavage is observed and the major product of the reaction is compound (2). This ring-cleavage product was exceptionally unstable and, on standing, the compound rapidly converted into the double-bond isomer (3). In contrast, reaction of compound (1*b*) with silver acetate resulted in the formation of the desired type of ring-cleavage product, *viz.* the *gem*-dichloro-[5.3.1]propellenone (4), although this was accompanied by significant quantities of the alcohol (1*c*) (Banwell & Pallich, 1997). In view of the different modes of ring cleavage possible within the framework of (1), we have sought to characterize unequivocally the products of such processes in order to identify spectroscopic parameters which would allow ready structure identification. As part of this effort, we now present the results of the X-ray analyses of compounds (3) and (4).



The cyclopentane ring in each structure adopts a C2-envelope conformation with pseudo-rotation parameters (Altona *et al.*, 1968)  $\Delta$  37.6 and  $\varphi_m$  9.0° for compound (3), and  $\Delta$  33.4 and  $\varphi_m$  13.6° for compound (4). The cyclohexadiene ring atoms in (3) are coplanar to within 0.019 (2) Å (r.m.s. deviation 0.014 Å). The conformation of (4) is similar to the conformation of the propellanone system in a benzannulated [5.3.1]propellanone (Mackay *et al.*, 1997). The cycloheptene ring is a fairly regular boat, as indicated by the conformational asymmetry parameter (Duax & Norton, 1975)  $\Delta C_s^{3a,8a}$  9.6°. Atoms C4, C3 $\alpha$ , C8 $\alpha$  and C8 are coplanar (r.m.s. deviation 0.009 Å) to within 0.011 (3) Å, and atoms C4, C5, C6 and C7 are coplanar (r.m.s. deviation 0.04 Å) to within 0.04 (1) Å, with the interplanar angle being 122.7 (2)°. All bond lengths and angles are similar to those found in comparable structures.