MOLECULAR-MECHANICAL CALCULATION OF TORSION POTENTIAL IN HEXANE

Ján GAJDOŠ and Tomáš BLEHA

Polymer Institute,
Slovak Academy of Sciences, 842 36 Bratislava

The report gives molecular-mechanical calculations of potential $V(\varphi)$ of internal rotation around the central C—C bond in n-hexane with full geometry optimization. Besides the conformational dependence of the potential energy (strain energy), also torsion dependence of vibration entropy, zero point energy (E_0) and heat of formation have been calculated for hexane. Limitations of bond-drive technique in application to quantitative static and dynamic characterization of internal rotation are pointed out. Effect of the condensed phase on $V(\varphi)$ has been assessed on the basis of a simplified model of medium as continuum.

Molecular-mechanical calculations (MMC) represent an efficient tool for determination of structure and thermodynamic properties especially of hydrocarbon molecules[1−4]. In terms of this calculation method the intramolecular energy is expressed by a set of parameters characterizing individual types of interactions in the molecule or the force field of the molecule. The individual contributions, as *e.g.* deformation energy of bond angles from their "standard" values, the van der Waals interactions of mutually non-bonded atoms, electrostatical interactions *etc.* are expressed on the basis of classical mechanics. The method was made perfect first of all by introduction of a set of mutually balanced parameters for the individual types of contributions to potential energy which are derived from experimental data as well as by assembling complete calculation programs for the routine exploitation[1−8].

The individual approaches differ in parametrization, selection of functions, applied optimization procedure, but in whole they provide reliable information about internal geometrical structure of hydrocarbon molecules and, in part, thermodynamic functions. It was stated[7] that structure determination of complex hydrocarbon molecules by means of MMC can be more accurate than that based on experimental data. In spite of MMC being successful especially for hydrocarbon molecules, attempts are made to extend the method to halogen derivatives and molecules containing oxygen, silicon, nitrogen, phosphorus and other heteroatoms.

The MMC's were used successfully for description of conformation properties of isolated hydrocarbon molecules. They predict the conformation energies and barriers of interconformational transitions in agreement with experiment. The comparison of theoretical and experimental values of internal rotation of hydrocarbons usually does not take into account effects of environment on shape of the potential $V(\varphi)$ of internal rotation around a C—C bond in the molecule, which is supported by the statement that dipole moments of hydrocarbons are negligible, and, hence, the hydrocarbons are affected only slightly by dielectric effects of medium. There is, however, growing evidence for possible existence of environmental effects on internal rotation even in the case of non-polar hydrocarbons[9−11]. Under such circumstances, there can be

a difference between the potential of internal rotation of isolated molecule $(V_{isol}(\varphi))$, which reflects the situation in the gas phase, and the torsion potential in the condensed phase $(V_{cond}(\varphi))$.

The present intensive attention paid to lipid bilayers, monolayers, micelles, microemulsions and other systems representing hydrocarbon aggregates as well as to structure of hydrocarbon polymers in solution and in solid state necessitates a more detailed study of the environmental effects (solvent, environmental matrix *etc.*) on conformation structure of hydrocarbons. *E.g.* it is necessary to find the differences between the conformation characteristics of an alkane molecule dissolved in non-polar solvent and those of the same molecule incorporated in an aggregate of the type of lipid bilayer. From theoretical point of view, a significant contribution to solution of the problem can be made by the molecular-mechanical calculations (MMC) carried out for a group of hydrocarbon molecules which suitably models the situation in real hydrocarbon structures. We decided to follow this path in a series of communications dealing with description of internal rotation in hydrocarbon aggregates with the use of the MMC method by Boyd[6]. With respect to the fact that the parameters in the MMC's should describe the intra- and the intermolecular interactions equally well, such application of the method does not bring any fundamental methodical problems. A similar calculation procedure is used for description of molecular crystals[12] as well as for the aggregates modelling the phospholipid bilayer in biological membranes[13]. In contrast to the above-mentioned approaches, our primary aim is to find the way in which a C—C bond torsional potential of a hydrocarbon molecule is changed on going from the isolated molecule to aggregate of the hydrocarbon molecules, and to find the optimum geometry arangements of such group of molecules. The present, first communication deals in more detail with the method used and with results of MMC's obtained for the isolated n-hexane molecule. The selection of hexane as a model for the study of polymolecular aggregates represents a compromise between the available computer capacity and a realistic model of longer linear n-alkanes. Also we determined the influence of the condensed phase modelled as a continuum on static and dynamic parameters of internal rotation of hexane.

Model and Calculation Procedure

We studied the internal rotation around the central $(C_3—C_4)$ bond in n-hexane molecule characterized by the torsional angle φ and potential of internal rotation $V(\varphi)$. The rotational isomers with φ 180° are denoted as antiperiplanar — *trans* (T), those with φ ±60° are denoted as synclinal — *gauche* (G^+ and G^-). The calculation was carried out by the modified MOLBL3 program by R.H. Boyd[14] using original parameters. As compared with the other MMC programs, the program used differs in the optimization method (it adopts the Newton–Raphson method) and in that the optimization results serve as a starting point for the vibrational analysis of the mole-

cule, too. The overall potential energy E_s (strain energy) is defined, according to Boyd, as a sum o several contributions,

$$E_s = V_\vartheta + V_r + V_t + V_n . \qquad (1)$$

The first two terms express the deformation energy of bond angles, $V_\vartheta = \sum_{i,j,k} \frac{1}{2} k_\vartheta (\vartheta_{i,j,k} - \vartheta^0_{i,j,k})^2$ (where $\vartheta_{i,j,k}$ is the bond angle between the atoms i, j, k, and ϑ^0 is "natural" or relaxed equilibrium bond angle; k_ϑ means the force constant of the bond angle strain), and the deformation energy of bond lengths $r_{i,j}$, $V_r = \sum_{i,j} \frac{1}{2} k_r (r_{i,j} - r^0_{i,j})^2$ (where the meaning of symbols is similar to that in the case of V_ϑ). The so called "inherent" three-fold potential of ethane type is $V_t = \sum_i \frac{1}{2} V_0 (1 + \cos 3\varphi_i)$, where V_0 means an adjustable parameter of the potential barrier height. The term V_n expresses the interactions between the mutually non-bonded atoms (except for the interactions of the atoms bound to a common atom) by means of (6-exp) potential. In the terms of the Boyd's program, the shape of torsion potential is easily obtained with the use of the bond-drive technique[4,15,16] which enables to adjust gradually one or more torsional coordinates (φ_i) at desired values. This effect is achieved by superposition of an additional function E_{extra} (whose minimum lies at the adjusted φ value) on the strain energy. The subsequent energy minimization leads to a geometry in which the φ angle has approximately the adjusted value[16]. The converged structure (with respect to one φ angle) serves as starting point for the further step. The calculation using an increment of 15° for the φ angle gave the reaction path of the conformational interconversion of hexane.

The minimization procedure of energy calculation is also used for determination of vibration frequencies ν_k of the molecule. These values along with the moment of inertia (I) of the molecule enable (in terms of the rigid rotor — harmonic oscillator approach) determination of the rotation and vibration contributions to the thermodynamic functions as $(H - H^0)/T$, S, C_p. Furthermore, it is possible to calculate the zero point energy (E_0) and predict the heat of formation (ΔH_f) of the hydrocarbon molecule. The latter quantity (at a temperature T) is given as the the sum[5,14]

$$\Delta H_f = E_s + E_0 + E_{th} + E_{gr} . \qquad (2)$$

The group energy (E_{gr}) is composed additively from contributions of individual atomic groups of the hydrocarbon molecule to its heat of formation[6]. The thermal energy (E_{th}) represents thermal excitations of individual degrees of freedom in the molecule: The translational and rotational excitations are expressed as multiples of RT (the same is true for PV term of volume work), and the vibrational excitations with temperature are determined as a sum of terms $RT\Theta/(e^\theta - 1)$ for all the $(3N - 6)$

vibration modes, where N means number of atoms in the molecule (for hexane it is $N = 20$), and $\Theta = hv/kT$.

Static Characteristics of Rotation

The curve given in Fig. 1 for torsional dependence of strain energy during rotation around the central C—C bond of hexane (calculated by the Boyd's method) represents the potential of internal rotation $(V(\varphi))$. Therefrom it follows that the conformation energy ΔE defined as the difference between the *gauche* and *trans* states has the value of 2·8 kJ/mol, the energy barriers $E_{TG}^{\ddagger}$ and $E_{GG}^{\ddagger}$ (from T to G and from G^+ to G^-, respectively) being 11·0 and 17·1 kJ/mol, respectively.

Also Fig. 1 gives the course of individual contributions to the overall strain energy. According to expectation, the most distinct torsion changes are exhibited by the V_n and V_t terms. However, the contribution of angle deformation is changed markedly, too, especially so near the eclipsed position with φ 0° when the C—C—C angles at the rotating bond are "opened" as wide as about 116°C. The contribution of bond deformation is almost conformation-independent. Figure 1 also demonstrates the effect of the optimization on the torsional potential. The optimized geometry calculated for all-*trans* extended hexane (where *e.g.* the C—C bond lengths lie between 0·1538 and 0·1536 nm, and the CCC bond angles are about 111·8°) is used in further calculation of the conformational dependence of $E_s^{\ast}$ without optimization (Fig. 1, curve $E_s^{\ast}$). It is seen that, first of all, the GG barrier is considerably increased, but the conformation energy ΔE is also increased to 3·8 kJ/mol, the minimum $\varphi \pm 67°$ being shifted to $\varphi \pm 75°$.

Most frequently the MMC method was used to study the rotation potential for the C—C bond of butane and its derivatives $(e.g.^{17})$ where the presence of a single angle φ makes the comparison with experimental data most reliable. However, experimental methods provide only differences between maxima and minima of the torsional potential $(as e.g. \Delta E, E_{TG}^{\ddagger}, E_{GG}^{\ddagger}$ etc.$)$, mutual agreement between the methods being little satisfactory. So *e.g.* the values given[18,19] for the conformational energy ΔE of shorter n-alkanes vary within the limits from about 1·8 to 4·1 kJ/mol. The MMC torsion potential agrees also with the best *ab initio* quantum-chemical calculations for butane[20]. Equally well the MMC method reflects the role of geometry optimization during rotation, which follows from comparison of Fig. 1 with analogous curves for butane obtained by *ab initio* and semi-empirical quantum-chemical methods[21]. For comparison we used (in the same way as MMC) also the standard semi-empirical methods PCILO and CNDO/2 which are generally relatively successful in predicting the conformational properties of molecules[3]. The non-optimized calculation with the geometry parameters corresponding to the all-*trans* conformation gives (in the case of PCILO method) the *trans* position more stable than the *gauche* position by only 0·4 kJ/mol, whereas in the case of CNDO/2 the *trans* position is even less stable than the *gauche* position by 0·8 kJ/mol (ref.[11]).

Limitations of the bond-drive technique for use in determination of the vibration terms. We calculated values of thermodynamic functions for the temperature 298·16 K and their changes with rotation by the angle φ. Beside the usual way of calculation

we also used the bond-drive technique with the aim to demonstrate unsuitability of this procedure for reliable determination of the vibrational contributions in internal rotation. Figure 2 gives the changes of entropy (S), zero point energy (E_0), and enthalpy of formation (ΔH_f) with the rotation, the full lines corresponding to the bond-drive calculation, whereas the standard approach is only applicable for stationary points at the hypersurface (the horizontal lines in the regions of minima and maxima of the E_s potential). The entropy values were calculated on the basis of standard thermodynamic relations in the rigid rotor — harmonic oscillator approximation[3]. As the translation contribution S_{tr} to entropy depends only on volume, temperature,
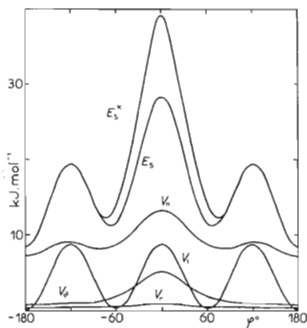

Fig. 1

Dependence of strain energy E_s (with optimization of geometry), E_s^* (without optimization) and individual contributions to E_s (according to Eq. (1)) on the angle φ of rotation around the central C—C bond in hexane
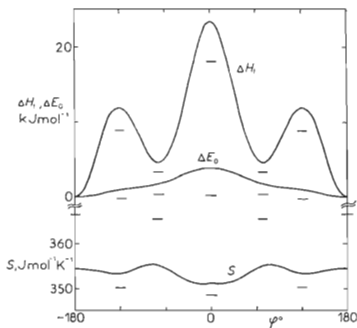
Fig. 2

Dependence of entropy S, relative changes (with respect to *trans* conformation) of the zero point energy E_0 and heat of formation ΔH_f on the angle φ of rotation around the central C—C bond in hexane obtained by the bond-drive technique. The horizontal lines represent the analogous changes (relative values in the case of E_0 and ΔH_f) obtained by the standard optimization procedure. Absolute values of E_0 and ΔH_f (in kJ/mol) for all-*trans* hexane are respectively: 483·1 and −167·5 (obtained by the bond-drive technique), 478·5 and −170·6 (obtained by the standard optimization procedure)

and molecular mass, its value does not change with internal rotation. Also relatively little conformation-dependent is the rotation contribution S_{rot} which is only affected by changes of the reduced moment of inertia (I_{red}) during internal rotation. The torsion dependence of the overall entropy is determined in the main by the change of the vibration contribution S_{vibr} with the rotation.

The entropy differences between the rotation isomers calculated by the two ways are not very large. The gauche-*trans* entropy difference is $-0.9 \text{ J mol}^{-1} \text{ K}^{-1}$ and $+0.9 \text{ J mol}^{-1} \text{ K}^{-1}$ according to the standard procedure and bond-drive technique, respectively. At normal temperatures such entropic values represent a correction of about 0.27 kJ/mol in the conformational free energy value (ΔF). Reisse[22] pointed out the importance of differences in vibration entropy of the individual conformers when submitting cyclic alkanes to precise conformational analysis. For linear alkanes, however, the vibration contribution to $T \Delta S$ appears to be not very significant.

Correct evaluation of the vibration entropic term depends critically on quality of vibrational analysis of the molecule. The Boyd's method seems to provide relatively reliable values of normal vibrational modes for stable conformations of hydrocarbon molecules as compared with experimental frequences[23]. Especially significant for calculation accuracy of thermodynamic functions are the low-frequency vibrations, which are most sensitive to conformation changes, too. Reliability of the vibrational analysis affects not only the S_{vibr} term, but also E_0 term, whose value is conformation-independent in such cases only, if $\sum\limits_{k}^{3N-6} v_k = \text{const.}$ for all the conformations. Really, the differences in the E_0 term of rotation isomers of n-hexane are minimum with application of the standard calculation procedure (Fig. 2).

The bond-drive technique, however, enables to calculate the S and E_0 terms also outside the points lying at the maxima and minima of the potential energy E_s. The minimization procedure leading to determination of molecular geometry of the individual stable rotation isomers in the MMC approaches[4–6] serves as the starting point for calculation of vibration frequences of the molecule. If the bond-drive technique[4,15,16] is used, however, the minimization procedure is carried out in such a way that $(3N - 7)$ internal coordinates converge to energetically optimum values, but the last coordinate — the dihedral angle φ — is kept at a fixed value[16] by the additional function E_{extra}. The vibrational analysis corresponds only to the quasi-equilibrium structure of the molecule, unless — by chance — the φ value represents just the *gauche* or *trans* minimum at the potential energy curve. The additional function E_{extra}, however, affects values of thermodynamic vibration functions also at the minima of potential energy E_s by increasing artificially the steepness of the potential wells on the hypersurface. Thus *e.g.* the zero point energy of the all-*trans* n-hexane conformation in the bond-drive approach (with a sixty-fold increase of the V_0 parameter) is $E_0^{drive} = 483.1 \text{ kJ/mol}$, whereas without using the E_{extra} function the value is $E_0 = 478.5 \text{ kJ/mol}$.

Especially marked are the differences between results of the bond-drive technique and those of the standard approach (without using the E_{extra} function) near the saddle points of the energy hypersurface, *i.e.* for n-hexane at the torsion angle values $\varphi = \pm 120°$ and 0°. These points represent transition states for rotation by angle φ, and the matrix of second derivatives of energy with respect to Cartesian coordinates (matrix of force constants) has six zero eigenvalues and at least one negative eigenvalue. The latter is ascribed to an imaginary frequency along the reaction coordinate (v_φ) which leads to decomposition of the transition state. Thus if energy of hexane is optimized near the saddle points (without the E_{extra} function), the imaginary frequency v_φ does not contribute to the vibrational energy terms belonging to these points. On the other hand, however, in the bond-drive procedure the E_{extra} function causes that the v_φ frequency is real and contributes to the vibrational terms also at the tops of the potential energy barriers.

Therefore, it is not surprising that the two methods give different courses of conformation dependences of vibration energy functions and the derived thermodynamic quantities. The v_φ frequency contributes with various weights to the overall values of S and E_0 quantities. As the low-frequency vibrations affect only insignificantly the E_0 term, neglection of one of them will change E_0 but little. Thus *e.g.* the typical value of C—C torsion vibration (about 100 cm^{-1}) corresponds to the energy of about 0·6 kJ/mol. On the other hand, the low-frequency vibration has the highest importance in determination of the S value, and the absence of the v_φ frequency causes a great decrease in the S value at the maxima of the potential energy curve, if the standard calculation procedure is used.

The energy course of internal rotation is described most frequently by plotting static potential energy as *e.g.* strain energy (E_s). But there are justified arguments that a better measure of stability of the individual steric isomers is obtained by plotting quantities involving also vibration energy contributions. Thus *e.g.* it is possible to correct the potential of internal rotation by introduction of differences in the E_0 energy of the rotation isomers. Figure 2 indicates that the E_0^{drive} values calculated by the bond-drive technique cannot be used for this purpose, and a correction of the $E_s(\varphi)$ potential by means of contribution of the $E_0^{drive}(\varphi)$ curve would be erroneous.

The exaggerated conformation dependence of the E_0^{drive} term can affect also the conformation dependence of heat of formation, if the bond-drive technique is used for the calculation. As the E_{gr} terms in Eq. (2) are constants, and the E_{th} term involves vibration thermal excitations which are, in fact, conformation-independent, too, the conformation dependence of ΔH_f is determined only by changes in the E_s and E_0 terms. The ΔH_f value represents a significant measure in comparison of molecular stability and in decisions about possible reaction paths of interconversions of stable conformers[17,24]. Application of the bond-drive technique is particularly useful in such cases, the ΔH_f dependence being obtained for the whole range of the

variable φ angle. If the used MMC's are based on schemes not involving explicitly the vibration effect[1], such procedure does not meet any difficulty. However, vibration terms are incorporated gradually into MMC computational schemes[5]. In such cases it seems problematic to express the energy course of interconformational transitions on the basis of the ΔH_f determined along the whole reaction path. Differences between the application of the standard and the bond-drive methods in calculation of ΔH_f for internal rotation of hexane are given in Fig. 2 which also indicates magnitude of the error which can be introduced during routine application of the bond-drive technique.

A certain analogy to the torsional dependences of ΔH_f and E_0 found by the bond-drive method can be encountered in the absolute reaction rate theory. There are attempts[25] to construct the reaction path on free energy hypersurfaces instead of potential energy hypersurfaces. Such approach necessitates determination of vibrational contributions to the activation entropy along the whole reaction coordinate, *i.e.* not only for equilibrium molecular structures.

Dynamic characterization of rotation. With regard to dynamic aspects of internal rotation viewed as a rate process, the *trans-gauche* isomerization is treated usually (on the basis of the absolute reaction rate theory) as a monomolecular reaction. The rate constant is

$$k_{TG} = \varkappa (kT/h) \exp(-\Delta F^* / RT), \qquad (3)$$

where k, h, R are universal constants, $\varkappa$ means the transmission coefficient which is usually considered equal to 1, ΔF^* is the activation free energy which can be separated into the enthalpy (ΔH^*) and entropy $(T \Delta S^*)$ terms. If ΔH^* of the *trans-gauche* interconformational transition is considered identical with the respective barrier at the $E_s(\varphi)$ curve (Fig. 1), then at T 298·16 K it is $k_{TG} = 10\cdot4$ ns^{-1}. The term $T \Delta S^*$ takes into account also the entropy difference between the positions with φ 180° and φ 120° (Fig. 2) obtained by the standard way without the additional function (E_{extra}).

Kinetics of internal rotation in hydrocarbons is also affected significantly by character of environment. In theoretical approaches the enviroment can be modelled in a discrete way, *i.e.* by a greater number of molecules surrounding the central molecule, or as a continuum. In the following text we will briefly deal with the latter approach, which we used recently[11,26]. We found that molecular surface and volume are substantially changed during internal rotation (by up to several per cent). In the case of n-alkanes the molecular volume is gradually increased during transition from *gauche* to *trans* position. If the molecule is immersed in a continuum, such rotation necessitates the corresponding increase of magnitude of the cavity occupied by the molecule in the medium, *i.e.* the energy $P_i \Delta V_w$ must be invested, where P_i

means internal pressure of the medium, and ΔV_w is the change in the van der Waals molecular volume. The torsional dependence of the product $P_i \, \Delta V_w$ can be considered to be a "perturbation" potential of the internal rotation which reflects effect of medium (solvent) in terms of this simple model, and its sum with the torsional potential of the isolated molecule $(V(\varphi))$ gives the torsional potential for the condensed phase $(V_{cond}(\varphi))$. We found[11] the *gauche–trans* volume change $\Delta V_w = -3.55$ cm^3/mol for hexane. The corresponding *gauche–trans* energy difference for liquid hexane also representing the environment $(P_i = 240 \text{ J/cm}^3)$ is $\Delta E = 1.95$ kJ/mol, which represents a lowering as compared with the isolated molecule (2.8 kJ/mol). The changed conformation energy in the condensed phase will manifest itself also in a marked shift of the *trans-gauche* conformation equilibrium as compared with the situation in gas phase[9,11].

The continuous model can also be used for expressing the influence of the condensed phase on kinetics of the internal rotation. From our calculation[11] it follows for the activation volume of the *trans-gauche* interconformational transition $\Delta V^{+} = -1.1$ cm^3/mol. This value makes about 31% of the value found for the equilibrium *gauche-trans* change ΔV_w $(-3.55 \text{ cm}^3/\text{mol})$. The only literature data suitable for comparison are those by Chandler and coworkers[9,27] who found a similar ratio of ΔV_w^{+} and ΔV_w $(-1.3 \text{ and } -4.7 \text{ cm}^3/\text{mol}, \text{ respectively})$ for butane in CCl$_4$. The activation anthalpy ΔH^{+} of the *trans-gauche* interconformational transition in the condensed state can be expressed by the sum:

$$\Delta H^{+} = \Delta E^{+} + \Delta E_0^{+} + P_i \, \Delta V^{+} . \qquad (4)$$

Introduction of Eq. (4) into Eq. (3) gives the rate constant values $k_{TG} = 12.0$ ns^{-1}. As compared with the isolated molecule, the continuous model of environment predicts an increase in the rate constant of the interconformational transition in the condensed phase.

The above-given calculations of kinetic parameters consider invariably the values obtained on the basis of the standard calculation procedure of vibrational contributions. A non-justified application of the vibrational contributions obtained by the bond-drive method would result in a considerable error even in determination of the rotation dynamic parameters. Thus *e.g.* introduction of the bond-drive values for the E_0 and S terms in Eqs (3) and (4) would give the value $k_{TG} = 47.3$ ns^{-1} instead of the above-mentioned value 12 ns^{-1}.

The continuous model of influence of the condensed phase on internal rotation in hydrocarbons represents undoubtedly a considerable simplification. However, it can also be qualitatively substantiated by the arguments based on the idea of discrete character of environment: The more is the hydrocarbon molecule globular $(i.e.$ it has a greater number of *gauche* conformations) the easier it is to place it among a set of spherical molecules $(e.g.$ CCl$_4)$ representing the neighbouring solvent.

A different situation, however, is encountered, if the medium is formed by more rigid rodlike molecules; then the hydrocarbon molecules tend to assume parallel arrangement and prefer *trans* conformations, which is denoted as local order in hydrocarbon systems. Discrete models of the hydrocarbon aggregates using the MMC's should elucidate molecular energetics of formation of the local order. A suitable comparison point for this purpose consists in the detailed characterization of internal rotation around C—C bond in hexane presented in this communication. Similarly inevitable is the knowledge of static and dynamic characteristics of internal rotation of isolated bond for examination of two or more simultaneous coupled rotations around C—C bonds. This case is particularly important as a model of motions of shorter segments of macromolecules in solid state and in solution or a model of mobility of hydrocarbon tails in membrane lipid bilayers.

REFERENCES

1. Allinger N. L.: *Advances in Physical Organic Chemistry 13*. Academic Press, London 1976
2. Altona C., Faber D. H.: *Topics in Current Chemistry* 45, 1. Springer, Berlin-Heidelberg 1974
3. Dashevskii V. G.: *Konformacii Organicheskikh Molekul*. Khimiya, Moscow 1974.
4. Ermer O.: *Structure and Bonding* 27, 161. Springer, Berlin-Heidelberg 1976.
5. Wertz D. H., Allinger N. L.: Tetrahedron *35*, 3 (1979).
6. Boyd R. H.: J. Chem. Phys. *49*, 2574 (1967).
7. Engler E. M., Andose J. D., von R. Schleyer P.: J. Amer. Chem. Soc. *95*, 8005 (1973).
8. Warshel A., Lifson S.: J. Chem. Phys. *53*, 582 (1970).
9. Pratt L. R., Hsu C. S., Chandler D.: J. Chem. Phys. *68*, 4202 (1978).
10. McCreery J. H., Christoffersen R. E., Hall G. G.: J. Amer. Chem. Soc. *98*, 7191 (1976).
11. Bleha T., Gajdoš J., Tvaroška I.: J. Mol. Struct. *68*, 189 (1980).
12. Kitaigorodskii A. I.: *Molekulyarnye Kristally*. Nauka, Moscow 1971.
13. Frischleder H., Lochman R.: Int. J. Quantum Chem. *16*, 203 (1979).
14. Boyd R. H., Breitling S. M., Mansfield M.: AIChE J. *19*, 1016 (1973).
15. Wiberg K. B., Boyd R. H.: J. Amer. Chem. Soc. *94*, 8426 (1972).
16. van de Graaf B., Baas J. M. A., van Veen A.: Rec. Trav. Chim. Pays-Bas *99*, 175 (1980).
17. Osawa E., Shirama H., Matsumoto T.: J. Amer. Chem. Soc. *101*, 4824 (1979).
18. Bothorel P.: J. Chim. Phys. Physicochim. Biol. *71*, 1133 (1974).
19. Colombo L., Zerbi G.: J. Chem. Phys. *73*, 2013 (1980).
20. Allinger N. L., Profeta S., jr: J. Comp. Chem. *1*, 181 (1980).
21. Scheiner S.: J. Amer. Chem. Soc. *102*, 3723 (1980).
22. Reisse J. in the book: *Conformational Analysis* (G. Chiurdoglu, Ed.). Academic Press, New York 1971.
23. Boyd R. H.: J. Amer. Chem. Soc. *97*, 5353 (1975).
24. Osawa E.: J. Amer. Chem. Soc. *101*, 5523 (1979).
25. Laidler K. J.: *Theories of Chemical Reaction Rates*. McGraw-Hill, New York 1969.
26. Bleha T.: Makromol. Chem., Rapid Commun. *2*, 35 (1981).
27. Montgomery J. A., Chandler D., Berne B. J.: J. Chem. Phys. *70*, 4056 (1979).

Translated by J. Panchartek.