

1,21-Henicosanediol

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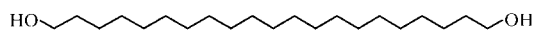
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In the molecular structure of the title compound, C₂₁H₄₄O₂, the hydrocarbon skeleton has an all-*trans* conformation. One of the terminal hydroxyl groups is also *trans* with respect to the skeleton, while the other is *gauche*. In the crystal structure, the molecules lie parallel to the *b* axis, forming layers with a thickness of *b*/2. The packing is similar to that in the smectic A phase of liquid crystals. These features are similar to those of the homologues with an odd number of C atoms, but different from those with an even number.

Comment

Long-chain aliphatic compounds tend to have a simple *trans* zigzag straight hydrocarbon chain skeleton. Thus, these compounds have been studied as basic models of polymers. In addition, the molecular shape can be regarded as rod-like, which is one of the typical features of liquid crystalline molecules. The molecules form a layered structure similar to the smectic phase of liquid crystals. As a result of this, these compounds have recently attracted attention not only as model compounds for polymers, but also as model compounds of liquid crystals.

Many researchers have studied the crystal structures of long-chain compounds since the early work on *n*-paraffins by Müller (1928). Recently, the present authors reported phase-transition phenomena of normal long-chain α,ω -alkanediols from C₁₃ to C₂₄ (Ogawa & Nakamura, 1999) and we have also reported the crystal structures of seven α,ω -alkanediols, namely 1,10-decanediol (Nakamura & Sato, 1999a), 1,11-undecanediol (Nakamura *et al.*, 1999), 1,12-dodecanediol (Nakamura & Setodoi, 1997), 1,13-tridecanediol (Nakamura *et al.*, 1997), 1,14-tetradecanediol (Nakamura & Sato, 1999b),



(I)

1,15-pentadecanediol (Nakamura *et al.*, 2000) and 1,16-hexadecanediol (Nakamura & Yamamoto, 1994). The molecular and crystal structures of 1,21-henicosanediol, (I), the chain

length of which is the longest we have studied, are described in this paper.

The molecular structure of (I) is shown in Fig. 1(a). The hydrocarbon skeleton has an all-*trans* conformation. The C—C distances are in the range 1.499 (3)–1.523 (4) Å and the C—C—C angles in the range 112.3 (3)–114.8 (3)°. The terminal C21—O2 bond is also *trans* with respect to the skeleton [O2—C21—C20—C19 torsion angle $-179.6(3)^\circ$], while the other terminal C1—O1 bond is *gauche* [O1—C1—C2—C3 torsion angle $65.1(5)^\circ$]. In the crystal structure of (I), the molecules lie parallel to the *b* axis, forming layers with a thickness of *b*/2, and they are arranged in an antiparallel fashion along the *a* axis within these layers, as shown in Fig. 1(b). The packing is similar to that in the smectic A phase of liquid crystals. The molecules also form two different types of

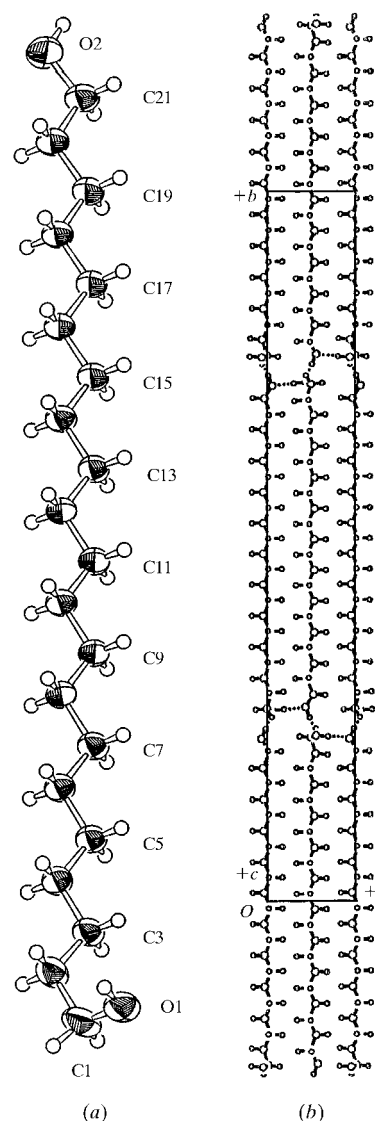


Figure 1

(a) An ORTEP (Johnson, 1976) view of the molecule of (I) showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. (b) The projection of the crystal structure of (I) along the *c* axis. Dotted lines indicate the hydrogen bonding.

hydrogen bond, *i.e.* interlayer and intralayer hydrogen bonds, with O1...O2 distances of 2.717 (3) and 2.778 (4) Å, respectively. These features are similar to those already reported for the homologues with an odd number of C atoms.

We have reported previously that the molecular and crystal structures of the homologues with an even number of C atoms (1,10-decanediol, 1,12-dodecanediol, 1,14-tetradecanediol and 1,16-hexadecanediol) are different from those of the homologues with an odd number of C atoms. In the molecular structures of long-chain α,ω -alkanediols with an even number of C atoms, the hydrocarbon skeleton has the all-*trans* conformation and both terminal C—O bonds are also *trans*. In the crystal structures of long-chain α,ω -alkanediols with an even number of C atoms, the centrosymmetric molecules form layers in which the long axis of the molecule is inclined to the layer plane and they are arranged in a zigzag fashion among the neighbouring layers to give a herring-bone motif. The packing is similar to that in the smectic C phase of liquid crystals. This herring-bone motif was also observed in 1,12-dibromododecane (Kupke *et al.*, 1981), 1,16-dibromohexadecane (Kobayashi *et al.*, 1995) and 1,18-dibromooctadecane (Nakamura *et al.*, 1993). In these structures, only interlayer hydrogen bonds are found.

Experimental

The title compound was synthesized as described previously by Ogawa & Nakamura (1999). The diacid was converted to the methyl ester by conventional procedures and the pure dimethyl ester was reduced to 1,21-henicosanediol, (I), using LiAlH₄. The single crystal of (I) used for X-ray analysis was grown by very slow evaporation from solution in a mixture of methanol, ethyl acetate and *n*-heptane (1:1:2).

Crystal data

C ₂₁ H ₄₄ O ₂	Cu K α radiation
$M_r = 328.58$	Cell parameters from 24 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 9.2\text{--}13.9^\circ$
$a = 7.247$ (4) Å	$\mu = 0.477$ mm ⁻¹
$b = 57.940$ (3) Å	$T = 296$ (2) K
$c = 5.048$ (4) Å	Plate, colourless
$V = 2119$ (1) Å ³	$0.50 \times 0.50 \times 0.05$ mm
$Z = 4$	
$D_x = 1.029$ Mg m ⁻³	

Data collection

Rigaku AFC-5R diffractometer	$R_{\text{int}} = 0.022$
ω scans	$\theta_{\text{max}} = 70.57^\circ$
Absorption correction: ψ scan	$h = -2 \rightarrow 8$
(North <i>et al.</i> , 1968)	$k = 0 \rightarrow 70$
$T_{\text{min}} = 0.825$, $T_{\text{max}} = 0.999$	$l = -1 \rightarrow 6$
3723 measured reflections	3 standard reflections
2355 independent reflections	every 150 reflections
1583 reflections with $I > 2\sigma(I)$	intensity decay: 4%

Refinement

Refinement on F	H-atom parameters constrained
$R = 0.051$	$w = 1/[\sigma^2(F_o) + 0.00106 F_o ^2]$
$wR = 0.083$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.896$	$\Delta\rho_{\text{max}} = 0.11$ e Å ⁻³
1583 reflections	$\Delta\rho_{\text{min}} = -0.22$ e Å ⁻³
208 parameters	

Table 1

Selected geometric parameters (Å, °).

O1—C1	1.424 (4)	O2—C21	1.417 (3)
O1—C1—C2	112.0 (3)	O2—C21—C20	108.9 (3)
O1—C1—C2—C3	65.1 (5)	O2—C21—C20—C19	-179.6 (3)

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); data reduction: *TEXSAN* (Molecular Structure Corporation, 1995); program(s) used to solve structure: *SAPI91* (Fan, 1991); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1020). Services for accessing these data are described at the back of the journal.

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