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Hydrogen-bonded networks in 1-(4-methoxyphenyl)-2,2-dimethylpropan-1-ol

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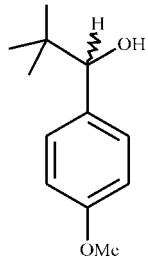
The asymmetric unit of the title compound, $C_{12}H_{18}O_2$, contains two independent molecules. They differ only slightly in conformation but form completely different intermolecular hydrogen-bonded arrays. One molecule exhibits disorder in the hydroxy group region, but this does not influence the formation of hydrogen bonds. The bulky *tert*-butyl group on one side of the carbinol C atom and the benzene ring on the other side promote the formation of discrete dimeric motifs *via* hydrogen-bridged hydroxy groups. Dimers are further joined by strong hydroxy–methoxy O—H···O bonds to form chains with dangling alcohol groups. Weaker intermolecular C—H···O interactions mediate the formation of a two-dimensional network.

Comment

Three different basic motifs have been described for the hydrogen-bonded networks found in crystals of mono-alcohols (Brock & Duncan, 1994). Two of the most important factors on which the formation of hydrogen-bonded systems depend are the number and size of the groups connected to the carbinol C atom. Primary mono-alcohols tend to form extended chain structures which contain ···O—H···O—H··· bond sequences (Taylor & Macrae, 2001). Secondary mono-alcohols tend to form chains or rings, and steric effects determine which motif is formed. Hence, secondary mono-alcohols with bulky groups connected to the carbinol C atom usually exhibit a finite motif, *i.e.* ring structures, instead of chains (McGregor *et al.*, 2006). As reported by Taylor & Macrae (2001), tertiary mono-alcohols either form finite motifs *via* O—H···O hydrogen bonds or do not exhibit any O—H···O hydrogen bonding. Furthermore, there is a third possibility, namely the formation of dimers: Brock & Duncan (1994) postulate that dimers form when an extended hydrogen-bonded structure is precluded. Closed dimers are said to be less likely to form than those with a dangling H atom and a free acceptor (Jeffrey & Saenger, 1991; Schweizer *et al.*, 1981). The title compound, (I), is a further interesting example, from the point of view of systematization of hydrogen-bonded networks displayed in mono-alcohols, of a secondary mono-alcohol with two bulky substituents at the carbinol C atom.



(I)

Since no separation of enantiomers had been undertaken after synthesis, the crystal examined was obtained from a racemic mixture. There are two independent molecules in the asymmetric unit of (I), labelled *A* and *B*. The only chiral centres of the molecules of (I) are at the carbinol C atoms, *i.e.* atoms C7 and C27. In the hydroxy group region of molecule *B*, disorder was identified and modelled as a superposition of two fragments, one defined by atoms C27, H27, O21 and H21, and the other by atoms C27*A*, H27*A*, O21*A* and H21*A*. Depending on which of the components is considered, the resulting conformation of molecule *B* is either *S* or *R*. This is reflected in the different values of the appropriate torsion angles (Table 1). In the following discussion, only the geometric parameters of the major component, *i.e.* that with an occupancy factor of 0.787 (3), will be presented.

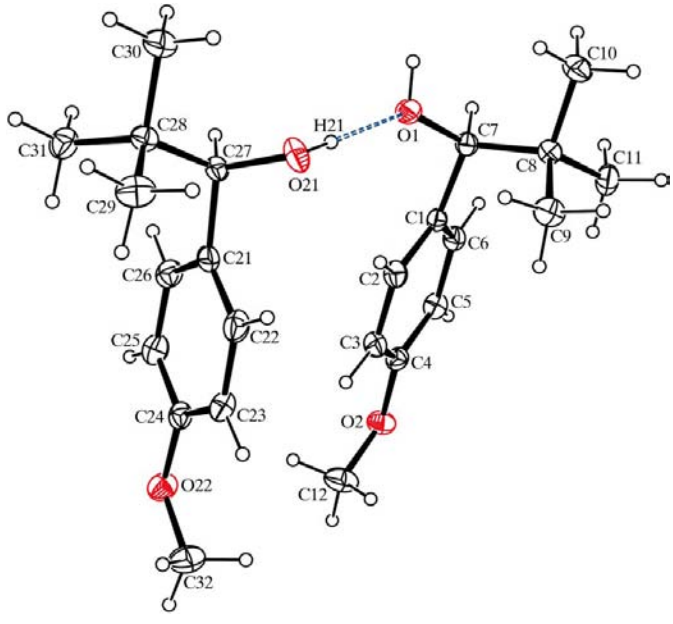


Figure 1
A plot of the two independent molecules of (I), *A* (right) and *B* (left), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The intermolecular hydrogen bond is indicated by a dashed line. The minor disorder component of molecule *B* (see *Comment*) has been omitted for clarity.

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The geometric parameters of molecules *A* and *B* are very similar and the most significant differences between the two unique molecules of (I) are found in the hydroxy and methoxy group regions (Table 1). For example, in molecule *A* the C1—C7 bond of 1.5138 (19) Å is about 0.011 (3) Å longer than C21—C27 in molecule *B*. These differences might be caused by the disorder. However, the fact that the O atom of the hydroxy group of molecule *A* forms two strong O—H···O hydrogen bonds may also be significant. The different strength of the intermolecular interactions in which atoms O2 and O22 participate (Table 2) may also be a reason for the small differences between the two unique molecules in the methoxy group region. Moreover, the anisotropic displacement coefficients of the C atoms which constitute the benzene ring of molecule *B* are larger than those of the corresponding atoms of molecule *A*.

The title compound exhibits a dimeric structure with graph-set notation *D* (Etter, 1990) formed by hydroxy–hydroxy O—H···O hydrogen bonding (Table 2) which links an *A* molecule and a *B* molecule (Fig. 1). This motif occurs irrespective of which disorder component is considered. Within each dimer, the major component of molecule *B* has the opposite configuration to that of molecule *A*. Although two bulky groups attached to the carbinol C atom hinder the association of more than two molecules *via* hydroxy–hydroxy O—H···O bonds, the O atoms from the methoxy groups enable the dimeric structure to form other more complex supramolecular networks. The geometric parameters of the hydrogen bonds which are present in the crystal structure of (I) are shown in Table 2.

The dimers are assembled into extended chains with dangling *B* molecules. This results from the fact that the dimers are not closed. Each molecule *A* is linked with two other symmetry-related *A* molecules by a strong hydroxy–methoxy O—H···O hydrogen bond (Table 2). These interactions link the dimers into a chain along the *c* axis (Fig. 2). This chain can be designated by the first-level graph-set notation $N_1 = C(8)[D]$ (Etter *et al.*, 1990). Another way of describing this chain is with the $p2_1$ rod group characterized by a 2_1 screw axis along the *c* axis (*International Tables for Crystallography*, 2002).

The chains further self-organize through weak C—H···O interactions to generate a layer. This is indicated by the geometry of the bond, as well as by the fact that the H atom is directed towards the O22 lone electron pair (Steiner, 2002). Within a layer, every *B* molecule is linked with two other *B* molecules to form a chain. The H31*C*···O22^{ii} distance is 2.53 Å [symmetry code: (ii) $-x + \frac{3}{2}, y, z + \frac{1}{2}$] and the C31—H31*C*···O22^{ii} angle is 163°. The supramolecular structure which results from these interactions is a layer with $pb2_1a$ symmetry (Fig. 2) (*International Tables for Crystallography*, 2002). These supramolecular layers are parallel to (010), hence the nonperiodic direction is that parallel to *b*. The basis vectors of the layer group, a_L and b_L, are consistent with the original *a* and *c* basis vectors, respectively. Within a layer, each chain is related to the adjacent chain by an *a*-glide plane.

In summary, the bulky *tert*-butyl group and the benzene ring on the carbinol C atom of (I) induce steric hindrance which effectively precludes the formation of a chain-like structure with hydroxy–hydroxy ···O—H···O sequences. Instead, molecules form dimers with a dangling H atom, and their open structure enables the dimers to arrange themselves into a hydrogen-bonded chain structure *via* interactions of methoxy O atoms with dangling H atoms.

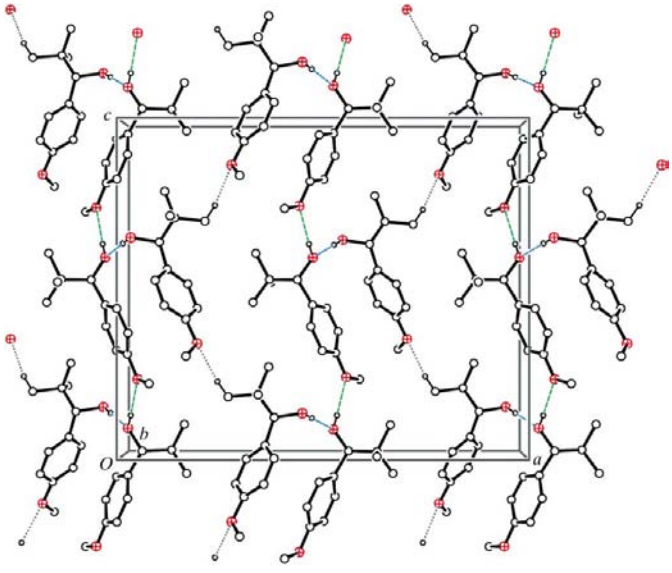

Figure 2
A projection of the crystal structure of (I) along the *b* axis, showing the layer of molecules linked by O—H···O (dashed lines) and C—H···O (dotted lines) interactions. H atoms not involved in intermolecular contacts have been omitted for clarity.

Experimental

The title compound was synthesized by the reduction of 1-(4-methoxyphenyl)-2,2-dimethyl-1-propanone with sodium borohydride. Into a methanol solution of 1-(4-methoxyphenyl)-2,2-dimethylpropan-1-one (7.7 g), a methanol solution of sodium borohydride was added dropwise at room temperature. The mixture was stirred for 6 h, hydrolyzed and the product extracted with *n*-hexane. The product, (I), was recrystallized from *n*-hexane (yield 5.8 g, 75%; m.p. 313–314 K). Prismatic colourless crystals suitable for diffraction study were obtained by recrystallization from toluene.

Crystal data

$C_{12}H_{18}O_2$
$M_r = 194.26$
Orthorhombic, $Pca2_1$
$a = 20.8868$ (6) Å
$b = 6.00175$ (18) Å
$c = 17.3531$ (5) Å
$V = 2175.34$ (11) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.08$ mm^{-1}
$T = 173$ (2) K
0.53 × 0.37 × 0.15 mm

Data collection

Oxford Diffraction KM-4 CCD area-detector diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2005)
$T_{min} = 0.956$, $T_{max} = 0.988$
33345 measured reflections
2812 independent reflections
2553 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	9 restraints
$wR(F^2) = 0.073$	H-atom parameters constrained
$S = 1.09$	$\Delta\rho_{max} = 0.20$ e Å^{-3}
2812 reflections	$\Delta\rho_{min} = -0.18$ e Å^{-3}
278 parameters	

Table 1
Selected geometric parameters (Å, °).

O1—C7	1.4428 (17)	O21—C27	1.437 (2)
C1—C7	1.5138 (19)	C21—C27	1.525 (2)
O2—C4	1.3809 (17)	O22—C24	1.3727 (18)
O2—C12	1.4294 (19)	O22—C32	1.4198 (19)
O21—C27—C21—C22	37.5 (2)	O21*A*—C27*A*—C21—C22	146.7 (3)
O21—C27—C21—C26	−144.65 (15)	O21*A*—C27*A*—C21—C26	−37.6 (5)
O21—C27—C28—C29	−64.98 (19)	O21*A*—C27*A*—C28—C29	−167.7 (6)
O21—C27—C28—C30	55.7 (2)	O21*A*—C27*A*—C28—C30	−54.6 (7)
O21—C27—C28—C31	173.00 (15)	O21*A*—C27*A*—C28—C31	72.8 (7)

Table 2
Hydrogen-bond and short-contact geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O21—H21···O1	0.84	2.04	2.883 (2)	179
O1—H1···O2^{i}	0.84	2.29	3.134 (2)	178
C31—H31*C*···O22^{ii}	0.98	2.53	3.481 (2)	163

Symmetry codes: (i) $-x+1, -y, z+\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y, z+\frac{1}{2}$.

The hydroxy group in molecule *B* is disordered. It was resolved by finding alternative positions from the difference Fourier map, and was subsequently refined over two positions with an occupancy of 0.787 (3) for the major conformer. To assist in the refinement process, both the C—C and C—O bonds in the disordered fragment were restrained to be equal, and displacement parameters on adjacent C atoms were restrained to be similar. Due to the absence of significant anomalous scattering effects, the measured Friedel pairs were merged. H atoms were positioned geometrically and constrained to ride on their parent atoms, with O—H = 0.84 Å and U_{iso}(H) = $1.5U_{eq}$(O) for the hydroxy group, and with C—H = 0.95–1.00 Å and U_{iso}(H) = $1.2U_{eq}$(C) or $1.5U_{eq}$(methyl C).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Version 1.08; Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data and an additional figure for this paper are available from the IUCr electronic archives (Reference: BM3037). Services for accessing these data are described at the back of the journal.

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