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The crystal structure of 14-heptacosanol.

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The crystal structure of secondary alcohols is of interest because of their dielectric properties described by Meakins & Sack (1951), who found them dependent on the method of preparation. Two forms were obtained, one by solidification of the melt, and the other by recrystallization from solution. An examination of the crystal structure of the form given by crystallization at room temperature is briefly reported here.

Crystals of 14-heptacosanol (m.p. 82° C.) were obtained as thin plates by evaporation of xylene solutions, the main face (001) having the shape of a parallelogram, with its longer diagonal parallel to *a* and shorter diagonal parallel to *b*, which is also a marked cleavage direction. Some hexagonal plates were also obtained, boundaries parallel to *b* being developed. Reasonable diffraction patterns were difficult to obtain.

Unit-cell dimensions were determined from rotating crystal and equi-inclination Weissenberg photographs using Ni-filtered Cu radiation. The crystal system is monoclinic, and cell dimensions are

$$a = 8\cdot14,\ b = 4\cdot95,\ c = 73\cdot2\ \text{Å},\ \beta = 104°.$$

The density, measured by flotation in alcohol–water mixture, was 0·90 g.cm.$^{-3}$, the value calculated for four units of $C_{27}H_{56}O$ per cell being 0·91 g.cm.$^{-3}$. Reflexions ($h0l$) with l odd and ($0k0$) with k odd were absent, so that the space group is $P2_1/c$.

Intensity data were obtained by the multiple-film technique, and, although an intensity range of 8000:1 was recorded, only 150 of the 400 possible ($h0l$) reflexions with $2 \sin \theta < 1\cdot5$ were of measurable intensity. Relative structure factors were placed on an absolute scale by comparison with calculated values, for which McWeeny's (1951) scattering curves for hydrogen, 'valence states' of carbon and $f = \frac{1}{3}(f_{\perp}+f_{\parallel})$ of oxygen were used.

Signs were determined by the application of subcell theory (Vand, 1951; Vand & Bell, 1951). The subcell is nearly orthorhombic, with a_s parallel to ($\bar{2}$,0,56), b_s to (010) and c_s to (402), having dimensions

$$a_s = 7\cdot8,\ b_s = 4\cdot95,\ c_s = 2\cdot58\ \text{Å},\ \beta = 92°.$$

It contains 4 CH_2 groups, 2 from each of adjacent molecular chains, the space group being $P2_1$. The length of a_s is considerably larger than that of the orthorhombic cell found in paraffins by Bunn (1939) and Vainshtein & Pinsker (1950), the other dimensions being similar.

The *b*-axis projection has been refined by Fourier methods to yield the electron-density map shown in Fig. 1. At this stage the reliability index is 0·25. Hydrogen atom positions have been estimated by placing them at points calculated with a C–H distance of 1·10 Å and tetrahedral angles at the carbons. Most lie on a set of parallel lines, so computation was reduced by making use of the sum of the series $\Sigma \cos(\alpha+(r-1)\beta)$. It has been found necessary to use a highly anisotropic temperature factor, having a value of $B = 2\times10^{-16}$ cm^2. in the direction of the chain and 10×10^{-16} cm.^{2} perpendicular to this direction, i.e. parallel to c_s and a_s.

With the oxygens related by the screw axis, the molecules are linked by a system of hydrogen bonds parallel to this direction and of length 2·75 Å, forming a planar zigzag, the O–O–O angle being 130°. The C–O bond is parallel to the plane of projection, the C–O–O angle being about 105°, so that there is distorted tetrahedral packing around the oxygen. The system of hydrogen bonds forces the paraffinic portions of the molecules apart in a direction more or less perpendicular to the molecular chains and the hydrogen bond chains but does not affect the component of separation parallel to *b* to any great extent. There is thus space for considerable freedom of movement of the carbon chains in the direction of expansion, giving rise to the large anisotropy in the temperature factor.

The hydrocarbon zigzags are inclined to the plane of projection at an angle of 55–60°, and there appears to be some distortion near the C–O group.

Examination of some distorted crystals cut from a mass solidified from the melt indicates that these have a different structure. The cell is nearly orthorhombic, with

$$a \sin \beta = 7\cdot9,\ b = 4\cdot97,\ c \sin \beta = 73\cdot3\ \text{Å}\,.$$

It has not been possible to determine β accurately, but

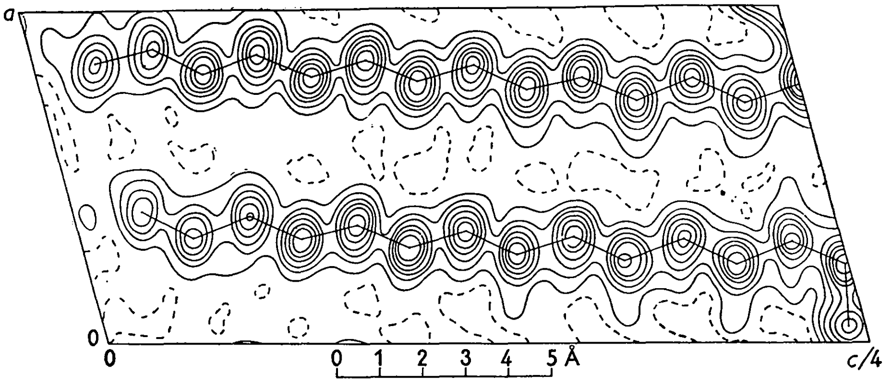

Fig. 1. Electron-density projection along the *b* axis. Contour interval 1 e.Å^{-2}; zero contour broken.

it is about 95°. The general distribution of intensities in diffraction patterns from rotation about corresponding short axes of the two forms are distinctly different, particularly in subcell regions. Though insufficiently sharp for accurate measurement, there is no doubt of the existence of different structures. These will be compared when more satisfactory data on the high-temperature form have been obtained.

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Conical crystals of graphite.

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In the course of an investigation of artificial graphite, using a three-stage electron microscope (HU-9 type made by the Hitachi Company Limited), we found apparently circular crystals (Fig. 1(*a*)) in addition to hexagonal crystals (Fig. 1(*b*)) (Tsuzuku & Komoda, 1955). The specimen examined was prepared from carbon black by a heat treatment at about 2500° C. A circular crystal gives spotty electron-diffraction rings accompanied by ellipses and diffuse bands (Fig. 1(*c*)), while an hexagonal one produces the ordinary diffraction pattern of a graphite monocrystal, i.e. an hexagonal net pattern accompanied by Kikuchi lines.

The spotty rings suggest that the circular crystal is a stack of thin graphite layers, each of which is successively rotated about a common axis in the *c* direction (Wilman, 1950). Moreover, the ellipses and diffuse bands suggest that the stack is not a plane disc but is slightly conical, somewhat like a lotus leaf. The conical form of the crystal is proved by the fact that the folded crystals do not show perfect semi-circles; for example, in Fig. 1(*d*) the two radii along the folded lines make an angle of about 167° instead of 180°. Such a conical crystal can be formed by spiral mechanism (Frank, 1949) if after mechanical buckling a thin layer of graphite overlaps, forming a cone (Fig. 2(*a*)). In the specimen shown in Fig. 1(*d*) it is easy to calculate that the angle formed by the overlapping is about 26°, which also represents the orientation difference between the adjacent layers in the stack. The circular loops observed in Fig. 1(*a*) seem to be the growth front, which is centred by the screw dislocation.

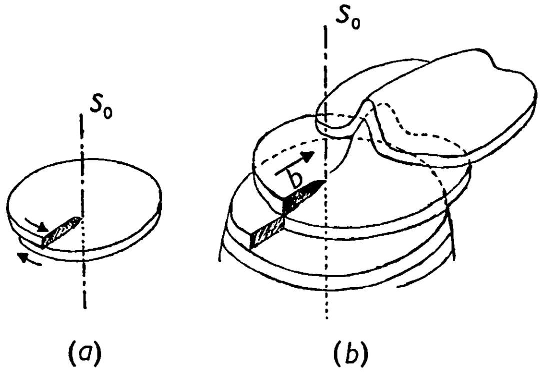

Fig. 2. (*a*) Deformation into a cone (S_0: screw dislocation). (*b*) Gliding of a helical stack of conical crystal sheets.

A remarkable gliding of an apparently circular crystal is reproduced in Fig. 1(*d*). At first it seems improbable that circular discs glide away from a helical stack of conical sheets. However, this is possible by the mechanism illustrated schematically in Fig. 2(*b*). According to this mechanism, the initial screw dislocation is successively cancelled in each disc (Dawson & Anderson, 1953) and a fairly sharp fold should be produced at the same time. It is most striking that the fold is generally observed as in Fig. 1(*e*). In Fig. 1(*f*) we can see some split sheets at the position indicated by the arrow *A*, which may suggest that the gliding in this case is not smooth. It is supposed that the initial screw dislocation is not cancelled in this case, but is cut into some shorter segments through the collapse of the stack, holding a spiral structure in each cleft sheet. The arrow *B* indicates a point of emergence of such a dislocation segment on a cleavage surface.

Finally, it is remarked that the gliding leads to the intersection of moving dislocations with the initial screw axis, which may occur in a very special manner owing to the characteristic conical structure. A detailed description of this mechanism, together with that of the experimental observation, will be published in the near future in the *Journal of the Physical Society of Japan.*

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