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Molecular Dynamics Study of the Conformational Properties of Branched Alkanes

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Molecular dynamics simulations were carried out to study the conformational properties of branched alkanes ($C_{40}H_{82}$). The populations of different isomeric conformers, cooperative transitions, and transition rates by analyzing a trajectory at 450 K in the gas phase were calculated. The results extracted from the molecular dynamics trajectory were mostly in very good agreement with the results for previously simulated *n*-alkanes.

Introduction

In nonrigid oligomers the basic motions underlying the relaxation processes are conformational transitions between rotational isomeric states: gauche+, gauche−, and trans. Conformational studies can be applied to a wide range of molecules: to molecules with small, highly constrained ring structures[1] and to those with large, open, linear chain structures.[2,3] The oligomers of 1-alkene are of particular interest because of their importance in the natural gas and petroleum industries.

Theoretical studies on the conformations of hydrocarbons can be classified into three categories according to the method of computation. The first category is quantum chemical methodology. Ab initio calculations are essential when the electronic structure of the system or other related properties are to be calculated. The ab initio method also allows investigation of the transition states in chemical reactions. Although quantum mechanics is unquestionably a superior method when the conformations of small molecules are of interest, some drawbacks are also encountered: calculations for large systems are computationally prohibitive, energies and geometries are dependent on basis set, and the calculations produce primarily static information.[4−11]

The second category of computations comprises molecular mechanics calculations based on the simple classical-mechanical model of molecular structure. The quality of the results of molecular mechanics calculations depend on the chemical accuracy of the force field parameters. The most favorable conformers are found by minimizing the energy of structures or by a search of the conformational space either systematically or randomly.[12−13]

The third category of conformational studies is simulation of systems, in which the static and dynamic properties of molecules are studied in detail by molecular dynamics methods. Computer simulation offers a primary source of information on the structures and dynamical properties of molecules, which can be compared with the experimental results. The conditions of the simulation can be allowed to vary during a trajectory, and studies can be made at higher temperatures and pressures than are possible experimentally. The static and dynamic properties of a material can also be calculated by Monte Carlo (MC) simulations.[13,14] The molecular dynamics methods to be applied to both equilibrium and nonequilibrium situations for the conformational and other properties of molecules. Molecular dynamics has widely been applied to the modeling of liquids.[15−22]

In this work we have studied the conformational properties of branched alkanes. The branched alkanes are used as model compounds of oligomers of 1-alkene: a dimer of eicosane, a tetramer of decane and a pentamer of octene by molecular dynamics (Figure 1).[23] The oligomers of 1-alkenes are important synthetic lubricants, and the knowledge of their dynamic behavior is being shown a growing interest by industry. Due to the size of the systems, theoretical studies on oligomers of alkanes are limited to low-energy conformers, and the conformers selected may not provide the best representation of the equilibrium statistics. Furthermore, the particular trajectory selected and the nonrigid nature of molecules may have an influence on the outcome of the study. Molecular dynamics has some definite advantages for the study of branched alkanes. For example, a large conformational space can be generated by using a long dynamics trajectory. Moreover, molecular dynamics allows the study of both equilibrium and nonequilibrium properties. Thus, molecular dynamics links the microworld and the macroworld.

Methods

1. Molecular Dynamics. Molecular dynamics is a powerful tool in molecular modeling.[24,25] Molecular dynamics considers the dynamics of a system in motion under the influence of Newtonian forces, where the system is allowed to change its properties as a function of time. In a simulation of a system, simplifying assumptions are used in the force field, which sometimes may not provide accurate predictions about the system in reality. For saturated hydrocarbons, however, such assumptions influence the result only slightly; and thus the differences in results due to different software packages are small.

We have studied the molecular dynamics of branched alkanes with the Sybyl program.[26] Branched alkanes were sketched, and a set of conformers was found by systematic search. After the systematic search, the conformers were energy-minimized to find the minimum-energy conformer, the structure of which represents the oligomer at 0 K in gas phase. The core structures of models are shown in Figure 2. The chains attached to the core structures of alkanes are in the *trans* state.[23] Sybyl[26] uses in the simulation a model based on molecular mechanics which includes hydrogen atoms.The lengths of the trajectories for the models are in Table 1. The simulations were carried out at

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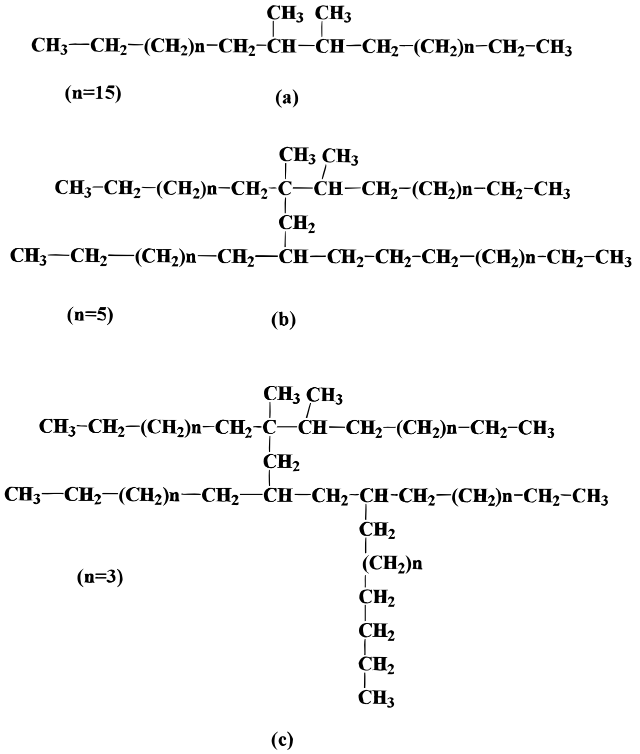

Figure 1. Structure of branched alkanes: (a) the dimer of eicosane, (b) the tetramer of decane, and (c) the pentamer of octane.

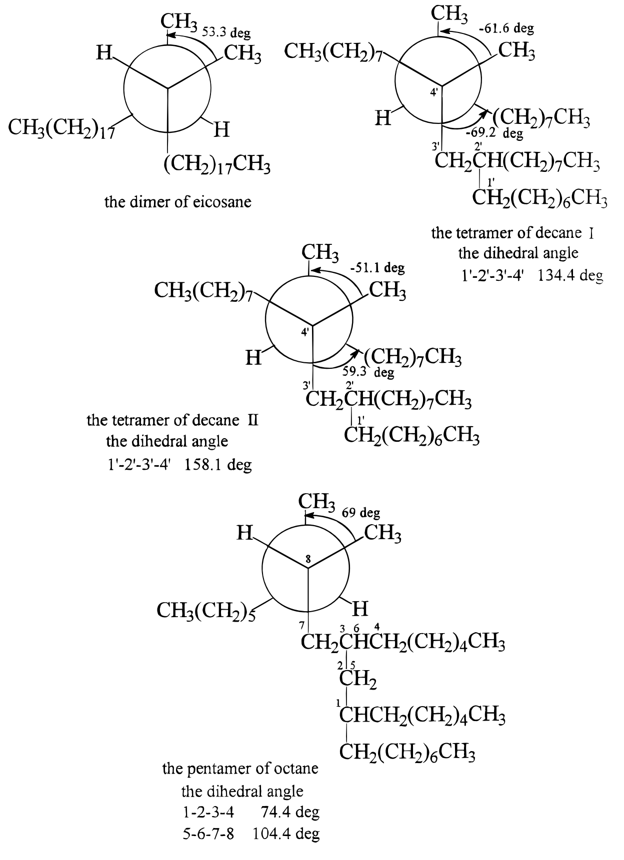

Figure 2. Core structure of branched alkanes.

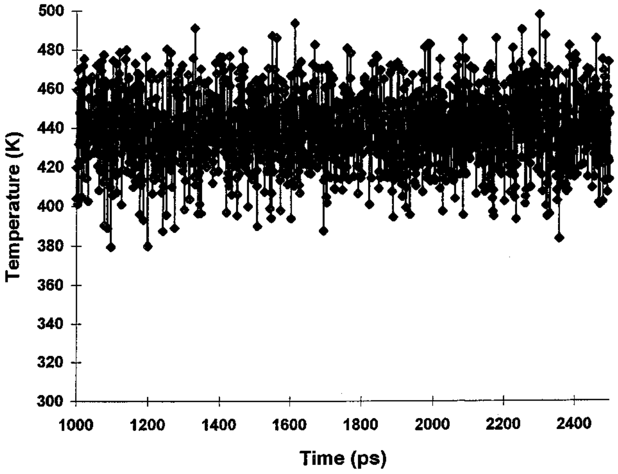

Figure 3. Evolution of the temperature during a part of trajectory.

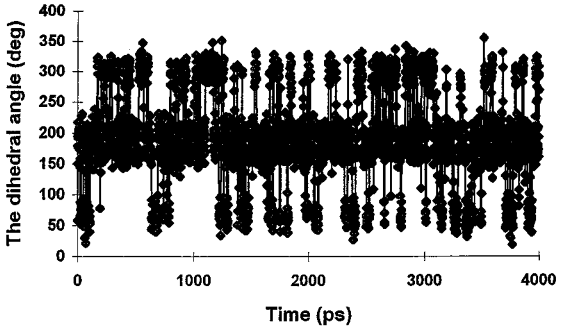

Figure 4. Typical internal C−C bond in a 4000 ps section of a trajectory of the pentamer of octane at 450 K.

TABLE 1: Results of the MD Simulations of Branched Alkanes

	dimer of eicosane	tetramer of decane (I)	tetramer of decane (II)	pentamer of octane
trajectory length (ps)	18 000	19 000	16 500	19 000
T (K)	450	450	450	450
trans (%)	60.6	18.5	55.8	59.0
gauche+ (%)	19.5	41.3	26.5	20.3
gauche− (%)	19.9	40.2	17.7	20.7
transitions	30 015	41 367	23 863	24 246
gauche pair	1208	376	779	576
gauche migration	1225	47	526	321

450 K in gas phase. An advantage of the high temperature is that the system reaches a state of equilibrium within a reasonable amount of computing time. The temperature fluctuates slightly during the trajectory (Figure 3). The results reported in this paper are limited for a low-density system. As the starting conformation we chose the low-energy conformation. The time step was 10 fs. The conformation of the molecule was recorded every 1 ps. The system allowed to preequilibrate 1 ns before collection of data. Most low-energy conformations can be assumed to be represented in the equilibrated trajectory and some transition-state conformers at higher energies. The result of the simulation should be independent of the starting conformation, unless the starting conformation is in the barrier region of the phase space or the trajectory is too short.

2. Bookkeeping on Conformers. The conformers of a saturated hydrocarbon can be studied through its torsion angles. The dihedral angle of the methylene−methylene bond fluctuates as a function of the molecular dynamics trajectory at 450 K (Figure 4). Three peaks are observed in the dihedral angle distribution averaged over the methylene−methylene bonds (Figure 5). Due to the 3-fold rotation of a C−C bond in a saturated hydrocarbon, these peaks are in the neighborhood of dihedral angles 60°, 180° and 300°. The corresponding rotational isomeric states are gauche+, trans, and gauche− (Figure 6). In this work a dihedral angle of 0° to 130° is defined as the gauche+ state, a dihedral angle between 131° and 230°

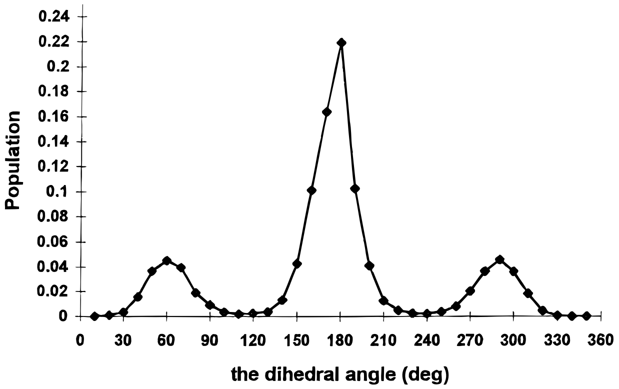

Figure 5. Population distribution of dihedral angles for an internal C−C bond at 450 K.

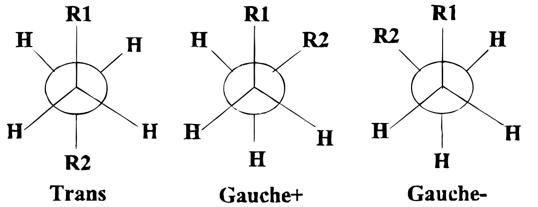

Figure 6. Rotational isomeric states.

as the trans state and a dihedral angle of 231° to 360 as the gauche− state.

At high temperature, one conformational state can change into another of each of the carbon−carbon bonds. Since isomeric transitions of any one of the C−C bonds will lead to a different conformer, the changes in conformation occur at frequent intervals. In clarifying the different conformers, we used t, g+, and g− to stand for trans, gauche+, and gauche− states. In the literature a conformer is denoted by the number of carbon−carbon bonds on each side of the polygon formed by its projection in the plane in which it lies.[1] In our algorithm for analyzing the molecular dynamics trajectory, we first numbered the bonds of the oligomers in the same way. We listed the transitions of each bonds and rotational isomeric states of dihedral angles and calculated the percentage of each state in the dihedral angle. The correlations between pairs of bonds have been analyzed by counting the number of simultaneous transitions of bond *i* and bond *j* at the time intervals of every 1 ps.

Results

1. Conformational Properties. In the next sections we analyze the results obtained in three sets of simulations, carried out on the dimer of eicosane, the tetramer of decane and the pentamer of octane. Figure 1a shows the structure of the dimer of eicosane. The dimer of eicosane has 30 015 transitions in a period of 18 ns compared to 2482 rotational isomeric transitions of n-$C_{50}H_{102}$ at 400 K (trajectory 3.7 ns).[2]

Using molecular dynamics, Ryckaert et al.[15] observed that for *n*-butane the proportion of trans state (291.5 K) was 66% in the gas phase and 54% in the liquid. For n-tridecane ($C_{13}H_{28}$) the population of the trans state was 58% (450 K).[27] According to Brown et al.[20] the proportion of trans states for linear alkane-like chains of 20 sites at 500 K is 71%. The population of the trans state for the dimer ($C_{40}H_{82}$) in our work was 60.6% (450 K) in the gas phase which is very close to the population of trans state for n-tridecane ($C_{13}H_{28}$) at same temperature. The populations of the gauche+ and gauche− states should be nearly identical; the trajectory assigns 19.5% to the gauche+ state and 19.9% to the gauche− state (Table 1).

The structure of the tetramer of decane is more sterically hindered than that of the dimer of eicosane (Figure 1b). The populations of isomeric states were calculated for two different conformers of the tetramer. The proportions of the conformers and the number of transitions were different for these two conformers. The population of rotational isomeric states for the conformer I were 18.5% trans, 41.3% gauche+, and 40.2% gauche−. The population of states for conformer II were 55.8% trans, 26.5% gauche+, and 17.7% gauche− (Table 1). The low trans population for conformer I may be due to the spatial properties of the central structure. The high amount of transitions for the tetramer of decane conformer I has been suggested to be caused by immediate reversal of transitions. This is due to the failure of neighboring bonds to adjust to the new state of the central bonds.[21] We have used the results of tetramer of conformer II for analysis. The population of trans state in both conformers was lower than the fraction of the trans state in either the dimer or the pentamer. The populations of the g+ (26.5%) and g− (17.7%) states are not identical in the tetramer of decene conformer II.

The pentamer of octane also has a highly crowded structure (Figure 1c). The number of trans state for the pentamer were 59.0%. The population of trans state of the pentamer is close to the amount of trans state in the dimer although the central structure has less space in the pentamer of octane. The population of gauche+ was 20.3% and gauche− 20.7% (Table 1).

2. Dynamic Properties. The transitions between isomeric states are predominantly of the type g+⇔t⇔g−, as can be seen by investigating the probabilities at 0°, 120°, and 240° (Figure 5). Direct transitions from gauche+ to gauche− are rare. Helfand et al. discovered a transition type ttg+⇔g+tt or ttg−⇔g−tt in their study of polyethylene by Brownian dynamics.[21] This transition is called gauche migration. The change of a single bond from gauche to trans (or from trans to gauche) may cause great strain, especially in the cycloalkanes.[1] The transition mode ttt⇔g+tg− (or ttt⇔g−tg+) is identified as gauche-pair creation.[21] The schemes of gauche migration and gauche-pair creation are strongly correlated with *i* and $i \pm 2$.[2,21] The transition rates were calculated by dividing the total number of transitions for the entire system during the trajectory by the product of the total number of C−C−C−C torsions and the time of the simulation.

The dimer of eicosane, which contains only slight steric hindrance (Figure 1a), has 30 015 transitions in a period of 18 ns compared to 2482 rotational isomeric transitions of n-$C_{50}H_{102}$ at 400 K (trajectory 3.7 ns).[2] Terminal dihedral angles (925 and 881 transitions) exhibit slightly more transitions between trans and gauche states than the internal angles (the average number of transitions is 871). Edberg et al.[22] have observed for both *n*-butane and *n*-decane that conformational change is faster at terminal angles than at internal angles. Moreover, several gauche⇒gauche transitions may occur at terminal dihedral angles, while for the other dihedral angles these transitions are uncommon, especially for branched structures. In the dimer of eicosane the trans population is significantly smaller at the terminal dihedral angles than at the internal angles due to the steric hindrace of transitions at the internal angles. In the trajectory, 1225 gauche migrations were identified in the different dihedral angles, and the mode of gauche pair was also seen, with as many as 1208 occurrences. Correlations of simultaneous transitions of a pair of bonds *i* and $i \pm j$ ($j = 1$, 3, 4, 5 ..., 10) were observed, but the proportions of such correlations were less than those for *i* and $i \pm 1$ and $i \pm 2$ (Table 2).

TABLE 2: Simultaneous Transitions of Bonds *i* and *i* ± *j*

j	dimer of eicosane	tetramer of decane	pentamer of octane
1	1231	239	217
2	2306	340	160
3	1088	142	149
4	1427	114	128
5	1150	112	79
6	1176	117	105
7	1033	160	15
8	1049	213	39
9	1085	174	55
10	979	173	37

Transitions between isomeric states dihedral angles were 23 863 for the tetramer of decane conformer II. The terminal dihedral angles had 804 transitions in average. Transitions in the internal angles move the large alkyl group through the local environment, which causes steric strain in the molecule due to that in the core dihedral angle of tetramer (Figure 1b) only two transitions were observed. Correlations of bonds i and $i \pm j$ ($j = 1, ..., 10$) were observed (Table 2). The number of gauche pairs were 779 and gauche migration 526 for the tetramer of decane.

On the ground that the pentamer of octane is more crowded than the dimer or tetramer, the pentamer has 24 246 transitions during the trajectory. The terminal angle has 973 transitions in average. The internal angle has many transitions too. The number of gauche-pairs 576 and gauche migrations 321 show considerable correlations between bonds i and $i \pm 1$ and i and $i \pm 2$, as has been also observed in the dimer and tetramer (Table 2).

Conclusions

In this paper we presented the conformational and dynamic properties of branched alkanes: the dimer of eicosane, the tetramer of decane and the pentamer of octane by molecular dynamics in gas phase. The proportion of the trans and both gauche states of bonds and the number of transitions were calculated. The average fraction of bonds in trans state for the dimer of eicosane agree well with previous calculations for *n*-tridecane.[27]

The population of trans state is the highest for the dimer of eicosane. Also, the transitions are the most favorable in the dimer of eicosane. The results of the tetramer of decane are in contrast to the results of the pentamer of octane. Despite the increased branching in the pentamer of octane, the fraction of bonds in the trans state and the number of transitions are higher than in the less-branched tetramer of decane. It is due to the fact that the mobile bonds near the end of the chain increases as the number of shorter chain increases. However, the gauche pair and the gauche migration are influenced by steric hindrace in a molecule. More space in a molecule, more gauche pairs and gauche migration. Strong correlations were found between bonds i and $i \pm 1$ and i and $i \pm 2$ in consistency with work done on polyethylene.

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