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The Low-Temperature Form of $C_{18}H_{38}$

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The low-temperature form of $C_{18}H_{38}$, which is iso-structural with that of other even paraffins from C_{22} down to C_6, is shown to be triclinic, with one molecule in the unit cell, which has dimensions

$$a = 4{\cdot}28_5\ \text{A.},\quad b = 4{\cdot}82_0\ \text{A.},\quad c = 23{\cdot}07_0\ \text{A.}$$
$$\alpha = 91^\circ\ 6',\quad \beta = 92^\circ\ 4',\quad \gamma = 107^\circ\ 18'.$$

Measurements were made of 118 spacings and 65 angles, by means of Laue, powder, rotation and Weissenberg photographs. The 'X-ray' density is 0·93 g.cm.$^{-3}$ at 21° C., as compared with the liquid density at the melting-point, 27° C., of 0·777 g.cm.$^{-3}$.

Introduction

It is known that $C_{18}H_{38}$, like a number of other hydrocarbons, can give two characteristic powder patterns. One is the 'normal' pattern, in which the chains are believed to be packed in a prismatic cell of rectangular cross-section, their lengths being perpendicular to the base of the cell. The long spacing is about 25·3 A. (Müller, 1930, 1932*a*). This form is observed at temperatures near to the melting-point, 27° C., and also at room temperatures if the octadecane contains more than about 2·2 % of the C_{16} or C_{20} paraffins (Ubbelohde, 1938). The long spacing in this form lies on a straight line (spacing versus number of carbon atoms) which extends from C_{11} upwards, including both odd- and even-numbered paraffins. There is, however, a second form of lower symmetry, having a long spacing of about 23 A., which is also typical of even paraffins from C_{22} (or possibly C_{24}) downwards to C_6, and which gives a characteristic pattern in which there are three strong side-spacing lines (at 4·56, 3·79 and 3·58 A. in $C_{20}H_{42}$ at room temperatures). It is the object of the present paper to describe this second modification, as found for pure octadecane at room temperatures. Single crystals were successfully grown from xylene. These were flakes, optically positive, with the acute bisectrix emerging at a small angle to the flake face normal.

Experimental

Laue photographs were first taken with the X-ray beam normal to the flake face; these photographs (which provide the most searching test of crystal perfection) showed that the flakes were somewhat distorted and possibly not single, but they also gave the directions of some important zone axes, about which rotation and Weissenberg photographs were subsequently taken. One very small and relatively undistorted crystal gave good photographs about axes which were chosen as the [100] and [010] zone axes, but it was twinned by reflexion on the (001) flake face. The crystals were proved to be triclinic, first of all from their optical properties, and then from photographs of a second crystal which was not twinned. This crystal, however, was bent, and although it gave Weissenberg photographs about the

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[*] Deceased. This work was begun by Dr Müller in 1940, and continued by K. Lonsdale during his absence through illness in the winter of 1940–1. It was written up after his death in 1947.

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[110] and [1$\bar{1}$0] axes from which reflexions could be identified and spacings measured with good accuracy, it did not give such accurate angle measurements as the first twinned crystal.*

The most accurate spacing measurements were, however, obtained from powder photographs, using a 29 cm. diameter camera, the lines being identified by comparison, in respect both of intensity and of spacing, with corresponding reflexions on the Weissenberg photographs. It was found that at first there was some difficulty in obtaining long-chain and side spacings on the same film, or indeed with the same specimen. If the hydrocarbon were melted on to a glass plate and then cooled on ice (to prevent the slow formation of large crystals), the side spacings were most intense; if it were allowed to crystallize out quickly from a solvent, the long spacings appeared; but one could not even be sure that the crystalline form was the same in both cases. Satisfactory powder photographs, showing both sets of lines, were finally obtained by using as specimen a thin coating of hydrocarbon on a fine aluminium wire, the wire being dipped into the melted hydrocarbon just as the latter was setting. A calibration photograph of the Al wire alone gave the reflexions 111, 200, 220 and 311, corresponding to $2\theta = 38{\cdot}47_0°$ (Cu $K\alpha_1$), $44{\cdot}71_8°$ (Cu $K\alpha_1$), $65{\cdot}09_3°$ (Cu $K\alpha_1$), $65{\cdot}27_5°$ (Cu $K\alpha_2$), $78{\cdot}22_4°$ (Cu $K\alpha_1$) and $78{\cdot}45_7°$ (Cu $K\alpha_2$). Photographs of the Al wire coated with $C_{18}H_{38}$ showed the Al calibration lines together with a considerable number of hydrocarbon lines. Each hydrocarbon line had a sharp absorption line at its centre, due to the relatively large absorption of the metal base; measurements were made on this sharp line, great care having been taken that the specimen should be accurately centred. The effective camera radius was calculated from the distances apart of the calibration lines, taken in pairs, and was found to be constant to within ± 1 in 2000 for any given film at any given time of measuring, except at the extreme ends of the film (near to $2\theta = 180°$). An average value of the effective camera radius was 14·33 cm., so that in the neighbourhood of the Al 311 lines a change of position of 0·1 cm. corresponded to a change of spacing of approximately 0·005 A. The $C_{18}H_{38}$ 0.0.19 reflexion could be measured with accuracy, because it was well resolved (the width of the α_1 and α_2 components being less than 0·025 cm. each) and because for Cu $K\alpha_1$ the value of 2θ was $78{\cdot}86_4°$, as compared with $78{\cdot}45_7°$ and $78{\cdot}22_4°$ for the α_2 and α_1 components of Al 311. The only other possible $C_{18}H_{38}$ reflexion in this neighbourhood, $1.\bar{1}.\overline{18}$, was observed on Weissenberg photographs to be much weaker than 0.0.19. All photographs were taken on the 50 kW. rotating anode tube at the Royal Institution, the time of exposure of a Weissenberg photograph using Ni-filtered Cu K radiation being 1–1½ hr. with a camera of 8 cm. diameter. The high-order reflexions on powder photographs were given twice the exposure of the low-order lines in order to make them of comparable intensity (the central part of the film being screened after half the time of the experiment). Accurate measurement was confined to those powder lines which were intense enough to show up, after enlargement, against the grain of the background. For such lines the positions of the centres could be determined with confidence to 0·001 cm. The temperature during the time of exposure varied from 20·9 to 21·8° C.

Since the determination of the triclinic unit-cell dimensions could be carried out only by the use of all four photographic methods (Laue, powder, rotation and Weissenberg), it is perhaps useful to indicate how this was done, at each stage.

Unit-cell size. Nine Laue photographs taken independently with the X-rays normal to the flake face of the crystal showed two prominent zone axes at an acute angle of 73·5 to 72·5°, the mean value being 72·9°. These zone axes were taken as [100] and [010], the angle therefore being γ or $(180° - \gamma)$. Rotation photographs gave the a and b axial lengths as 4·29 and 4·82 A. respectively (from layer-line distances). A c-axis rotation photograph could not be obtained. From Weissenberg photographs about [100] and [010] the angles 010 : 001 and 001 : 100 were found to be $A = 88{\cdot}2°$, $B = 87{\cdot}3°$, and the spacings of the axial planes (identified on Weissenberg photographs and more accurately measured on powder photographs) were $d_{100} = 4{\cdot}08_2$ (weak powder line), $d_{010} = 4{\cdot}59_9$ (strong, well-defined powder line), $d_{001} = 23{\cdot}041$ A. (from 0.0.19 powder line; excellent agreement with all other observable orders). The values of d_{010} and d_{001} were taken as being accurate enough for calculation of other spacings. The observed values of A and B, obtained from the small twinned crystal, were also sufficiently exact, since small changes in these angles did not alter the calculated spacings. The observed values of d_{100} and of γ were not, however, of equal accuracy with those of the other axial spacings and angles, and it was found, in particular, that the calculated (hhl) and $(h\bar{h}l)$ spacings were very sensitive to changes in γ. 'Trial and error' values giving the best agreement with observation for all planes were $d_{100} = 4{\cdot}08_6$ A. and γ (or $180° - \gamma$) $= 72{\cdot}7°$.

Two unit cells are possible from the observed values of A, B and γ. Using the formulae

$$\left.\begin{aligned}\tan\tfrac{1}{2}(\alpha+\beta) &= \cos\tfrac{1}{2}(A-B)\sec\tfrac{1}{2}(A+B)\tan\tfrac{1}{2}\gamma,\\ \tan\tfrac{1}{2}(\alpha-\beta) &= \sin\tfrac{1}{2}(A-B)\operatorname{cosec}\tfrac{1}{2}(A+B)\tan\tfrac{1}{2}\gamma,\end{aligned}\right\}\quad(1)$$

we obtain either

$$\alpha = 87°\,20', \quad \beta = 86°\,50', \quad \gamma = 72°\,42', \qquad (1)$$

or

$$\alpha = 91°\,6', \quad \beta = 92°\,4', \quad \gamma = 107°\,18'. \qquad (2)$$

We can decide definitely between these two possible unit cells by a determination of the spacings of planes (hkl) having no zero index and/or by the angles between

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* The mortality among these little flakes was high, partly owing to the fact that at the time of the experiments the laboratory was subject to considerable vibration.

planes not in the same axial zone. Both methods were used. Taking $d_{100}=4\cdot08_6$, $d_{010}=4\cdot59_9$ and $d_{001}=23\cdot041$ A., we have the following spacings and angles in the two cases:

(1)

$d_{111}=3\cdot62_5$ A., $111:001=84\cdot6^\circ$
$d_{11\bar{1}}=3\cdot55_5$ A., $11\bar{1}:00\bar{1}=77\cdot5^\circ$
$d_{112}=3\cdot53_1$ A., $112:001=75\cdot8^\circ$
$d_{11\bar{2}}=3\cdot40_5$ A., $11\bar{2}:00\bar{1}=69\cdot2^\circ$
$d_{1\bar{1}2}=2\cdot62_2$ A., $1\bar{1}2:001=77\cdot5^\circ$
$d_{1\bar{1}\bar{2}}=2\cdot61_0$ A., $1\bar{1}\bar{2}:00\bar{1}=76\cdot3^\circ$

(2)

$d_{1\bar{1}\bar{1}}=3\cdot60_5$ A., $1\bar{1}\bar{1}:00\bar{1}=81\cdot8^\circ$
$d_{1\bar{1}1}=3\cdot58_9$ A., $1\bar{1}1:001=80\cdot2^\circ$
$d_{1\bar{1}\bar{2}}=3\cdot48_7$ A., $1\bar{1}\bar{2}:00\bar{1}=72\cdot6^\circ$
$d_{1\bar{1}2}=3\cdot45_9$ A., $1\bar{1}2:001=71\cdot7^\circ$
$d_{11\bar{2}}=2\cdot64_0$ A., $11\bar{2}:00\bar{1}=79\cdot5^\circ$
$d_{112}=2\cdot58_6$ A., $112:001=74\cdot3^\circ$

The second, fourth and sixth of these gave relatively strong reflexions for which the observed values were

$3\cdot58_9$ A. ($80\cdot0^\circ$), $3\cdot45_9$ A. ($72\cdot0^\circ$), $2\cdot58_8$ A. ($73\cdot5^\circ$),

agreeing well with unit cell (2) but not with (1). In fact, all the observed data were much more consistent with (2) than with (1).

The formulae used for the calculation of spacings and angles were

$$\left(\frac{1}{d_{hkl}}\right)^2=\Sigma\frac{h^2}{N^2a^2}\sin^2\alpha+2\Sigma\frac{kl}{N^2bc}(\cos\beta\cos\gamma-\cos\alpha), \tag{II}$$

where

$$N^2=4\sin\tfrac{1}{2}(\alpha+\beta+\gamma)\sin\tfrac{1}{2}(-\alpha+\beta+\gamma)\times\sin\tfrac{1}{2}(\alpha-\beta+\gamma)\sin\tfrac{1}{2}(\alpha+\beta-\gamma),$$

whence

$$a=\frac{d_{100}}{N}\sin\alpha,\quad b=\frac{d_{010}}{N}\sin\beta,\quad c=\frac{d_{001}}{N}\sin\gamma;$$

and

$$h_1k_1l_1:h_2k_2l_2=\cos^{-1}\left\{d_1d_2\left[\Sigma\frac{h_1h_2}{N^2a^2}\sin^2\alpha+\Sigma\frac{k_1l_2+k_2l_1}{N^2bc}(\cos\beta\cos\gamma-\cos\alpha)\right]\right\}. \tag{III}$$

The finally accepted values of the unit-cell dimensions were

$$\begin{array}{lll} d_{100}=4\cdot08_6\text{ A.}, & \alpha=91^\circ 6', & a=4\cdot28_5\text{ A.},\\ d_{010}=4\cdot59_9\text{ A.}, & \beta=92^\circ 4', & b=4\cdot82_0\text{ A.},\\ d_{001}=23\cdot04_1\text{ A.}, & \gamma=107^\circ 18', & c=23\cdot07_0\text{ A.} \end{array}$$

(in terms of

Cu $K\alpha_1=1\cdot54050$ A. and Cu $K\alpha_2=1\cdot54435$ A.).

These dimensions give 0·01–0·1 % agreement in spacing measurement for all but the very weakest reflexions; in all, some 118 spacings and 65 angles were measured.

From these dimensions we have:

Volume of unit cell $=a.b.c.N=454\cdot40$ A.^{3}

Mass of one molecule $=(254\cdot30\div6\cdot0228)\times10^{-24}$ g.

$$\frac{\text{Mass of molecule}}{\text{Volume of unit cell}}=\frac{\text{Density}}{\text{Number of molecules}}=\frac{0\cdot929}{n}\text{ g.cm.}^{-3}$$

The density of $C_{18}H_{38}$ could not be directly determined on account of its solubility in all suitable suspension liquids, but it is certainly less than that of water at room temperatures. The unit cell must therefore contain one molecule and the density, as determined by the above X-ray method, is 0·93 g.cm.$^{-3}$ at 21° C. The density of liquid $C_{18}H_{38}$ at the melting-point is 0·7770 g.cm.$^{-3}$ (*International Critical Tables*), the spacing corresponding to the 'liquid ring' being 4·6 A. (Müller, 1932*b*), which is very close to the strong side-spacing of the triclinic unit cell. This decrease in density indicates that although some measure of parallelism of the molecules must be retained on melting, much of the molecular order has disappeared. The crystalline structure will be discussed in a subsequent paper.

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