
**STABILITY OF MOLECULAR AGGREGATES OF HYDROCARBONS
WITH ALL-*trans* CHAINS AND TRANSLATION OF THE MOLECULES**Ján GAJDOŠ^a and Tomáš BLEHA^b^a *Institute of Chemistry and*^b *Polymer Institute, Centre of Chemical Research,
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Potential energy has been calculated for molecular aggregates formed of all-*trans* extended hexanes with various arrangements of the central molecule surrounded by the first coordination sphere. Differences in stabilities of the aggregates are connected with biaxial character of asymmetry of the interaction energy of extended paraffins. When investigating the multiparameter interaction potential of the partially ordered systems of hydrocarbon chains, the first step consisted in determination of the energy barriers to longitudinal shifts of the central molecules at various distances of the surrounding molecules. Destabilization of the aggregates with displaced molecules is due to both the mismatch of the central molecule to the matrix and effective shortening of that part of the central molecule which is "immersed" in the aggregate. The energetics of the model aggregates is made use of in elucidating the role of translation of paraffins and cognate molecules in rotational phase, in mesophases, and at a forced shortening of the chains connected with conformational transition.

A number of technically and biologically important structures include molecules with linear hydrocarbon chains. The most closely packed and most regular arrangement in solid state is encountered — within this group of compounds — with molecular crystals of paraffins. However, even in this case crystallographical modifications (particularly the so-called rotator phase) with increased mobility of molecules and higher degree of lattice disorder are observed at enhanced temperatures near the melting point¹. Density and regularity of arrangement of molecules in the crystal is further decreased in more complex molecules containing other groups besides the paraffinic chain, as *e.g.* fatty acids, lipids, *etc.* With these types of compounds a number of aggregate states are observed which lie between molecular crystals and liquid state (mesophases). As compared with an ideal crystal, dynamics of molecular motions is increased due to weaker intermolecular mean field in the individual mesophases. Hence, there emerges necessity of energy characterization of the individual modes of motion and their distinct anisotropy can be expected due to the chain character of the molecules.

Molecular mechanics² calculations appear to be very useful for obtaining information on static and dynamic properties of chain hydrocarbons. In continuation of our previous treatment^{3,4} of pairs and triads of paraffins, this paper deals with energetics of extended paraffinic chains surrounded by the first crystallographical layer of molecules in the lattice with arrangements of various symmetries. We also examined the energy required for one particular type of molecular motions in the

aggregate – translation of molecules along their longitudinal axis in the force field of the other molecules in the aggregate.

Method and Model

The potential energy calculations were carried out in the same way as those in the previous communications^{3,4} using the molecular mechanics method with parameters and procedure according to Boyd⁵. The potential energy E_s of a molecular assembly is expressed in this method by the relations based on classical mechanics, and minimization of the E_s energy provides the equilibrium intra- and intermolecular parameters of the aggregate. As our previous work³ showed no significant internal geometry changes of the all-*trans* molecules which would be caused by the presence of other molecules in the vicinity, we neglected the optimization of intramolecular parameters in the calculation. Thus the potential energy of molecular set is given by the van der Waals intermolecular interaction energy. All-*trans* n-hexane was used as a model of longer hydrocarbon chains, its geometry parameters being optimized³.

The investigated aggregates of parallel hexane molecules are represented schematically in Fig. 1. The hexagonal arrangement (formed of seven molecules) is typical for various less ordered aggregate states of molecules with paraffinic chains. It is encountered, *e.g.*, in the rotator phase of paraffinic crystals^{1,6}, in lipid mono- and bilayers⁷, and in the inclusion adducts of paraffins and urea⁸. The hexagonal arrangement H_A was used by Belle and Bothorel⁷ for modelling the interactions in phospholipid aggregates. Cooperative rotation of all the molecules by 30° around their longitudinal axes transforms this arrangement into H_B . The S aggregate (formed of five molecules) represents a hypothetical model of tetragonal arrangement. The orthorhombic

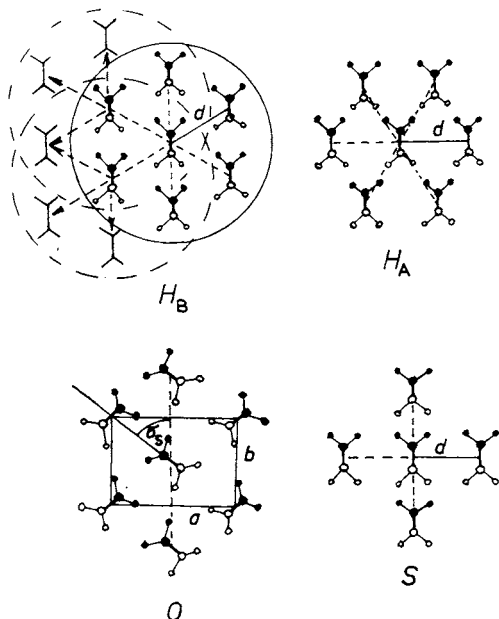


FIG. 1

Arrangement of the molecules in the aggregates represented in the plane perpendicular to their longitudinal axis. The different values of the z coordinates (crystallographic axis c) are represented by full and empty circles. In the H_B aggregate a part of the molecules of the outer layer are also represented so that the calculation of the stabilization energy e_{int}^c may be demonstrated more clearly

structure *O* is typical for the paraffins with odd number of carbon atoms and for the polymethylene macromolecule¹.

The dependence of intermolecular interaction energy E_{int} on the distance d between the central molecule and the surrounding molecules was examined for the aggregates H_A , H_B , and S . The stabilization energy is $E_{\text{int}} = E_s - nE^{\text{isol}}$, where n means number of the molecules in the aggregate, and E^{isol} stands for the energy of an isolated hexane molecule. In the orthorhombic aggregate the static potential energy E_{int} was calculated for experimental value of lattice parameters $a = 0.744$ nm and $b = 0.496$ nm corresponding to long-chain paraffins⁹. For the setting angle σ_s (Fig. 1) the value 34.5° was used which corresponds to the minimum of the potential energy E_s in the *O* aggregate, although the experimental value is somewhat higher (41.3°). The displacement of the central molecule along the longitudinal axis was expressed in multiples of z , where $z = 0.254$ nm corresponds to the repetition period of CH_2 groups in a long paraffinic chain along the crystallographic axis c .

RESULTS AND DISCUSSION

Stabilization energies. The dependence of the intermolecular van der Waals energy of the chains on the distance d of the first coordination sphere is given in Fig. 2 for the aggregates H_A , H_B , and S . The interaction potential shows a deep minimum in each of the three cases. Out of the two hexagonal structures, H_B appears to be more stable and has considerably smaller equilibrium distance d_{min} as compared with H_A . The stabilization energy of the orthorhombic structure (-146.0 kJ mol⁻¹ for $\sigma_s = 34.5^\circ$ and -144.0 kJ mol⁻¹ for $\sigma_s = 41.3^\circ$) lies between the values of the two hexagonal structures. Table I gives the stabilization energies e_{int} of the aggregates calculated per one methylene group, the effect of the methyl end groups being neglected. It can be seen that the stabilization increases with increasing number of the mole-

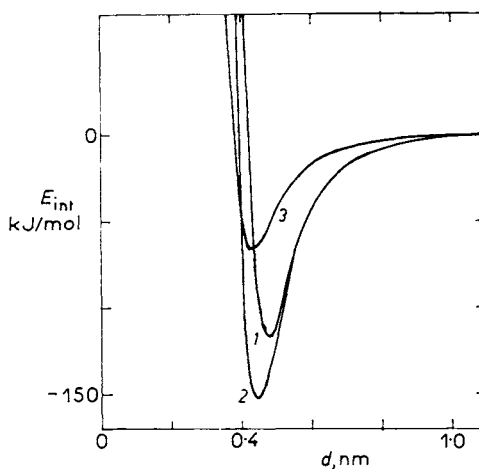


FIG. 2

Dependence of the intermolecular interaction energy on the distance d between the molecules. 1 H_A aggregate, 2 H_B , 3 S

cules in the aggregate. The e_{int} value (Table I) was obtained by simple dividing the total stabilization energy of the aggregate by the number of all the CH_2 groups present (*i.e.* 35 and 42 for 5 and 7 molecules, resp.). This value, however, reflects the stabilization for such model in which the central molecule is surrounded by the first coordination sphere only ("isolated aggregate"). It is unsuitable for comparison with the lattice energy of the molecular crystals of paraffins, because it does not take into account the interactions of the "isolated aggregate" with the neighbouring molecules in the crystal lattice. The "binding" energy of the aggregate in the lattice was assessed in the following way.

The interactions were calculated between the central molecule and each of the surrounding molecules in the aggregate, neglecting the mutual interactions of the surrounding molecules. The obtained E'_{int} values were -57.03 , -73.91 , and -70.55 kJ mol^{-1} for the aggregates H_A , H_B , and O , respectively. The stabilization energy E_{int}^c of the aggregate in the lattice is given by the sum of E_{int} of the "isolated" aggregate (represented schematically in Fig. 1 by the molecules encircled by full line) and the contributions $E'_{\text{int}}/4$ determined for each of the six molecules in the first coordination sphere (encircled by dashed line in Fig. 1). Reduction of E'_{int} to one quarter eliminates the repetition of the interactions already involved in E_{int} . Finally, the stabilization energy obtained in this way was divided by the number of CH_2 groups in the aggregate, similarly as in the calculation of e_{int} .

The values e_{int}^c obtained in this way are given in Table I. The experimental stabilization energy of the crystal¹⁰ is still not attained, which is mainly due to "insufficient"

TABLE I

The stabilization energies e_{int} (kJ mol^{-1}) of the molecular aggregates of hexane per one $-\text{CH}_2-$ group for the intermolecular distance d (nm), number of molecules n , and the stabilization energy per one $-\text{CH}_2-$ group (e_{int}^c , kJ mol^{-1}) of the aggregates "bound" in the lattice in the respective arrangement

Arrangement	n	d	e_{int}	e_{int}^c
Pair ^a	2	0.405	-1.45	
Triad ^a	3	0.445	-1.55	
S	5	0.435	-2.24	
H_A	7	0.477	-2.80	-4.84
H_B	7	0.449	-3.66	-6.30
O^b	7		-3.48	-6.00
Crystal ^c	∞			-7.70

^a The maximum stabilization energies of several configurations of pairs and triads³; ^b for the distances corresponding to a , b from ref.⁹ and to $\sigma_s = 34.5^\circ$; ^c the lattice energy of the polymethylene crystal¹⁰.

length of the hexane molecules and/or to the fact that further molecular layers "above" and "below" the aggregate were not involved. Practical range of the applied van der Waals atom-atom potentials is about 1 nm, whereas the length of the hexane molecule is only about 0.6 nm. The same factors may explain the calculated preference of the H_B aggregate to the O aggregate. It is also noteworthy that the H_B structure (in contrast to H_A) differs but slightly from the monoclinic structure in its laterally shifted sandwich arrangement, the monoclinic structure being observed as the most stable one with higher even paraffins¹. The mutual subtle balance between the length of the paraffinic chain, even or odd number of the chain carbon atoms, and apparently also size of the aggregate (number of the coordination spheres) determine the preference of the final crystallographic structure in the paraffin-like molecules.

The diversity of crystalline modifications of chain hydrocarbons is closely connected with the biaxial character of anisotropy of the interaction potential of the extended chains. Besides the dominant anisotropy along the longitudinal axis these molecules also show another anisotropy between the "width" and "thickness" of electron density in the plane of the zig-zag carbon backbone of the chain. This asymmetry is responsible for the interaction energy differences between pairs and triads of extended paraffins in various parallel configurations³ and it is transferred to the static energy of the aggregates in Fig. 1. Semiempirical assessments of the interaction energy start sometimes from monoaxial anisotropy of the chain and from the idea of cylindrical symmetry of the interaction energy around the longitudinal axis of the chain¹¹; such approximation, however, wipes off slight differences in stabilities of the individual assemblies of extended chains. The fact that it is necessary to consider the biaxial anisotropy of the extended paraffins complicates considerably general expression of E_{int} , and, in principle, different shapes of the potential are obtained for each configuration as it can be seen in Fig. 2. The curves in Fig. 2 were expressed by means of the biparametric potential of the type 6–12

$$E_{\text{int}} = \varepsilon(x^{-12} - 2x^{-6}), \quad (1)$$

where ε means the depth of the potential minimum and $x = d/d_{\text{min}}$ (Table II). Fitting of the curves by means of the 5–11 potential (which is recommended¹¹ for parallel chains with cylindrically symmetrical potential) proved unsuitable in our case.

Application of the potentials from Fig. 2 to real aggregates of hydrocarbon chains at greater distances d , however, is connected with difficulties. If the molecules are more separated, further degrees of freedom are made available for molecular motions, *viz.* for rotation around the longitudinal axis by an angle σ , for a shift of the molecules along the long axis by z , as well as for tilting of the whole aggregate of extended parallel molecules by an angle Θ from the normal. Finally, at large d values the parallel arrangement is disturbed as a consequence of internal rotation

by an angle φ around C—C bonds in the molecules from *trans* to *gauche* positions. Hence, a description of interaction in aggregates with chain molecules necessitates knowledge of the more general potential $E_{\text{int}}(d, \sigma_n, z_n, \Theta_n, \varphi_{nj})$, where n means number of molecules and j corresponds to the number of carbon atoms in the chain minus three. Sometimes a single parameter d suffices for determination of mutual position of the molecules (hexagonal arrangement), several parameters being needed for other symmetries. Although the dependence of the E_{int} potential on the intermolecular distance is dominant, its dependence on other parameters cannot be neglected.

Analytical form of the general interaction potential for chains with any combination of the mentioned parameters is not known, and it will be extraordinarily difficult to find it. This potential, however, is indispensable for simulating thermodynamic properties of partially ordered condensed phases composed of chain molecules. In simple liquids this problem is solved by application of the procedures based *e.g.* on the Kihara model of the pair potential of anisotropic molecules or on various potentials for dumb-bell-shaped molecules, *etc.* In the case of hydrocarbon chains the most passable way to obtain a general pair interaction potential seems to consist in its numerical determination on the basis of the atom-atom potential energies.

Shift of molecules in the aggregate. If the hypersurface $E_{\text{int}}(d, \sigma_n, z_n, \Theta_n, \varphi_{nj})$ were known, it would be possible to evaluate also probability of individual modes of motion of the molecules in the aggregate and their mutual coupling. The coupling can apply to the same mode in several molecules, as it is the case of the tilting angle Θ which is usually the same for all the molecules in an aggregate (the preference of parallel arrangement of the chains), or it can involve two different modes of the same molecule. Just in the latter case there already exists a unique picture of the part of the mentioned hypersurface for the coupling of translation with molecular rotation in orthorhombic structure¹². Variation of parameters of the interaction potential enables to construct parts of energy hypersurface and to find energy requirements for the individual modes of motion. Especially interesting are the situations involving

TABLE II

Parameters of the potential function (6–12) for molecular aggregates of n-hexane. The ϵ values are in kJ mol^{-1} , d_{min} in nm

Arrangement	ϵ	d_{min}
H_A	117.53	0.477
H_B	153.66	0.449
S	67.23	0.435

molecular distances slightly greater than those required by the dense packing of molecules in ideal crystals of paraffins. This region corresponds to less stable crystalline configurations as *e.g.* the rotator phase of paraffinic crystals as well as to various mesophases, where there are substantially greater possibilities of molecular motions than in an ideal crystal.

In the first step of characterization of energetics of molecular motions in the aggregates we examined the feasibility of the shifts of the extended chains along the longitudinal axis. The energy barrier to the translation of the central molecule was determined for the aggregates H_A , H_B , and S at two extreme distances, *viz.* d_{\min} in the given aggregate and $d = 0.55$ nm. In the orthorhombic aggregate the computation started again from experimental parameters of the unit cell⁹ and $\sigma_s = 34.5^\circ$. For the densely arranged aggregates corresponding to the equilibrium distances d_{\min} we found relatively high barriers to the translation along the longitudinal axis by one period $z = 0.254$ nm (two methylene groups) (Fig. 3). Out of the two hexagonal structures, H_B exhibits a higher barrier in accordance with smaller distance d_{\min} . However, as it can be seen from Fig. 3 the energy maximum does not appear at the expected shift by $z/2$ (0.127 nm) but at about 0.14 nm or even at 0.15 nm in the case of the O aggregate. This fact is due to two factors determining the destabilization of the aggregate which accompanies the shift of the central molecule. The first factor consists in formation of a structure exhibiting a mismatch of the chains in the aggregate when the central molecule is displaced by $z/2$; the configuration thus formed was denoted as BB' in the case of the chain pairs³, and it is characterized by a lowered stabilization energy. The second factor consists in the fact that the translation of the central molecule out of the aggregate effectively shortens that part of the central chain which is immersed in the aggregate, and the missing $-\text{CH}_2-$

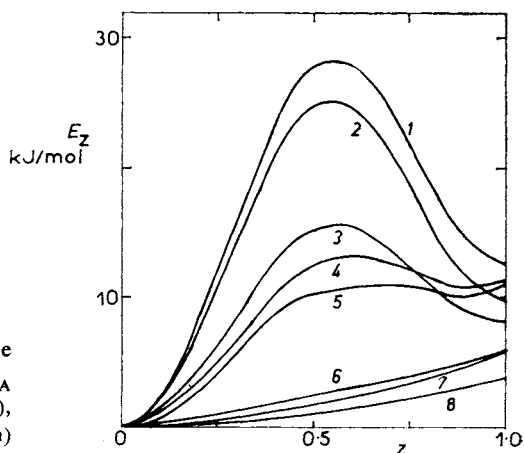


FIG. 3

The translation of the central molecule in the aggregates. 1 H_B aggregate (d_{\min}), 2 H_A (d_{\min}), 3 S (d_{\min}), 4 O , 5 H_B (0.48 nm), 6 H_A (0.55 nm), 7 H_B (0.55 nm), 8 S (0.55 nm)

groups cause a lowering of stability of the aggregate. The second factor is also responsible for the fact that energy of the aggregates shifted by the entire period ($z = 1$) is smaller than that at $z = 0$ (Fig. 3). Obviously, the energy barrier to the shift in the aggregate will increase with the length of the chains. Therefore, it is more advantageous to express the barrier to the longitudinal translation per one $-\text{CH}_2-$ group shifting through the lattice points in the individual aggregates (Δe_z) (Table III), neglecting the effects of methyl end groups.

The effect of the "lost" interaction energy as the consequence of displacement of the molecule from the aggregate into vacuum decreases with increasing chain length and disappears for the infinite chain. Its contribution to the barrier to the longitudinal shift was assessed in the following way. The E_{int} value was determined for the shift of the central molecule by an integer multiple of z (when the central molecule fits the crystallographical register of the surrounding molecules). The points obtained were fitted to a parabolic function enabling determination of the contribution of the energy "loss" also for any arbitrary non-integer z values. This procedure gives "corrected" barriers ΔE_z^{corr} and Δe_z^{corr} (Table III) located precisely at $z/2$ and representing only the destabilization of the aggregates due to mismatch of the chain configuration. Table III shows that the individual densely arranged molecular aggregates (with $d = d_{\text{min}}$) differ considerably in the energy restrictions on the translation of the central molecule.

Figure 3 gives — as an opposite to the dense arrangements — also the results for $d = 0.55$ nm. At this distance of surrounding molecules from the central molecule no barrier exists at $z/2$, and the whole energy increase from $z = 0$ to $z = 1$ is due to the "loss" of stabilization energy accompanying the shift of the CH_2CH_3 part of the central molecule out of the aggregate. After correction for long chains it fol-

TABLE III

The barriers ΔE_z to longitudinal translation of the central chain in the aggregates with the d_{min} intermolecular distances. Δe_z are the barriers per one $-\text{CH}_2-$ group. ΔE_z^{corr} and Δe_z^{corr} are the values of the translational barriers corrected for long chains (in kJ mol^{-1})

Arrangement	ΔE_z	Δe_z	ΔE_z^{corr}	Δe_z^{corr}	
H_A	24.9	4.1	22.0	3.7	
H_B	28.1	4.7	24.5	4.1	
H_B^a	10.9	1.8	6.7	1.1	
O^b	12.6	2.1	9.2	1.5	2.1 ^c
S	15.2	2.5	12.6	2.1	

^a For $d = 0.48$ nm; ^b for a, b from ref.⁹ and for $\sigma_s = 34.5^\circ$; ^c ref.¹².

lows that the distance $d = 0.55$ nm is already large enough in order the mismatch arrangements along translation have no effect on the E_{int} value.

With the hexagonal H_B arrangement we also examined the translation energetics at the intermediate distance $d = 0.48$ nm. Such distances are usually observed between paraffin molecules in the rotator phase and in various mesophases of more complicated molecules with hydrocarbon chains. From Fig. 3 and Table III it can be seen that, according to expectation, the translational barriers are distinctly lowered as compared with those for the densely arranged chains. Moreover, the calculated energies show that in the hexagonal arrangement of the molecules with $d = 0.48$ nm there exists a larger freedom of the longitudinal translation as compared with the orthorhombic arrangement O .

For the aggregates H_A , H_B , and S we also carried out calculations of the stabilization energy $E_{int}(d, z)$ at the arrangement of the central molecule being displaced by $z/2$ along the longitudinal axis. It was found that the maximum stabilization in the aggregates is attained at the intermolecular distance d greater by about 0.03 nm than that of the aggregates having non-shifted molecules. The stability order of the aggregates (expressed by the magnitude of the stabilization energy) remained unchanged, the most stabilized aggregate being H_B (-130.0 kJ mol $^{-1}$), followed by H_A (-93.5 kJ mol $^{-1}$) and by S (-54.4 kJ mol $^{-1}$) which is composed of 5 molecules. The results given show that a forced translation of some chain in the hydrocarbon crystal should be accompanied by expansion in perpendicular direction to this shift, *i.e.* by an increase of intermolecular distances of the chains. It is obvious, however, that this expansion would be almost suppressed by involvement of the second and further coordination spheres in the model.

The barriers to the longitudinal translation of the central molecule were calculated with the presumption that the translation is not accompanied by simultaneous rotation of the whole molecules. It is probable, however, that at small distances near d_{min} these two modes will be coupled, and the translation of a chain accompanied by its simultaneous rotation to the optimum angle σ will result in a lowering of the calculated barriers. On the other hand this coupling becomes weaker with increasing distance d , and the two modes can be considered independent at higher distances.

Translation of paraffinic chains in condensed phases. The molecular energetics of the translation of the central molecule in the aggregates can be related with the translational motion observed in various types of aggregate states with paraffinic chains. The greatest amount of information of this type was accumulated on n-alkanes. Phase behaviour of alkanes is very complex, and only recently it was found that higher odd-number alkanes exhibit – between the low temperature stable crystalline modification and the melting point T_m – further three⁶ or even four (for the region of $C_{25} - C_{29}$) modifications¹³. The especially detailed study by Strobl and coworkers⁶

on the derivative C_{33} clearly showed gradual increasing of the chain mobility in the individual solid–solid phase transitions. The transition from the low-temperature stable A modification to the B modification is connected with release of cooperative rotation of the chains around the longitudinal axis by about $\sigma = 180^\circ$. On transition from B to C modification it is possible already to observe a limited motion along the longitudinal axis of the chain, too, which is partially coupled with molecular rotation. Finally, in the quasihexagonal D modification (denoted usually as the rotator phase), which lies closely below the melting point, there takes place rotation of the extended chain, longitudinal diffusion, as well as formation of intrachain conformation defects. By means of quasielastic neutron diffraction the cited authors⁶ determined the translational diffusion coefficient $(1.2 \pm 0.2) \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ in the D modification, the molecular dynamics in this modification being describable as a diffusion process with independent rotational and translational components.

The diffusion coefficient of the longitudinal translation can also be assessed on the basis of the calculated barriers in the individual aggregates from the relation¹⁴

$$D = a^2 \nu_t \exp((\Delta S - \Delta H)/RT), \quad (2)$$

where a is the lattice parameter (the distance of two equilibrium positions), ν_t is thermal vibration frequency of the molecule in the lattice, and the activation entropy and enthalpy have the usual meaning as in the theory of rate processes. Let us restrict the discussion only to the assessment of D in the case of H_B aggregate with $d = 0.48 \text{ nm}$ which could most probably correspond to the situation in the rotator phase of paraffins. The thermal vibration frequency of the paraffins in the lattice is about 10^{12} s^{-1} , the distance of the minima $a = 0.254 \text{ nm}$, and the assessed value of the entropy factor $\exp(\Delta S/R)$ is 10. Application of $\Delta E_z^{\text{corr}} = 6.7 \text{ kJ mol}^{-1}$ from Table III and introduction into the equation for the diffusion coefficient of hexane at 300 K gives the value $4.4 \cdot 10^{-8} \text{ m}^2 \text{ s}^{-1}$. The analogous value for the C_{33} paraffin (with the use of the calculated barrier Δe_z^{corr} per one shifting methylene group) is $D = 3.08 \cdot 10^{-13} \text{ m}^2 \text{ s}^{-1}$. It must be noted that the calculated values correspond to the diffusion coefficient D_{\parallel} in the direction of the longitudinal axes of the chains. The diffusion coefficient D_{\perp} for the direction perpendicular to the chains will obviously be lower by several orders of magnitude.

When comparing the calculated diffusion coefficients with the above-mentioned experimental value, D (and hence also ΔE_z) seems not to increase proportionally with the chain length. In contrast with the idealized H_B aggregate, the diffusion in the rotator phase of paraffins is also significantly affected by the presence of various defects (partially protruded molecules from the lamella surface, conformational defects, etc.). This is also confirmed by long-range migrations of the chains between crystallites¹⁵. Such macroscopical transfer of the matter is explained by the authors¹⁵ on the basis of longitudinal rototranslational jumps of the molecules in their extended

form. This idea presumes a relatively easy penetration of the diffusing molecule into the host aggregate, a possibility of formation of holes in the latter. Thus crystal modifications of alkanes must have considerably "plastic" character near T_m , and it is stated¹⁵ that up to 15% of alkane chains of the rotator modification slipped out from the crystal lamella.

There exist different opinions with regard to the extent of conformational disorder in the rotator modification. Translation of virtually rigid molecules in this phase is presumed¹⁵, or other authors⁶ suppose that the intrachain defects do not substantially affect the rotational chain radius. Still other results¹³ confirm — on the contrary — a considerable proportion of non-planar conformations in the rotator phase caused by both the intrachain conformational defects and the end defects. Gradual shifting of the chains out from the aggregate leads to disturbance of the long-range lamellar arrangement and represents an analogy of transition of smectic into nematic structure in the case of liquid crystals. In contrast to these crystals, however, the alkane molecules are flexible, and their protruded ends undergo rotational isomerization to the gauche conformations.

A similar trend to increase the gauche defects at the ends of chains is also observed with the double chain molecules of lipids in mono- or bilayers, where one chain extends over the end of the other. Also in the solid–solid type phase transitions of more complex paraffin-like molecules it is possible to expect a similar situation as in alkanes. The individual phase transitions, *e.g.* of lipids¹⁶, denoted as the pre-melting, can, also here, be considered a reaction of the crystal lattice on the onset of certain molecular motions which introduce elements of disorder into the crystal.

The problem of dynamics of molecular motions is also important in solid state polymers. In the case of long chains, our result for Δe_z in the orthorhombic aggregate can be compared with the already published data from a more complex treatment of rotational and translational motions in polymethylene¹². The barrier to the chain shift by $z/2$ per one —CH₂— group (about 2.1 kJ mol⁻¹) found at rigid values of the rotation angles σ_n agrees well with our result (Table III). The difference can be connected with different choice of the atom–atom interaction potentials and the setting angle σ_s in the orthorhombic structure.

The translational energy barriers are also important for evaluation of probability of formation of various conformational defects in crystals of macromolecular chains. Formation of any conformational defect in all-*trans* extended chain is accompanied by shortening of the chain and, hence, by a forced shift of the remaining part of the chain in the lattice. The most frequently assumed conformational defects in crystal are the so called kink^{17,18} (a *gauche*⁺, *trans*, *gauche*⁻ sequence of bonds in the chain) and the Reneker defect¹⁹, where the gauche internal rotation is accompanied also by rotation of the rest of the molecule as a whole by $\sigma = 180^\circ$. Such defects result in effective shortening of the chain in the lattice by one or two —CH₂— groups and, hence, in a shift of chain by the distance $z/2$ or z . The energy demands

of the forced displacement of the whole rest of the molecule behind the conformational defect contribute to the static energy of the defect and, hence, to the probability of its formation and/or possibility of its migration along the chain. In accordance with our results it was really found that the longer is the chain the greater energies are needed for formation of the kink^{17,18}. The energy requirements for displacement, however, show no strictly additive dependence on the number of —CH₂—groups in the slipping part of the chain. This section of the chain gradually accommodates to the crystallographic register by deformation of the intrachain geometry, particularly the bond angles. The energetics of the translation coupled with the rotation of the chain as a whole and with deformation of its internal geometry will be dealt with in following communications.

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