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Study of Internal Rotation of Radical Center in *n*-Alkyl Radicals

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Abstract—A quantum-mechanical study of internal rotation around C–C• bond in *n*-alkyl radicals from C_2H_5 to C_7H_{15} was carried out using B3LYP/6-311++G(3df, 3pd) approach. The values of barriers and local minima were found. Analysis of the distribution of electron density was carried out. By application of the methods of mathematical statistics different types of representation of the potential functions of internal rotation were analyzed and the optimal approximation was revealed. Contributions to the thermodynamic properties of the considered radicals were calculated. The generalized function of internal rotation was suggested for the radicals of the type C_nH_{2n+1}, $n > 4$.

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Quantitative evaluation of parameters of chemical reactions is impossible without the knowledge of thermodynamic properties of compounds. These properties reflect all motions of molecules as a whole and its individual parts. We believe that in the literature not enough attention has been paid to the study of the regularities concerning the contributions of internal rotation to the thermodynamic properties. In the previous article [1] we reported on the investigation of potential functions of internal rotation in *n*-alkanes and they were generalized in the framework of quantitative correlations "structure-property." The aim of this work is to study such regularities for *n*-alkyl radicals.

Thermodynamic properties of substances in the approximation of the separation of motions [2] are calculated by the methods of statistical physics [3], by summation of translational, rotational and vibrational contributions. Internal rotation, being substantially inharmonic motion [4], usually is extracted from vibrations and is considered by means of the relations whose parameters are potential functions of internal rotation $V(\varphi)$ and reduced moments of inertia *Ir*. Function $V(\varphi)$ is a cross section of the potential energy surface (PES) along the dihedral angle φ. It is possible to estimate the value of *Ir*, the values of barriers on PES (V_{max}) and the approximate $V(\varphi)$ from the data of microwave spectra and electron diffraction [5, 6]. However, for radicals, for several reasons, such measurements are extremely difficult, so for them the basic tool for the study of internal rotation is quantum-mechanical calculations. Such high-level calculations are still very resource-consuming and for the radicals in question have not been performed. At a lower level, for ethyl and propyl radicals [7–25] in small bases geometric parameters, barriers and potential functions have been calculated, and a calculation of the barrier in the *n*-butyl has been performed [8]. Comparing results of these calculations with the ESR spectrum of C_3H_7 gives an estimation of the barrier value 1.67 [23] and 1.72 [24] kJ mol^{-1}, the value of the barrier in the C_2H_5 from the data of the infrared spectrum is 0.24 [21] and 0.20 [22] kJ mol^{-1}.

We performed a quantum-mechanical study of conformations of *n*-alkyl radicals from C_2H_5 to C_7H_{15}, appearing at the internal rotation of group C•H$_2$ group around the C–C• bond, determined the relative values of their electron-nuclear energy (global and local minima (V_{min}), and the energy barriers between them ($V_{max} = V_{glob}$, V_{loc}), found values of *Ir* and plots for $V(\varphi)$. The different types of representation of the potential function were analyzed and the best characteristics were suggested: the type of approximation of $V(\varphi)$, the number of the members of expansion, the initial conformation corresponding to $\varphi = 0$.

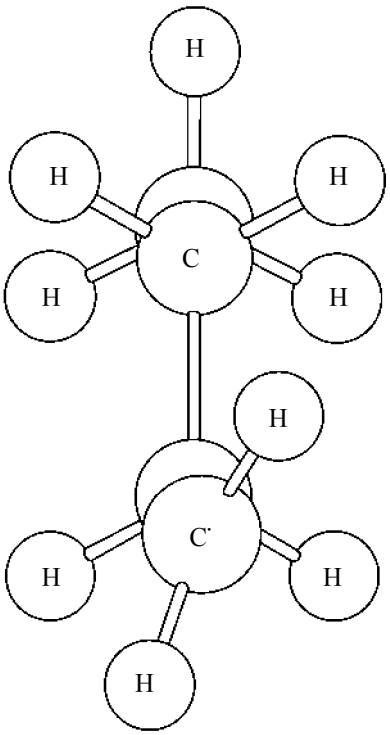

Fig. 1. Locations of the atoms of butyl radical for the conformation of the global minimum (*2* in Fig. 2). Group $C^{\bullet}H_2$ in the foreground.

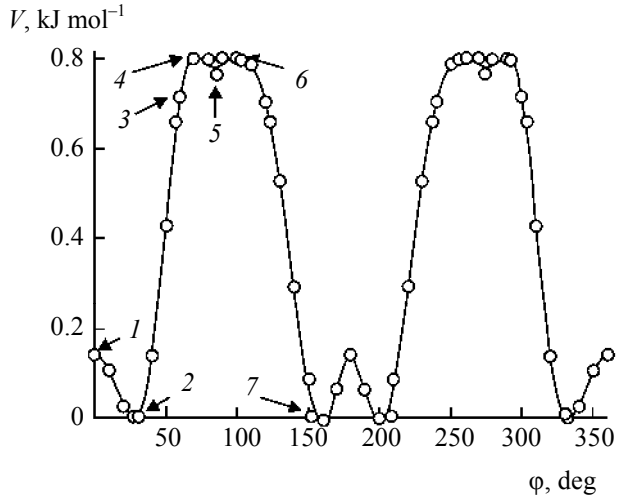

Fig. 2. Type of potential function $V(\varphi)$ C_nH_{2n+1}, $n > 2$, at the rotation of group $C^{\bullet}H_2$ around the C–C$^{\bullet}$ bond, of the dihedral angle C–C–C$^{\bullet}$–H (see also Tables 1 and 2). By arrows and numbers are marked: (*1*) local maximum V_{loc}, eclipsed position of atoms C and H at the variations of dihedral angle C–C–C$^{\bullet}$–H; (*2, 7*) global minima; V_{min} is the ground state (Fig. 1), optical isomers; (*3*) V_{ecl}, eclipsed location of atoms H^2 and H^1 at variation of the dihedral angle H^2–C–C$^{\bullet}$–H^1; (*4*) V_{glob}, global maximum value at the angle C–C–C$^{\bullet}$–H equal to 68.3°; (*5*) local minimum, V_{min}, at the C–C–C$^{\bullet}$–H angle equal to 85.8°. Situation (*5*) corresponds to the point group symmetry C_s.

All calculations were made using G98 program [26] in B3LYP/6-311++G(3df, 3pd) approximation. The comparison of the calculated and experimental values of barriers V_{glob}, V_{loc}, and V_{min} for *n*-alkanes carried out in [1] showed good reproducibility of results obtained with this method and basis set. *n*-Alkyl radicals C_3H_7 to C_7H_{15} are the optical isomers of the position of hydrogen atoms of $C^{\bullet}H_2$ group (Fig. 1). The transition from one conformation of the ground state to another proceeds by turning the group of H–C$^{\bullet}$–H around the C–C$^{\bullet}$ dihedral angle C–C–C$^{\bullet}$–H to 56°, the plane of the H–C$^{\bullet}$–H is tilted to C–C$^{\bullet}$ bond at an angle of 7.1°. C_2H_5 belongs to point group symmetry C_s, the remaining *n*-alkyl to C_1, the carbon atoms of the chain form therewith a non-planar backbone.

In the main calculations of $V(\varphi)$ the step of dihedral angle $\Delta\varphi$ (φ is the reaction coordinate) was taken as 10°. Additionally the conformations were examined corresponding to a local minimum (*5* in Fig. 2), to global and local maxima that cooresponded to trasnsition states (TS, *4, 6, 1* in Fig. 2), and to eclipsed location of hydrogen atoms (*3* in Fig. 2). The worst value of the convergence of iterative procedure was on the slope of the potential energy surface: by the energy 1.7×10^{-9} au and by the gradient 1.5×10^{-4} au/Bohr. It should be noted that the TS position in the C_nH_{2n+1}, $n > 2$ corresponding to V_{glob} (*4* in Fig. 2), does not coincide with the eclipsed position of atoms (V_{ecl} corresponds to *3* in Fig. 2). In C_4H_9 the V_{glob} corresponds to dihedral angle α(C–C–C$^{\bullet}$–H) = 68.3°, and for V_{ecl} α(C–C–C$^{\bullet}$–H) = 56.4°. For all eclipsed positions V_{ecl} and V_{loc} (see Fig. 2) α(C–C–C$^{\bullet}$–N) = 0°, the group of nuclei C–C$^{\bullet}H_2$ is planar, that is, the state of inversion of the tail $C^{\bullet}H_2$ does not coincide with V_{glob}, but occurs at V_{ecl} and V_{loc}. The symmetrical arrangement of atoms in the C_nH_{2n+1}, $n > 2$ [*5* in Fig. 2, angle α(C–C–C$^{\bullet}$–H) = 85.8°, the plane of the H–C$^{\bullet}$–H is inclined to the C–C$^{\bullet}$ bond at the angle 8.1°, close to equilibrium], is a local minimum with a very low value of barrier and does not represent any stable state.

The consideration of potential functions showed that the dependence of $V(\varphi)$ for C_2H_5 is different from those for other radicals, so it was approximated separately. The $V(\varphi)$ plot for C_2H_5 is well described by 6-fold cosine curve *1* with V_{max} = 0.233 kJ × mol^{-1} ($V_{max} = V_6$) (Table 1).

$$V(\varphi) = V_6/2[1 - \cos(6\varphi)]. \quad (1)$$

Table 1. The values of reduced moment of inertia *Ir* for the local maximum (*1* in Fig. 2), in parentheses for the global minimum (*2* in Fig. 2), of barriers *V* including $V_{gen}(\varphi)$ and contributions to the thermodynamic properties for the internal rotation around (C)–C$^{\bullet}$H$_2$ bond in *n*-alkyl radicals

Molecule	V_{glob}, kJ mol^{-1}	V_{loc}, kJ mol^{-1}	V_{ecl}, kJ mol^{-1}	V_{min}, kJ mol^{-1}	*Ir*, kg m^2	H_{298}–$H_{(0)int.rot}$,[c] kJ mol^{-1}	G_{298}–$G_{(0)int.rot}$,[c] kJ mol^{-1}	$S_{(298)int.rot}$,[c] J mol^{-1} K^{-1}	$Cp_{(298)int.rot}$,[c] J mol^{-1} K^{-1}
Ethyl	0.233[a]	–	–	–	1.85×10^{-47}	1.35 (1.24)	–2.96 (–3.07)	14.47 (14.47)	4.17 (4.16)
Propyl	1.31[b]	0.11	1.02	1.30	2.65×10^{-47} (2.66×10^{-47})	1.76 (1.24)	–4.53 (–5.10)	21.11 (21.28)	4.50 (4.16)
Butyl	0.80	0.15	0.66	0.77	2.70×10^{-47} (2.71×10^{-47})	1.60 (1.24)	–4.74 (–5.13)	21.29 (21.37)	4.30 (4.16)
Pentyl	0.81	0.16	0.67	0.79	2.80×10^{-47} (2.81×10^{-47})	1.62 (1.24)	–4.77 (–5.17)	21.44 (21.52)	4.30 (4.16)
Hexyl	0.77	0.13	0.65	0.69	2.82×10^{-47} (2.82×10^{-47})	1.57 (1.24)	–4.83 (–5.18)	21.48 (21.55)	4.28 (4.16)
Heptyl	0.79	0.12	0.67	0.72	2.85×10^{-47} (2.85×10^{-47})	1.59 (1.24)	–4.83 (–5.20)	21.52 (21.59)	4.29 (4.16)
$V_{gen}(\varphi)$	0.78	0.14	–	0.73	2.9×10^{-47}	1.60 (1.24)	–4.84 (–5.22)	21.60 (21.66)	4.29 (4.16)

[a] Experimental value from the infrared spectrum is equal to 0.24 [21] and 0.20 [22], kJ mol^{-1}. [b] Experimental value from the ESR spectrum is equal to 1.67 [23] and 1.72 [24], kJ mol^{-1}. [c] In parentheses are given the contributions related to the free-rotation.

Table 2. The values of the coefficients of series (6) in the *n*-alkyl radicals, including those of the $V_{gen}(\varphi)$, for the rotation around (C)–C$^{\bullet}$H$_2$ bond, kJ mol^{-1}

Molecule	V_0	V_1	V_2	V_3	V_4	V_5	V_6	V_7	V_8	V_9	V_{10}	V_{11}	V_{12}
Propyl	0.630	–0.039	–0.720	0.022	0.055	0.050	0.143	0.000	–0.011	–0.036	0.007	0.004	0.005
Butyl	0.402	–0.016	–0.440	0.021	0.055	0.029	0.117	–0.008	0.005	–0.026	–0.002	0.000	0.006
Pentyl	0.419	0.000	–0.439	0.000	0.045	0.000	0.124	0.000	0.008	0.000	0.002	0.000	0.005
Hexyl	0.371	0.000	–0.389	0.000	0.057	0.000	0.129	0.000	–0.002	0.000	–0.009	0.000	–0.004
Heptyl	0.392	0.000	–0.419	0.000	0.040	0.000	0.126	0.000	–0.002	0.000	–0.002	0.000	–0.006
$V_{gen}(\varphi)$	0.394	0.000	–0.416	0.000	0.047	0.000	0.126	0.000	0.001	0.000	–0.003	0.000	–0.002

For the C_nH_{2n+1}, $n > 2$, a description of the rotation of group C$^{\bullet}$C$_3$H$_7$ around the C–C$^{\bullet}$ bond requires a larger number of members of the Fourier series than in (1). This is defined by the presence and alternation of different size maxima (Fig. 2, Table 2). Such a curve for the C_3H_7 was obtained in the UHF/3-21G calculation, but in another, rather rough, approximation [25].

To find the valid $V(\varphi)$ representation, we considered the approximations by the series (2)–(7) with $k = 6, 12, 15, 20$.

$$V(\varphi) = V_0 + \sum_{i=1}^{k} V_i\cos(i\varphi) + \sum_{j=1}^{k} V_j\sin(j\varphi), \quad (2)$$

$$V(\varphi) = \sum_{i=1}^{k} V_i/2\,[1 - \cos(i\varphi)] + \sum_{j=1}^{k} V_j/2[1 - \sin(j\varphi)], \quad (3)$$

$$V(\varphi) = \sum_{i=1}^{k} V_i/2\,[1 - \cos(i\varphi)], \quad (4)$$

$$V(\varphi) = \sum_{j=1}^{k} V_j/2\,[1 - \sin(j\varphi)], \quad (5)$$

$$V(\varphi) = V_0 + \sum_{i=1}^{k} V_i\cos(i\varphi), \quad (6)$$

$$V(\varphi) = V_0 + \sum_{j=1}^{k} V_j\sin(j\varphi). \quad (7)$$

As a test molecule was taken the butyl radical C_4H_9, as an error (divergence) was taken the average sum of squares of deviations (dispersion). It turned out that the choice of initial configuration significantly affect the divergence. Therefore, in order to minimize the divergence, as the initial conformation with $\varphi = 0$ were considered successively various structures: with eclipsed atoms, V_{ecl}, TS, global and local minima (in Fig. 2 they are marked by numbers). In other words, in various approximations of the functions $V(\varphi)$, different structures of the molecule corresponded to the reaction coordinate $\varphi = 0$, differing by the dihedral angle C–C–C$^{\bullet}$–H. That is, for any conformation from which the calculation starts, for the first point on the graph $V(\varphi)$ was taken $\varphi = 0$, and the change of the conformation corresponded to the shift of initial potential function along the abscissa. For each series (2) to (7) and each sum with $k = 6, 12, 15, 20$ six expansions were carried out corresponding to the six reaction coordinates $\varphi = 0$

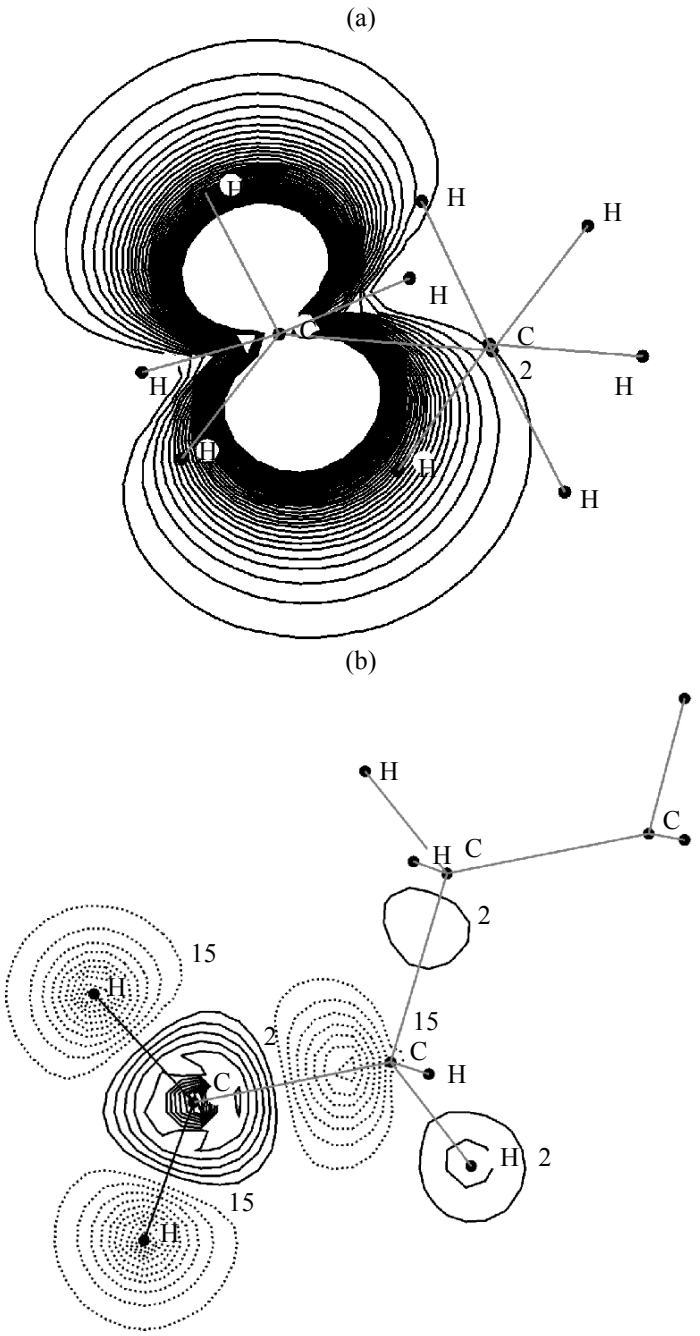

Fig. 3. Distribution of the unpaired electron spin density for the global minimum conformation (Fig. 1, Fig. 2, *2*). (a) In the plane including the nucleus C• and perpendicular to C–C•; (b) in the plane coinciding with the plane of the nuclei H–C•–H. Spin density: (α) solid lines; (β) dotted lines. Numbers 2 and 5 near the contours correspond to iso-surface 0.001 au Bohr^{-3}, (2) α density; (15) β density. Figure is drawn using MolDen program [29].

at different initial points (Fig. 2, numbers *1, 2, 4–7*). Thus, for C_4H_9 144 calculations were made.

Statistical analysis showed that the most accurate description of $V(\varphi)$ for C_4H_9 (lowest divergence) is achieved with a series (2) if as $\varphi = 0$ is taken the state corresponding to TS (V_{glob}, *4* in Fig. 2). At the variation in the number of summands in (2) it was obtained that starting from $k = 15$ the differences in dispersion with a large k, according to Fisher's criterion [27], were statistically insignificant. As a result, the best approximation of $V(\varphi)$ for C_nH_{2n+1}, $n > 2$,

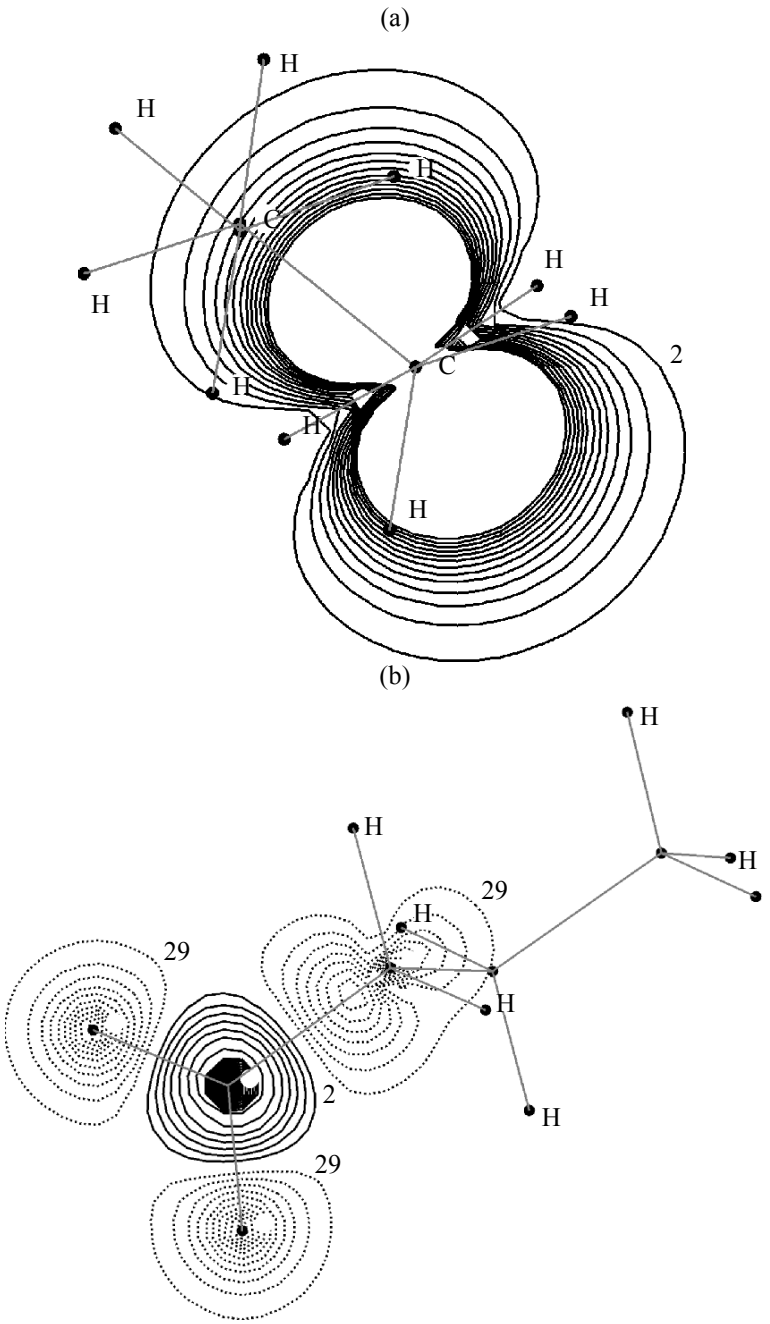

Fig. 4. The distribution of the unpaired electron spin density for the conformation of the global maximum (Fig. 2, *4*). (a) In the plane including the nucleus C• and perpendicular to C–C•; (b) in the plane coinciding with the plane of the nuclei H–C•–H. Spin density: (α) solid lines; (β) dotted lines. Numbers 2 and 29 near the contours correspond to iso-surface 0.001 au Bohr^{-3}, (2) α density; (29) β density. Figure is created using MolDen program [29].

is of type (2) with k = 15. Such a representation of $V(\varphi)$ contains 31 summands, hence, as many calculations should be carried out. This is not always possible, so we looked for the expansion of $V(\varphi)$ with fewer points retaining the divergence with this rougher model within acceptable limits. To this requirement corresponds another starting conformation, also TS (V_{loc}, *1* in Fig. 2), reducing k to 12 and taking zero coefficients before sin points, namely, series (6). With this expansion of $V(\varphi)$ the divergence becomes smaller. The use of a series (2) for this initial conformation does not improve it, because the coefficients at the sin (V_j) are small and do not affect the accuracy. Other representations (other initial

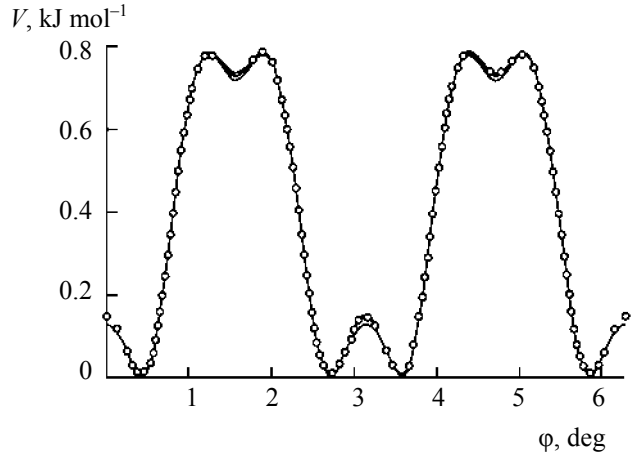

Fig. 5. The dependence of $V(\varphi)$ for (solid line) *n*-butyl and (points) the generalized potential function $V_{gen}(\varphi)$ for C_nH_{2n+1}, $n > 4$ (Table 2).

conformation and the types of expansion) or decrease in the number of components leads to either the disappearance of V_{min}, or to the appearance of additional minima and maxima. The values of V_{glob}, V_{loc}, V_{min}, V_{ecl} of radicals corresponding to Fig. 2 are summarized in Table 1, the coefficients of $V(\varphi)$ for (6) are given in Table 2.

The values of V_{glob} of the studied *n*-alkyl radicals do not exceed 1.5 kJ mol^{-1} (Table 1), therefore, the rotation around the C–C$^{\bullet}$ bond at $T = 298$ K and higher temperatures can be considered as free rotation. At low temperatures ($V_{loc} << RT$) the compounds C_nH_{2n+1}, $n > 2$ exist as a racemic mixtures. The electron density of unshared electron (free valence) is located mostly at the radical center (C$^{\bullet}$) as a very diffuse dumbbell-like cloud perpendicular to the H–C$^{\bullet}$–N plane (*p*-orbitals) (Fig. 3) [28]. The shape and size of the clouds almost do not depend on the dihedral angle C–C–C$^{\bullet}$–H (Figs. 3 and 4). Thus, at the rotation around the C–C$^{\bullet}$ the "tail" alkyl radical bearing the radical center is surrounded by a cloud of electron density of free valence that facilitates the attack by another compound and leads to high reactivity of these radicals. Complete analysis of the electron density of *n*-alkyl radicals in the framework of "Quantum theory of atoms in molecules" (QTAIM) [30, 31] is given in [28].

Study of the electron density of the tested *n*-butyl radical showed that, firstly, the localization of unpaired α-electron ($e^{\bullet}$) on C$^{\bullet}$ significantly polarizes the density of β electrons in the shells of neighboring atoms (Figs. 3 and 4) and, secondly, $e^{\bullet}$ at the rotation around the C–C$^{\bullet}$ bond remains by 0.87–0.88 localized on C$^{\bullet}$ at any φ. The volumes (V) of all atoms, including the largest $V(C^{\bullet})$, also changed slightly, in all conformation $V(C^{\bullet})$ is 103.03–102.50 au with a maximum value at V_{glob} (*1* in Fig. 2) and lowest in V_{min} (*5* in Fig. 2). The charges of atoms different from group $C^{\bullet}H_2$ are changing little. In $HC^{\bullet}H$ upon rotation occurs smooth transition of charge from one hydrogen atom in the group to another (from –0.003 to –0.009 au) and a sharp jump on both the hydrogen to about –0.041 au near V_{min} (*5* in Fig. 2). The charge is transferred from the hydrogen atoms of neighboring CH_2 groups.

In [28] it was shown that the inductive effect of $C^{\bullet}H_2$ extends over two adjacent CH_2 groups and that of CH_3 over one CH_2 groups. Therefore, starting with *n*-pentyl, the interaction of CH_3 with $C^{\bullet}H_2$ can be neglected, and further elongation of the chain (due to the locality of the inductive effect) should not affect the $V(\varphi)$. According to the Tables 1 and 2 the value of the barriers (within the errors of calculation) is not changed since C_4H_9, that is further extension of C–C chain does not affect the value of the barrier and the s$V(\varphi)$. This confirms the local nature of the internal rotation. In other words, the magnitudes of barriers $V(\varphi)$ are determined by the distribution of the electron density of atoms belonging to the rotating bond and to their valence environment. On this basis, we have proposed a generalized potential function [$V_{gen}(\varphi)$] for the rotation of $C^{\bullet}H_2$ around the C–C$^{\bullet}$ bond for C_nH_{2n+1}, $n > 4$ (Table 2). For the $V_{gen}(\varphi)$ are found hypothetical values of V_{glob}, V_{loc}, V_{min} which are added to Table 1.

Table 1 summarizes the contributions of internal rotation of group $C^{\bullet}H_2$ to the thermodynamic properties of the considered radicals. For comparison are shown the contributions calculated with $V_{gen}(\varphi)$ at *Ir* equal to 2.9×10^{-47} kg m^2. The enlarged value of *Ir* is taken for modeling elongation of the carbon backbone outside the considered compounds. Fig. 5 shows the plots of $V(\varphi)$ for *n*-butyl, and $V_{gen}(\varphi)$. Tables 1 and 2 and Fig. 5 shows that the proposed values of $V_{gen}(\varphi)$ and *Ir* well describe the behavior and contribution of this degree of freedom to the thermodynamic properties. The differences in the contributions to the Gibbs free energy [$G_{298} - G_{(0)int.rot.}$] and entropy [$S_{(298)int.rot.}$] in most cases can be neglected. In this approximation, $V(\varphi)$ does not depend on the length of carbon chain C_nH_{2n+1}, $n > 4$, and the function itself as well as contributions obtained with this function can be used for calculation of energy and thermodynamic properties of *n*-alkyl radicals and the radicals of the type R –$(CH_2)_n$–$C^{\bullet}H_2$, $n > 3$.

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