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Polytypic Structures of n-C₂₈H₅₈ (Octacosane) and n-C₃₆H₇₄ (Hexatriacontane)

BY R. BOISTELLE, B. SIMON AND G. PÈPE

Laboratoire des Mécanismes de la Croissance Cristalline,
Université d'Aix Marseille III, Centre Scientifique Saint Jerôme, 13397 Marseille/Cedex 4, France

Octacosane ($C_{28}H_{58}$) and hexatriacontane ($C_{36}H_{74}$) obtained by crystallization at room temperature from light petroleum solutions are polytypic modifications of the monoclinic structures. Their structure is a stacking of alternate monoclinic layers, related one to the other by a twofold axis perpendicular to the (001) plane. Space group *Pbca*, $Z=4$. Cell parameters $a=7\cdot42$, $b=5\cdot59$, $c=66\cdot50$ or $84\cdot50$ Å for $C_{28}H_{58}$ and $C_{36}H_{74}$ respectively. The paraffinic chains are regular with C–C and C–H mean distances of $1\cdot526$ and $1\cdot00$ Å. The mean C–C–C angle is $113\cdot9°$. Thermal motion is anisotropic, weak in the direction of the chain. Lateral contacts between chains are the same in this structure as in the monoclinic structure.

Introduction

In a previous growth kinetics study of n-$C_{36}H_{74}$ crystallizing from light petroleum solutions (Simon, Grassi & Boistelle, 1974) we had to identify the crystalline phase by X-ray diffraction, since two polymorphic modifications are known. With identical morphologies (rhombic platelets), the polymorphs differ only in the orientation of the paraffinic chains: in the monoclinic phase the chains are inclined relative to the (001) plane (Shearer & Vand, 1956), whereas in the orthorhombic phase they are perpendicular to this plane (Teare, 1959). The crystals obtained belonged to neither phase, but to a new orthorhombic phase, space group *Pbca* with $a=7\cdot42$, $b=5\cdot59$, $c=84\cdot5$ Å, $Z=4$. By comparison of these parameters with those of the monoclinic phase, we made the hypothesis that the new phase was a polytypic modification. But, due to the low thicknesses of the crystals, it was not possible to support this hypothesis by a structure determination. The same abnormal orthorhombic phase was later obtained with n-$C_{28}H_{58}$ in another growth kinetics study (Doussoulin, 1975; Boistelle & Doussoulin, 1976). Owing to the better quality of the crystals and to their greater thickness, it was then possible to perform a structure determination. The present study is a first contribution to the problem of polytypism in n-paraffins.

Experimental data

According to the crystallization conditions (temperature, nature of the solvent, purity of the products) a given paraffin crystallizes in different polymorphic structures (Holder & Winckler, 1965; Smith, 1953). For this reason we describe exactly the experimental conditions.

Light petroleum, frequently used as a solvent for paraffins, is a comparatively complex mixture. The commercially available product (Prolabo), has a mean molar mass of 78·5 g, and contains essentially pentane, 2-methylpentane, cyclopentane, and 3-methylpentane in the proportions of 39·4, 27·4, 12·2, 8·1 moles per 100 moles of solvent. As for the paraffins, their purity is better than 95% (Fluka), the 'impurities' probably being paraffins with slightly different numbers of carbon atoms in the chain.

Morphology

Octacosane and hexatriacontane crystals, obtained at 20°C by slow evaporation or slow cooling of the solution, are (001) rhombic platelets with [110] edges, the acute angle of the lozenge being about 72°. Observation of the (001) surfaces by electron microscopy with the platinum–carbon replica technique is comparatively easy only for $C_{36}H_{74}$, owing to its higher

melting point (72 °C). Surfaces of $C_{28}H_{58}$ are more or less destroyed by the carbon flux (melting point 61 °C), and we only describe the phenomena observed with hexatriacontane crystals.

The (001) faces, as is usual with paraffins (Dawson & Vand, 1951), exhibit polygonized growth spirals, but here two new points are of interest. First, the step height which can be observed in these conditions is always 90 ± 20 Å, which corresponds to a bimolecular layer, according to the length of a paraffinic chain. Second, the edges in one of the obtuse angles of the spiral are always split in two steps (Figs. 1 and 2). As we will see later, this splitting reflects the polytypic structure. On the one hand, these edges could be a slight interlacing of steps during growth; on the other hand, the splitting could result from a different behaviour of the two edges, during the heating of the crystals, due to the platinum–carbon deposition. Furthermore, the fragility of such double steps is evidenced by a beginning of fusion when the (001) faces are heated, for instance by a small carbon particle. Paraffin droplets form along the steps, with the diameter decreasing with increasing distance from the heat source (Fig. 3); when the heating is uniform, the fusion of steps and the diameter of the droplets are also uniform (Fig. 4).

Cell parameters

The cell parameters and space group of the new orthorhombic phases have been determined by rotating crystal and precession photographs with Cu $K\alpha$ radiation. Space group $Pbca$, $Z = 4$. Cell parameters are given in Table 1. Since the diffraction patterns of both paraffins are closely similar, we assume that their structures are isotypes.

Table 1. *Cell parameters of polytypic octacosane and hexatriacontane crystals*

n-Paraffin	a(Å)	b(Å)	c(Å)	d_{calc}	d_{obs}
$C_{28}H_{58}$	7·42 (1)	5·59 (1)	66·50 (5)	0·948	0·954
$C_{36}H_{74}$	7·42 (1)	5·59 (1)	84·50 (5)	0·959	0·953

Structure determination of the orthorhombic octacosane

The first structure hypothesis had been made (Simon et al., 1974) by comparison of the cell parameters of the new orthorhombic phase of $C_{36}H_{74}$ with those of the monoclinic (m) phase, the structure of which has been determined by Shearer & Vand (1956). In this monoclinic phase $a_m = 5\cdot57$, $b_m = 7\cdot42$, $c_m = 48\cdot35$ Å, $\beta = 119\cdot6°$; the paraffinic chains are inclined with an angle of nearly 30° relative to the normal to the (001)

Table 2. *y and z coordinates* ($\times 10^4$) *of carbon and related hydrogen atoms*

(Standard deviations: 0·002 on *y*, 0·0002 on *z*.)

	y	*z*		*y*	*z*
H(1)	−8293	161	H(15)	−9831	1202
C(1)	4	107	C(8) −8223	1263
H(2)	36	95	H(16)	−8160	1268
H(3)	−3590	176	H(17)	−6826	1529
C(2)	−2047	238	C(9) −8370	1472
H(4)	−1919	242	H(18)	−8497	1463
H(5)	−585	503	H(19)	−1911	1544
C(3)	−2220	450	C(10) −523	1595
H(6)	−2256	437	H(20)	−240	1610
H(7)	−5670	518	H(21)	−8907	1871
C(4)	−4089	573	C(11) −436	1804
H(8)	−3999	584	H(22)	−578	1805
H(9)	−2666	845	H(23)	−3991	1886
C(5)	−4191	786	C(12) −2334	1945
H(10)	−4370	779	H(24)	−2320	1952
H(11)	−7751	860	H(25)	−2658	2147
C(6)	−6348	916	C(13) −2477	2150
H(12)	−6080	926	H(26)	−987	2213
H(13)	−4746	1187	H(27)	−5971	2238
C(7)	−6373	1125	C(14) −4312	2297
H(14)	−6417	1121	H(28)	−4300	2305

Table 3. *Anisotropic thermal factors* β ($\times 10^4$) *of carbon atoms, and corresponding isotropic factors,*
$$B_{eq} = \tfrac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2)$$

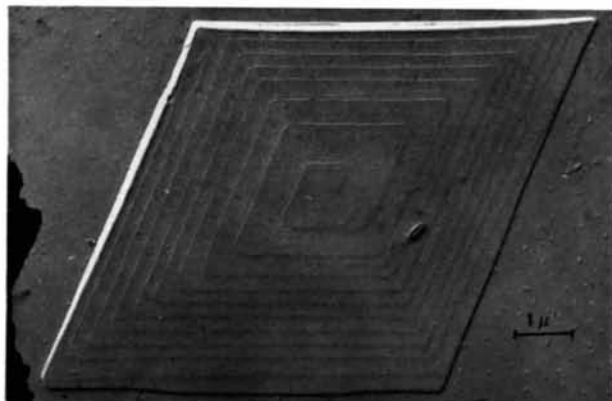| Carbon atoms	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{eq}
1, 3, 5, 7, 9, 11	146 (18)	437 (42)	1 (0)	35 (35)	9 (2)	14 (2)	3·485
2, 4, 6, 8, 10, 12	214 (25)	316 (42)	3 (0)	0 (30)	−4 (2)	12 (3)	4·660
13	514 (44)	531 (60)	3 (0)	209 (44)	18 (3)	9 (3)	7·175
14	726 (57)	805 (79)	6 (0)	−222 (64)	15 (5)	40 (6)	12·233

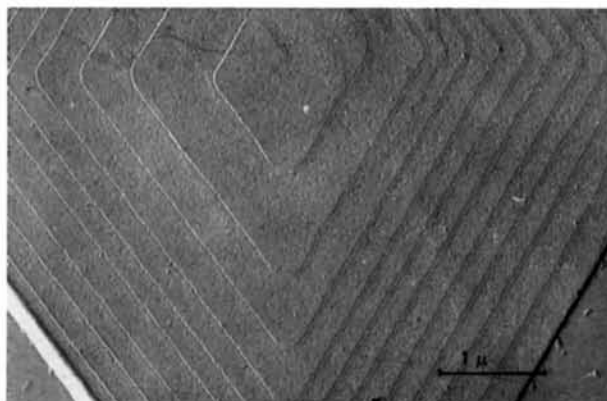Fig. 1. Growth spiral on (001) of $C_{36}H_{74}$.

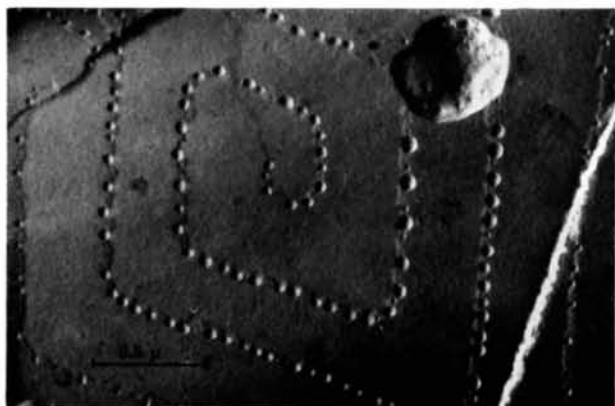Fig. 2. Bimolecular steps (height 90 Å) split in two mono-molecular steps in one of the obtuse angles.

Fig. 3. Droplets of molten paraffin along steps, due to the heating by a carbon particle from the electrodes.
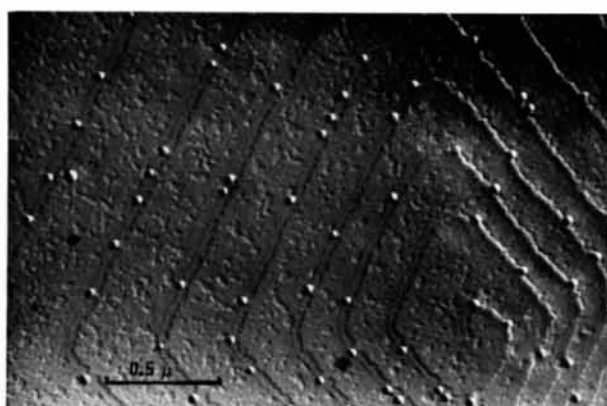

Fig. 4. Droplets of molten paraffin along steps, due to uniform heating of the crystal.

plane. Since the reticular distance $d_{(002)}$ of the new phase is nearly equal to $d_{(001)}$ of the (m) phase (42·25 and 42·29 Å respectively), and since $a = b_m$, and $b = a_m$, it had been assumed that the new phase was a polytypic modification of the monoclinic structure, consisting of a stacking of monoclinic layers related one to the other by a twofold axis normal to the (001) plane.

Similar assumptions were later made with C$_{28}$H$_{58}$ (Doussoulin 1975; Boistelle & Doussoulin, 1976). Here the new orthorhombic phase has $d_{(002)} = 33·25$ Å, which is nearly equal to the experimental monoclinic long spacing $d_{(001)}$ (Broadhurst, 1962) and to the predicted value (Nyburg & Potworowski, 1973) (33·60 and 33·21 Å respectively). Finally, the coordinates of the carbon atoms have been supposed to be the same as those of the first 28 carbon atoms in the monoclinic phase of C$_{36}$H$_{74}$.

In order to determine the structure of orthorhombic octacosane, we have used a nearly spherical crystal of about 0·1 mm in diameter, obtained by fast dissolution of a thick crystal. The intensities were recorded on a Nonius CAD 4 automatic diffractometer, using the Mo $K\alpha$ radiation, with the θ–2θ scan technique. The counting time was inversely proportional to the intensities, which were corrected for Lorentz–polarization, but not for absorption. Reflexions with intensities lower than $3\sigma(I)$ were automatically rejected (about 400 reflexions) and only 417 independent reflexions were considered.

Considering only the carbon atoms in the positions described above, and using the $SFLS$ 5 program (Prewitt, 1966) and the scattering factors given by Moore (1963), the first refinement led to a reliability index $R = 0·21$ with isotropic temperature factors, reduced to 0·15 with anisotropic temperature factors. Hydrogen atoms were then placed in their theoretical positions with a distance C–H = 1·08 Å and an angle HCH = 107°. They were given an isotropic temperature factor $B = 5$ Å^2, except those of the end CH$_2$ group ($B = 7$ Å^2), and those of the terminal CH$_3$ group ($B = 12$ Å^2) placed in a *trans* conformation.

A new refinement of the coordinates and temperature factors of the only carbon atoms led then to $R = 0·12$. It was also apparent that, within experimental error, the axis of the paraffinic chain was in the (100) plane, and that the carbon atoms had the same temperature factors, except those at the end of the chain. Refinement of y and z coordinates and of the temperature factors of the carbon atoms was then continued, all the carbons in x being given the same temperature factor, and the atoms in $\bar{x}$ another. The final reliability factor with the 417 reflexions decreased thus only to $R = 0·118$. The weighted factor of reliability $R_w = [\sum w |F_o|^2 - |F_c|^2]/\sum|F_o|$ with $w = [\sigma^2 I_o + K I_o]^{-1}$ was equal to 0·124. It should be noted that taking into account only the 300 most intense reflexions the reliability index is $R = 0·05$. Table 2 gives the y and z coordinates of the atoms, obtained in the last refinement using all the measured reflexions. All odd carbons

have the same $x = 0·0392$ (8), their corresponding hydrogen atoms having $x = 0·0089$ and $x = 0·1725$. All even carbon atoms have the same $x = -0·0392$ (8) and their related hydrogen have $x = -0·0089$ and $x = -0·1785$.

The structure of orthorhombic hexatriacontane, which is isotypic with this structure, can now be obtained by a simple extrapolation, in the manner described by Nyburg & Potworowski (1973) for the monoclinic phases.*

Table 3 gives the temperature factors of carbon atoms, but the differences between odd and even atoms are not significant. On the other hand, thermal motion is high for the last two atoms of the chain, especially for C(14). This is normal, according to the weaker bonds of these atoms with their own chain, and to their large distances to the chains in the next layer (Fig. 5).

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* A list of structure factors for both compounds has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31410 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
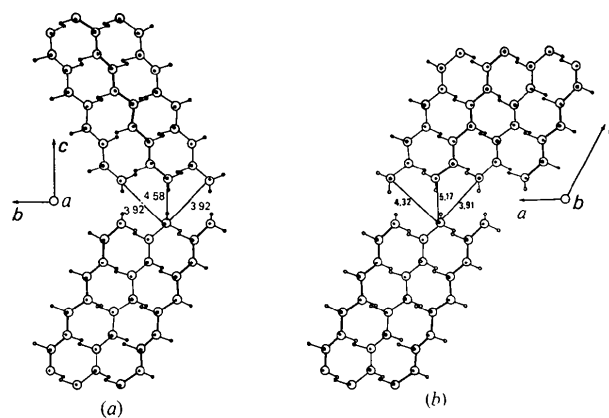

Fig. 5. (a) Structure of the new orthorhombic phase of C$_{28}$H$_{58}$. Distances between carbon atoms of adjacent layers are indicated. (b) Structure of the 'normal' monoclinic structure of C$_{28}$H$_{58}$.
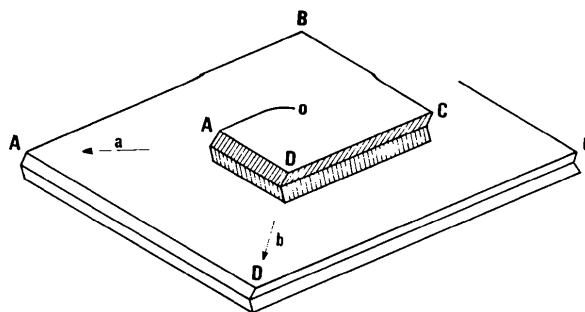

Fig. 6. Growth spiral on (001) of the polytypic structure due to the emergence of a screw dislocation at O (from Simon *et al.*, 1974).

Description of the structure

The new phases of octacosane and hexatriacontane consist of a stacking of monoclinic layers, one layer being related to the adjacent one by a twofold axis [001]. In these layers, the chains are nearly regular, planar, with their axis in the (100) plane and their centres at the symmetry centre. The chains make an angle of about 27° with the [001] direction. If C'(1) is symmetric to C(1), the distances C'(1)C(1), C(1)C(2) $\cdots$C(13)C(14) are 1·537, 1·554, 1·532, 1·450, 1·536, 1·596, 1·510, 1·502, 1·512, 1·567, 1·511, 1·532, 1·488, 1·533 Å. The average value is 1·526 Å. The angles C'(1)C(1)C(2), C(1)C(2)C(3)$\cdots$C(12)C(13)C(14) are 112·14, 115·01, 114·51, 113·42, 113·02, 111·58, 114·98, 116·92, 112·14, 108·07, 113·40, 116·88, 118·33°. The average value is 113·90°.

As the carbon atoms have been refined after the introduction of hydrogen atoms in fixed positions, the hydrogen atoms have not kept their theoretical positions relative to the carbon atoms. The CH distances range between 0·88 and 1·02 Å, with a mean value of 1·00 Å, and the HCH angles range between 104 and 115° with a mean value of 108·24°. A monolayer in the new phase is then, within experimental errors, identical with a layer of the corresponding monoclinic phase and accordingly it can be said that these new structures are polytypic modifications of the monoclinic ones. Our former structure hypothesis is thus confirmed. According to Ramsdell (1947), the designation of these orthorhombic structures must be $2O[180]$ which means that: in the period [001] there are two monolayers – the structure is orthorhombic – each layer is related to the adjacent one by a rotation of 180° around [001]. The monoclinic structures should be written $1M[0]$. Fig. 5 shows the terminal CH_2 and CH_3 groups in both structures: the stackings are closely similar.

Discussion

Thermal motion along the chain axis (Table 3) is very low ($\beta_{33} \sim 0$), owing to the high intramolecular forces compared with the intermolecular forces. This point was already apparent from the experimental results of Müller (1930, 1932) who showed that the thermal expansion along the c axis of normal orthorhombic paraffins is negligible, whereas it is 4% and 1% along a and b respectively. According to Müller's results, β_{11} should be greater than β_{22}, but it must be noted that in the polytypic phase $a = 7·42$ and $b = 5·59$ Å, while in the normal orthorhombic phase $a = 7·42$, but $b = 4·92$ Å.

The morphological features of the growth spirals on the (001) faces may be understood in the following way: if there is a screw dislocation with a Burgers vector having a component perpendicular to (001) equal to $d_{(001)}$, the step thus created is of bimolecular height (Fig. 6). It can be seen that in one of the obtuse angles the two layers make a re-entrant angle, whereas in the other they form a salient angle. There appears an asym-

metry in the configuration of the steps, which can be reflected in the growth features: from these configurations, one could expect an interlacing of the growth spirals. Furthermore, recent study in our laboratory (D. Aquilano – private communication) led to the conclusion that other polytypic structures exist. Such structures consist of p monolayers of the monoclinic structure parallel one to the other, followed by q monolayers of the same structure, the q monolayers being related to the p layers by a twofold axis normal to (001). The values of p and q are unknown at the present time but, from ordinary microscopic examination, it may be concluded that p and q are fairly high, probably with different values. Such structures should be called $(p+q)M[(0)_{p-1}180(0)_{q-1}180]$.

A more general question may be asked concerning the conditions necessary for the formation of a polymorph or of a polytype. As has been pointed out by Ubbelohde (1938) and Smith (1953), it seems that 'normal' monoclinic paraffins are obtained in very pure conditions while the 'normal' orthorhombic phases form when the starting product contains about 2% of neighbouring homologues. But this is not the only condition, because the formation of polymorphs and polytypes depends also on the solvent.

Furthermore, it must be emphasized that growth kinetics also play an important role in the formation of the different phases. All other conditions being the same, octacosane crystallizes at low supersaturation (i.e. at low growth rate) in the polytypic modification, while at high supersaturation (i.e. at high growth rate) it crystallizes in a triclinic structure. This influence of the growth kinetics on crystal structure will be discussed later.

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