CALCULATION OF STABILIZATION ENERGY OF PARALLEL HEXANE MOLECULES

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Molecular-mechanics method has been used for calculation of stable configurations of n-hexane pairs and triads in extended all-*trans* conformations with full translational and rotational freedom of the molecules during optimization. The calculated stabilization energies and equilibrium distances have been compared with the experimental data obtained for molecular crystals of paraffins. The comparison enables to distinguish the effects characteristical of the collective packing forces in the crystal. The optimum configurations of some hexane pairs have also been calculated by the quantum-chemical PCILO method. The results indicate superiority of MMC to the quantum-chemical methods and other empirical calculation procedures for the purposes of the stabilization energy determination.

Stability of various aggregated systems of hydrocarbon molecules and dynamics of molecular motions therein are determined by intra- and intermolecular forces in the aggregate. This rule applies invariably to various hydrocarbon structures occurring in solutions (monolayers, bilayers, micells, emulsions), to liquid crystals, as well as to amorphous and crystalline systems in solid state. The molecular-mechanics calculations[1-3] (MMC) represent nowadays the most reliable tool for theoretical determination of geometry parameters and inter- and intramolecular interactions of hydrocarbons. The success of the MCC method is based on the fact that it utilizes a great number of parameters determined empirically from abundant experimental data about hydrocarbons.

We were particularly interested in reexamination of influence of medium on character of internal rotation in saturated hydrocarbons, applying the MMC method to suitable hydrocarbon aggregates represented by n-hexane molecules. In the previous communication[4] we focused our attention to detailed analysis of torsional potential during rotation around the central C—C bond in the isolated hexane molecule and effects of surroundings modelled as continuum[5]. In the present paper we use the simplest discrete model of the surroundings, *i.e.* the presence of further (one or two) hexane molecules in the neighbourhood of the reference molecule. We calculated the stabilization energies of hexane pairs and triads in various configurations in all-*trans* extended conformation. Analogous calculation was also carried out by semi-empirical quantum-chemical PCILO method, which is frequently and successfully used not only for investigation of conformational structure of molecules[1] but also for calculation of intermolecular interactions[6,7]. Comparison of the

MMC and the PCILO results for the stabilization energies represents an important test of reliability of the PCILO method in quantitative predictions of behaviour of saturated hydrocarbons and their systems.

The Used Method and Model

We used the Boyd's version of MMC described in the original paper[8] and also in our previous communication[4]. The total potential energy E_S of the molecule (set of molecules) is expressed as a sum of a number of contributions depending on the internal coordinates and intermolecular distances of the mutually non-bonded atoms. Minimization of the E_S energy by means of the Newton–Raphson method gives the equilibrium intramolecular parameters of hexane and stable configurations of the set of hexane molecules.

The semi-empirical quantum-chemical PCILO method was used in the standard version with CNDO/2 parametrization[9]. In contrast to MMC, the PCILO calculations only optimized the mutual position of hexane molecules in individual configurations. The rigid hexane geometry used as PCILO input corresponded to the optimized all-*trans* conformation of isolated hexane molecule calculated by MMC method[4].

The intermolecular interaction energy is determined as $E_{int} = E_S(d) - E_S(\infty)$, where $E_S(d)$ means energy of the supersystem (pair or triad of hexane molecules) at the distance d between the hexane molecules. Expressed in this way, the stabilization energy E_{int} from MMC involves also change of intramolecular contributions to the potential energy E_S, because internal geometry of the aggregated molecule can differ from that of an isolated one due to the effect of surroundings. If these intramolecular changes are negligible, then the stabilization energy E_{int} is determined in MMC only by the sum of non-bonding interactions of atoms from different molecules (E_n).

The calculation was carried out for several configurations of the pairs and triads of hexane molecules (Fig. 1). Structure A represents schematically the isolated hexane molecule in all-*trans* extended conformation. The chain axis is denoted as n_1, and σ_1 means the angle of rotation of the whole chain around the n_1 axis in clockwise direction. The figure also gives projection of the hexane molecule into the plane perpendicular to the n_1 axis. The empty circles denote the nearer CH_3 end groups when viewing the molecule from the bottom and the more distant C atom of CH_2 group is denoted by the full circle. Similarly it is possible to define the n_2 axis and σ_2 angle of the other hexane in the pair and n_3, σ_3 in the hexane triad.

The AA arrangement in Fig. 1 represents a sandwich configuration of a hexane pair with coplanar position of the planes involving the carbon skeleton of the molecules and with parallel orientation of the n_1 and n_2 axes. The rotation angles of the complex AA are chosen $\sigma_1 = \sigma_2 = 0$. Gradual rotation of the molecules around the

rotation axes generates many configurational pairs out of which some are given in Fig. 1. The individual structures have the following rotation angles σ_1, σ_2: AA′ (0°, 180°), BB (90°, 90°), BB′ (90°, 270°), AC (0°, 90°), AC′ (0°, 270°). Similarly the triads AAA and BBB can be characterized by the angles 0°, 0°, 0° and 90°, 90°, 90°, respectively. The quantity d gives the distance between the rotation axes of the molecules in the individual configurations.

Stabilization Energies from MMC *Method*

Table I lists the values of potential energy E_S and stabilization energy E_{int} at equilibrium distances d for hexane pairs and triads obtained by the MMC method. The configurations given in Fig. 1 with the initial value d 0·4 nm were optimized with full freedom of translation and rotation motions of all the molecules in all-*trans* conformation. The configurations resulting form the optimization retained precisely the original character of the arrangement with parallel rotation axes, the distance d only being increased without mutual translation in direction of the rotation axis. The only exception was the AC configuration (equienergetical with AC′) in which the increasing distance of the molecules was accompanied by their mutual deviation. In the deviated configuration the rotation axes n_1 and n_2 form an angle of about 15° (0° in the original parallel orientation), and the rotation axis n_2 of the upper molecule is parallel with the plane crossing the carbon skeleton of the lower molecule. In the case of the hexane triads the central molecule was located symmetrically at the distance d from the both neighbouring molecules.

Potential energies E_S of the supersystems exhibit stabilization with respect to the value of the isolated *n*-hexane in all-*trans* conformation (8·4 kJ/mol, see also ref.[4]). It was found that E_{int} was determined almost exclusively by the non-bonding interactions E_n, the contribution of changes of intramolecular interactions to E_{int} being only about 0·1 kJ/mol. The AA′ pair was shown to be the most stable energetically,

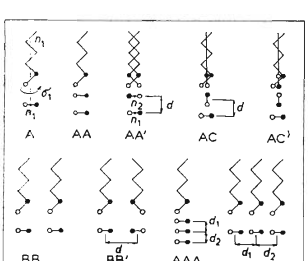

FIG. 1

Types of arrangement of pairs and triads of hexane molecules. For explanation of symbols see the text

its antiparallel chain arrangement enabling mutual approach of the chains to an extremely low d values. Noteworthy is the found approximate agreement in energetic stability of the pairs and triads type AA and BB at different d values. The d and E_{int} values of the hexane triads indicate rough additivity in the sense "a triad = two pairs".

The stabilization energy E_{int} divided by the total number of carbon atoms in the interacting molecules (12 in pairs, 18 in triads) gives the e_{int} value of the stabilization energy per one CH_2 unit, the effects of the CH_3 end groups being neglected.

Stabilization Energies from PCILO *Calculations*

As the PCILO calculations are much more time consuming than the MMC's, they were limited to two configurations only (AA, BB). Similar to MMC's, the optimization started from the configurations represented in Fig. 1, however, with presumption of rigid internal structure of the molecules. In the AA complex full freedom of translational and rotational motions of the two molecules was considered during the optimization. Nevertheless, only the distance d changed, the character of the arrangement being precisely maintained. Therefore, in the BB complex the distance d was only optimized. The calculation results are summarized in Table I.

Comparison with the MMC results reveals that the PCILO method predicts a substantially smaller stabilization energy for the both types of complexes. Furthermore, the two complexes being equienergetic in the MMC approach, the PCILO method predicts an almost four-fold stability of the AA complex related to BB,

TABLE I

Energy and geometry parameters of stable configurations of pairs and triads of extended hexane molecules (the energy values in kJ/mol, the distances in nm)

Arrangement	AA	AA′	BB	BB′	AC[a]	AAA	BBB
d	0·425	0·405	0·452	0·476	0·43	0·424	0·445
E_s	3·0	− 0·6	3·0	5·5	2·0	− 2·2	− 2·7
E_{int}	−13·8	−17·4	−13·8	−11·3	−14·8	−27·4	−27·9
e_{int}	− 1·15	− 1·45	− 1·15	−0·94	− 1·23	− 1·52	− 1·55
d (PCILO)	0·400		0·466				
E_{int} (PCILO)	− 5·9		− 1·5				
e_{int} (PCILO)	− 0·49		− 0·13				

[a] In stable configuration after optimization the rotation axes n_1 and n_2 form the angle 15°. Both AC and AC′ are equienergetical configurations.

which is apparently connected with the extremely small PCILO optimum distance d in the AA complex. Comparison with the MMC results indicates that the PCILO results for stability of paraffinic complexes cannot be simply corrected by any multiplication factor to give an acceptable quantitative assessment of magnitude of the stabilization energy.

Implication of Results for Stability of Molecular Crystals

The individual idealized hydrocarbon configurations represented in Fig. 1 have their counterparts in the crystalline structures formed by paraffins[10] and cognate molecules as *e.g.* lipids[11]. The extended chains of all-*trans* conformation with parallel axes form a number of crystalline modifications, the most frequently occurring elementary crystal cells being represented schematically in Fig. 2. It can be seen that in the molecular crystals there are only the structures similar to the configurations of Fig. 1 with parallel or perpendicular orientation of the planes of C—C bonds corresponding to an integer multiple of 90° for the difference $(\sigma_1 - \sigma_2)$.

Comparison of experimental lattice energies and lattice constants (a, b, c) with the calculations of stability and equilibrium distances (d) for pairs (triads) of paraffins enables a deeper understanding of energetics of crystal packing. In this way it can be decided to what extent the stability of the observed structures is determined by pure interactions of the adjacent pairs and what is the contribution of collective crystal packing forces. Relations between the AA′ pair and position of molecules in (parallel) orthorhombic cell, between the AC configuration and (perpendicular) orthorhombic cell, between BB (AA) pair and orientation of molecules along the b_c (a_c) axis in monoclinic cell *etc.* can be seen at first sight.

The MMC results in Table I show that parallel orientation of the chain axes occurring in molecular crystals is the most stable in the pairs of molecules already.

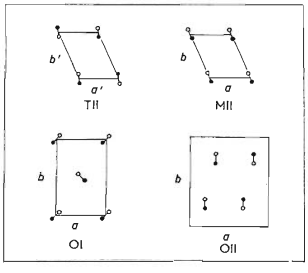

FIG. 2

Arrangement of hydrocarbon chains in some types of lattices. The axes of the molecules perpendicular to the projection plane lie in the crystallographic axis c_c. O,M,T mean orthorhombic, monoclinic, and triclinic symmetries, respectively, ∥ and ⊥ mean the mutual orientation of the chain planes. In the triclinic structure a' and b' represent projections of the lattice constants into the plane perpendicular to c_c

The only exception is the AC (or AC') configuration for which the MMC results indicate that the molecular axes are arranged parallel in the crystal only as a consequence of the presence of additional molecules. The crystal forces cause also shifts of positions of the molecules as compared with the idealized pair structures in Fig. 1, so that the plane defined by the two rotation axes n_1, n_2 does not remain perpendicular to (or parallel with) the planes of carbon skeleton of the molecules. Thus *e.g.* the pair of molecules along the a_e axis in monoclinic lattice (Fig. 2) corresponds to a "shifted" AA configuration. This shift complicates immediate comparison of the calculated and experimental values. Nevertheless a good agreement is observed, *e.g.* for *n*-hexane which crystallizes in triclinic system[12] with *a* 0·417 and *b* 0·470 nm. Judging from the MMC's in Table I, the monoclinic lattice should have $b > a$ and, furthermore, the *a* constant of triclinic and parallel orthorhombic cell (corresponding to the AA' pair) should be smaller than the *a* values of the other cells. It must not be forgotten, however, that long-range crystal forces cause a decrease of inter-chain distances (from the optimum values of the pairs), *i.e.* an effective "compression" of the crystal.

The long-range crystal forces are even more distinct when comparing the energy quantities. From Table I it is seen that in hexane pairs the stabilization energy increment per one CH_2 group is about $-1{\cdot}25$ kJ/mol CH_2, whereas in the triads the respective value is about $-1{\cdot}5$ kJ/mol CH_2. With increasing number of the nearest neighbours of the central chain the stabilization energy would gradually increase, and for an infinite crystal its value should approach experimental value[13] $e_{int} = -7{\cdot}7$ kJ/mol. Since the calculation showed that the E_{int} energy in MMC is determined substantially by the E_n contribution, the energy increment e_{int} is determined by characters of potentials of the interaction between the pairs of atoms C···C, C···H, and H···H in the neighbouring chains. In the Boyd parametrization of MMC the E_n term is expressed on the basis of the modified potentials proposed by Williams[14].

Comparison with Previous Calculations

There exist surprisingly few pieces of theoretical information on molecular energetics in smaller clusters of hydrocarbon molecules. Usually, the behaviour of a whole molecular crystal is modelled as the opposite alternative to the isolated molecule study. Energy description of packing in molecular crystals contributed substantially to our knowledge of stability and mobility of molecules in crystals[14,15]. Furthermore, the molecular calculations for crystals serve as the most reliable source of parameters for the empirical methods of the MMC or force field types[16,17]. In the packing calculations, however, the primary part is played by the exclusion of the structures with repulsion short-range interactions, the problem of a reliable description of long-range attractive London interactions being not yet satisfactorily solved.

In literature there are only few calculations with which our results can be compared. Thus Wertz and Allinger[3] used another parametrization of the MMC method and found the value 0·414 nm for the equilibrium distance of *n*-hexane pair in the position determining the *a* constant of the lattice of crystalline hexane. Brosio and coworkers[18] presented simplified hard-core energy maps for "energy-allowed" regions of mutual orientation of two extended paraffinic chains. They expressed the interaction energy on the basis of empirical potentials for non-bonding van der Waals energy and considered the *d* distance to be the only degree of freedom. In contrast to our calculations, their results show that for *d* 0·4 nm the energy-allowed structures are not only AA′ but also AC and BB. For values *d* 0·44 nm they found that all structures (except for BB′) of Fig. 1 are energy-allowed, and at *d* 0·48 nm almost all combinations of the σ_1 and σ_2 angles are allowed from the point of view of energy. It must be noted, however, that at longer distances intramolecular flexibility would predominate over the packing forces in crystal, and the *trans-gauche* rotation isomerization would result in deviation of the chain from the all-*trans* conformation.

So far the most reliable values of interaction energies between hydrocarbon chains obtained on the basis of quantum-chemical second order perturbation theory are those of refs[19,20]. Salem[19] based his calculations on the presumption of pair additivity of attraction of CH_2 units in two parallel chains, using isotropic bond polarizabilities found experimentally. By using the familiar London relation he found the mutual attractive energy between two CH_2 groups at distances r (in 10^{-10} m) to be $-2{\cdot}35 \,.\, 10^4/r^6$ kJ/mol. The total attraction of two parallel paraffinic chains composed of N methylene groups is

$$E_{\mathrm{attr}} = -5{\cdot}19 \,.\, 10^3 N/d^5 \text{ kJ/mol}\,, \qquad (1)$$

if their distance d is in 10^{-10} m. Hence, the attraction of chains is inversely proportional to the fifth power of their distance. Although Salem derived Eq. (*1*), considering only the configuration BB (Fig. 1), the Eq. (*1*) can also be used with the orientation-averaged experimental bond polarizabilities for other configurations. Introduction of the equilibrium distances *d* from the MMC's (Table I) of the hexane complexes AA, AA′, BB, and BB′ into Eq. (*1*) gives the values $-22{\cdot}5$, $-28{\cdot}6$, $-16{\cdot}5$, and $-12{\cdot}7$ kJ/mol, respectively. As the Salem's relation (*1*) considers only the attractive interactions between the chains, it is not surprising that it gives greater stabilization energies than our MMC.

In contrast to Salem, Shapiro and Ohki[19,20] involved explicitely in their procedure also the repulsive interactions of the methylene groups on the basis on the Kihara potential. Fitting of the calculation results of the interaction energy by means of the standard $m-n$ Lennard–Jonnes potential gave $m = 11$ and $n = 5$. As the authors presumed free rotation of the both chains around the n_1 and n_2 axes, their procedure

ascribes only one value of stabilization energy to all the configurations given in Fig. 1, *viz.* the value about $-1{\cdot}93$ kJ per one pair of interacting C_2H_4 groups, *i.e.* about $-0{\cdot}5$ kJ/mol CH_2 at the distance d about 0·5 nm.

Comparison of this value with the e_{int} values from MMC's (about $-1{\cdot}25$ kJ/mol CH_2) indicates an underestimation of stabilization energy in the calculation according to ref.[20]. This fact is probably due to excessive weight of repulsion term in the interaction potential, which shifts the equilibrium distance d of two chains down to 0·5 nm, the contribution of attraction being weakened. Furthermore, our calculations show the importance of respecting of real chain configuration in determination of stabilization energy (Table I), whereas the differences are lost in chain rotational averaging.

In literature there are also quantum-chemical studies of stabilization of pairs of saturated hydrocarbons. Lochmann and coworkers[6,7] tested the PCILO method for use in prediction of intermolecular forces of molecular complexes inclusive of paraffins in various configurations. As the most stable structure for paraffins they found the BB configuration with d about 0·475 nm for two nonane chains, which agrees approximately with our PCILO results for hexane (Table I). The AA configuration was apparently not taken into account in papers[6,7]. The authors also found a negligible influence of optimization of the internal geometry on the PCILO stabilization energies of saturated hydrocarbons. In the pair of nonanes the contribution of one methylene group to the stabilization energy was about $-0{\cdot}19$ kJ/mol CH_2, *i.e.* its absolute value is somewhat greater than our PCILO results for the BB complex. The BB and BB′ complexes of longer paraffins (C_5, C_7, and C_9) were also studied by the INDO method[21]. Stabilization energy of the two complexes differed but little, being about -4 kJ/mol for nonane dimers with d about 0·49 and 0·51 nm for the BB and BB′ complexes, respectively. Thus similar to PCILO, the INDO method also strongly underestimates the stabilization energy (e_{int}(INDO) is about $-0{\cdot}2$ kJ/mol CH_2), and, in addition, the INDO method is inferior in describing the shape of interaction potential, as it overestimates intermolecular attraction at longer d distances (0·6 nm and above)[21]. Hence it is seen that in spite of a deeper insight into the reasons of stabilization of the dimers and a separation of contributions of the type of dispersion, charge-transfer energy *etc.*, resulting from the PCILO and INDO calculations quantum-chemical methods give a markedly lower stabilization energy as compared with experiment. Therefore, at the present state of knowledge, the effective energy values determined by the MMC method should be preferred in quantitative determination of intermolecular interactions in hydrocarbons.

On the whole, the molecular energetics of the extended paraffinic chains is important for interpretation of static structure and dynamics of molecular crystals and particularly for study of changes in orientation of molecules and orientation disorder during phase transitions of solid-solid type in the case of longer paraffins with all-*trans* conformation. At longer d distances, when the *trans-gauche* rotation isomerization takes place, however, the energy relations will be different. Our forthcomming

communication will deal with study of the interaction energies and potential of internal rotation in the model systems of the mentioned type.

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REFERENCES

1. Dashevskii V. G.: *Konformacii Organicheskikh Molekul.* Khimia, Moscow 1974.
2. Altona C., Faber D. H.: Topics Curr. Chem. *45*, 1. Springer, Berlin—Heidelberg 1974.
3. Wertz D. H., Allinger N. L.: Tetrahedron *35*, 3 (1979).
4. Gajdoš J., Bleha T.: This Journal *47*, 2323 (1982).
5. Bleha T., Gajdoš J., Tvaroška I.: J. Mol. Struct. *68*, 189 (1980).
6. Lochmann R., Weller T.: Int. J. Quantum Chem. *10*, 909 (1976).
7. Lochmann R., Hobza P.: Int. J. Quantum Chem. *15*, 73 (1979).
8. Boyd R. H.: J. Chem. Phys. *48*, 2574 (1968).
9. Diner S., Malrieu J. P., Claverie P.: Theor. Chim. Acta *13*, 1 (1969).
10. Kitaigorodskii A. I.: *Molekulyarnye Kristally.* Nauka, Moscow 1971.
11. Abrahamsson S., Dahlén B., Löfgren H., Pascher I., Sundell S. in the book: *Structure of Biological Membranes* (S. Abrahamsson, I. Pascher, Eds). Plenum Press, New York 1977.
12. Norman N., Mathisen H.: Acta Chem. Scand. *15*, 1755 (1961).
13. Billmeyer F. W.: J. Appl. Phys. *28*, 1114 (1957).
14. Williams D. E.: J. Chem. Phys. *47*, 4680 (1967).
15. Timofeeva R. V., Chernikova N. Yu., Zorkii P. M.: Usp. Khim. *49*, 966 (1980).
16. Warshel A., Lifson S.: J. Chem. Phys. *53*, 582 (1970).
17. Momany F. A., Carruthers L. M., McGuire R. F., Scheraga H. A.: J. Phys. Chem. *78*, 1595 (1974).
18. Brosio E., Conti F., DiNola A., Kovacs A. L.: J. Theor. Biol. *67*, 319 (1977).
19. Salem L.: J. Chem. Phys. *37*, 2100 (1962).
20. Shapiro E., Ohki S.: J. Colloid Interface Sci. *47*, 38 (1974).
21. Bell G. M., Combs L. L., Dunne L. J.: Chem. Rev. *81*, 15 (1981).

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