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Conformational Preference of Perhydro-1,3,2-dioxazine Inside Nanotubes

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Abstract—Conformational changes of perhydro-1,3,2-dioxazine in open single-walled carbon nanotubes have been studied by hybrid DFT PBE/3z method. It was established that relative stability of equatorial and axial chair conformers of encapsulated molecule has been inverted, the latter form becoming favorable. In this case the barrier of pyramidal inversion of nitrogen atom has been slightly decreased.

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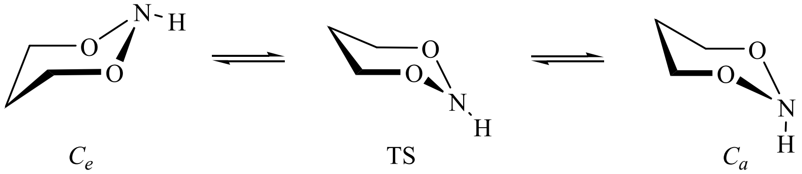
The importance of conformational studies of perhydro-1,3,2-dioxazines, saturated heterocyclic analogs of cyclohexane containing O–N–O ring fragment, is connected with structural peculiarities that are caused by the high conformational stability of nitrogen atom [1–5]. Recent investigation of conformational properties of unsubstituted perhydro-1,3,2-dioxazine in the frame of HF/6-31G(d) and MP2-RI/λ2 approximation [6] has revealed that the main minimum at potential energy surface corresponds to equatorial *chair* conformer (C_e), the axial *chair* (C_a) is the nearest form. Conformational isomerization $C_a \leftrightarrow C_e$ occurs via pyramidal inversion of nitrogen; the structure of transition state (TS) corresponds to the planar state of nitrogen. The isomerization potential barrier was fairly high, close to the experimentally determined value in the case of acyclic *N,N*-dialkoxyamines [7].

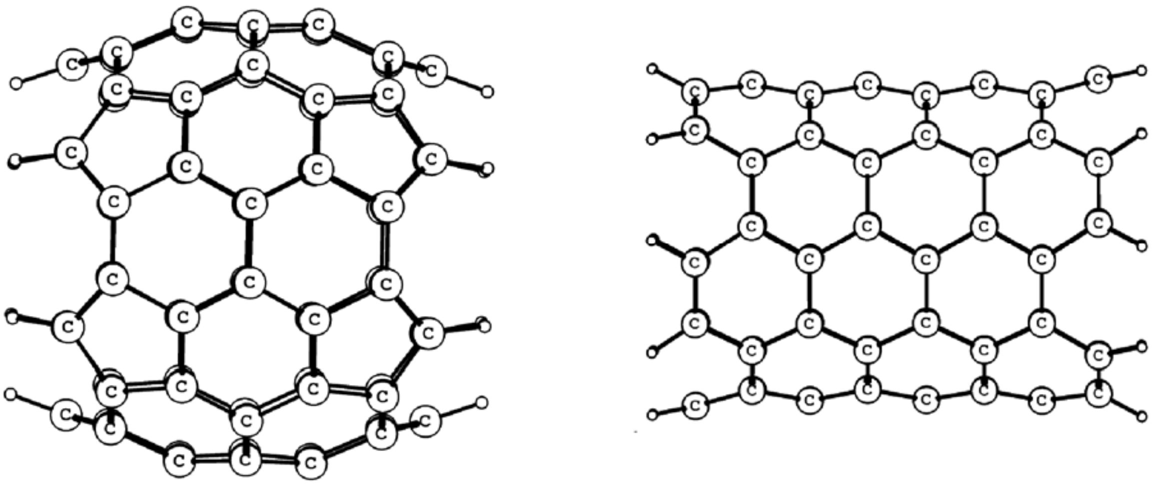


On the other hand, nanosized objects has excited much interest due to their utilitarian properties: high catalytic activity, unique optical features, biochemical properties, etc. [8, 9]. Moreover, nanosized molecules significantly alters the properties of encapsulated molecules. In particular, recent computer simulation studies have revealed that barrier of pyramidal inversion of nanotube-encapsulated ammonia was 2.5–5.8 times higher as compared with isolated NH_3 [10]. In view of that, conformational properties of nitrogen-containing heterocycles incorporated into nanotubes inner cavity are of significant importance. In this work, the DFT PBE/3z method (PRIRODA software package [11]) was applied to study the $C_a \leftrightarrow C_e$ conformation transition of perhydro-1,3,2-dioxazine inside model single-walled nanotubes **I** and **II** (Scheme 1).

Simulation of isolated perhydro-1,3,2-dioxazine molecule confirmed that the C_e conformer is the main minimum at the potential energy surface and indicates that calculation result is rather close to experimentally determined barrier of inversion of nitrogen in C_2O_2N fragment (21.7–24.6 kcal/mol) [7]) (Table 1).

In the case of the dioxazine–**I** system (with distance between hydrogen atoms of the encapsulated molecule and the nanotube wall of 2.3–2.4 Å), three orientations of dioxazine were found: longitudinal (**A**), orthogonal (**B**), and angular (**C**) (Scheme 2).

Scheme 1.



I: $C_{72}H_{12}$; *l* 6.6 Å, ∅ 8.4 Å

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

System **C** was the most stable, the energy of its C_e conformer; the differences from that of clusters **A** and **B** by 0.9 and 1.3 kcal/mol, respectively. Further simula-tions were performed using system **C** as an example. In that case, angle between the longitudinal symmetry axes of nanotube and of dioxazine molecule was 51°.

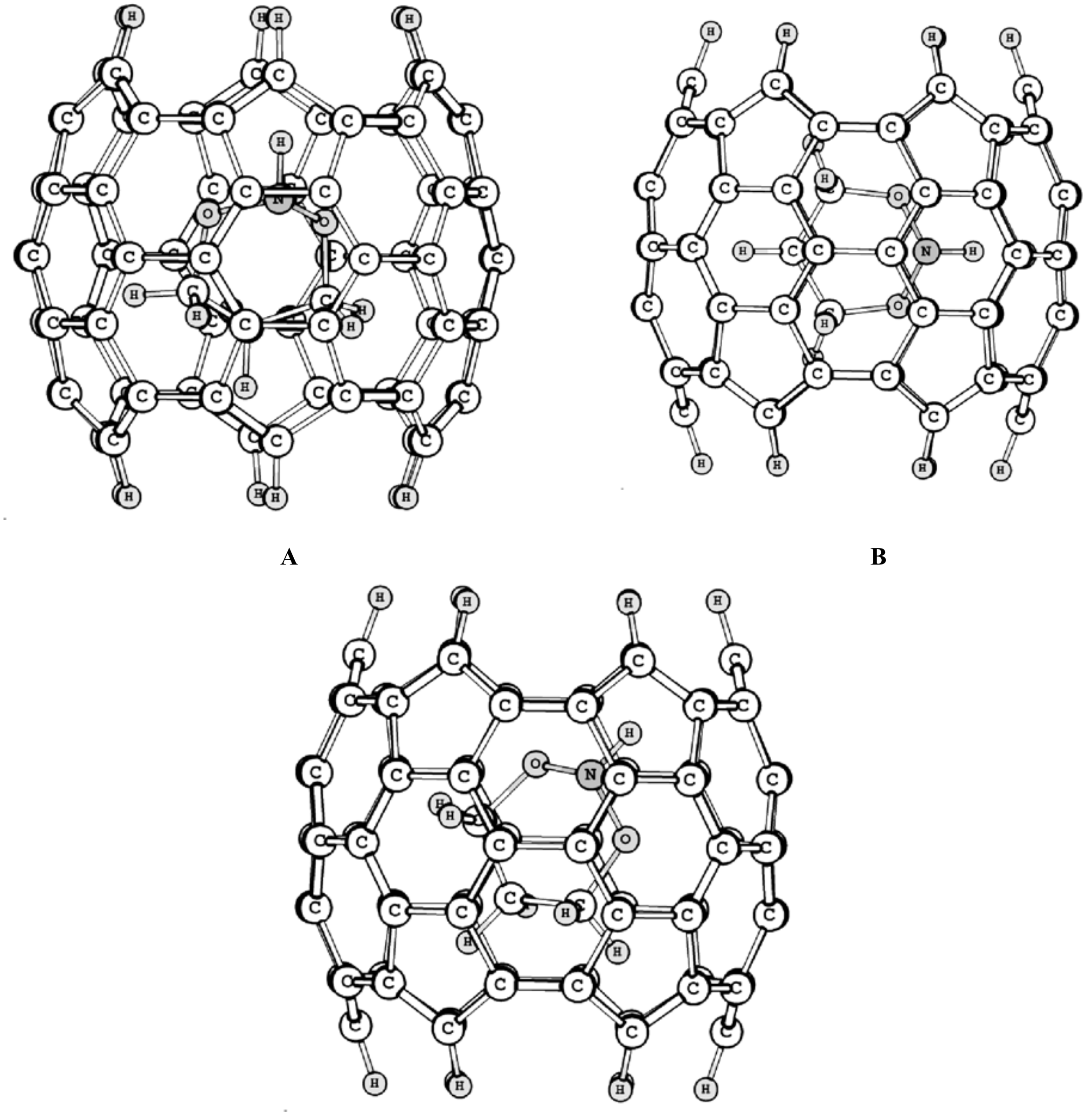
The studied cluster reveals the change in the relative stability of the *chair* forms: the main minimum at potential surface energy corresponds to the C_a conformer (see values of ΔE^0, ΔH^0, and ΔG^0, Table 1). Moreover, the geometry of dioxazine was distorted: distances between the cycle hydrogen atoms and NH

Table 1. Energy parameters of perhydro-1,3,2-dioxazine molecule according to the PBE/3z simulation

Form	$-E_0$[a], hartree	ΔE_0^0	ΔH_{298}^0	ΔG_{298}^0	ΔS_{298}^0	$\Delta E_0^{\neq}$	$\Delta H_{298}^{\neq}$	$\Delta G_{298}^{\neq}$	$-\Delta S_{298}^{\neq}$, cal mol^{-1} K^{-1}	$P_{N–O}$	Charge ($-q$)
		kcal/mol									
					Perhydro-1,3,2-dioxazine						
C_a	323.267225	2.3	2.3	2.3	0.0	–	–	–	–	0.92	0
C_e	323.270920	0	0	0	0	0	0	0	0	0.91	0
TS	323.236466	–	–	–	–	21.6	21.5	21.7	0.6	0.92	0
					Perhydro-1,3,2-dioxazine–**I**						
C_a	3071.011212	0	0	0	0	0	0	0	0	0.91, 0.93	0.6479
C_e	3071.010046	0.7	0.2	2.1	–6.6	–	–	–	–	0.86, 0.89	0.6108
TS	3070.978051	–	–	–	–	20.8	19.7	23.4	12.5	0.89, 0.92	0.4698
					Perhydro-1,3,2-dioxazine–**II**						
C_a	3380.349516	0	0	0	0	0	0	0	0	0.87, 0.89	0.6530
C_e	3380.347203	1.5	1.5	1.1	1.3	–	–	–	–	0.86, 0.89	0.6042
TS	3380.317321	–	–	–	–	20.2	20.1	20.2	0.3	0.82, 0.91	0.5615

[a] In view of ZPE.

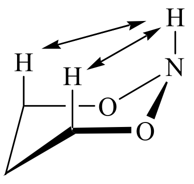
Scheme 2.



A **B**

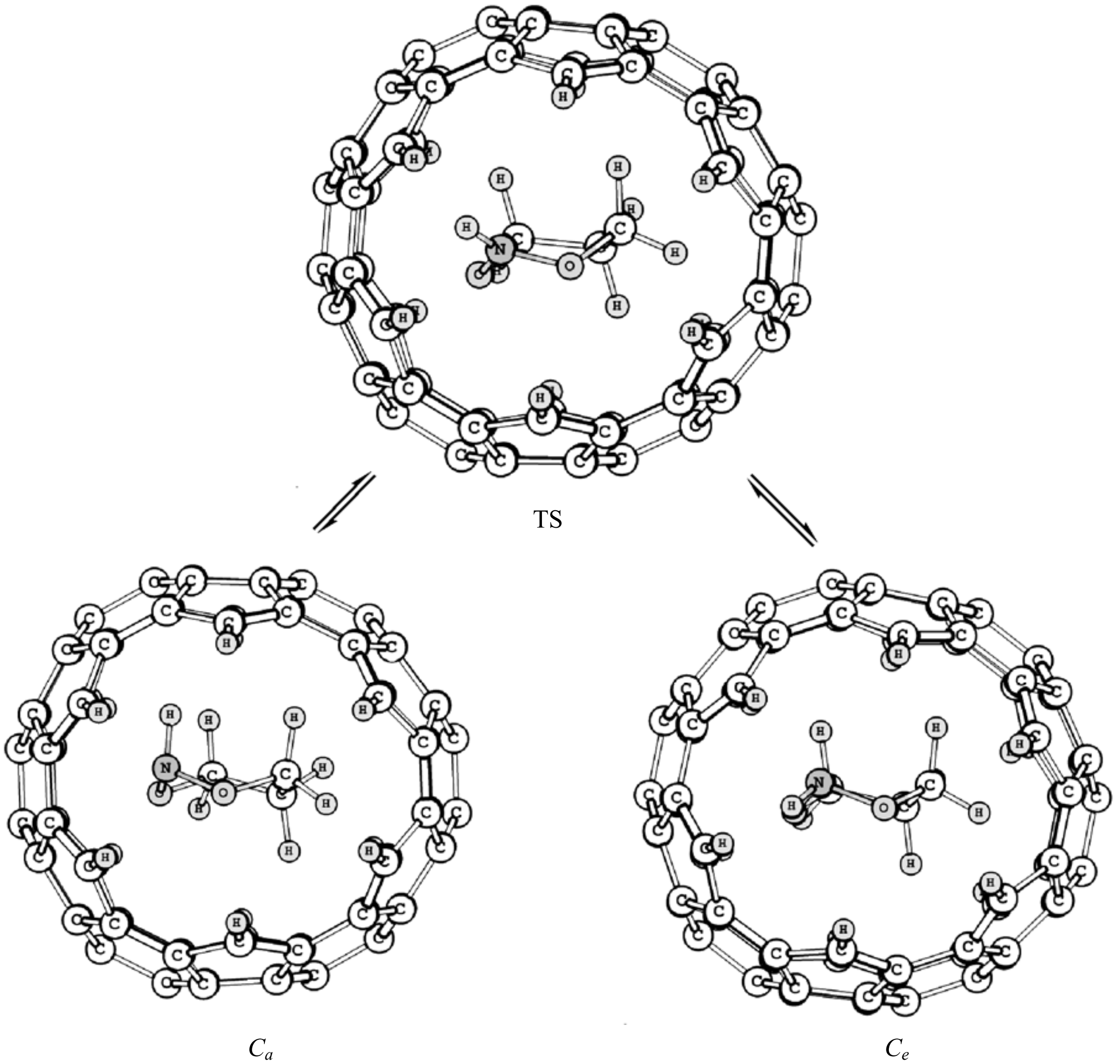
C

proton of the axial conformer ($r_{H\cdots H}$) were 2.129 Å (C^4–H) and 2.209 Å (C^6–H) as compared with 2.248 Å in the free heterocyclic molecule. The decrease in the $r_{H\cdots H}$ value demonstrates that the force field inside the nanotube “squeezes” the encapsulated molecule (Scheme 3).



The energy barrier to the pyramidal inversion of nitrogen atom ($\Delta E^{\neq}$, $\Delta H^{\neq}$, and $\Delta G^{\neq}$) was slightly decreased upon encapsulation; simultaneously, the order of the N–O bond ($p_{N–O}$) practically did not change as compared with the free dioxazine molecule (Table 1). It should be stressed that, the Hessian of the C_e form contains one imaginary frequency that corresponds to vibrations of the encapsulated molecule as a whole, whereas the Hessian of transition state has three imaginary frequencies. Two of the latter ones were assigned to vibrations of the whole dioxazine

Scheme 3.



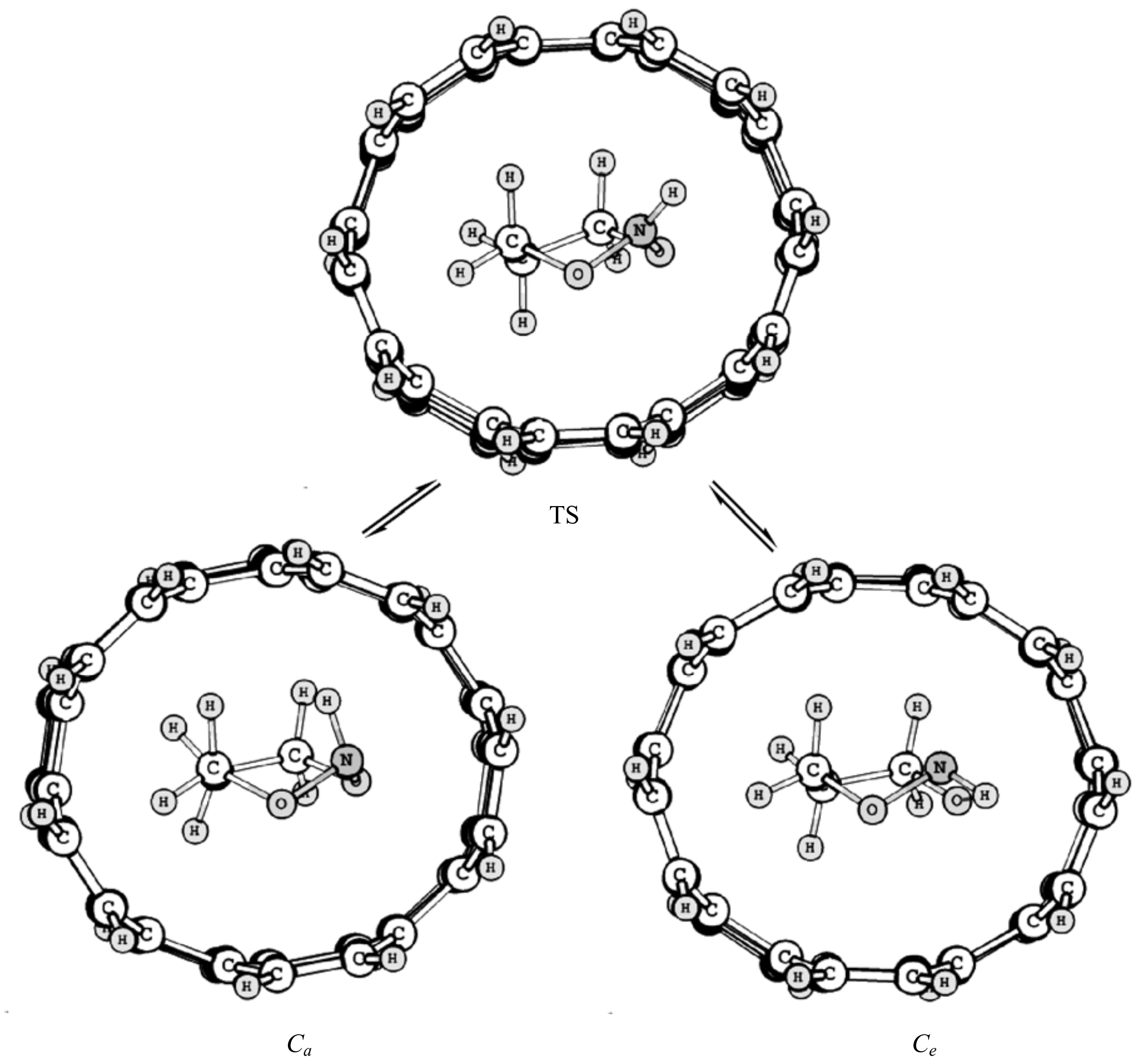
molecule, the third being due to scissor vibrations of the N–H fragment; thus, the form with planar structure of the nitrogen corresponds to the transition state.

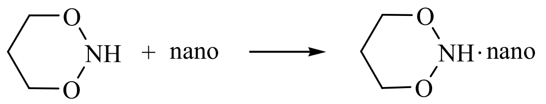
In the case of the dioxazine–**II** system (with smaller diameter of the nanotube) the minimal distance between hydrogen atoms of the encapsulated molecule and the nanotube wall was 1.9–2.1 Å, and only the cluster with angular orientation of dioxazine molecule was possible. The angle between the longitudinal symmetry axes of nanotube and dioxazine molecule was 51°.

In the latter cluster, the heterocyclic molecule was more distorted: distances between the cycle hydrogen atoms and NH proton were 1.939 Å (C^4–H) and 2.578 Å (C^6–H). At the same time, the preference towards the axial form of *chair* became more evident. Energy barrier of pyramidal inversion of nitrogen was close to that computed in the case of dioxazine-**I** system, being lower than that of the free molecule by 1.5 kcal/mol (Table 1). The order of the N–O bond remained practically unchanged. Hessians of clusters with C_a and C_e conformers are free of imaginary frequencies; the transition state contains only one imaginary frequency that corresponds to scissor vibrations of N–H (Scheme 4).

Negative charge at the encapsulated molecule was a general feature of both systems with nanotubes **I** and **II**; however, the systems as a whole were neutral (Table 1).

Scheme 4.





In order to estimate the relative preference towards formation of dioxazine cluster with nanotube, thermodynamic parameters of the formally written reaction were calculated with C_a conformer taken as an example.

Results collected in Table 2 demonstrated that the formation of the studied clusters was accompanied by the positive ΔE^0, ΔH^0, and ΔG^0 as well as negative ΔS^0 changes; therefore, the process could not occur spontaneously. However, the increase of the thermodynamic parameters from clusters **I** to **II** demonstrates the growth of the barrier of the molecule encapsulation inside the tube with the decrease of its diameter.

To conclude, computer simulation demonstrated that force field of nanotubes significantly changed structural and energy parameters of the molecule upon encapsulation.

Table 2. Thermodynamic parameters of the formation of cluster from nanotubes and perhydro-1,3,2-dioxazine (C_a)

Cluster	ΔE_0^0	ΔH_{298}^0	ΔG_{298}^0	$-\Delta S_{298}^0$, cal mol^{-1} K^{-1}
	kcal/mol			
Dioxazine–**I**	23.3	23.3	36.5	44.2
Dioxazine–**II**	126.7	125.6	142.5	56.7

EXPERIMENTAL

Simulation of conformation transitions of dioxazine inside nanotubes consisted of several steps. First, using the HyperChem software [12], the corresponding nanotube was constructed, and then its geometry was optimized in the frame of semi-empirical AM1 approximation (HyperChem) followed by PBE/3z optimization (PRIRODA) [11]. Similarly, all the forms of perhydro-1,3,2-dioxazine were simulated. Then, the C_e conformer (AM1) was put into the inner cavity of the nanotube and geometry of this system was optimized. In the obtained structure, nitrogen conformation was set to be planar in HyperChem software, and this system was simulated as transition state with the AM1 method. Then, the energy of the obtained structure was minimized; the structure was thus transformed into the C_a form inside the nanotube. (The described procedure was targeted at obtaining all forms of the encapsulated molecule without changing its position inside the nanotube). Further, all three optimized structures were simulated using the PBE/3z method. The conformity of the stationary points to energy minima was confirmed by the absence of imaginary frequencies (except for the C_e–**I** cluster); the conformity of the stationary points to transition state was confirmed by the presence of only imaginary frequency (except for the TS–**I** cluster). Thermodynamic parameters of cluster formation (Table 2) were calculated following the Hess law: $\Delta E^0 = E^0_{\text{nano–doixazine}} - (E^0_{\text{nano}} + E^0_{\text{dioxazine}})$, $\Delta H^0 = H^0_{\text{nano–doixazine}} - (H^0_{\text{nano}} + H^0_{\text{dioxazine}})$, $\Delta G^0 = G^0_{\text{nano–doixazine}} - (G^0_{\text{nano}} + G^0_{\text{dioxazine}})$, $\Delta S^0 = S_{\text{nano–doixazine}} - (S^0_{\text{nano}} + S^0_{\text{dioxazine}})$.

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