

**(2*RS*)-5,6:7,8-Dibenzobicyclo[2.2.2]-
octan-2-ol**Kenneth W. Muir,^{a*} David G. Morris^a and Karl S. Ryder^b^aDepartment of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland, and ^bDepartment of Chemistry, Loughborough University, Loughborough LE11 3TU, England

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Received 7 February 2003

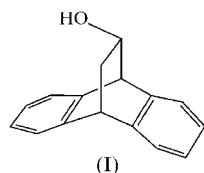
Accepted 27 March 2003

Online 10 May 2003

The racemic form of the title secondary monoalcohol, C₁₆H₁₄O, forms crystals in which the molecules are linked into chains by hydrogen bonding. The chain architecture is unusual; adjacent molecules are related pseudosymmetrically, by either a pseudo-diad or a pseudo-glide plane, while alternate molecules are related exactly by a crystallographic glide plane.

Comment

Our interest in the modes of hydrogen bonding adopted by polycyclic monoalcohols (Morris *et al.*, 2001, 2002) has led us to determine the crystal structure of the racemic form of the secondary alcohol (I) (Fig. 1 and Table 1). Monoalcohols in general show a preference for trigonal and tetragonal space groups and their crystal structures frequently contain more than one crystallographically independent molecule (*i.e.* $Z' > 1$) (Brock & Duncan, 1994). These preferences are thought to arise from steric constraints in forming hydrogen bonds. Consistent with this view, we have recently shown (Fraile *et al.*, 2003) that tertiary monoalcohols display these preferences in a particularly pronounced fashion.

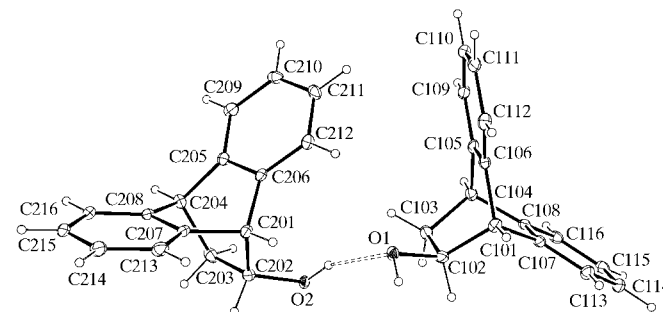


The polycyclic and sterically hindered secondary alcohol (I) crystallizes in the non-centrosymmetric but non-chiral space group *Pca*2₁ (No. 29) with $Z' = 2$. Chains of molecules running parallel to the short *c* axis are linked by conventional hydrogen bonds (Table 2, and Figs. 2 and 3). In itself, this is not an unusual arrangement in homomolecular monoalcohol crystal structures (Brock & Duncan, 1994). However, the translationally repeated unit of the chain, consisting of four

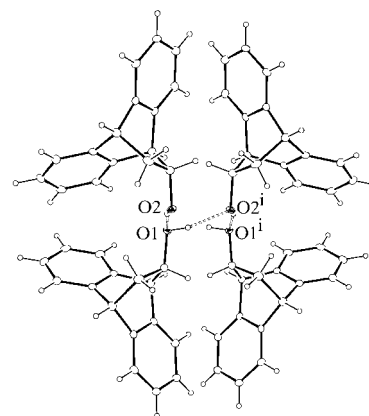
molecules related by an exact *c*-glide plane normal to *a* and by additional pseudosymmetry, is unusual and merits discussion.

The asymmetric unit we have chosen contains two enantiomeric molecules, and the coordinates of the atoms of molecule 2 are approximately related to those of the corresponding atoms of molecule 1 by the pseudosymmetric operation $(x, \frac{1}{2} - y, \frac{1}{2} + z - \delta)$; δ is 0.01–0.09 for individual C atoms, rising to 0.13 for the two O atoms, and its mean value is 0.038. If δ were 0, this operation would correspond exactly to that of a *c*-glide plane normal to the *b* axis, and the space group would become *Iba*2 (No. 45). The pseudosymmetry causes the *hkl* reflections to be systematically weak when $h + k + l = 2n + 1$, this pseudo-absence being especially pronounced for the *hk0* zone.

In each chain, the unit repeated by translation comprises four molecules linked by $\cdots\text{H}-\text{O}1^i\cdots\text{H}-\text{O}2^i\cdots\text{H}-\text{O}1\cdots\text{H}-\text{O}2\cdots$ hydrogen bonds. The symmetry operation [*viz.* (i) $\frac{3}{2} - x, y, z - \frac{1}{2}$] defines a *c*-glide plane normal to *a*, and the molecule containing O1 is related to that containing O2 and O2ⁱ by pseudo-operations approximating respectively to a *c*-glide normal to *b* (see above) and to a diad axis parallel to *c* ($\frac{3}{2} - x, \frac{1}{2} - y, z - \delta$). Thus the chain sequence is $\cdots R S S R \cdots$, where *R* and *S* indicate the configuration at C_nO2 ($n = 1$ or 2) in successive molecules. The hydrogen bonds in each chain

**Figure 1**

A view of the two independent molecules of (I), showing displacement ellipsoids at the 20% probability level. Dashed lines represent O—H...O hydrogen bonds. For clarity, the minor disorder sites of the two O atoms are not shown.

**Figure 2**

One of the hydrogen-bonded chains, viewed along the *c* axis. The *a* axis runs from left to right and the *b* axis points upwards in the plane of the drawing. [Symmetry code: (i) $\frac{3}{2} - x, y, z - \frac{1}{2}$]

therefore connect pairs of molecules that may be of the same, or of opposite, chiralities.

The tendency for monoalcohols to crystallize with two or more molecules in the asymmetric unit is well established, and this feature of the structure of (I) is therefore not surprising. However, in their survey of hydrogen-bonding motifs adopted by monoalcohols, Brock & Duncan (1994) found only five out of 55 structures in which four molecules make up the translational repeat unit. Of these, only one, namely ethanol, resembles (I) in generating the chain by application of a glide operation to two independent molecules. However, the two independent ethanol molecules are not pseudosymmetrically related (Jönsson, 1976).

The two crystallographically independent molecules of (I) are structurally nearly identical. A least-squares fit of the positions of corresponding C or O atoms gives an r.m.s. deviation, Δ , of 0.057 Å, with the O atoms showing the largest individual discrepancy [0.174 (5) Å]. Furthermore, for bond lengths and angles, the r.m.s. Δ values are, respectively, 0.011 Å and 1.1° (PLATON; Spek, 2003). Table 1 lists the distances and angles in the CH(OH)—CH bridging units where the differences between the two molecules are greatest. Though complicated by minor disorder of the O atoms (see below), these differences are probably a consequence of the differing orientations of the OH bonds [Cn01—Cn02—On—H = −85 (4) and 8 (4)° for $n = 1$ and 2, respectively]. This result illustrates the factors that cause sterically hindered alcohols to crystallize with $Z' > 1$; a pseudosymmetric relationship between molecules 1 and 2 permits differing hydrogen-bond orientations, which would be precluded if molecules 1 and 2 were related exactly by space-group symmetry. Each molecule contains two C_8 units (defined by an aromatic ring plus the two C atoms directly attached to it), which are coplanar to within 0.05 Å and which define dihedral angles of 53.4 (1) and 52.8 (1)°. The mean $C_{ar}-C_{ar}$ and $C_{ar}-C_{sp^3}$ bond lengths are 1.391 and 1.516 Å, and their respective ranges are 1.380 (6)–1.405 (5) and 1.508 (4)–1.526 (4) Å. The atomic U^{ij} values are moderately well reproduced by a TLS

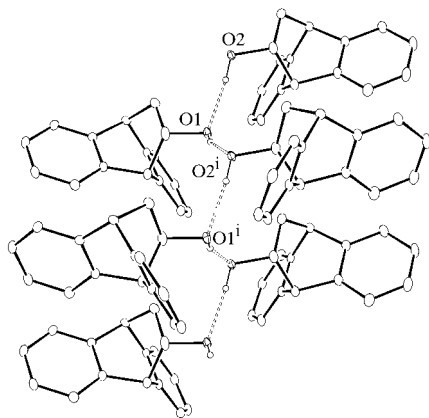


Figure 3
A hydrogen-bonded chain, viewed along the a axis. The c axis points upwards and the b axis runs horizontally from left to right. H atoms not involved in hydrogen bonding have been omitted. The symmetry code is as in Fig. 1.

analysis [Schomaker & Trueblood, 1968; $R2 = (\Delta U^2/U^2)^{1/2} = 0.16$ and 0.14 for individual molecules]. The worst discrepancy in the Hirshfeld (1976) rigid-bond test is the value of ΔU for C202—C203 [0.008 (2) Å²].

Experimental

The title compound was first synthesized by Wawzonek & Hallum (1953). The sample used for the present analysis was provided by Professor Marie-Joséphe Brienne, Collège de France, Paris.

Crystal data

$C_{16}H_{14}O$	Mo $K\alpha$ radiation
$M_r = 222.27$	Cell parameters from 2967 reflections
Orthorhombic, $Pca2_1$	$\theta = 2.9$ – 27.5°
$a = 14.3719$ (3) Å	$\mu = 0.08$ mm ^{−1}
$b = 22.8650$ (6) Å	$T = 100$ (2) K
$c = 7.0703$ (1) Å	Needle, colourless
$V = 2323.40$ (8) Å ³	0.40 × 0.17 × 0.12 mm
$Z = 8$	
$D_x = 1.271$ Mg m ^{−3}	

Data collection

Nonius KappaCCD area-detector diffractometer	$R_{int} = 0.057$
Thick-slice scans	$\theta_{max} = 27.5^\circ$
17 231 measured reflections	$h = 0 \rightarrow 18$
2863 independent reflections	$k = 0 \rightarrow 29$
2385 reflections with $I > 2\sigma(I)$	$l = 0 \rightarrow 9$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + 1.24P]$
$R(F) = 0.055$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.141$	$(\Delta/\sigma)_{max} = 0$
$S = 1.03$	$\Delta\rho_{max} = 0.34$ e Å ^{−3}
2863 reflections	$\Delta\rho_{min} = -0.24$ e Å ^{−3}
324 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (Å, °).

C101—C102	1.568 (5)	C201—C202	1.533 (5)
C102—O1	1.424 (4)	C202—O2	1.445 (4)
C102—C103	1.531 (5)	C202—C203	1.538 (5)
C103—C104	1.548 (4)	C203—C204	1.564 (4)
O1—C102—C103	107.5 (3)	O2—C202—C201	111.1 (3)
O1—C102—C101	114.7 (3)	O2—C202—C203	111.4 (3)
C103—C102—C101	109.2 (2)	C201—C202—C203	108.9 (2)
O1—C102—C103—C104	133.8 (3)	O2—C202—C203—C204	−126.0 (3)
C101—C102—C103—C104	8.8 (3)	C201—C202—C203—C204	−3.2 (3)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots O2 ⁱ	0.87 (5)	1.91 (5)	2.761 (4)	165 (4)
O2—H2 \cdots O1	0.87 (7)	1.94 (7)	2.768 (4)	159 (5)

Symmetry code: (i) $\frac{3}{2} - x, y, z - \frac{1}{2}$.

The absolute structure has not been determined experimentally. Our coordinates and drawings arbitrarily show *S* and *R* configurations at C102 and C202, respectively. All H atoms appeared in difference syntheses in stereochemically acceptable positions. In the final calculations, hydroxyl H atoms were refined freely. The other H atoms were placed in positions calculated using the HFIX option in *SHELXL97* (Sheldrick, 1997) and then refined riding on their parent C atoms, with C–H distances of 1.00, 0.99 and 0.95 Å, respectively, for H atoms on methine, methylene and aromatic C atoms, and $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$. At a late stage in the analysis ($R1 = 0.068$ for observed data and $wR = 0.180$ for all data), two peaks of $0.8 \text{ e } \text{Å}^{-3}$ with coordinates derived from those of O1 and O2 by inversion through the origin were found in the difference map. Accordingly, O1 and O2 were assumed to be disordered over two sites with occupancies of α and $1 - \alpha$ [$\alpha = 0.856(8)$] after refinement. This disorder model led to significantly lower agreement indices and a featureless difference synthesis. There is no indication that disorder affects any of the C atoms.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

We thank Professor Marie-Joséphe Brienne for the gift of the crystals of the title compound, and the EPSRC and Glasgow University for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1526). Services for accessing these data are described at the back of the journal.

References

- Brock, C. P. & Duncan, L. L. (1994). *Chem. Mater.* **6**, 1307–1312.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Fraile, A. G., Morris, D. G., Martinez, A. G., de la Moya Cerero, S., Muir, K. W., Ryder, K. S. & Teso Vilara, E. (2003). *J. Org. Biomol. Chem.* **1**, 700–704.
Hirshfeld, F. L. (1976). *Acta Cryst.* **A32**, 239–244.
Jönsson, P.-G. (1976). *Acta Cryst.* **B32**, 232–236.
Morris, D. G., Muir, K. W. & Ryder, K. S. (2002). *Acta Cryst.* **C58**, o615–o618.
Morris, D. G., Ryder, K. S., Walker, S., Muir, K. W., Hix, G. B. & Maclean, E. J. (2001). *Tetrahedron Lett.* **42**, 319–322.
Nonius (1997–2000). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Wawzonek, S. & Hallum, J. V. (1953). *J. Org. Chem.* **18**, 288–291.