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Inverted thermochemistry of "norbornadiene–quadricyclane" molecular system inside fullerene nanocages

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ABSTRACT

Currently, endofullerenes become common compounds that enrich chemistry by novel opportunities for molecular engineering. The influence of the fullerene cages on the behavior of guest molecules is obvious and not limited to simple encaging. Unfortunately, its quantitative estimation is difficult but this information may provide insights into regulating reactions by encapsulation. In the present work, we have applied the accurate DFT techniques to elucidate how encapsulation into the fullerene cages changes thermodynamic parameters and polarizability of "norbornadiene ↔ quadricyclane" interconversion (a classic example of molecular systems for solar energy accumulation). As it is turned out, decreasing the size of the cage enhances thermodynamic favorability of the norbornadiene conversion. Moreover, when appropriately encapsulating, the primarily endothermic direct reaction becomes exothermic. This also holds true in the case of inorganic (boron–nitrogen) fullerenes with rigid structures. Thus, the found regularity is a general trend and encapsulation can be recommended as one of the ways to tune thermodynamic parameters of chemical reactions.

1. Introduction

Fullerene molecules have empty space inside. This fact was immediately used to put atoms and molecules into their cages that result in endofullerenes (or endohedral complexes), a new class of topological compounds promising for wide-range applications such as radiofarmaceuticals, quantum bits, or photoswitchable devices [1]. Such encapsulation may change molecular properties of both the host fullerene and the guest atom/molecule. As a consequence, this causes changes in the exoherdal reactivity of the fullerene moieties of such complexes [1–3] as well as the measurable physicochemical properties of the atoms trapped [1,4–10]. Thus, the encapsulation causes the formation of hoping metal–metal bonds inside the cage [6], stabilization of nonconventional fullerenes [8] and compression of the encapsulated atoms [4] or clusters [7].

Nowadays, most of the synthesized endofullerenes contain atoms or metal ions inside but not the molecules [1]. However, the stability of endofullerenes with molecular fillings have been predicted based on quantum chemical calculations (see, *e.g.*, works [6,8,9,11–15]). Though endofullerenes with guesting molecules are mainly hypothetical now, synthetic methods for their preparation are rapidly developed. These methods, called molecular surgery [16], allow chemical opening the cages, putting a desirable molecule inside, and restoring the initial structure of the cage. Endofullerenes $H_2@C_{60}$, $H_2O@C_{60}$, and analogous compounds have been successfully produced by means of molecular surgery [17–20]. In this context, the forthcoming opportunity of carrying out chemical reactions inside fullerene vessels does not seem fantastic.

The theoretical works, devoted to the distinctiveness of chemical processes inside carbon fullerenes, are scarce. These are limited to quantum-chemical modeling on the conformational transits on the trapped molecules [21,22] and reactions of the encapsulated molecules with the inner surface of the fullerene cage [23] (note that chemical reactions and conformational transits inside nanotubes are also studied [24–26]). Therefore, the question of how encapsulation influence on the inner chemical reaction in general is currently open. We can propose the reversible reaction that takes place inside a fullerene:

$$aA + bB + \ldots dD \leftrightarrow kK + lL + \ldots nN \quad (1)$$

Extrapolating Le Chatelier's principle to molecular level, the equilibrium should be shifted to the right part if the number of molecules of products $k + l + \ldots n$ is less than the respective number for reactants $a + b + \ldots d$ (and if both products and reactants do not interact with the fullerene cage). However, such considerations are

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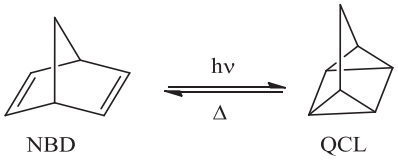
unhelpful when $k + l + \ldots n = a + b + \ldots d$. Monomolecular reactions (*e.g.*, isomerization of organic compounds) is a simplest example of the mentioned case.

We have theoretically investigated such a monomolecular case in the present work. For this purpose, we have chosen a striking example of "norbornadiene–quadricyclane" (NBD–QCL) isomerization, well-studied in previous works [27–37]. This bistable molecular system is a classic example of molecular accumulation of solar energy [27,28].



Thermodynamically, NBD state is more stable. When treated by irradiation, it converts into the less stable QCL (tetracyclo [3.2.0.0^{2,7}.0^{4,6}]heptane), which contains highly constrained cyclobutane and cyclopropane fragments. Therefore, the reverse reaction QCL → NBD has a sufficient heat effect (-89.3 ± 1.18 kJ mol^{-1} for liquid-phase reaction [29]). In spite of the fact that the NBD–QCL system is known for a long time [27–33] and has some disadvantages (described in detail in review [28]), the interest in it does not wane. Thus, theoretical studies are performed to elucidate the routes of the photochemical transformations of norbornadiene [34] and to find analogs of NBD–QCL system with higher propensity for energy accumulation (*e.g.*, example, due to the introduction of substituents in the norbornadiene molecule [35,36] or replacement of carbon by heteroatoms in the carbon skeleton of NBD [37]). Peculiarities of interconversions between NBD and QCL system have been studied in many theoretical and experimental works. All of them undoubtedly state the higher stability of norbornadiene compared to quadricyclane (this holds true for numerous derivatives of the mentioned compounds) [27–37].

In the present work using modern DFT techniques, we predict for the first time that encapsulation of the mentioned compounds into the fullerene cages makes QCL state more stable than NBD and allows tuning the equilibrium NBD ↔ QCL.

2. Calculation details

All optimizations have been performed with density functional theory method PBE/3ζ [38] implemented in the Priroda program [39]. The 3ζ basis set describes electronic configurations of molecular systems by the orbital basis sets of contracted Gaussian-type functions (5s,1p)/[3s,1p] for H, (15s,11p,2d)/[10s,6p,2d] for Si, (11s,6p,2d)/[6s,3p,2d] for B, C, N and O, and which have been used in combination with the density-fitting basis sets of uncontracted Gaussian-type functions (5s,2p) for H, (14s,3p,3d,1f,1g) for Si, (10s,3p,3d,1f) for B, C, N and O atoms. As previously shown in detail [21–23,26,40–45] the PBE/3ζ method reproduces structures and physicochemical characteristics of fullerenes and their derivatives with high accuracy. Additionally, it correctly reproduces the experimental regularities on the volumes of the C_{60} and C_{70} fullerenes [23,45], their mean polarizabilities [23,40–44] and distribution of electronic density in C_{60} derivatives [43]. Recently, it has been successfully applied to study conformations of the molecules, trapped by fullerenes [21,22] and nanotubes [26].

After DFT-optimizations and vibration modes solving by standard techniques (to prove that all the stationary points, respective to the molecules under study, are minima of the potential energy surfaces), the heat effects ΔH_r° and Gibbs energies ΔG_r° of the reactions have been calculated as the differences between the total energies E of the products and the reactants with inclusion of zero-point vibrational energy corrections ε_{ZPV} and the temperature corrections A_{corr} (H_{corr} or G_{corr}) for $T = 298$ K:

$$\Delta H_r^\circ = \sum_{\text{products}} (E_{tot} + \varepsilon_{ZPV} + A_{corr}) - \sum_{\text{reactants}} (E_{tot} + \varepsilon_{ZPV} + A_{corr}) \quad (2)$$

Components of polarizability tensors have been calculated in terms of finite field approach as the second order derivatives of the total energy E with respect to the homogenous external electric field. The tensors have been calculated in the arbitrary coordinate system and then diagonalized. Their eigenvalues α_{xx}, α_{yy}, α_{zz} have been used for the calculation of the mean polarizabilities of the molecules:

$$\alpha = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (3)$$

Volumes of the carbon fullerene cages in the empty and the encapsulated states have been calculated using our original algorithm, based on the partition of polyhedra into disjoint simplexes (triangular pyramids) [45]. Previously, we successfully tested this approach on the calculation of fullerene ions [45] and endofullerenes [23]. Atomic charges and bond orders have been calculated according to standard techniques in terms of Hirschfeld and Mulliken approaches, respectively, as implemented in Priroda program [39].

3. Results and discussion

To monitor how the heat effect of the title transformation depends on the volume of the molecular vessel, we have considered diverse fullerene molecules, which are able to host NBD and QCL molecules. These are conventional fullerenes: (1) the experimentally known fullerenes C_{70} (D_{5h}) [46] and I_h-C_{80} [47–49] and (2) the hypothetical fullerenes C_{90} (C_{2v}) [50], C_{100} (D_5) [11] and C_{120} (T_d) [51–53] (there are experimental evidences for their existence) (Fig. 1).

Note that we have not succeeded considering the C_{60} buckminsterfullerene as a molecular vessel for the reaction NBD ↔ QCL because the optimization of both initial structures, proposed for NBD@C_{60} and QCL@C_{60}, results in QCL@C_{60}. It means that the inner space of the C_{60} cage is sufficient to provide conditions for the only stable state, *viz.* QCL@C_{60} (the animations of the relaxed optimizations for NBD@C_{60} is available as Video Data). Therefore, we have started with C_{70}, the nearest buckminsterfullerene's kin. Before scrutinizing thermochemistry, we have examined structural aspects of NBD/QCL encapsulation into the fullerenes.

The norbornadiene and quadricyclane molecules are characterized with a C_{2v} point symmetry group. According to PBE/3ζ calculations, they lose their symmetry after the encapsulation resulting in C_1 symmetry structures due to the compression (see Supplementary material). Nonetheless, the character of double bonds in NBD, which are principal for its isomerization, is unchanged upon encapsulation. It is illustrated by the calculated Mulliken bond orders, being 1.89 and 1.40–1.83 in the intact and encapsulated states, respectively (see Supplementary material). After the encapsulation, small charges $-0.50\ldots-0.02$ and $-0.25\ldots-0.04$ arise on the NBD and QCL molecules, respectively (calculated in terms of Hirschfeld scheme, see Supplementary material). The computational data above indicate the weak interaction between the NBD/QCL molecules and the fullerene cages. Note that the fact of the compression of the encapsulated molecules is well agrees with the known compression of atoms [4] and clusters [7] inside the fullerene cages.

In addition, the empty fullerene cages negligibly differ from the filled ones. To estimate the structural changes, we have studied nuclear volumes of the fullerenes (V_X) and their increase upon