

Tricosane-1,23-diol

Naotake Nakamura,^{a*} Kenjiro Uno^a and Yoshihiro Ogawa^b^aDepartment of Applied Chemistry, Faculty of Science and Engineering, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577, Japan, and ^bDepartment of Chemistry, Faculty of Science, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, JapanCorrespondence e-mail:
nakamura@se.ritsumei.ac.jp

Key indicators

Single-crystal X-ray study

T = 296 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.044

wR factor = 0.192

Data-to-parameter ratio = 10.7

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $\text{C}_{23}\text{H}_{48}\text{O}_2$, one of the hydroxy groups adopts a *gauche* conformation with respect to the hydrocarbon skeleton, whereas the other hydroxy group adopts a *trans* conformation. The molecules form a layer structure similar to that found in the smectic A phase of liquid crystals. Inter- and intralayer hydrogen bonds are formed in the crystal. These features are similar to those of the homologues with an odd number of C atoms. The calculated density, however, deviates from that predicted by a relation between the density and the number of C atoms in alkane- α,ω -diols with an odd number of C atoms.

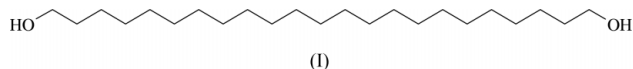
Received 9 October 2001

Accepted 16 October 2001

Online 20 October 2001

Comment

Normal long-chain aliphatic compounds have been investigated recently as models for smectic liquid crystals. Phase-transition phenomena in alkane- α,ω -diols containing 13–24 C atoms have been studied (Ogawa & Nakamura, 1999). It was found that alkane- α,ω -diols containing 13–24 C atoms, except for the diol containing 14 C atoms, had a rotator phase in which molecules were assured greater motional freedom, compared to that observed in liquid crystals. In addition, it was reported that the analogous compounds with two hydroxy groups at one or both chain ends had a liquid crystal smectic phase (Hentrich *et al.*, 1994). Therefore, the crystal data of alkane- α,ω -diols are important in order to explain the phase-transition.



The crystal structures of 11 alkane- α,ω -diols containing 10–19 and 21 C atoms have been investigated by Nakamura and co-workers: 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), 1,15-pentadecanediol (Nakamura, Uno, Watanabe *et al.*, 2000), 1,16-hexadecanediol (Nakamura & Yamamoto, 1994), 1,17-heptadecanediol (Nakamura *et al.*, 2001a), octadecane-1,18-diol (Nakamura & Watanabe, 2001), nonadecane-1,19-diol (Nakamura *et al.*, 2001b) and 1,21-henicosanediol (Nakamura Uno & Ogawa, 2000). These structures divide into two groups; one series has an even number of C atoms and the other series has an odd number of C atoms. In this paper, the crystal structure of tricosane-1,23-diol, (I), is described and compared with the other alkane- α,ω -diols.

Fig. 1 shows the molecular structure of (I). The terminal torsion angles $\text{O1}-\text{C1}-\text{C2}-\text{C3}$ and $\text{O2}-\text{C23}-\text{C22}-\text{C21}$

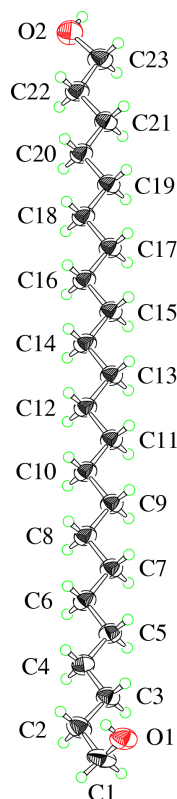


Figure 1

An ORTEP (Johnson, 1976) view of the molecule of (I) showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

are 63.9 (4) and $-179.6 (2)^\circ$, respectively. This means that the former has a *gauche* conformation and the latter a *trans* conformation. Fig. 2 shows the projection of the crystal structure of (I) along the *c* axis. The long axis of the molecule is normal to the *ac* plane, and the molecules form layers with a thickness of $b/2$. The packing is similar to that in the smectic *A* phase of liquid crystals. The molecules also form two different types of hydrogen bond, *i.e.* interlayer and intralayer. The donor–acceptor distances of the inter- and intralayer hydrogen bonds are 2.711 (2) and 2.778 (4) Å, respectively. These features are similar to those of other alkane- α,ω -diols with an odd number of C atoms.

The calculated densities of the odd-numbered alkane- α,ω -diols containing 11–21 C atoms are 1.050, 1.045, 1.041, 1.037, 1.034 and 1.029 Mg m $^{-3}$, respectively. As the X-ray structure analyses were carried out at nearly the same temperature, the density of tricosane-1,23-diol was estimated to be less than 1.029 Mg m $^{-3}$. However, it is 1.031 Mg m $^{-3}$. This value is not in accord with the tendency to decrease slightly with increasing chain length in the odd-numbered alkane- α,ω -diols. This feature is in agreement with that observed in the relation between the crystal-rotator phase-transition temperature (T_t) and the number of C atoms in the compounds. The T_t of tricosane-1,23-diol is a little higher than the T_t predicted from the relationship (Ogawa & Nakamura, 1999).

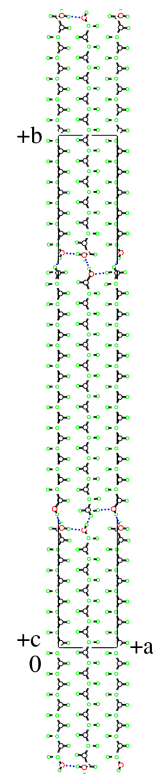


Figure 2

The projection of the crystal structure of (I) along the *c* axis. Dotted lines indicate the hydrogen bonding.

Experimental

The title compound was synthesized as described previously (Ogawa & Nakamura, 1999). The diacid was obtained from short-chain diacids by a ketene dimerization synthesis (Blomquist *et al.*, 1952) and was converted to the methyl ester by conventional procedures. The pure compound was obtained through fractional distillation and recrystallization, and the purity was 99.9% or higher. The single crystal used for the analysis was grown by slow evaporation from a solution containing a mixture of methanol, ethyl acetate and *n*-heptane (1:1:1).

Crystal data

C₂₃H₄₈O₂
 $M_r = 356.61$
 Orthorhombic, $P2_12_12_1$
 $a = 7.230 (6) \text{ \AA}$
 $b = 63.045 (5) \text{ \AA}$
 $c = 5.041 (4) \text{ \AA}$
 $V = 2298 (2) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.031 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation
 Cell parameters from 19 reflections
 $\theta = 9.8\text{--}13.3^\circ$
 $\mu = 0.47 \text{ mm}^{-1}$
 $T = 296.2 \text{ K}$
 Plate, colorless
 $0.60 \times 0.30 \times 0.03 \text{ mm}$

Data collection

Rigaku AFC-5R diffractometer
 ω scans
 Absorption correction: ψ scan
 (North *et al.*, 1968)
 $T_{\min} = 0.851$, $T_{\max} = 0.986$
 4062 measured reflections
 2538 independent reflections
 1692 reflections with $F^2 > 2\sigma(F^2)$

$R_{\text{int}} = 0.009$
 $\theta_{\text{max}} = 70.6^\circ$
 $h = -2 \rightarrow 8$
 $k = 0 \rightarrow 77$
 $l = -1 \rightarrow 6$
 3 standard reflections
 every 150 reflections
 intensity decay: 3.3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.192$
 $S = 1.41$
 2491 reflections
 233 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + \{0.09[\text{Max}(F_o^2, 0) + 2F_c^2]/3\}^2]$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.25 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.20 \text{ e } \text{Å}^{-3}$
 Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
 Extinction coefficient: 0.047 (7)

Table 1

Selected geometric parameters (Å, °).

O1—C1	1.423 (4)	C11—C12	1.517 (3)
O2—C23	1.427 (3)	C12—C13	1.520 (3)
C1—C2	1.507 (3)	C13—C14	1.518 (3)
C2—C3	1.520 (3)	C14—C15	1.521 (3)
C3—C4	1.521 (3)	C15—C16	1.521 (3)
C4—C5	1.519 (3)	C16—C17	1.521 (3)
C5—C6	1.521 (3)	C17—C18	1.521 (3)
C6—C7	1.523 (3)	C18—C19	1.522 (3)
C7—C8	1.521 (3)	C19—C20	1.522 (3)
C8—C9	1.524 (3)	C20—C21	1.522 (3)
C9—C10	1.519 (3)	C21—C22	1.519 (3)
C10—C11	1.520 (3)	C22—C23	1.507 (3)
O1—C1—C2—C3	63.9 (4)	O2—C23—C22—C21	-179.6 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1 ^o \cdots O2 ⁱ	0.82 (3)	1.96 (3)	2.778 (4)	170 (3)
O2—H2 ^o \cdots O1 ⁱⁱ	0.75 (3)	1.96 (3)	2.711 (2)	174 (3)

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

The measured fraction ($\theta_{\text{max}} = 70.6^\circ$) of 0.952 is relatively low, which is due to the blind region of the χ -90 setting. The absolute configuration was tentatively assigned. The methylene-H atoms were

located at idealized positions, and were allowed to ride on the parent C atoms (C—H = 0.95 Å). The hydroxy-H atoms were located from a difference Fourier map, and were allowed to refine isotropically for the final refinements [O—H = 0.75 (3) and 0.82 (3) Å]. The H-atom isotropic displacement parameters were set to be $1.2U_{\text{eq}}$ of the parent atom.

Data collection: *MSC/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFD Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *SAPI91* (Fan, 1991); program(s) used to refine structure: *TEXSAN*; software used to prepare material for publication: *TEXSAN*.

References

- Blomquist, A., Johnson, J., Diuguid, L., Shillington, J. & Spencer, R. (1952). *J. Am. Chem. Soc.* **74**, 4203–4204.
 Fan, H.-F. (1991). *SAPI91*. Rigaku Corporation, Tokyo, Japan.
 Hentrich, F., Diele, S. & Tschierske, C. (1994). *Liq. Cryst.* **17**, 827–840.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Molecular Structure Corporation (1992). *MSC/AFD Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
 Molecular Structure Corporation (2000). *TEXSAN*. Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.
 Nakamura, N. & Sato, T. (1999a). *Acta Cryst.* **C55**, 1685–1687.
 Nakamura, N. & Sato, T. (1999b). *Acta Cryst.* **C55**, 1687–1689.
 Nakamura, N. & Setodoi, S. (1997). *Acta Cryst.* **C53**, 1883–1885.
 Nakamura, N., Setodoi, S. & Ikeya, T. (1999). *Acta Cryst.* **C55**, 789–791.
 Nakamura, N., Tanihara, Y. & Takayama, T. (1997). *Acta Cryst.* **C53**, 253–255.
 Nakamura, N., Uno, K. & Ogawa, Y. (2000). *Acta Cryst.* **C56**, 1389–1390.
 Nakamura, N., Uno, K. & Ogawa, Y. (2001a). *Acta Cryst.* **C57**, 585–586.
 Nakamura, N., Uno, K. & Ogawa, Y. (2001b). *Acta Cryst.* **E57**, o485–o487.
 Nakamura, N., Uno, K., Watanabe, R., Ikeya, T. & Ogawa, Y. (2000). *Acta Cryst.* **C56**, 903–904.
 Nakamura, N. & Watanabe, R. (2001). *Acta Cryst.* **E57**, o136–o138.
 Nakamura, N. & Yamamoto, T. (1994). *Acta Cryst.* **C50**, 946–948.
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 Ogawa, Y. & Nakamura, N. (1999). *Bull. Chem. Soc. Jpn.* **72**, 943–946.
 Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.