

Syntactic Coalescences between the Monoclinic and Orthorhombic Polymorphs of the Long-Chain Even n -Alkane, n -C₃₄H₇₀

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Abstract

Crystals of pure n -C₃₄H₇₀ grown from heptane solutions at low temperature (278–283 K) exhibit syntactic coalescences between monoclinic and orthorhombic polymorphs. The stackings of the vertical paraffin chains on the tilted ones are revealed by growth spirals which develop on the (001) common faces of the aggregates. From the interaction energy calculations performed with a Lennard-Jones 6–12 potential function, it is shown that coalescences are possible from both structural and energetical points of view.

1. Introduction

Even normal alkane crystals (C_{*n*}H_{2*n*+2}) are known to exhibit an important polymorphism mainly depending on the parity of n and on their chain lengths. The short members of the series are triclinic (Müller & Lonsdale, 1948; Smith, 1953; Norman & Mathisen, 1960, 1961*a,b*; Mathisen, Norman & Pedersen, 1967; Crisemann, Passaglia, Eby & Colson, 1970; Nyburg & Lüth, 1972) whereas the long members are either monoclinic (Smith, 1953; Shearer & Vand, 1956) or orthorhombic (Kohlhaas & Soremba, 1938; Teare, 1959). In addition, normal alkanes above C₁₈H₃₈ can crystallize in different modifications according to the purity of the material and to the growth conditions such as temperature, supersaturation and nature of the solvent (Ubbelohde, 1938; Smith, 1953; Lundager Madsen & Boistelle, 1976). Finally, in the neighbourhood of the melting points appears a hexagonal modification called the rotator phase or rotational crystalline state (Müller, 1932).

All crystal structures were predicted by Nyburg & Potworowski (1973) while polymorphism and phase

transitions were discussed by Schoon (1938), Kitaigorodskii (1957*a,b*), Mnyukh (1960, 1963), Atkinson & Richardson (1969), Broadhurst (1962) and Teare (1959).

Normal alkane crystals are built up of paraffin layers stacked one upon another, the contact plane between adjacent layers being (001). In most cases the end-group packing between molecules belonging to these layers is normal and the crystals have the usual and simple structures quoted above. Nevertheless, in some cases, complex structures built up of the basic ones also appear in the growth morphology of the crystals on which they are made evident by interlaced growth spirals developing on the (001) faces. These complex structures consist of an anomalous stacking of the paraffin layers giving rise in monoclinic long-chain alkanes either to polytypes or to periodic polysynthetic twins (Amelinckx, 1956; Simon, Grassi & Boistelle, 1974; Boistelle, Simon & Pépe, 1976; Aquilano, 1977; Boistelle & Aquilano, 1977). Inside such crystals the layers are rotated with respect to each other around an axis normal to (001), the number of anomalous (001) interfaces depending on the crystal size and on the height of the normal component of the Burgers vectors of the spirals which generate both polytypes and twins. If the rotation angle between layers is 0 or 180° the resulting crystals are polytypes, whereas for all other rotation angles they are periodic polysynthetic twins (PPT) (Aquilano, 1977). At least for the latter, the (001) interfaces between the two individuals of the twin may be considered as completely anomalous from a geometrical standpoint, whereas calculations of end-group packing energies show that they are stable, the stability of the twins being nevertheless mostly provided by the side-packing energies inside the adjacent layers (Boistelle & Aquilano, 1977).

It must be emphasized here that in all polytypes or PPT the layers on both sides of the (001) interfaces are

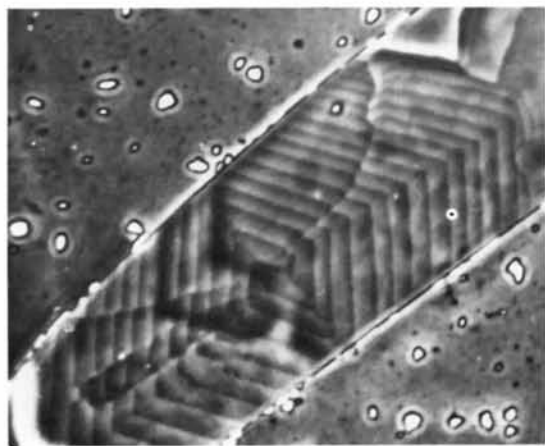
all monoclinic. In a few other cases the complexity of the structure is higher since the crystals are built up of monoclinic and orthorhombic layers at the same time. Such aggregates have been observed in $n\text{-C}_{34}\text{H}_{70}$ crystals grown from solution and the aim of this paper is to find the conditions necessary for their stability from both a structural and an energetic standpoint.

2. Experimental and results

The $n\text{-C}_{34}\text{H}_{70}$ crystals were grown from heptane solutions by slow evaporation of the solvent in a temperature range of 278 to 283 K and observed microscopically with reflected light after silvering of their (001) faces. Most of the crystals exhibited the usually lozenge-shaped monoclinic morphology but a few were very elongated and presented at the same time growth spirals characteristic of both monoclinic and orthorhombic modifications (Figs. 1, 2). In Fig. 3(a),



(a)



(b)

Fig. 1. (a) Crystal of $n\text{-C}_{34}\text{H}_{70}$ developing the {001} form elongated along [100]. The micromorphology of the upper face exhibits the coalescence of two spiral patterns. (b) Enlarged view of the left part of the crystal represented in (a).

(b), which is the schematic representation of Fig. 1, the crystal association is mainly formed by a monoclinic individual elongated along \mathbf{a} , as may be seen from the obtuse angle $\beta_M = 106^\circ$ between the steps of the growth spiral (Fig. 3a). The (001) faces have the largest extension but unlike the usual growth habit, on which {010} generally does not appear, the (010) are here much more developed than the (110) faces. In addition, at the extremity of the crystal, the second and orthorhombic individual is made evident by a growth spiral, the steps of which spread over the monoclinic crystal. It is this spiral, actually formed by two series of interlaced steps, which reveals the existence of the orthorhombic polymorph; in fact the acute angle between the steps near the spiral core is about 67° (Fig. 3b). When the distance from the core of the spiral increases the acute angle increases too and tends towards a final value of 74° characteristic of the monoclinic polymorph. As both orthorhombic (O) and monoclinic (M) spirals are oriented in the same direction, $[100]_O$ coincides with $[010]_M$ and in the (001) interface between the two polymorphs exists a two-dimensional coincidence lattice common to both individuals, the translation vectors of which are:

$$\mathbf{T}_1 = \mathbf{a}_O = \mathbf{b}_M, \quad |\mathbf{T}_1| = 7.42 \text{ \AA},$$

$$\mathbf{T}_2 = 9\mathbf{b}_O \simeq 8\mathbf{a}_M, \quad |\mathbf{T}_2| = 44.46 \text{ \AA}.$$

In this coincidence lattice, 18 molecules are involved on both sides of the interface, and the (001) cell multiplicity is nine for the orthorhombic and eight for the monoclinic layer.

In Fig. 4, which is a schematic representation of Fig. 2, the crystal has the same habit as that described above. The growth layers are either monoclinic or orthorhombic and are generated by a screw dislocation emerging near a $(010)_M$ face of the crystal.



Fig. 2. Crystal of $n\text{-C}_{34}\text{H}_{70}$ showing the same development as in Fig. 1(a). The micromorphology of the upper face exhibits in this instance a coalescence of growth steps having their mutual orientation rotated $\pm 90^\circ$ with respect to that of Fig. 1(a).

Nevertheless, unlike the crystal shown in Figs. 1 and 3(a), (b), the orthorhombic is rotated with respect to the monoclinic layer by an angle of 90 or 270°. The acute angle of the monoclinic growth spiral is contained in the obtuse angle of the orthorhombic one. The two-dimensional coincidence lattice in the (001) contact plane has for translation vectors:

$$\begin{aligned} \mathbf{T}_3 &= 3\mathbf{b}_O = 2\mathbf{b}_M, & |\mathbf{T}_3| &= 14.88 \text{ \AA}, \\ \mathbf{T}_4 &= 3\mathbf{a}_O = 4\mathbf{a}_M, & |\mathbf{T}_4| &= 22.26 \text{ \AA}. \end{aligned}$$

As previously, there are 18 molecules involved in the coincidence lattice, the cell multiplicity being nine and eight for the orthorhombic and monoclinic layers, respectively. In both cases considered above the relative orientation of the orthorhombic with respect to the monoclinic layers cannot be determined unambiguously. It is not possible to know in Fig. 3(a), (b) whether this relative orientation is 0 or 180° and, in Fig. 4, whether it is 90 or 270°. In monoclinic crystals the steps of the growth spirals usually show a marked anisotropy in their advancement velocities (Aquilano, 1977) but the growth steps of the orthorhombic modification do not show this effect due to the *mm* symmetry of their growth patterns.

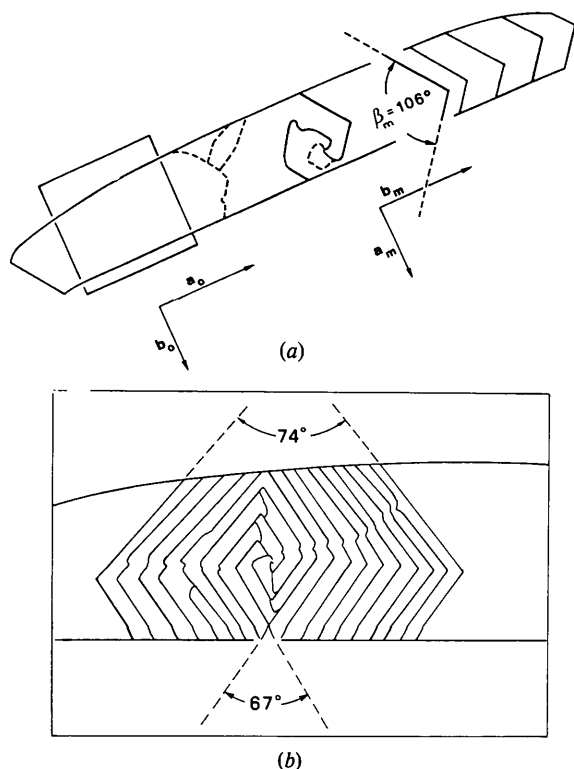


Fig. 3. (a) Schematic drawing of the crystal in Fig. 1(a). The steps $\langle 110 \rangle$ in the central and right part of the crystal form an obtuse angle of 106°, the supplementary of which (74°) corresponds to the monoclinic polymorph. (b) Schematic drawing of the enlarged view in Fig. 1(b). The steps of the interlaced spirals form an angle of 67° in the core region, corresponding to the orthorhombic polymorph.

3. Interaction energies

The method used for the calculation of the interaction energies between orthorhombic and monoclinic layers across their common (001) interface is based on the Lennard-Jones 6–12 potential, each C atom of the paraffin chain being an interaction centre. It is the same as that previously used for the calculation of heats of sublimation (Lundager Madsen & Boistelle, 1976) and of molecular interactions between (*hk*0) orthorhombic twinned crystals (Boistelle & Aquilano, 1978) or between monoclinic PPT (Boistelle & Aquilano, 1977). As for the latter, the problem consists here in finding the best stacking between adjacent layers in order to get the lowest potential energy. In addition, near the anomalous interface the two layers do not have the same structure, so it is necessary to estimate on the basis of structural considerations the interlayer distance *Z* between the planes passing through the C atoms of the terminal CH₃ groups on both sides of the interface (Fig. 5), since *Z* = 2.86 and 3.08 Å in the usual monoclinic and orthorhombic modifications, respectively. Taking into account the positions of the uppermost H atoms extrapolated from the structures determined by Shearer & Vand (1956) and Teare (1959), it turns out that, structurally, the densest possible packing of a molecule in a vertical structure (orthorhombic) on a layer of tilted molecules (monoclinic) corresponds to a distance *Z* ≈ 3.00 Å.

Even if it were impossible for steric reasons to build up a complete and rigid orthorhombic layer on a monoclinic substrate with such a small interlayer distance (overlapping of the hydrogen spheres), this distance was nevertheless chosen in the first step of the calculations. In order to minimize the potential energy it is sufficient to minimize the repulsive forces across the (001) interface by shifting the orthorhombic layer parallel to the monoclinic layer along the translation vectors \mathbf{T}_i (*i* = 1, 2, 3, 4) quoted above. As the repulsive forces are only sensitive to the smallest

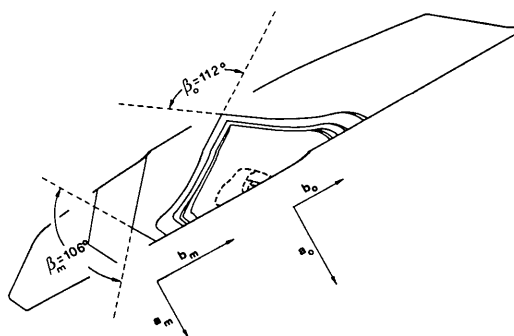


Fig. 4. Schematic drawing of the step patterns in Fig. 2. In the central part the obtuse angle $\beta_o = 112^\circ$ reveals the appearance of the orthorhombic polymorph whilst in the left part the obtuse angle $\beta_m = 106^\circ$ reveals the existence of the monoclinic modification.

C—C distances it is also sufficient to perform the initial calculations by taking into account only three C atoms on both sides of the interface. When the best stackings of the coincidence lattices are found this way, more realistic values of the interaction energies can be found if all C atoms of the paraffin chains are considered in the calculation. Actually, as the potential converges very rapidly when the number of C atoms in the chains increases (Boistelle & Aquilano, 1977), the results given hereafter concern paraffin chains built up of only seven C atoms on both sides of the interfaces. Finally,

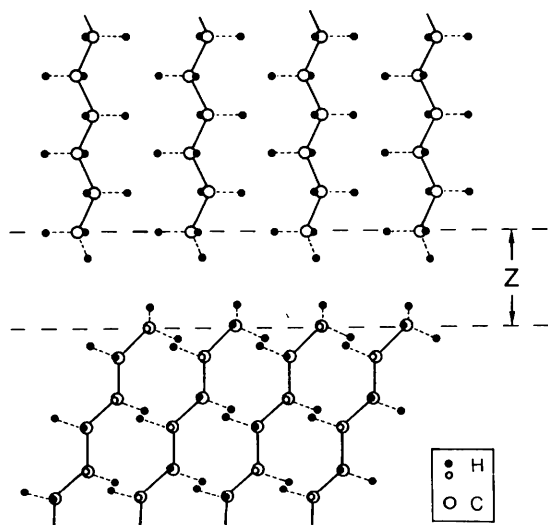


Fig. 5. Schematic drawing of an orthorhombic paraffin layer stacked on a monoclinic one with distance Z between the planes of the end-group C atoms. This stacking refers to a rotation angle of $\pm 90^\circ$ (as in Fig. 4).

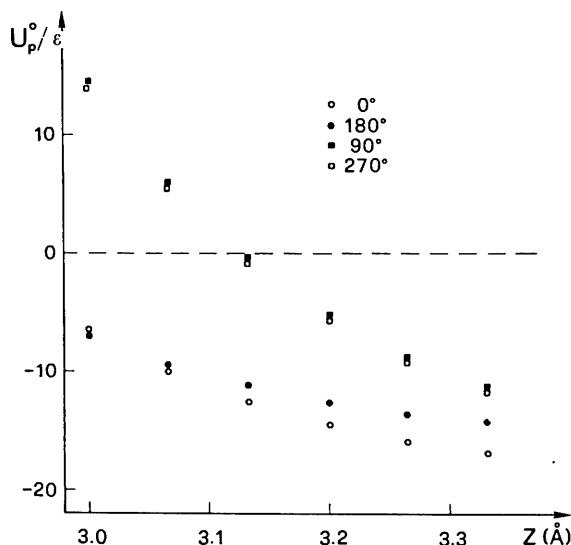


Fig. 6. U_p^0/ϵ values representing the interaction energies between a monoclinic paraffin layer stacked on an orthorhombic one for different rotation angles. Z represents (as in Fig. 5) the distance between the interface end-group C atoms.

the calculations were also performed as a function of Z , bearing in mind that from a structural standpoint the true value of Z probably ranges between 3 and 3.5 Å which is the distance for which the vertical and tilted structures can be superposed without overlapping of the hydrogen spheres.

The results of these calculations are shown in Fig. 6 where the interaction energy between the monoclinic and orthorhombic layers is plotted as a function of the distance Z for different angular stackings quoted above. One unit of U_p^0/ϵ is equivalent to 0.46 kJ mol⁻¹ and the U_p^0/ϵ values plotted in Fig. 6 represent the mean interaction energy per molecule of the two-dimensional coincidence cells considered above.

4. Discussion

It is not possible to obtain the distances Z experimentally. However, looking at the curves in Fig. 6 we can make the following observations:

(i) for the syntactic coalescences at 0 and 180° the stability is reached at $Z = 3$ Å with corresponding values of U_p^0/ϵ ranging between -6 and -7, about 2.5 kJ mol⁻¹;

(ii) on the other hand, for the syntactic coalescences at 90 and 270°, the crystal aggregate becomes stable only for values of $Z \geq 3.12$ Å. The same values of U_p^0/ϵ as in (i) are obtained in this case for Z distances of about 3.22 Å.

It is worthwhile to compare these values with those obtained previously for a monoclinic or an orthorhombic crystal, for the polytype 2O[180] and for the $[\bar{1}10]$ twin law which corresponds to the stablest PPT (Boistelle & Aquilano, 1977). The calculations also performed with seven C atoms on both sides of the (001) interface gave for U_p^0/ϵ : -25.12, -24.75, -23.00 and -13.45 respectively. Obviously these crystals are more stable than the aggregates obtained by syntactic coalescences of monoclinic and orthorhombic polymorphs. That is not surprising for the orthorhombic, the monoclinic 1M [0] and the polytypic 2O[180] structures; however we should have expected the same interaction energies for the $[\bar{1}10]$ twin law and for the syntactic coalescences because in all these cases the coincidence cell areas and multiplicities are the same. Actually, from the considerations (i) and (ii) and from previous work (Aquilano, 1977; Boistelle & Aquilano, 1978), it turns out that there is no simple correspondence between coincidence cell areas and interaction energies. The existence of common lattices in crystal aggregates is a condition which is necessary but not sufficient for their stability, as becomes clear when the corresponding interaction energies are calculated.

Nevertheless, the observed syntactic coalescences show that it is possible for an orthorhombic growth layer to spread over a monoclinic substrate in spite of

the fact that the end-group packing energy is less than in a normal crystal or in polytypes. In our opinion, this may be due to the presence, on the (001) faces of these crystals, of growth spirals repeating periodically the stacking sequence which depends on the content of the exposed ledge. In this way, near the anomalous interfaces, stability is mainly provided by the side-packing energy which remains unaltered. Furthermore, the highly repulsive forces at the interface may be cancelled if the interlayer spacings are increased by a few tenths of an Å or by the rearrangement of relaxed end-groups which was not taken into account in our model.

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Temperature Effects on the X-ray Scattering Factors of Crystals in the LCAO Approximation

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Abstract

A new convolution method is presented for a rigorous LCAO calculation of the lattice-vibration effects on the X-ray scattering factors of crystals. The theory is applied to a lithium hydride crystal and a good agreement with experiment is obtained.

Introduction

Previous calculations of the X-ray scattering factors of crystals within the LCAO approximation have included

the lattice vibrations in a similar way to the free ion (or free atom) picture (Aikala & Mansikka, 1970, 1971, 1972; Grosso & Parravicini, 1978). These calculations have involved the conception of crystal ions (or atoms). This inconsistency is avoided in the present work where the lattice vibrations are treated rigorously in the LCAO approximation with a convolution method.

The most suitable crystal for an experimental check of this method is lithium hydride because it is the simplest ionic crystal with only four electrons per ion pair. Recently, several theoretical investigations have been published on this crystal. These include studies on directional and isotropic Compton profiles (Aikala,