INTERACTION AND FLEXIBILITY OF MOLECULES IN HYDROCARBON AGGREGATES. TORSIONAL POTENTIAL IN A GROUP OF HEXANES

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The molecular-mechanics method has been used for calculation of the torsional potential $V(\varphi)$ of internal rotation around central C—C bond in hexane with one or two other hexane molecules in the neighbourhood and with full optimization of external and internal degrees of freedom. The optimum energy arrangement of the hydrocarbon molecules has been determined for various values of the φ angle as well as the optimum intramolecular geometry parameters. The adjacent molecules with all-*trans* conformation accommodate to the shape variation of the rotating molecule by means of translation motion. The adjacent molecules can change substantially the form of $V(\varphi)$ potential as compared with the isolated molecule, and they increase rigidity of the hydrocarbon chain. For some types of mutual arrangement, however, it has been found that the other molecule in the vicinity decreases the conformational energies and barriers of transitions between the rotation isomers as compared with the isolated molecule. Thus the inter-chain forces can induce also an effective coiling of the chain. Implications of these findings have been discussed with respect to structural properties of various real hydrocarbon aggregates in solution and in solid state.

The conformation mobility of hydrocarbons is determined principally by the potential $V(\varphi)$ of internal rotation around the C—C single bonds in the molecules. Quite often it is simply presumed that this potential is the same in the isolated molecule, in the molecule of the pure liquid hydrocarbon, in an organic solvent, or in various hydrocarbon aggregates as liquid crystals, monolayers, bilayers, micelles *etc*. The environment, however, appears to be able to affect the conformation equilibrium even in the cases of non-polar hydrocarbons, *viz.* either as a solvent or by the matrix effect.

In a series of communications we deal with the effect of environment using semi-empirical calculations, particularly the molecular-mechanics calculation (MMC) method[1,2]. A detailed analysis of the torsion potential of n-hexane (as a model of linear hydrocarbons) and influence of the environment (solvent) modelled as continuum was dealt with in the previous communications[3,4]. Some simplest configurations of pairs and triads of hexane molecules and their stabilization energies in the extended all-*trans* conformation were presented in ref.[5].

The aim of the present paper is to calculate the interaction energies and potential $V(\varphi)$ of internal rotation for the individual configurations of the hexane pairs and triads with full optimization of translational and rotational degrees of freedom of the molecules and to quantify influence of inter-chain forces on flexibility of the hydro-

carbons by comparison of $V(\varphi)$ with the torsion potential of the isolated molecule $V_{isol}(\varphi)$. Our approach uses the well-tried way of discrete modelling of environment by the presence of further (one or two) molecules of extended hydrocarbons in the vicinity of the reference hexane molecule whose internal rotation around the central C—C bond is investigated.

THEORETICAL

The model used. Fig. 1 represents schematically mutual positions of the pairs and triads of hexane molecules studied in the present paper. Because of the time-consuming calculation we omitted the pair BB′ and the triad AAA (ref.[5]). We examined the torsion potential $V(\varphi)$ in the rotation around the central C—C bond of one hexane molecule by the angle φ. The φ angle is 180 and $\pm 60°$ in antiperiplanar (*trans*) and synclinal (*gauche*) positions, respectively. The second molecule of the pair was in its extended all-*trans* conformation. Similarly, in the hexane triad the hexane reference molecule with internal rotation was placed between two other all-*trans* hexanes.

The intermolecular distance d was determined by the distance between rotation axes of the molecules along their carbon backbones. In the case of the molecule with internal rotation this axis belongs to first four carbon atoms of the chain. Mutual orientation of the planes formed by carbon atoms of the chains in extended all-*trans* conformation is characterized[5] by means of the angles σ_1, σ_2 and σ_3 (Fig. 1) describing rotation of the whole chain around the rotation axis n. The basic orientation is that of the pair AA in which $\sigma_1 = \sigma_2 = 0°$, and n_1, n_2 denote parallel rotation axes of the carbon skeleton in all-*trans* conformation.

The method used. The interactions of the reference molecule with the adjacent molecule(s) are manifested in shape of the torsional potential $V(\varphi)$ which can thus be expressed as a sum of an intra- and an intermolecular contributions.

$$V(\varphi) = V_{isol}(\varphi) + E_{int}(\varphi) \qquad (1)$$

For calculation of $V(\varphi)$ the Boyd's version of MMC (ref.[6,7]) was used as in the previous papers[4,5]. The total potential energy E_s of a set of molecules is expressed in this method by a sum of several potential contributions. The $V(\varphi)$ potential was determined with the use of the bond-drive technique[8,4] in which the torsion angle φ is fixed at a chosen value and then all remaining degrees of freedom (*i.e.* internal coordinates and also translation and rotation coordinates of two or three molecules) are optimized. Some calculations without optimization and with fixed mutual distance of the molecules during rotation served as a reference point for determination of steric interactions in the hexanes system.

Calculations. With some pairs and triads investigated, difficulties were encountered concerning convergence of the calculation. It was necessary to increase the geometry parameter[7] RMS of the calculation convergence as compared with the calculations of the isolated molecule and pairs of molecules in extended all-*trans* conformation. The convergence rate of the calculation depends considerably also on choice of the $\Delta\varphi$ increment for the rotation around the C—C bond, since final geometry of one calculation represents the input data for the subsequent one. The calculation was carried out with the $\Delta\varphi$ values 15 and 25° for the pairs and triads, respectively.

The calculations were carried out with a Siemens 4004/150 computer. The Boyd's modification of the MMC program needed 403 kByte CPU memory. Time of the optimization of one hexane conformation with two adjacent molecules (a triad) was about 1 000 s (the whole rotation 360° by the 25° increments lasted about 15 000 s).

RESULTS AND DISCUSSION

Interaction Energy

In the expression (2) of intermolecular stabilization energy E_{int} the values of the isolated molecules are subtracted from total strain energy of the supersystem (pair, triad).

$$E_{int}(\varphi) = E_S^{sup}(\varphi) - E_T^{is}(\varphi) - nE_T^{is}(trans) . \tag{2}$$
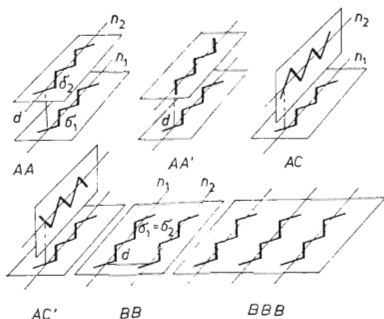

FIG. 1

Geometrical arrangement of the studied pairs and triad of hexane molecules

The value $n = 1$ for the pairs and $n = 2$ for the triads of hexane molecules. This calculation method also involves intramolecular energy contributions to the strain energy E_s which can vary due to influence of the adjacent molecules. If this change does not take place, then E_{int} is determined by the sum of non-bonding interactions E_{nb} of the atoms in vicinal molecules.
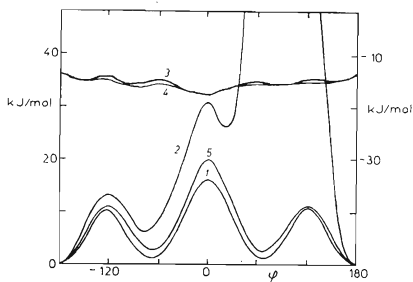

FIG. 2

Calculated torsional potentials ($V(\varphi)$) and interaction energies, $E_{int}(\varphi)$, $E_{nb}(\varphi)$, vs conformation angle φ for a pair of hexane molecules in the AA arrangement. 1 $V(\varphi)$, 2 $V^*(\varphi)$, 3 $E_{int}(\varphi)$, 4 $E_{nb}(\varphi)$, 5 $V_{isol}(\varphi)$
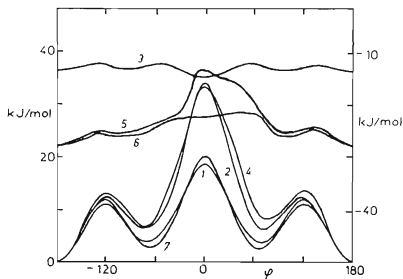

FIG. 3

Calculated torsional potentials ($V(\varphi)$) and interaction energies, $E_{int}(\varphi)$, $E_{nb}(\varphi)$, vs conformation angle φ for a pair type BB and a triad type BBB of hexane molecules. 1 $V(\varphi)$, BB; 2; $V^*(\varphi)$, BB; 3 $E_{int}(\varphi)$, BB; 4 $V(\varphi)$, BBB; 5 $E_{int}(\varphi)$, BBB; 6 $E_{nb}(\varphi)$, BBB; 7 $V_{isol}(\varphi)$

Figs 2 and 3 give dependences of E_{int} on φ for full optimization of all parameters of the pairs AA, BB and triad BBB. Similar energy dependences were also obtained for the other pairs of Fig. 1. From Figs 2 and 3 it is seen that the stabilization energy E_{int} in the pairs (except for small differences in the case of the AA pair) is determined principally by the non-bonding interactions E_{nb}. Hence, practically no further intramolecular geometry changes accompanied the internal rotation of the molecule (and no changes in internal geometry of the other molecule with all-*trans* conformation) as compared with the optimized geometry of the isolated molecule. In the case of the BBB triad, greater changes in internal geometry of the central molecule were only found near the *cis* position of φ. The E_{int} values for $\varphi = \pm 180°$ correspond to configurations with all-*trans* extended hexane molecules reported in the previous paper[5]. It is seen that in the AA configuration absolute value of the stabilization energy always increases after rotation from the position $\varphi = 180°$. A different situation is found in BB configuration and, especially, in BBB configuration, where the most stabilized structure is the all-*trans* extended structure.

No data have been found in literature on stabilization energies of hydrocarbon aggregates which could be compared with our results. Most calculations concern only the extended all-*trans* molecules[5] or model the interactions in greater sets of hydrocarbon molecules by means of the Monte Carlo[9] or molecular-dynamic methods[10] presuming equilibrium population of the gauche conformations in each chain characteristical of liquid state. Thus *e.g.* ref.[9] gives the value of average interaction energy 9·3 kJ/mol at 450 K for a pair of n-pentane molecules, the value being made average for all conformations and mutual configurations. Our previous
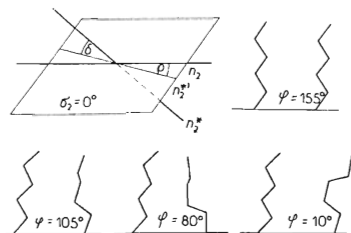

Fig. 4

Geometry changes in arrangement of the BB pair during internal rotation of the reference molecule and the parameters characterizing this arrangement ($n_2^{*'}$ is projection of n_2^* in $\sigma_2 = 0°$). The molecules are represented in their projection in the plane $\sigma_1 \equiv \sigma_2 = 0°$

calculations[5] have already shown that the E_{int} interaction energy depends greatly on particular configuration of the all-*trans* chains in a pair. In the case of internal rotation of one of the chains this dependence is even more distinct.

Potential of Internal Rotation

Combination of the E_{int} contribution with torsional potential of isolated hexane[4] V_{isol} makes it possible to find the rotation potential $V(\varphi)$ for the pair or triad. Figs 2, and 3 give the results for AA, BB and BBB configurations. Table I summarizes basic characteristics of the $V(\varphi)$ potential for the mentioned and other calculated configurations of Fig. 1. The values found for the arrangements AC and AC′ (Fig. 1) were the same. Difference in the *trans* and *gauche* minima is denoted as ΔE; the values $E_{tg}^{\ast}$ and $E_{gg}^{\ast}$ denote the barriers to the *trans–gauche* and *gauche–gauche* transitions, respectively. In the case of the isolated molecule[5] the *gauche*–minimum of potential energy lies at φ about 67°. In the pairs calculated in the present paper (AA, AA′, BB, AC) this angle changed but little, its values being 69°, 68°, 69°, 65°, respectively.

For a more clear comparison of influence of optimization on sterical interactions of the pairs, Figs 2 and 3 also give the potentials $V^{\ast}(\varphi)$ which consider the φ angle to be the only degree of freedom, *i.e.* the internal geometry of the molecules was considered rigid, and the d distance was constant (0·425 and 0·452 nm for AA and BB, respectively) and corresponding to the minimum of potential energy of two all-*trans* molecules[5]. The course of the $V_{\ast}(\varphi)$ potential reflects different behaviour of AA and BB. In the AA configuration the rotation from the angle 0° to 180° results in approaching of the rotating end of reference hexane to the close vicinity of neighbour molecule which is accompanied by an extremely high repulsive interaction. The internal rotation of hexane in the BB complex leads invariably to the increase of its

TABLE I
Conformational energy and *trans-gauche* and *gauche-gauche* transition barriers of isolated hexane molecule and various configurations of pairs and a triad of hexane molecules (in kJ/mol)

Energy	Isolated molecule	AA	AA′	BB	AC	BBB
ΔE	2·8	1·2	4·3	3·7	4·9	6·3
$E_{tg}^{\ast}$	11·0	10·6	13·1	11·9	13·5	14·3
$E_{gg}^{\ast}$	17·1	12·6	14·7	14·9	15·4	28·7

distance from the other molecule, and the course of $V^*(\varphi)$ is principally determined by the $V^*_{isol}(\varphi)$ potential of the isolated hexane molecule[4] without optimization of internal geometry during the rotation.

On the contrary, the calculation of the "optimized" potential $V(\varphi)$ gives, for the both pairs, a curve analogous in shape to that of the potential of the isolated molecule, which indicates that the optimization of the AA pair was connected with a distinct separation of the second extended chain from the reference chain due to internal rotation. In non-optimized pairs AA and BB the gauche energy minimum was found at φ about 75°. A qualitatively same character of the potentials $V^*(\varphi)$ with the angle φ being the only degree of freedom was also obtained when using the quantum-chemical PCILO method with the equilibrium distance d (0·400 and 0·466 nm for AA and BB, respectively) for the all-*trans* structures obtained by the PCILO method[5].

Positional Motion of Molecules at Internal Rotation

In describing the motion of the molecules we shall focus our attention to the structures AA and BB which reflect two opposite characters of arrangement of the molecules. In the AA arrangement the molecules are placed "sandwich" in parallel planes, and rotation of one molecule moves its parts towards or from the other molecule. In the BB arrangement the molecules lie "side by side", and the rotating parts of the first molecule "pass by" the other one. This different character of the arrangement is also reflected in the energy parameters (Table I).

At the beginning of the calculation of the AA configuration the molecules are mutually parallel. Due to internal rotation of the first molecule, the other molecule moves to the position characterized by the rotation axis n_2^*. The ϱ angle describes the deviation of n_2^* axis from n_2 in the plane $\sigma_2 = 0^0$, the δ angle is formed by n_2^* axis and the plane $\sigma_2 = 0^0$ (Fig. 4). The m_1 axis of the first (reference) molecule is defined as the longitudinal axis connecting centres of the C—C bonds determining the dihedral angle φ (the second and the fourth C—C bonds). This axis reflects rotation (deviation) of a part of the first molecule. When the dihedral angle of the first molecule begins to change from 180°, the rotating —CH$_2$—CH$_3$ group begins to move away from the other molecule. The latter molecule "follows" the rotating molecule by gradual tilting (changing of the δ angle). At the same time also the ϱ angle is changed so that the molecular axes m_1 and n_2^* remain roughly parallel. The second molecule is also gradually shifted along the longitudinal direction by the distance equal to about one half of C—C bond length. For the dihedral angle 0° of the first chain, the chain axes m_1 and n_2^* are parallel, their distance being about 0·40 nm. Next, during internal rotation of the first molecule from 0° to 180° (when the rotating part of the molecule begins to deviate towards the second molecule) the angle σ_2 of the rotation around the n_2^* axis is changed (rotation around the longitudinal axis of the

molecule). At the dihedral angle 180°, however, the planes are parallel again, and position of the molecules is identical with that at the beginning of the rotation. During all the rotation no significant changes of dihedral angles of the second molecule took place.

With the BB pair we could also observe a tendency to parallel arrangement of the m_1 and n_2^* axes during rotation. However, in contrast to the AA pair the rotation was not accompanied by a change of the σ_2 angle (twist of the zigzag plane). Hence the second molecule did not rotate as a whole around the n_2^* axis. Figure 4 gives geometry arrangement of this pair during the internal rotation characterized by the φ angle of the reference molecule for four selected configurations (projection in the plane defined by $\sigma_1 = 0°$). No significant mutual shift of the molecules along their longitudinal axes was observed, too. At the dihedral angle $0°$ of the rotating molecule the other molecule lies at a distance of about 0·47 nm. During further rotation from 0° the second molecule again "follows" (in an unchanged all-*trans* conformation) the rotation of the part of the first molecule in the opposite direction as far as the original value of the dihedral angle 180°.

Internal Rotation in the Triads of Molecules

In the case of a triad the internal geometry variation of the central molecule is famore distinct. However, also in this case internal rotation of the central moler cule did not cause any significant changes in dihedral angles of the neighbouring molecules. From the beginning of internal rotation of the central molecule in the BBB aggregate at 180° up to the dihedral angle about 250°, the internal geometry of the molecules remains practically identical to that of the isolated molecule. However, from the said angle (250°) the internal geometry of the central rotating molecule begins to change significantly as compared with analogous rotation around the C—C bond in the optimized isolated molecule. Thus *e.g.* the C—C bond angles adjacent to the rotating bond are increased by 2—3°. Starting from dihedral angle about 15° also the other dihedral angles of the rotating end of the central molecule begin to change partially (from 180°). At $\varphi = 30°$ *e.g.* these two latter dihedral angles (of the group —CH_2—CH_2—CH_3) have the values 162 and 157°, respectively. Further rotation brings their values back to 180°. The internal rotation in the central molecule caused practically no mutual shift of the molecules in this triad along their longitudinal axes.

From the point of view of energy, comparison of the hexane pairs and triads shows that *cis* position of the rotating molecule is the most stabilized one in the pairs, being the most destabilized one in the triads. It seems likely that the triads show already a tendency to parallel alignment of the molecules and to preference of their extended all-*trans* conformation. The central molecule tends to adopt the orientation dictated by the matrix of two adjacent all-*trans* molecules.

Barriers, Conformation Energy, and Orientational Correlation

Table I shows that the presence of the second molecule in all the pair complexes lowers the barrier of the *gauche–gauche* transition E_{gg}^{*} as compared with that of the isolated molecule. The *trans–gauche* barrier E_{tg}^{*} is, however, slightly higher with all the types of pairs (except for AA). The highest values of the both barriers were obtained for the BBB triad. In the case of the *gauche–gauche* barrier the reason partially consists in that the inter-chain interactions destabilize the *cis* position with respect to *gauche* position by about 5·5 kJ/mol (Fig. 3). Another difference is due to changed internal geometry of the central molecule. Recent experimental value[11] for gaseous butane (a molecule with one rotation angle as in our case), for comparison, are $E_{tg}^{*} = 9\cdot2$ kJ/mol, $E_{gg}^{*} = 9\cdot6$ kJ/mol.

The changed shape of the $V(\varphi)$ potential as compared with that of $V_{isol}(\varphi)$ makes itself felt also in different values of conformation energies ΔE with respect to the isolated molecule (Table I). As expected, the results for most pairs and for the triad of hexane molecules predict an increased preference of *trans* to *gauche* conformation as compared with the situation in the isolated molecule. In other words, the presence of additional one or two molecules with unrestricted translation freedom results in effective stiffening of the reference hexane molecule. Surprisingly, however, in the AA pair, on the contrary, the preference of the *trans* conformation is relatively lowered due to inter-chain stabilization of the gauche position by 1·6 kJ/mol (if the E_{nb} interactions were only considered, this decrease would be as much as 2·0 kJ/mol).

Obviously the mutual orientation of chains in direction of their long axes exerts an important influence not only on magnitude of the stabilization energies but also on the conformation equilibrium. In the case of the AA complex the matrix effect simulated by the second extended hexane molecule predicts effective coiling of the alkane chain similar to that observed in application of the continuum model of the solvent effect to the conformation equilibrium in n-hexane[3,4]. This treatment[3,4] of solvent effect was based on assessment of energy changes of cavity formation with changes of n-hexane (the solute) conformation, the van der Waals interactions with environment being considered conformation-independent. The matrix effect, as it is simply simulated in the present paper, reflects, on the contrary, only the van der Waals interactions.

In spite of the simplifications of model, the calculation of the $V(\varphi)$ potential can contribute to elucidation of some problems concerning structure and interactions in real hydrocarbon systems. An object of intensive discussion[12−15] is the problem of existence of short-range orientational order in condensed state of longer hydrocarbons for which there exists evidence from experimental measurements using the depolarized Rayleigh scattering[12] and calorimetry[13]. It is presumed that the same type of order could exist in the case of macromolecules as *e.g.* amorphous polyethylene. Recently Flory[14] ascribed relative increase of mutual orientation

of paraffine chains in liquid phase only to simple "steric" effect: to the inaccessible volume excluded from the surroundings of the molecule as a consequence of the presence of neighbouring hydrocarbon molecules. Similarly, application of a computer simulation[15] of molecular arrangement of paraffinic liquid revealed a slight tendency to orientation correlation which is restricted to short distances (the nearest vicinal groups). The conformational energies of Table I show that in most cases the presence of a extended molecule in the neighbourhood induces "structural order", even though the complex AA indicates also an opposite possibility. It is obvious that the adopted model with limited number of neighbouring molecules which are considered rigid and having all-*trans* conformation and full translational freedom reflects the situation of real alkane liquid only very roughly.

The presence of rod-like all-*trans* molecules near the reference molecule simulates well especially the situation of liquid crystals with nematic or smectic type of increased order as compared with an isotropic liquid. It is known that probability of occurrence of *trans* conformation in paraffinic chain increases in the series: isotropic liquid — liquid crystal — crystal. Our calculation gave quantitative data supporting the mentioned trend as well as their dependence on mutual orientation of molecules. The results of Table I agree well with statistical-thermodynamic treatment of flexibility of n-alkyl chains in liquid-crystalline dialkoxyazoxybenzene[16], where the most probable mean conformation energy ΔE was found to be by 2·3 kJ/mol higher than that of the isotropic phase (isolated molecule).

Simple phospholipid bilayers or lipid matrix of biological membranes represent a similar type of lyotropic liquid crystals. Seelig[17] examined flexibility of hydrocarbon chains in phospholipid bilayers in smectic state. He found that intermolecular interactions tend to lower the probability of gauche conformations and to make the chains more rigid. He assessed the value ΔE about 6·3 kJ/mol, which indicates a similar force action in the lipid bilayer as we have found for the BBB triad (Table I). Such an average value of ΔE, however, does not naturally reflect the differences between flexibility of hydrocarbon tail of the lipid near the non--ordered centre of the bilayer and the part of the molecule near the polar head of the bilayer. An increased structural order exists probably also in some regions of other hydrocarbon aggregates in water as *e.g.* micelles, microemulsions *etc.*

Besides paraffinic liquids and liquid crystals, the rotational isomerization around C—C bonds plays a part as the most frequently considered defect in crystalline hydrocarbons, especially so near the points of their phase transitions. In this and also other cases it is presumed (especially for long chains) that there exist coupled rotations of the *gauche* type with opposite direction, so called kinks. The motions of kink of a "crankshaft" type serve as models for relaxation modes of polymeric hydrocarbons in solid state. Natural extension of the model used in the present work, *i.e.* considering several rotation angles φ, will enable to examine the energy conditions of formation of the kink. The extended model, which is being elaborated,

will enable to decide whether molecules of globular shape assist in breaking the short range orientational order in solutions of hydrocarbons with extended anisotropic molecules[13].

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