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Conformational Preferences of 2,2-Dimethylpropane in Nanotubes

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Abstract—Structural and conformational study of 2,2-dimethylpropane in open single-walled carbon nanotubes by means of the PBE/3z hybrid DFT method showed that the barrier to hindered rotation around the C–C bond appreciably increases as the nanotube diameter decreases. Concurrently, the orders and lengths of C–C bonds in the encapsulated molecule also decrease.

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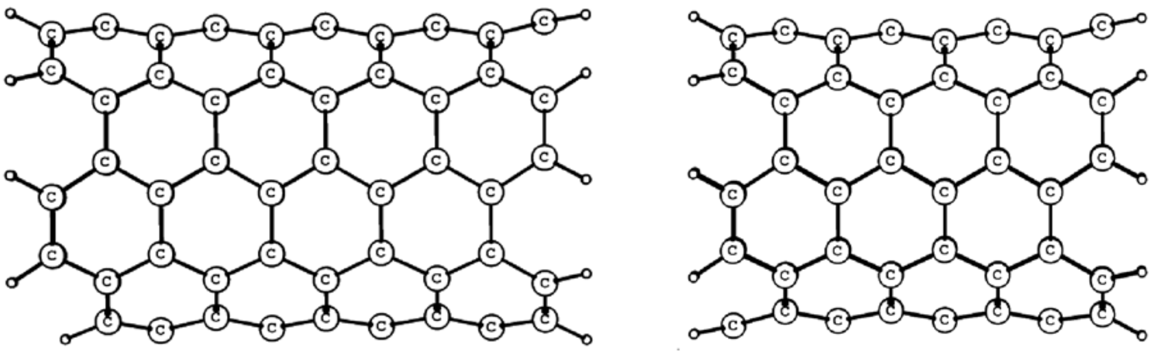
The interest in nano-objects is associated with their valuable properties: high catalytic activity, specific optical characteristics, unique biochemical potential, etc. [1, 2]. Moreover, nanosized structures appreciably affect the properties of encapsulated molecules. In particular, as shown recently by computer simulation, the barrier to pyramidal inversion of ammonia in a nanotube increases 2.5–5.8 times compared to that for free NH_3 [3], whereas an encapsulated molecule of diazadifluoride shows an inverted relative stability of the *cis* and *trans* isomers [4]. By semiempirical and DFT calculations in [5] we established that the minimum-energy conformation of ethane in the cavity of nanotube corresponds to the eclipsed form in contrast to the staggered conformation in the free molecule. In this connection it was interesting to analyse the conformational properties. In the present work the conformational behavior of 2,2-dimethylpropane (DMP) inside of model singlewalled nanotubes **I**–**IV** (hereinafter, nano-**I**–**IV,** see Schemes 1, 2) was studied for the first time by using the DFT PBE/3z method (PRIPODA software [6]).

The experimental barrier to hindered rotation in DMP is 4.3 kcal/mol in favor of the staggered conformer [7, 8].

The calculations of free DMP, too, give evidence for the preference of the staggered form, but the calculated activation barrier is lower by 0.5–1.3 kcal/mol compared to the experimental one (Table 1).

In contrast to the ethane in nanotubes [5], in the system DMP–nano-**I** (Scheme 3), where the distance

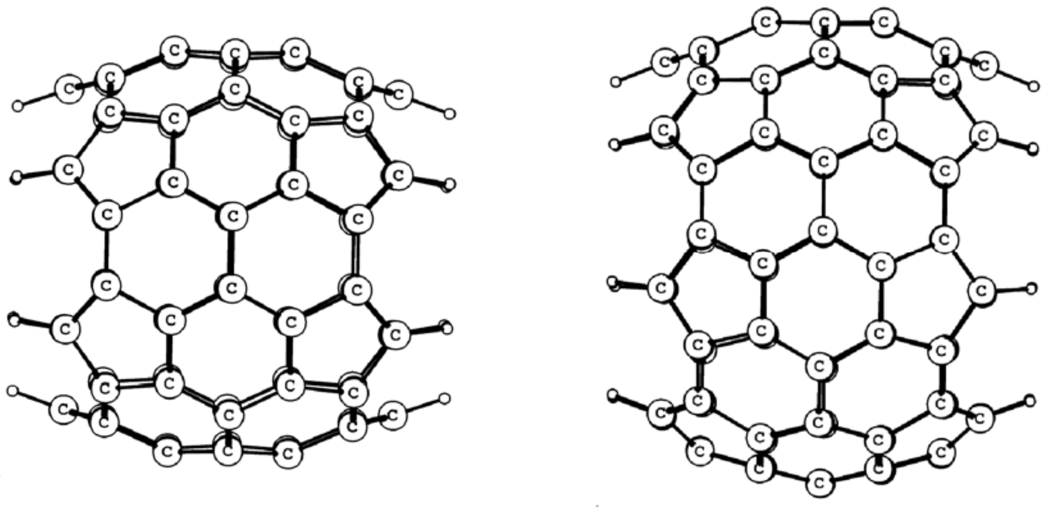
Scheme 1.



I: $C_{98}H_{20}$; *l* 9.8 Å, ∅ 6.8 Å

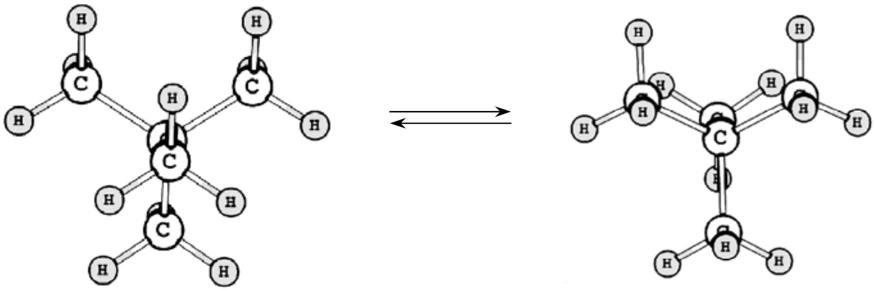
II: $C_{80}H_{20}$; *l* 7.4 Å, ∅ 6.8 Å

Scheme 2.



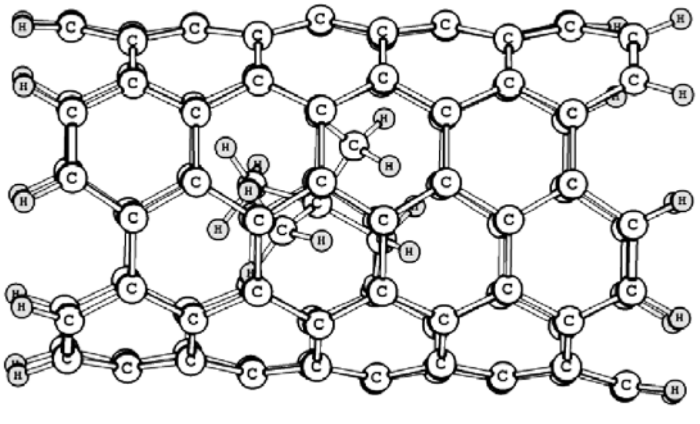
III: $C_{72}H_{12}$; *l* 6.6 Å, ∅ 8.4 Å

IV: $C_{84}H_{14}$; *l* 6.5 Å, ∅ 9.6 Å



between hydrogen atoms of the encapsulated molecule and nanotube walls is 1.9–2.0 Å, a 3-fold increase of the barrier of hindered rotation in favor of the staggered conformer is observed together with the appreciable decrease of the C–C bond length ($r_{\mathrm{C–C}}$) compared to free DMP. In addition, a distortion of DMP geometry, which reveals itself in varied distances between C and H in the eclipsed conformer ($r_{\mathrm{C\cdots H}}$), as well as a decrease of the C–C bond order ($P_{\mathrm{C–C}}$), should be mentioned (Table 1). The Hessian of the eclipsed form contains one imaginary frequency; its character (torsional vibrations about the C–C bond)

Scheme 3.



DMP–nano-**I**

Table 1. Energy and structure parameters of the DMP molecule by PBE/3z calculations

Form	$-E_0$[a], Ha	$\Delta H^{\neq}_{0}$	$\Delta H^{\neq}_{298}$	$\Delta G^{\neq}_{298}$	$\Delta S^{\neq}_{298}$, cal mol^{-1} K^{-1}	$r_{\mathrm{C-C}}$	r_{CH}[b]	$P_{\mathrm{C-C}}$	Charge
		kcal/mol				Å			
				DMP					
Staggered	197.393994	0	0	0	0	1.539	–	1.00	0
Eclipsed	197.389482	3.5	3.0	3.8	–2.6	1.558	2.523	0.91	0
				DMP–nano-**I**					
Staggered	3939.602907	0	0	0	0	1.467	–	0.79	–0.7235
Eclipsed	3939.584956	11.3	11.2	11.1	0.2	1.492	2.099–2.700	0.88	–0.5257
				DMP–nano-**II**					
Staggered	3254.286297	0	0	0	0	1.522	–	0.75	–0.6038
Eclipsed	3254.272230	8.8	9.2	7.7	5.1	1.518	2.060–2.735	0.77	–0.8076
				DMP–nano-**III**					
Staggered	2945.073054	0	0	0	0	1.530	–	0.77	–0.9205
Eclipsed	2945.068330	3.0	2.5	3.4	–3.0	1.548	2.535	0.70	–0.8637
				DMP–nano-**IV**					
Staggered	3403.194782	0	0	0	0	1.538	–	0.93	–0.4930
Eclipsed	3403.187984	4.3	3.9	4.6	–2.6	1.557	2.510–2.523	0.87	–0.5023

[a] Including ZPE correction. [b] Considered in the eclipsed form only.

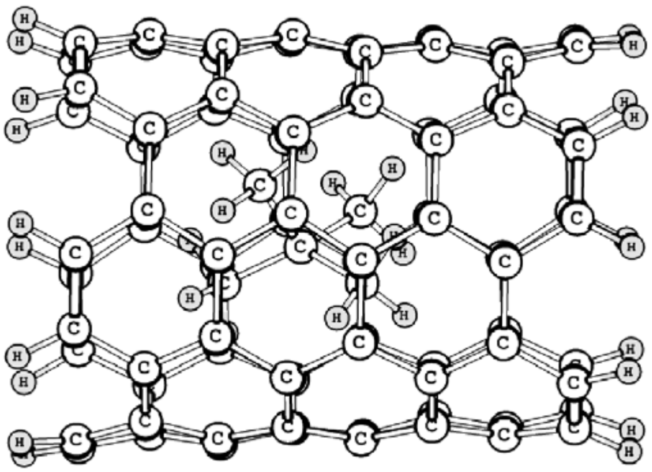
provides unequivocal evidence showing that this form belong to a transition state between staggered conformers.

The same tendencies are observed in the DMP–nano-**II** system (Scheme 4), in which the shortest distance between hydrogen atoms of the encapsulated molecule and nanotube walls is 1.8–2.1 Å.

In this system, the length and order of the C–C bond around which rotation occurs are appreciably decreased, whereas the staggered form is 2.1–3 times more stable compared with free DMP (Table 1). It should also be noted that the Hessian of the eclipsed form contains an expected imaginary frequency (torsional vibrations about the C–C bond). At the same time, the Hessian of the staggered form contains one imaginary frequency too, which, however, is associated with rotation of the DMP molecule as a whole.

Increase of the nanotube diameter gives rise to opposite effects. In the case of the DMP–nano-**III**

Scheme 4.



DMP–nano-**II**

system (Scheme 5) (the minimum distance to nanotube walls is 2.4–2.6 Å), the staggered conformer, again, corresponds to a minimum on the potential energy surface, but its preference over the eclipsed form is not so great as in the free molecule.

A similar tendency is observed in the DMP–nano-**IV** system (Scheme 6) (the minimum distance to nanotube walls is 2.8–3.0 Å).

In the latter case, the C–C bond length in the encapsulated molecule almost does not differ from that calculated for free DMP; the difference in the bond orders becomes smaller too.

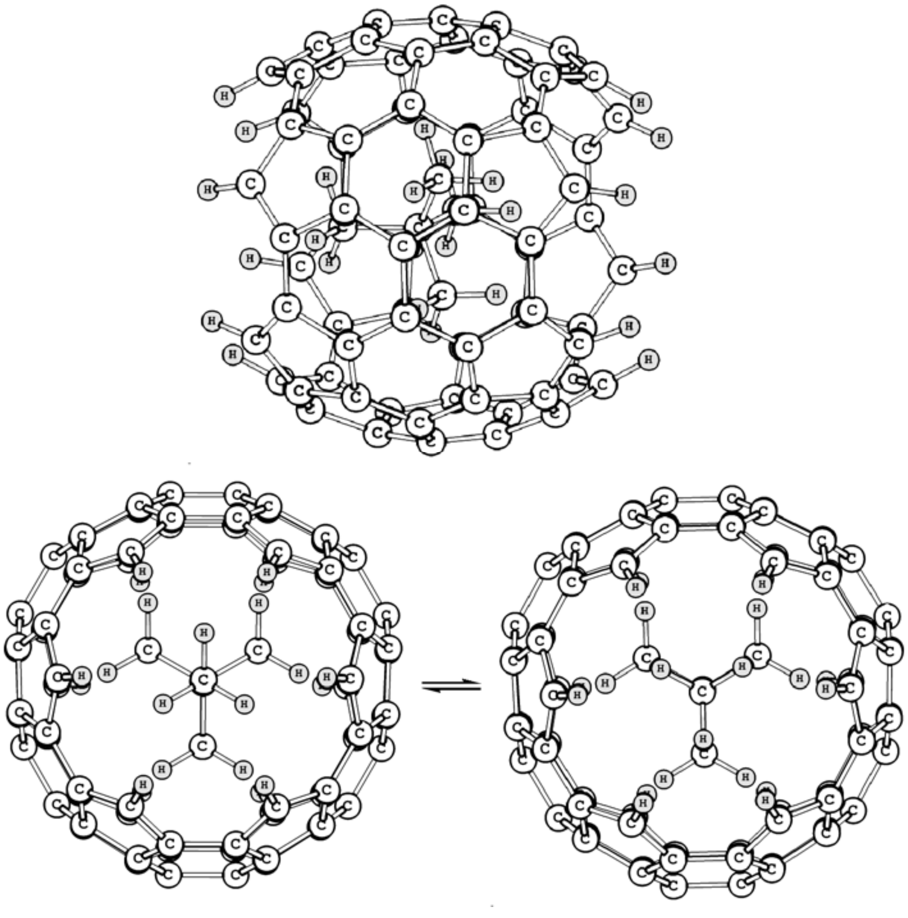
The general feature of all the considered "clusters" is that the encapsulated molecule bears a negative charge, even though the whole DMP–nanotube system is electrically neutral (Table 1).

To estimate the relative energy gain from the formation of the DMP–nanotube system, we calculated the thermodynamic parameters of the formal reaction: DMP + nano → DMP · nano.

The results presented in Table 2 show that the process of "clusters" formation has positive ΔH^0 and ΔG^0 values and a negative ΔS^0 value, and, therefore, this reaction cannot occur spontaneoulsy. At the same time, the decrease of these parameters in going from DMP–nano-**II** to DMP–nano-**IV** suggests that the molecule can potentially freely enter into the nanotube when the diameter of the latter increases.

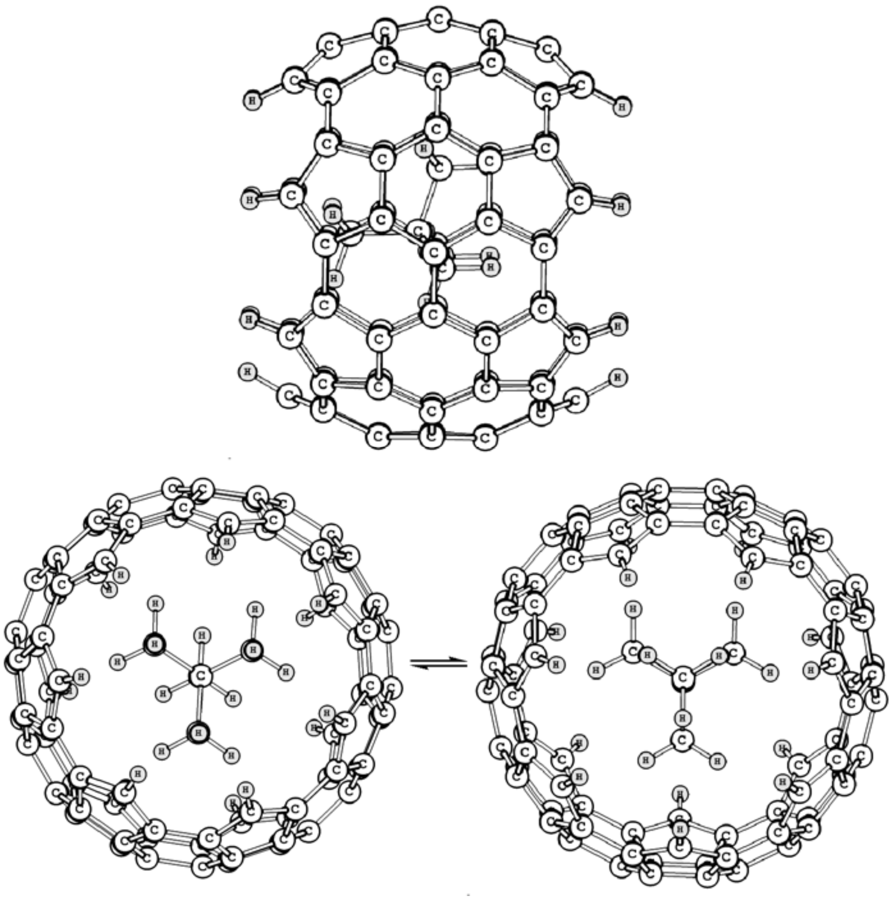
Thus, the results of computer simulation show that the effect of the nanotube force field on the structure and energy parameters of the encapsulated molecule depends on the nanotube diameter. At relatively short distances to nanotube walls (less than 2.4 Å), the force field compresses the molecule in the cavity and leads to the significant changes in the conformational behavior of the encapsulated molecule.

Scheme 5.



DMP–nano-**III**

Scheme 6.



DMP–nano-**IV**

EXPERIMENTAL

Conformational transformations of DMP in nanotubes were simulated in several steps. First, using HyperChem software [9], we created the corresponding nanotube, after which its geometry was optimized by the semiempirical AM1 method (HyperChem) and then by the PBE/3z method (PRIPODA). Both DMP conformations were calculated in a similar way. Then the staggered form (AM1) was placed, through the exchange buffer, inside the nanotube, and this system was optimized by the same method. In the resulting structure hydrogen atoms in the encapsulated molecule were moved to the eclipsed position using HyperChem procedure and this system was calculated by the AM1 method as a transition state. Both thus optimized DMP–nano systems were further calculated by the PBE/3z method. The Stationary points on the potential

Table 2. Thermodynamic parameters of nano–DMP clusters

Cluster	ΔH_0^0	ΔH_{298}^0	ΔG_{298}^0	$-\Delta S_{298}^0$, cal mol^{-1} K^{-1}
	kcal/mol			
DMP–nano-**I**	241.0	238.2	258.7	68.6
DMP–nano-**II**	246.5	243.7	264.1	68.5
DMP–nano-**III**	64.7	63.9	79.9	53.7
DMP–nano-**IV**	6.1	5.7	21.2	52.0

energy surface were identified by the lack of imaginary frequency (except for the DMP–nano-**II** system) and as transition states, by the presence of one imaginary frequency in the corresponding Hessian. The thermodynamic parameters of DMP–nano "clusters" formation (Table 2) were calculated by the Hess law with the lowest enthalpies and Gibbs energy characteristic of this system.

$$\Delta H^0 = H^0_{\text{nano–DMP}} - (H^0_{\text{nano}} + H^0_{\text{DMP}}),$$

$$\Delta G^0 = G^0_{\text{nano–DMP}} - (G^0_{\text{nano}} + G^0_{\text{DMP}}).$$

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