

Analysis of the molecular structure and the terminal groups packing of n-alkanes of different parities

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A scheme of the contact region structure of the terminal methyl groups of molecules of neighboring lamellae in n-alkanes of different parities is proposed. The penetration depth of the lamellae into each other was calculated depending on the orthorhombic or triclinic symmetries of the molecular arrangement in the lamella crystalline cores. A greater depth of van der Waals contact between the terminal groups in even n-alkanes than in odd ones was revealed, which indicates a denser packing of molecules with triclinic symmetry compared to orthorhombic.

Keywords: n-alkanes, molecular structure, unit cells, lamellae.

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Normal alkanes $\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_3$ are representatives of the long-chain molecular crystals (LCMCs) with the simplest chemical structure. The possibility of industrial synthesis of LCMCs with the number of methylene groups $n = 10-40$, a high degree of chemical purity and in the absence of structural and conformational defects allows us to consider n-alkanes as finite-size models for describing phase transitions, which is of significant interest for polymer physics.

Identification of the features of the polymorphic rearrangement of the crystal structure of LCMC n-alkanes during temperature phase transitions raises the need for additional fundamental studies. In particular, studies are being carried out on the kinetics of the development of the solid-phase transition of first kind first-order solid-solid phase transition [1,2] to establish the step-by-step mechanism of structural transformations. Increased attention is paid to comparing the progress of phase transitions in n-alkanes of different parities due to the difference in the symmetry of molecular packing in lamellae with vertical and inclined chains [3].

The most convenient objects for studying structural transformations are n-alkanes that are solid at room temperature: tricosane $\text{C}_{23}\text{H}_{48}$ (C23) and tetracosane $\text{C}_{24}\text{H}_{50}$ (C24), which have a unique property associated with the temperature separation by several degrees of the solid-solid phase transition and the phase transition of order-disorder type (melting/crystallization).

To explain the processes occurring during the solid-solid phase transition, namely, various conformational transformations of molecules and modifications in the symmetry of their mutual stacking, it is necessary to clarify the structure of the thin interlayer formed by the van der Waals contact (VDWC) of the terminal CH_3 groups of molecules in adjacent lamellae.

In the literature the sizes of interlamellar layers were estimated as the distances between the planes formed by the end carbon atoms in neighboring lamellae [4]. However, until now no attention drawn to a detailed analysis of the structure and arrangement of end groups. One of the actual problems is the study of the structure of the contact between the end groups of molecules in neighboring lamellae of n-alkanes, which is the goal of this paper.

Calculations concerning the structure of the interlamellar space are often based on the length of the molecule, during calculation of which the authors usually do not take into account several factors discussed below. The spatial structure of the n-alkane molecule is a planar trans-zigzag, the basis of the spatial configuration of which is sp^3 -hybrid carbon atoms. According to [5], the characteristic parameters of the trans-zigzag of n-alkane molecule, namely, the lengths of carbon-carbon C–C and carbon-hydrogen C–H bonds, and the valency angles of the carbon skeleton, in fact, increase slightly from the end of the molecule towards its middle (Figure 1). This is due to the influence of the end methyl CH_3 group on the rest part of the chain, the disturbance from which, however, attenuates by the nearest neighboring methylene group $\omega\text{-CH}_2$. Thus, we assume that the unperturbed section of the chain is characterized by the following parameters: length of carbon-carbon bond $L(\text{C}-\text{C}) = 1.5418 \text{ \AA}$, valency angle of the carbon skeleton $(\text{C}-\text{C}-\text{C}) = 112.7^\circ$, length of carbon-hydrogen bond $L(\text{C}-\text{H}) = 1.0859 \text{ \AA}$ and angle $(\text{H}-\text{C}-\text{H}) = 107.0^\circ$. For end CH_3 and its neighbouring $\omega\text{-CH}_2$ groups we will use special parameters according to Figure 1.

Obviously, the length of the unperturbed trans-section of the molecule is determined by the expression:

$$L_{\text{unpert. trans}} = (n - 5) (\text{C}-\text{C})_x,$$

where n — number of carbon atoms in molecule of n-alkane, $(\text{C}-\text{C})_x$ — projection of unperturbed C–C-bond

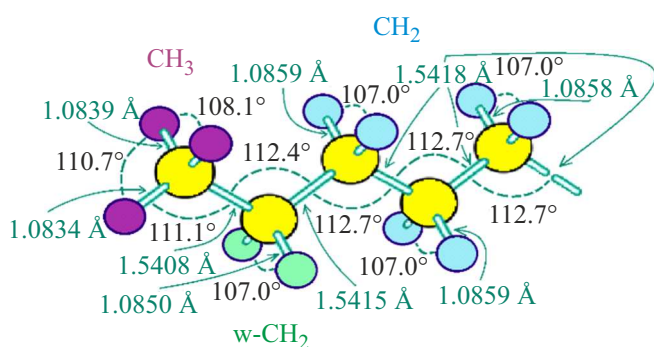


Figure 1. Calculated parameters of the n-alkane molecule [5].

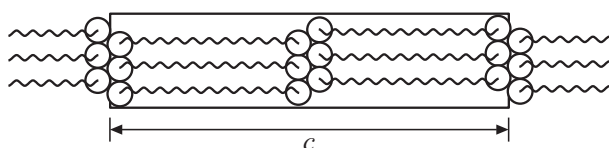


Figure 2. Scheme of molecules arrangement in orthorhombic cell.

on molecule axis. The total projection of perturbed bonds onto the axis of the molecule can be expressed as follows:

$$L_{\text{pert.trans}} = 2(C-C)_x + 2(C_\omega - C_{\text{end}})_x,$$

where C_ω and C_{end} — carbon atoms belonging to ω -CH₂ and CH₃ groups, respectively. Then the length of the trans-zigzag molecule is determined by the expression

$$L_{\text{trans}} = L_{\text{unpert.trans}} + L_{\text{pert.trans}} \quad (L_{\text{trans}}(\text{C23}) = 28.23 \text{ \AA})$$

and

$$L_{\text{trans}}(\text{C24}) = 29.51 \text{ \AA}.$$

When calculating the total length of the molecule, it is necessary to take into account the specific structure of the two end methyl groups, in which single C–H-bonds are located in the trans-zigzag plane. The corresponding contribution to the total length is equal to $2(C-H)_x$, where $(C-H)_x$ — projection of the end C–H-bond to the axis of the molecule. Among other things, it is necessary to take into account the radii of hydrogen atoms, for which generally van der Waals radii are used when describing the molecular structure and interactions. The latter are $R_0(\text{H}) = 1.16 \text{ \AA}$ for hydrogen, and $R_0(\text{C}) = 1.71 \text{ \AA}$ for carbon [6]. Since the van der Waals radii can only be determined up to 0.01 \AA , in further calculations one should keep in mind precisely this accuracy in determining the lengths of the chains.

Taking into account the above structural features, the total length of the n-alkane molecule is determined by the relation

$$L = L_{\text{trans}} + 2(C-H)_x + 2R_0(\text{H}),$$

which makes it possible to estimate the chain lengths of tricosane $L(\text{C23}) = 32.34 \text{ \AA}$ and tetracosane $L(\text{C24}) = 33.62 \text{ \AA}$.

The general formula for the n-alkane chain length depending on n is as follows:

$$L = 1.2835n + 2.8165 (\text{\AA}). \quad (1)$$

We believe that expression (1) for calculating the length of the molecule will be valid for all n-alkanes with linear chain structure, starting with $n = 5$, since in such homologous series the end groups have a similar effect on the trans-zigzag.

Let us find out the differences in the interlamellar space of most even and odd n-alkanes. It is known that rather pure n-alkanes with even n ($6 \leq n \leq 26$) crystallize in the triclinic system, while with odd n ($9 \leq n \leq 45, 61, 65, 69$) — in the orthorhombic system [7,8], while all n-alkanes exhibit either a true hexagonal phase or its distorted modification near the melting point. The „key“ structure of the representative with odd n was determined for tricosane C₂₃H₄₈ [9], and analysis of the even molecule was given by the example of octadecane C₁₈H₃₈ [10]. Even-odd differences are associated with the type of symmetry of molecules (trans or cis), which is significantly manifested in the packing of end groups and leads to the appearance of inclined phases, which are more energetically favorable specifically for even chains.

According to [9], the orthorhombic main unit cell C23 is characterized by the parameters $a = 4.97 \text{ \AA}$, $b = 7.48 \text{ \AA}$, $c = 62.31 \text{ \AA}$. As can be seen from Figure 2, a distance equal to c falls on 2 molecules, taking into account the overlap of their end groups. Therefore, using the length of the tricosane molecule calculated from expression (1), we can estimate this overlap or the depth of the VDWC of the end groups of neighboring molecules in the orthorhombic cell:

$$R_{\text{vdW}} = L - c/2 = 1.19 \text{ \AA}.$$

In turn, the following parameters were determined for the triclinic unit cell C24 [11]: $a = 4.29 \text{ \AA}$, $b = 4.82 \text{ \AA}$, $c = 32.50 \text{ \AA}$, $\alpha = 86.43^\circ$, $\beta = 68.71^\circ$, $\gamma = 72.70^\circ$, which are predicted based on the „key“ structure of octadecane [10]. As obtained above, the length of the tetracosane molecule is $L(\text{C24}) = 33.62 \text{ \AA}$, which exceeds the largest cell parameter c . Thus, the depth of the VDWC of the end groups of neighboring molecules in triclinic cell along the molecule axis is determined by the relation

$$R_{\text{vdW}} = L - c = 1.12 \text{ \AA}.$$

Note that overlap was found along the axis of the molecule. We are interested in the true depth of the VDWC along the axis of the lamella or perpendicular to its base plane, i.e. it is necessary to take into account the inclination of the molecules in the unit cell. Based on the parameters and angles of the triclinic cell, it was possible to calculate the angle between the axis of the molecule and the axis of the lamella $\varphi = 21.48^\circ$. Therefore, the projection of the parameter c onto the lamella axis is $h = c \cos \varphi = 30.24 \text{ \AA}$, which completely coincides with

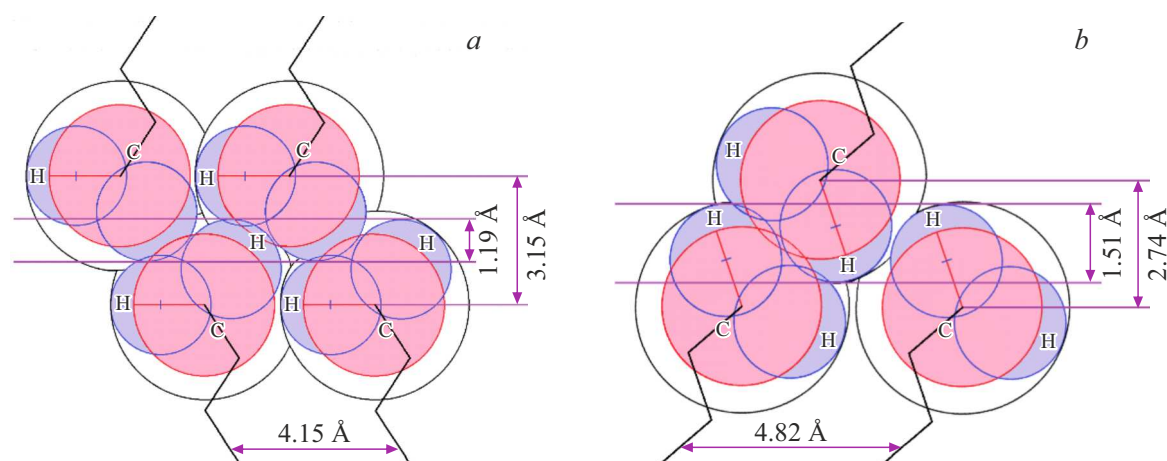


Figure 3. Scheme of contact of molecules in neighboring lamellae with cells of orthorhombic (a) and triclinic (b) symmetry.

the literature specified calculated value of the long period $d(001)$ [11] and is in good agreement with the experiment $d(001) = 30.32 \text{ \AA}$ [12]. To find the projection of the length of the tetracosane molecule $L(C_{24})$ onto the lamella axis, it is necessary to determine for greater accuracy the angle θ formed by a single end C–H bond and the lamellar axis. Since the spatial location of this bond is not obvious, we use the bond length $L(C_{\omega}-C_{\text{end}}) = 1.5408 \text{ \AA}$ [5] and its projection onto the lamella axis, which, based on the coordinates of the end carbon atoms [11], is $L(C_{\omega}-C_{\text{end}})^* = 1.11 \text{ \AA}$. The data obtained ensure based on the geometric considerations determination of angle $\theta = 24.95^\circ$. Thus, the total projection of the length of C24 molecule onto the lamellar axis

$$L^* = L_{\text{trans}} \cos \varphi + 2L(C-H)_{\text{end}} \cos \theta + 2R_0(H) \\ = 31.75 \text{ \AA}.$$

It can be concluded that the depth of the VDWC along the lamella axis in triclinic cell has the value $R_{\text{vdW lam}} = L^* - h = 1.51 \text{ \AA}$.

Comparison of the calculated penetration depths of the lamellae into each other confirms that the triclinic packing is the most dense for LCMCs [13], since the greater depth of the end groups of VDWC indicates a narrower interlamellar space. Our calculations are consistent with the consideration of the packing density of the end groups in inclined and vertical chains [7], as well as with estimates of the distances between the planes of the end methyl groups of neighboring lamellae: 2.74 and 3.15 Å for triclinic and orthorhombic structures, respectively [4].

Figure 3 shows diagrams of the contact of the end groups of neighboring lamellae C23 (a) and C24 (b) based on the data obtained above. The distance between molecules inside one lamella for orthorhombic cell is taken in accordance with the shortest contact between chains 4.15 Å [14], and for triclinic cell — as the parameter $b = 4.82 \text{ \AA}$.

From Figure 3 it is clear that in the case of triclinic symmetry (tetracosane), the contact of the end groups is

indeed more dense (it should be understood that actually there is no intersection of atoms, since the molecules in neighboring lamellae are displaced along the axis perpendicular to the plane of the Figure). Thus, the analysis of interlamellar space in n-alkanes of different parities allows us to quantitatively consider changes in the structure of n-alkanes at the molecular and supramolecular levels of organization.

Conflict of interest

The authors declare that they have no conflict of interest.

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