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The Crystal Structure of the Monoclinic Form of *n*-Hexadecanol

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The γ-form of *n*-hexadecanol, $C_{16}H_{33}OH$, is monoclinic with

$$a=8{\cdot}95,\ b=4{\cdot}93,\ c=88{\cdot}1\ \text{Å},\ \beta=122^\circ\ 23'.$$

The cell contains eight molecules, the space group is C_{2h}^6–$A2/a$, and the packing of the hydrocarbon chains is of the common orthorhombic type. Hydrogen bonds link the molecules together in one direction. Symmetry requires the protons to have a disordered distribution between two possible positions.

Introduction

It is well known that normal fatty alcohols, like other fatty compounds, exhibit polymorphism (cf. Tanaka *et al.*, 1957). The alcohols between dodecanol and eicosanol have a hexagonal high-temperature form (α) stable just below the melting point. Those having an even number of carbon atoms possess two low-temperature forms; one orthorhombic (β), with the chains normal to the planes formed by the hydroxyl groups, and one monoclinic (γ) with inclined chains. The odd alcohols have only the orthorhombic low-temperature phase.

Preparation of crystals

The pure hexadecanol was provided by Prof. E. Stenhagen and his collaborators (Ställberg *et al.*, 1952). The melting point was 48·5–49·0 °C. Crystals were grown from different solvents and from the melt. A mixture of both low-temperature forms was normally obtained, but when using an easily volatile solvent like ether the monoclinic form dominated. The crystals grew in thin plates with an acute angle of $57\pm4^\circ$ though (β) and (γ) forms could not be distinguished by any differences in this angle as Amelinckx (1955) found possible with higher alcohols. The crystals were biaxial positive and showed twinning.

X-ray data

Rotation and Weissenberg photographs were taken about the *a*- and *b*-axes using Cu *K* radiation. The cell dimensions were calculated from calibrated powder photographs obtained with Guinier cameras using Cu $K\alpha$ and Cr $K\alpha$ radiation.

Molecular formula: $C_{16}H_{34}O$
Molecular weight: 242·45
Unit cell: Monoclinic

$$a=8{\cdot}95\pm0{\cdot}03,\ b=4{\cdot}93\pm0{\cdot}02,\ c=88{\cdot}1\pm0{\cdot}3\ \text{Å},$$
$$\beta=122^\circ\ 23'\pm30',\ d(001)=74{\cdot}4\pm0{\cdot}3\ \text{Å}$$

Eight molecules per unit cell
Number of electrons: 1104
Density calculated: $0{\cdot}982\pm0{\cdot}010$ g.cm.$^{-3}$
Density measured: 0·982 g.cm.$^{-3}$
Absent reflections: hkl for $k+l=2n+1$
$h0l$ for $h\ =2n+1$

Possible space groups were C_s^4–Aa and C_{2h}^6–$A2/a$, of which the centrosymmetrical one, C_{2h}^6–$A2/a$, was chosen. The following structure refinement did not contradict the choice. The intensities of the $h0l$ and the $0kl$ reflections were estimated visually, over a range of about 3000:1, by two observers using the multiple-film technique. The data were converted to an absolute scale by comparison with calculated factors after correction for the Lorentz and polarization factors. No absorption corrections were applied.

Subcell

As usual with compounds having a periodic hydrocarbon chain, a pronounced sub-lattice was found in

Table 1. *Atomic coordinates*

Atom	x/a	y/b	z/c
O	0·1400	0·1750	0·0060
C_1	0·2010	0·3130	0·0227
C_2	0·1145	0·1890	0·0319
C_3	0·1993	0·3100	0·0513
C_4	0·1042	0·1900	0·0604
C_5	0·1863	0·3090	0·0794
C_6	0·0962	0·1912	0·0885
C_7	0·1770	0·3080	0·1077
C_8	0·0866	0·1922	0·1170
C_9	0·1668	0·3078	0·1365
C_{10}	0·0755	0·1925	0·1455
C_{11}	0·1604	0·3070	0·1651
C_{12}	0·0641	0·1933	0·1739
C_{13}	0·1519	0·3058	0·1938
C_{14}	0·0544	0·1945	0·2027
C_{15}	0·1425	0·3044	0·2221
C_{16}	0·0429	0·1958	0·2305

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Table 2. *Observed and calculated structure factors*

hkl	F_o	F_c
0,0,0	*	1080
2	*	40·0
4	*	−42·7
6	*	37·7
8	*	−41·9
10	49·0	43·4
12	30·2	−34·4
14	43·7	49·3
16	30·2	−33·2
18	39·3	45·4
20	33·5	−32·3
22	37·1	35·8
24	38·0	−36·9
26	35·0	29·2
28	44·6	−44·5
30	33·6	35·2
32	81·0	−81·4
34	93·5	82·6
36	179·1	172·3
38	37·3	−30·5
40	< 7·2	15·4
42	15·7	−15·7
44	< 7·2	1·4
46	11·8	−10·3
70	33·5	−35·4
72	27·8	−31·3
74	< 7·2	− 7·5
2,0,$\overline{104}$	< 7·4	44·5
$\overline{102}$	16·6	−15·5
$\overline{100}$	< 7·4	2·0
$\overline{74}$	< 7·4	3·9
$\overline{72}$	47·2	−41·8
$\overline{70}$	85·1	96·7
$\overline{68}$	73·6	78·2
$\overline{66}$	< 6·2	−11·2
$\overline{64}$	29·8	30·2
$\overline{62}$	< 6·2	4·7
$\overline{60}$	25·1	23·2
$\overline{58}$	< 5·8	8·1
$\overline{56}$	24·3	20·1
$\overline{54}$	< 5·8	12·4
$\overline{52}$	23·2	24·3
$\overline{50}$	18·2	22·4
$\overline{48}$	24·0	28·2
$\overline{46}$	21·7	19·3
$\overline{44}$	26·3	30·3
$\overline{42}$	25·9	23·6
$\overline{40}$	25·1	32·9
$\overline{38}$	32·5	29·6
$\overline{36}$	26·3	32·9
$\overline{34}$	36·7	32·9
$\overline{32}$	25·9	31·3
$\overline{30}$	36·3	34·4
$\overline{28}$	26·7	28·6
$\overline{26}$	35·9	34·0
$\overline{24}$	22·4	20·9
$\overline{22}$	40·6	35·6
$\overline{20}$	17·0	18·1
$\overline{18}$	41·4	39·5
$\overline{16}$	15·1	17·0
$\overline{14}$	45·3	51·5
$\overline{12}$	8·5	11·2
$\overline{10}$	53·0	61·5
$\overline{8}$	< 3·1	8·9
$\overline{6}$	87·0	91·3
$\overline{4}$	< 3·1	3·5
$\overline{2}$	186·9	204·3
2,0,0	20·9	19·0
2	336·3	−373·0
4	12·7	− 7·7
6	85·9	−84·3
8	13·5	− 9·7
10	47·0	−45·3
12	13·5	−14·7
14	29·8	−26·7
16	13·9	−19·3
18	20·1	−17·8
20	13·5	−19·7
22	13·5	− 9·7
24	12·0	−16·3
26	< 5·0	3·6
32	15·5	−13·2
34	78·8	91·0
36	71·6	−78·0
38	85·1	−90·3
40	< 6·6	16·3
4,0,$\overline{108}$	< 7·0	—
$\overline{106}$	21·3	27·1
$\overline{104}$	< 7·0	−11·6
$\overline{102}$	16·6	−21·3
$\overline{100}$	< 7·0	10·4
$\overline{86}$	< 6·6	20·5
$\overline{84}$	13·9	20·1
$\overline{82}$	< 6·6	6·2
$\overline{80}$	20·1	19·3
$\overline{78}$	< 6·6	11·6
$\overline{76}$	30·5	25·9
$\overline{74}$	24·4	28·6
$\overline{72}$	59·2	50·7
$\overline{70}$	11·2	10·5
$\overline{68}$	99·8	−106·8
$\overline{66}$	43·3	−36·4
$\overline{64}$	< 6·2	− 0·4
$\overline{62}$	18·6	−18·2
$\overline{60}$	< 5·8	0·8
$\overline{58}$	16·2	−15·0
$\overline{56}$	< 5·4	5·0
$\overline{54}$	12·3	− 8·9
$\overline{52}$	< 5·4	6·2
$\overline{50}$	10·4	−13·4
$\overline{48}$	15·5	10·4
$\overline{46}$	13·9	−18·9
$\overline{44}$	20·1	12·8
$\overline{42}$	18·2	−22·8
$\overline{40}$	34·0	30·9
$\overline{38}$	17·0	−15·1
$\overline{36}$	92·5	86·7
$\overline{34}$	43·7	35·9
$\overline{32}$	123·7	−134·0
$\overline{30}$	27·4	−23·2
$\overline{28}$	43·7	−48·0
$\overline{26}$	25·1	−29·0
$\overline{24}$	34·0	−34·0
$\overline{22}$	24·4	−27·1
$\overline{20}$	26·7	−27·1
$\overline{18}$	23·6	−25·1
$\overline{16}$	24·0	−25·5
$\overline{14}$	22·8	−25·5
$\overline{12}$	22·4	−27·1
$\overline{10}$	22·4	−24·4
$\overline{8}$	24·4	−27·8
$\overline{6}$	21·3	−23·5
$\overline{4}$	32·9	−34·0
$\overline{2}$	20·1	−28·2
4,0,0	106·0	−104·1
2	< 5·8	− 7·8
4	54·6	43·3
6	< 5·0	−17·0
32	< 5·8	− 1·6
34	22·8	−21·3
36	64·2	−70·0
38	31·4	32·1
40	27·1	26·7
42	< 6·2	—
6,0,$\overline{76}$	< 7·0	2·7
$\overline{74}$	22·4	−18·9
$\overline{72}$	< 6·6	− 1·6
$\overline{70}$	61·1	−55·0
$\overline{68}$	69·3	−65·3
$\overline{66}$	37·5	36·3
$\overline{64}$	< 6·6	−12·7
$\overline{48}$	< 5·8	− 6·2
$\overline{46}$	11·2	− 8·1
$\overline{44}$	5·8	− 1·6
$\overline{42}$	12·7	−10·0
$\overline{40}$	< 5·8	5·0
$\overline{38}$	23·2	−21·7
$\overline{36}$	10·5	11·3
$\overline{34}$	99·8	−89·0
$\overline{32}$	37·1	−28·1
$\overline{30}$	33·2	26·3
$\overline{28}$	< 5·0	−19·4
6,0,0	< 5·0	13·1
2	29·0	−10·0
4	< 5·0	16·2
34	< 5·4	−12·0
36	14·3	18·6
38	25·5	30·9
40	< 5·4	− 5·0
8,0,$\overline{106}$	< 7·0	4·6
$\overline{104}$	17·0	−11·3
$\overline{102}$	34·1	−20·5
$\overline{100}$	< 7·0	3·5
$\overline{74}$	< 6·6	− 8·9
$\overline{72}$	< 6·2	− 5·0
$\overline{70}$	15·5	− 8·1
$\overline{68}$	27·8	19·0
$\overline{66}$	25·5	13·5
$\overline{64}$	< 5·8	−12·0
$\overline{36}$	< 5·4	−17·8
$\overline{34}$	19·0	−10·8
$\overline{32}$	74·6	75·4
$\overline{30}$	24·0	15·5
$\overline{28}$	< 5·4	9·6
10,0,$\overline{36}$	< 7·3	5·4
$\overline{34}$	17·8	6·6
$\overline{32}$	< 7·3	17·0
$\overline{30}$	22·4	− 6·2
$\overline{28}$	< 7·3	− 2·3
0,1,1	14·3	−13·9
3	16·3	−12·4
5	22·3	−17·3
7	17·9	−14·7
9	18·5	−22·2
11	13·5	−15·4
13	16·1	−24·3
15	10·2	−13·8
17	15·6	−23·3
19	6·4	−10·4
21	15·3	−21·1
23	6·4	− 8·2
25	21·0	−23·9
27	< 4·9	− 6·9
29	34·4	−29·9
31	< 4·9	− 3·4
33	67·2	−71·9
35	39·0	−41·9
37	74·0	65·1
39	11·5	6·9
41	19·2	19·7
43	8·8	3·7
45	11·7	9·3
47	< 1·0	3·7
0,2,0	231·0	−299·0
2	< 7·2	− 9·8
4	15·3	8·5
6	< 7·2	−13·7
8	11·2	8·2
10	< 7·2	−16·8
12	10·0	6·8
14	< 7·2	−18·0
16	9·9	8·0
18	< 7·2	−16·4
20	8·4	9·4
22	< 7·2	−13·2
24	10·6	12·0
26	6·9	−11·9
28	15·7	15·5
30	13·9	−14·8
32	22·8	31·8
34	39·8	−33·6
36	69·1	−73·2
38	< 7·2	14·9
0,3,23	< 8·0	9·4
25	12·2	19·2
27	< 8·2	7·6
29	18·0	23·4
31	< 8·2	3·7
33	54·3	57·0
35	29·7	34·8
37	60·5	−56·7
39	< 8·7	—

* These lower orders of 00*l* were not within range of the goniometer.

the reciprocal lattice. The systematic absences in the sub-lattice and the calculated subcell dimensions indicated that the chain packing was of the common orthorhombic type, 0 ⊥, (space group *Pbnm*) as first described by Bunn (1939).

The dimensions are:

$$a_s = 4{\cdot}93,\ b_s = 7{\cdot}42,\ c_s = 2{\cdot}53\ \text{Å}\,.$$

The orientation of this subcell within the main cell is such that a_s coincides with b and c_s is roughly parallel to the (202) planes.

Structure determination

The hydrocarbon chains were placed according to the orthorhombic subcell and its orientation within the main cell being as above for the trial structure. The oxygen atoms were placed in the most probable way for hydrogen bonding. The molecules are thought to be linked together in infinite chains, e.g. as found in methyl alcohol (Zachariasen, 1935; Tauer & Lipscomb, 1952) or as in 14-heptacosanol (Welsh, 1956). There are however two possible ways of building the structure with respect to the hydrogen bonding. Hydrogen-bond spirals can be formed along the screw axes parallel to the *b*-axis but alternatively infinite chains in the *a* direction are also possible with hydrogen bonds between centres of symmetry and twofold axes. The latter case corresponds to a structure centred in the polar groups and therefore seemed more likely. It was also the only structure giving agreement between observed and calculated structure factors.

Cycles of structure-factor calculations and electron-density maps along the *a*- and *b*-axes were carried out. The structure factor calculations were made on the BESK-computer of the Swedish Board for Computing Machinery using the atomic scattering values of Vand *et al.* (1957). The Fourier summations were performed with Beevers–Lipson strips (3°) and the Hägg–Laurent machine (1946).

The hydrogen atoms, except the hydroxyl hydrogen, were included in the structure-factor calculations as a later refinement. Their positions relative to the carbon atoms were calculated from the standard shape of the CH_2-group (Vainshtein & Pinsker, 1950). As the *h*0*l*-difference maps clearly indicated an anisotropic thermal motion, an anisotropic temperature factor of the form

$$\exp -(B + C\cos^2\psi)\sin^2\theta/\lambda^2$$

was applied (Hughes, 1941; Cochran, 1951, 1954), where B and C are constants with the final values of 1·2 and 2·8 Å^2 respectively and ψ is the angle between the direction of the maximum vibration and the normal to the reflection plane. Omitting non-observed reflections the reliability index R_{h0l} is 13%.

The 0*kl* projections show no such anisotropy which is in accordance with the observations that the thermal motions of the orthorhombic packing, O ⊥, take place predominantly along the long subcell axis (cf. Degerman & von Sydow, 1959, and Teare, 1959). The final reliability index of the 0*kl* reflections is 13% when non-observed and 020 reflections are omitted, (the latter probably suffers from extinction).

Atomic coordinates were derived from the difference maps and are given in Table 1. Observed and calculated structure factors are listed in Table 2. One very high order reflection index $2,0,\overline{104}$ shows poor agreement. The standard deviations of the atomic

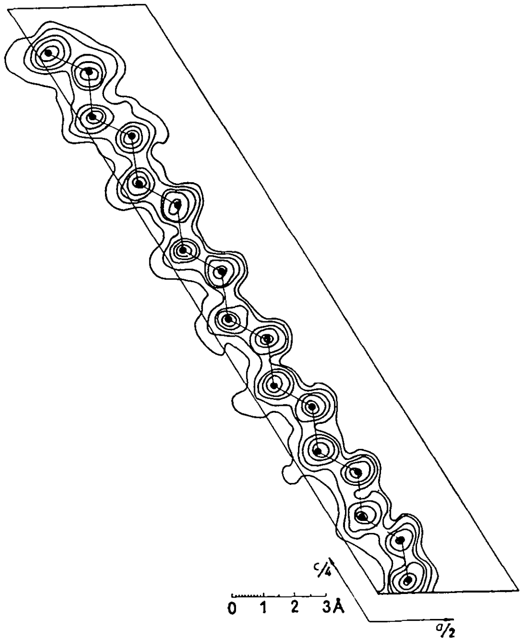

Fig. 1. Electron-density projection along the *b* axis. Contours are given at intervals of 1 e.Å^{-2} starting with 1 e.Å^{-2}.

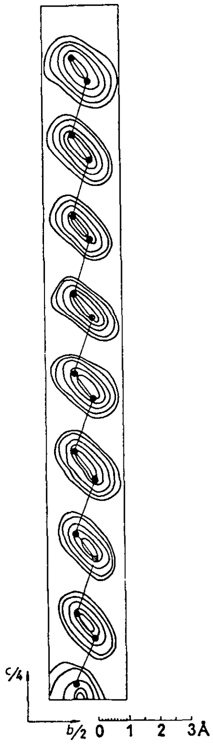

Fig. 2. Electron-density projection along the *a* axis. Contours are given at intervals of 1 e.Å^{-2} starting with 1 e.Å^{-2}.

Table 3. *Standard deviations*

$\sigma(x) = \sigma(y) = 0{\cdot}01$ Å
$\sigma(z) = 0{\cdot}015$ Å
σ (bond length) = 0·02 Å
σ (bond angle) = 1° 30′

coordinates, bond lengths and bond angles, given in Table 3, were calculated by Cruickshank's formulae (1949, 1953). The electron-density maps of the *h0l*- and the *0kl* projections are given in Fig. 1 and Fig. 2 respectively.

Discussion of the results

The bond lengths within one molecule are given in Table 4 and the bond angles in the chain in Table 5. According to Table 4 there seems to be two alternating carbon–carbon lengths in the chain but these differences are more apparent than real as experimental error in a structure having a zigzag chain like this should lead to an alternation of bond lengths.

Table 4. *Bond lengths*

$O-C_1$	1·44 Å	C_8-C_9	1·57 Å
C_1-C_2	1·52	C_9-C_{10}	1·52
C_2-C_3	1·57	$C_{10}-C_{11}$	1·57
C_3-C_4	1·56	$C_{11}-C_{12}$	1·54
C_4-C_5	1·54	$C_{12}-C_{13}$	1·59
C_5-C_6	1·52	$C_{13}-C_{14}$	1·55
C_6-C_7	1·55	$C_{14}-C_{15}$	1·55
C_7-C_8	1·54	$C_{15}-C_{16}$	1·53

$C_{2n}-C_{2n+1}$ 1·563 Å (parallel with C_1-C_2)
$C_{2n-1}-C_{2n}$ 1·535 Å (parallel with $O-C_1$)
Average 1·545 Å

Table 5. *Bond angles*

(Bond angles in the order $O-C_1-C_2$ $C_1-C_2-C_3$ . . .)

109° 18′ 110° 6′ 109° 36′ 109° 54′ 110° 30′ 111° 30′
111° 54′ 112° 42′ 112° 6′ 111° 6′ 110° 36′ 110° 24′
110° 48′ 110° 6′ 109° 12′

Average 110° 24′

The average carbon–carbon distance is 1·545 Å which is slightly longer than is found in hydrocarbons, e.g. monoclinic and orthorhombic *n*-hexatriacontane which give 1·534 Å and 1·537 Å respectively (Shearer & Vand, 1956; Teare, 1959); the average carbon–carbon angle (110° 24′) is accordingly little less than the values for *n*-hexatriacontane (Shearer & Vand 112° 1′, Teare 111° 54′) but these deviations are within experimental error.

The arrangements of the molecules are shown schematically in Figs. 3 and 4. The straight, regular hydrocarbon chains are arranged according to the orthorhombic packing, 0 ⊥, with alternate chain planes roughly perpendicular to each other.

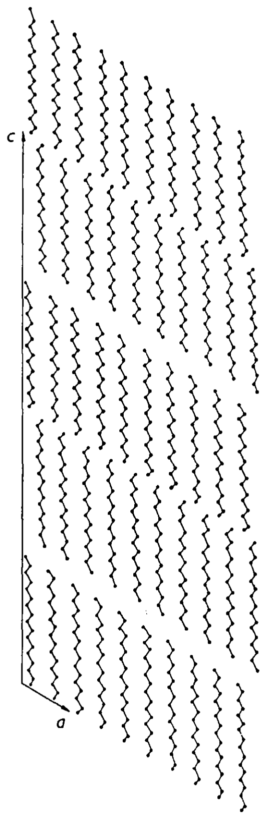

Fig. 3. Molecular arrangement as viewed along the *b* axis.

The molecules are linked together by infinite chains of hydrogen bonds along the *a*-axis. The closest oxygen–oxygen approaches are 2·74 Å over centres of symmetry and 2·69 Å over twofold axes. This difference is insignificant. The infrared absorption spectrum gives a value of 2·74 Å for the asymmetric hydrogen bond taken from a curve given by Lippincott & Schroeder (1954).

As the hydrogen bonds are between centres of symmetry and twofold axes, the protons must be distributed at random over two possible positions *if* they belong to a lattice of the same statistical symmetry as the heavier atoms.

Hydrogen bonds can also be formed if the hydroxyl groups belong to a lower symmetry as *Aa*; of course these two cases cannot be distinguished by X-ray methods but on general grounds randomly distributed protons seem more probably.

Centrally located protons are unlikely because of the comparatively long oxygen–oxygen distance.

Disordered protons in crystalline primary alcohols have been suggested earlier on the basis of dielectric measurements (Dryden, 1952; Hamon & Meakins, 1952) and of specific-heat measurements (Kakiuchi, 1954).

The closest carbon–carbon distance in the methyl group contact layers are 3·93 Å and 4·24 Å which agrees with the distance in monoclinic *n*-hexatriacontane 3·91 Å.

Thanks are due to Prof. G. Hägg and Prof. E. Sten-

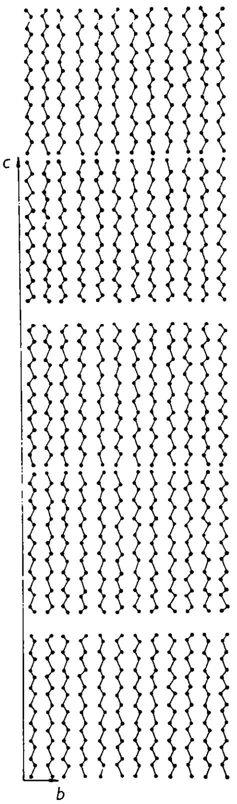

Fig. 4. Molecular arrangement as viewed along the *a* axis.

hagen for their interest. The expenses involved have been defrayed by grants from the Swedish Natural Science Research Council and the Swedish Board for Computing Machinery.

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The Required Precision of Intensity Measurements for Single-Crystal Analysis*

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A discussion is given of the requirements necessary for determining bond lengths crystallographically within a limit of error of 0·01 Å. A simple approximate formula is given relating the residual R to the co-ordinate estimated standard deviation.

The required standard of coordinate accuracy

The primary problem in single-crystal structure analysis is the determination of sufficiently accurate atomic coordinates. A great step forward in the detailed understanding of chemical valency would be possible if the accuracy were such that one could assert with confidence that *a measured difference of* 0·01 Å *between two bond lengths corresponded to a genuine difference*. Such a precision would allow the assignment of multiple bond orders within 0·05, would distinguish between the predictions of the molecular-

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