

The γ -form of *n*-eicosanolFrançois Michaud, Lourdes Ventolà, M. Teresa Calvet,
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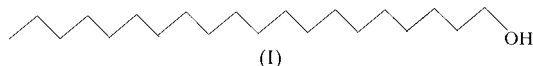
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In the crystal of the title compound, $C_{20}H_{42}O$, the molecules are packed in layers parallel to the (100) plane. The alkyl chains are parallel to the $[30\bar{2}0]$ direction and these molecular chains are hydrogen-bonded into chains parallel to the c axis. All C—C bonds of the alkyl chain show an antiperiplanar (*trans*) conformation, with a slight deviation from the ideal value (180°) in the C—C bonds close to the hydrogen bonds. The length of the alkyl chain is $27.92(2)$ Å and the tilt angle is $59.7(2)^\circ$.

Comment

The *n*-alkanols (normal fatty alcohols $C_nH_{2n+1}OH$) show a complicated polymorphic behaviour, only partially characterized to date. The principle of a common structural description is summed up by Small (1986). This description is based on the assumption that the presence of long alkanol chains packed in a regular and parallel crystallographic array would contribute a small periodic structure within the real unit cell that defines the repeating unit of the whole structure. For a given mode of alkanol chain packing, this small internal periodic structure describes the three-dimensional relationship between equivalent positions of translationally related positions within a single alkanol chain and between its lateral neighbours. This three-dimensional subcell is defined by three axes: c_s for the translation between equivalent positions within a chain and a_s and b_s for the lateral translations. In the title compound, (I), $c_s = 2.553$ Å and a_s and b_s are given by the rectangular planar subcell, 4.889×6.032 Å.



When the long axis of the molecule tilts over the short axis of the rectangular planar subcell (4.889 Å), the modification is called γ , and if the long axis of the molecule tilts over the long axis of the rectangular subcell (6.032 Å), the modification is called β . The γ -modifications are typically exhibited by even-numbered *n*-alkanols. They are subdivided into several forms γ_i , depending on the degree of tilting of the molecules with

respect to the molecular layers (Precht, 1974). The structure of two such crystals, *n*-hexadecanol (Abrahamsson *et al.*, 1960) and *n*-octadecanol (Seto, 1962; Fujimoto *et al.*, 1985), have already been determined. They were proved to be of the γ_4 form and were reported in the space group $A2/a$. The cell transformation between the conventional and the reported cell is $a_R = c$, $b_R = -b$ and $c_R = a - nc$, where n is 5 for *n*-octadecanol and 6 for *n*-hexadecanol. For the rest of the series, as well as for other γ_i forms, powder diffraction patterns are indexed by extrapolation, using a constant orthorhombic subcell connected with the $-CH_2-$ repetition in the structure (Precht, 1974, 1976). In spite of the consistency of the subcell description, a complete and unambiguous indexing of the patterns becomes difficult as the length of the chain increases. The present study is part of our work dedicated to *n*-alkanol mixed crystals. The investigation of the crystal structure of (I) was undertaken in order to support powder diffraction analyses.

The average C—C bond length is $1.515(7)$ Å. All C—C bonds show an antiperiplanar (*trans*) conformation. The C2—C3—C4—C5 [$177.86(8)^\circ$], C1—C2—C3—C4 [$-179.04(9)^\circ$] and O—C1—C2—C3 [$175.77(9)^\circ$] torsion angles all deviate significantly from the ideal 180° . This is explained by the steric hindrance produced by the hydrogen bond. The chains are parallel to the $[30\bar{2}0]$ direction, while they are parallel to $[10\bar{6}]$ in *n*-octadecanol and $[30\bar{1}7]$ in *n*-hexadecanol if the conventional cell is used. Precht (1974) classified the three compounds in the $[10\bar{6}]$ group.

The length of the alkyl chain is $27.92(2)$ Å. This value is obtained by dividing the modulus of the $[30\bar{2}0]$ vector by 12, the number of chains in this period; the value is 27.08 Å if Precht's approximation is used. The corresponding chain lengths are 24.9 for *n*-octadecanol and 21.6 Å for *n*-hexadecanol. The chain length for (I) can also be obtained in Å from the equation $l = 1.246n + 3$, where n is the number of C atoms. The long axis of the molecule in (I) tilts $59.7(2)^\circ$ over the short axis (4.889 Å) of the orthorhombic subcell defined by Precht (1974), so the structure corresponds to the γ_4 form according to the classification of Precht.

A rigid body treatment of the atomic displacement parameters for the whole chain has been carried out, using the

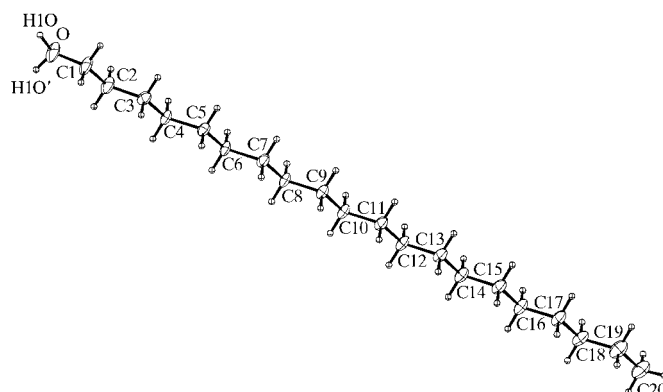


Figure 1

The molecular structure of (I), showing 50% probability displacement ellipsoids and the disorder of atom H1O.

EKRT program (Craven *et al.*, 1992). The inertial axes are defined as follows: the first is normal to the plane of the chain, the second is in the plane of the chain and perpendicular to the long axis of the molecule and the third is the long axis of the molecule. The principal values of the translational tensor are 0.043, 0.051 and 0.019 Å², where the first two principal axes of the translational tensor are the first two inertial axes rotated 60° around the third inertial axis and the third is parallel to the long axis of the molecule. The principal values of the librational tensor are 0.4, 1.0 and 97.2°², where the first two principal axes of the librational tensor are the first two inertial axes rotated 74° around the third inertial axis and the third is parallel to the long axis of the molecule. These results could explain the formation of *gauche* conformers in the phases at high temperature.

The alkyl chains are hydrogen-bonded, producing chains parallel to the c axis. The direction of the alkyl chains and the direction of the hydrogen bond produce a layered structure, with the layers parallel to the (100) plane. This fact explains the pseudo-rhombohedral morphology of the crystals with two more-developed opposite faces, which are {100}. The short diagonal of these rhombic faces is the direction of the b axis. The angles between the edges of the main face are close to 120 and 60°.

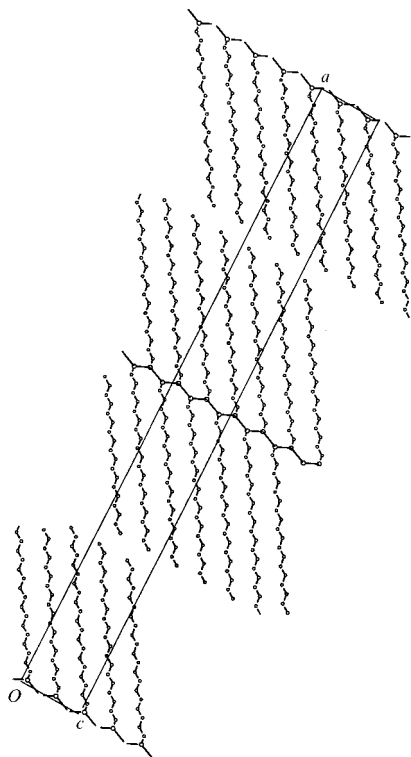


Figure 2
The projection of the cell content parallel to the (010) plane, showing the hydrogen bonds.

Experimental

Crystals of (I) were obtained by slowly evaporating saturated solutions of the compound in 4-chlorotoluene at room temperature.

Crystal data

$\text{C}_{20}\text{H}_{42}\text{O}$
 $M_r = 298.54$
 Monoclinic, $C2/c$
 $a = 91.116(17) \text{ \AA}$
 $b = 4.932(4) \text{ \AA}$
 $c = 8.997(10) \text{ \AA}$
 $\beta = 93.01(4)^\circ$
 $V = 4038(6) \text{ \AA}^3$
 $Z = 8$

$D_x = 0.982 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25
 reflections
 $\theta = 8\text{--}15^\circ$
 $\mu = 0.057 \text{ mm}^{-1}$
 $T = 293 \text{ (2) K}$
 Lozenge, colourless
 $0.6 \times 0.6 \times 0.2 \text{ mm}$

Data collection

Enraf-Nonius CAD-4 diffractometer
 ω - 2θ scans
 4539 measured reflections
 3932 independent reflections
 2007 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.023$

$\theta_{\max} = 26.01^\circ$
 $h = -110 \rightarrow 112$
 $k = 0 \rightarrow 6$
 $l = 0 \rightarrow 10$
 3 standard reflections
 frequency: 120 min
 intensity decay: none

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.159$
 $S = 0.978$
 3932 reflections
 198 parameters

H-atom parameters mixed
 $w = 1/[\sigma^2(F_o^2) + (0.0879P)^2]$ where
 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.009$
 $\Delta\rho_{\max} = 0.15 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.12 \text{ e } \text{\AA}^{-3}$

Table 1
Selected geometric parameters (Å, °).

O—C1	1.407 (1)	C1—C2	1.498 (2)
O—C1—C2	112.5 (1)		
O—C1—C2—C3	175.77 (9)	C2—C3—C4—C5	177.86 (8)
C1—C2—C3—C4	−179.04 (9)		

Table 2
Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O-H1O \cdots O^i$	1.00 (2)	1.73 (2)	2.688 (3)	159 (2)
$O-H1O' \cdots O^{ii}$	1.00 (2)	1.87 (2)	2.700 (3)	139 (2)

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

The H atom linked to O was located from a difference map and found to be on a disordered site. An occupancy factor of 0.5 was assigned according to the peak heights in the difference map. Each O atom is close to two further O atoms (related by an inversion centre and a twofold axis) at a distance appropriate to a hydrogen bond, so an ordered hydrogen-bond scheme is incompatible with the space group symmetry. An overall isotropic displacement parameter for the H atoms was used in the refinement and all H(—C) atoms were refined using a riding model. The anisotropic displacement parameters for the O atom revealed a possible disorder in the localization of this atom. The maximum and minimum principal axes of the displacement ellipsoids are 0.131 (1) and 0.015 (1) Å², respectively. The direction of that corresponding to the maximum eigenvalue is very nearly perpendicular to the C—O bond.

Data collection: *CAD-4/PC* (Kretschmar, 1996); cell refinement: *CAD-4/PC*; data reduction: *CFEO* (Solans, 1978); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1965; Brueggemann & Schmid, 1990); software used to prepare material for publication: *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1435). Services for accessing these data are described at the back of the journal.

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