

Computations on Ba@C₇₄ and Yb@C₇₄

Zdeněk Slanina,^{*,**} Filip Uhlík^{***} and Shigeru Nagase*

*Department of Theoretical Molecular Science
Institute for Molecular Science

Myodaiji, Okazaki 444-8585, Aichi, Japan

**Institute of Chemistry, Academia Sinica

Nankang, Taipei 11529, Taiwan - ROC

***School of Science, Charles University

128 43 Prague 2, Czech Republic

ABSTRACT

Empty C₇₄ is still not available in condensed form, however, its endohedral derivatives are already known. The report surveys computations for two such C₇₄-based endohedrals - Ba@C₇₄ and Yb@C₇₄. A set of six C₇₄ cages is considered, namely one cage with isolated pentagons, three isomers with a pentagon-pentagon junction, two structures with one pentagon-pentagon pair and one heptagon. Special interest is paid to the Gibbs-energy evaluations for estimations of the relative isomeric populations and also of the production abundancies for different metallofullerenes. The C₇₄-based metallofullerenes are discussed in a wider context of nanoscience and nanotechnology applications of fullerene endohedrals.

Keywords: Metallofullerenes; carbon-based nanotechnology; molecular electronics; optimized syntheses; Gibbs-energy evaluations.

1 INTRODUCTION

Although empty C₇₄ fullerene [1] is not yet available in solid form, several related endohedral species have been known like Ca@C₇₄ [2,3], Sr@C₇₄ [4], Ba@C₇₄ [5], La@C₇₄ [6-8], Eu@C₇₄ [9], Yb@C₇₄ [10], Sc₂@C₇₄ [11] or Er₃@C₇₄ [12]. In the Yb@C₇₄ case, two isomers were in fact isolated [10]. This isomerism finding is particularly interesting as there is just one [13] C₇₄ cage that obeys the isolated pentagon rule (IPR), namely of D_{3h} symmetry. The cage was experimentally confirmed in Ca@C₇₄ [2], Ba@C₇₄ [4] and La@C₇₄ [8]. Obviously, with Yb@C₇₄ a non-IPR cage should be involved as it is the case of Ca@C₇₂ [14] (empty C₇₂ could also not be isolated yet, possibly owing to solubility problems [2,15-17]).

The metallofullerene family is naturally of computational interest. First such computations were performed for Ca@C₇₄ with considerations of selected non-IPR cages [2,16,18,19]. However, the non-IPR encapsulations are not significant with Ca@C₇₄, in contrast to Ca@C₇₂ [20,21]. The present paper surveys the computations also for the Ba@C₇₄ and Yb@C₇₄ species. In order to respect high temperatures in fullerene/metallofullerene preparations, the Gibbs energies are to be used [22,23] in relative stability considerations rather than the mere potential energy terms.

** The corresponding author e-mail: zdenek@ims.ac.jp

2 COMPUTATIONS

The computations treat a set of six metallofullerene isomers, using the carbon cages investigated with Ca@C₇₄, namely the three structures selected from dianion energetics [2,18], and three additional cages with non-negligible populations as empty C₇₄ cages [24,25]. In the computations [18,19,24] the cages have been labeled by some code numbers that are also used here, combined with the symmetry of the complexes: 1/C_{2v}, 4/C₁, 52/C₂, 103/C₁, 368/C₁, and 463/C₁. The 1/C_{2v} endohedral is the species derived from the unique C₇₄ IPR structure. The previously considered [16] two non-IPR C₇₄ cages are now labeled by 4/C₁ and 103/C₁. A pair of connected pentagons is also present in the 52/C₂ structure. The remaining two species, 368/C₁ and 463/C₁, contain a pentagon/pentagon pair and one heptagon.

The present geometry optimizations were primarily carried out using density-functional theory (DFT), namely employing Becke's three parameter functional [26] with the non-local Lee-Yang-Parr correlation functional [27] (B3LYP) in a combined basis set. As an example, the computational details are further given for Yb@C₇₄ where 3-21G basis for C atoms and the CEP-4G basis set [28-30] with the CEP effective core potential for Yb was applied (the combined basis set is denoted here by 3-21G~CEP-4G). The B3LYP/3-21G~CEP-4G geometry optimizations were carried out with the analytically constructed energy gradient, using results from preliminary B3LYP/CEP-4G optimizations. The reported computations were performed with the Gaussian 03 program package [31].

In the optimized B3LYP/3-21G~CEP-4G geometries, the harmonic vibrational analysis was carried out with the analytical force-constant matrix. In the same B3LYP/3-21G~CEP-4G optimized geometries higher-level single-point energy calculations were also performed, using the standard 6-31G* basis set for C atoms, i.e., the B3LYP/6-31G*~CEP-4G level. Moreover, the SDD (Stuttgart/Dresden) basis set [32,33] was also employed (with the SDD effective core potential for Yb) for the single point calculations, however, for the carbon atoms the SDD, 6-31G*, or 6-311G* basis set was stepwise used. In addition, for the three lowest isomers, the geometry optimizations were also carried out at the B3LYP/6-31G*~SDD level. The electronic excitation energies were evaluated by means of time-dependent (TD) DFT response theory [34] at the B3LYP/3-21G~CEP-4G level.

Relative concentrations (mole fractions) x_i of m iso-

mers can be evaluated [35] through their partition functions q_i and the enthalpies at the absolute zero temperature or ground-state energies $\Delta H_{0,i}^o$. Rotational-vibrational partition functions were constructed from the calculated structural and vibrational data using the rigid rotator and harmonic oscillator (RRHO) approximation. No frequency scaling is applied as it is not significant [36] for the x_i values at high temperatures. The geometrical symmetries of the optimized cages were determined not only by the Gaussian built-in procedure [31], but primarily by a procedure [37] which considers precision of the computed coordinates. The electronic partition function was constructed by directed summation, for example, for Yb@C_{74} of the TD B3LYP/3-21G~CEP-4G electronic excitation energies. Finally, the chirality contribution was included accordingly [38].

In addition to the conventional RRHO treatment with eq. (1), also a modified approach to description of the encapsulate motions can be considered [39], following findings [14,16,40] that the encapsulated atoms can exercise large amplitude motions, especially so at elevated temperatures (unless the motions are restricted by cage derivatizations [41]). One can expect that if the encapsulate is relatively free then, at sufficiently high temperatures, its behavior in different cages will bring about the same contribution to the partition functions. However, such uniform contributions would then cancel out in eq. (1). This simplification is called [39] free, fluctuating, or floating encapsulate model (FEM) and requires two steps. In addition to removal of the three lowest vibrational frequencies (belonging to the metal motions in the cage), the symmetries of the cages should be treated as the highest (topologically) possible, which reflects averaging effects of the large amplitude motions. There are several systems [39,42] where the FEM approach improves agreement with experiment.

As for the temperature intervals to be considered, it is true that the temperature region where fullerene or metallofullerene electric-arc synthesis takes place is not yet known, however, the new observations [43] supply some arguments to expect it around 1500 K. It has also been pointed out that very low excited electronic states can be present in some fullerenes like C_{80} [44] or even the C_{74} IPR cage [45], thus influencing the electronic partition function significantly. Interestingly enough, there is a suggestion [25] that the electronic partition function, based on the singlet electronic states only, could actually produce more realistic results for fullerene relative concentrations in the fullerene soot. Incidentally, the electronic excitation energies can in some cases be evaluated by means of a simpler ZINDO method [46,47] (known also as the ZINDO/S method), a semiempirical SCF method combined with the configuration interaction technique and specifically parametrized for electron excited states.

3 RESULTS AND DISCUSSION

Let us first survey the empty C_{74} cages (B3LYP/6-31G*/B3LYP/3-21G energetics, ZINDO electronic partition functions). The computed relative populations show that the sole IPR cage (D_{3h}) is prevailing. Shinohara *et al.* [48] recently recorded electronic spectrum of C_{74} anion and concluded that the cage could have D_{3h} symmetry. Moreover, it was observed by Achiba *et al.* [3] that the only available IPR C_{74} cage is actually

employed also in the Ca@C_{74} endohedral species. At a temperature of 1500 K, the $1/\text{C}_{2v}$ (related to the C_{74} IPR species), $4/\text{C}_1$, and $103/\text{C}_1$ Ca@C_{74} isomeric populations are computed [19] in the FEM scheme as 88.4, 8.0, 3.5 %, respectively.

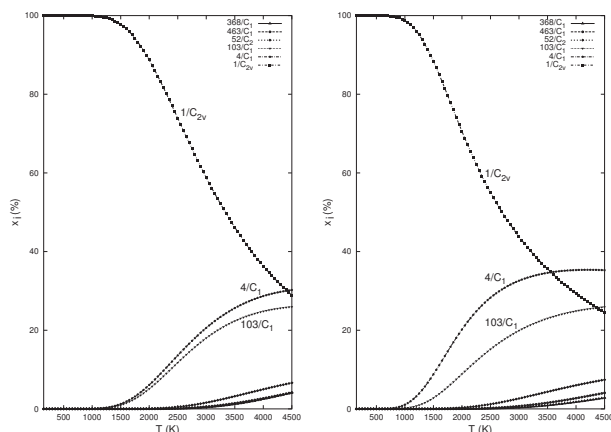


Fig. 1. Ba@C_{74} (left: B3LYP/6-31G*~dz energetics, B3LYP/3-21G~dz entropy, FEM treatment) and Yb@C_{74} (right: B3LYP/6-311G*~SDD energetics, B3LYP/3-21G~CEP-4G entropy, FEM treatment) relative concentrations.

Ba@C_{74} relative stability proportions (Fig. 1) differ from those previously computed [19] for Ca@C_{74} . For example, at a temperature of 1500 K the $1/\text{C}_{2v}$, $4/\text{C}_1$, and $103/\text{C}_1$ species when evaluated with the conventional RRHO treatment should form 99.5, 0.3, 0.2 % of the equilibrium isomeric mixture, respectively. With the more realistic FEM scheme, the relative concentration are changed to 97.8, 1.2 and 1.0 %. The proportions are in agreement with the observation of Reich *et al.* [5] in which just one Ba@C_{74} species was isolated, namely possessing the IPR carbon cage.

For the other system computed here, Yb@C_{74} , Xu *et al.* [10] isolated two isomers and even found their production ratio as 100:3. Fig. 1 converts the computed Yb@C_{74} energy and entropy parts into the relative concentrations. In order to reproduce the observed [10] production isomeric ratio (100:3) within the conventional RRHO approach temperature should reach about 1850 K when the $1/\text{C}_{2v}$, $4/\text{C}_1$, and $103/\text{C}_1$ species compose 95.7, 2.8, and 1.5 % of the equilibrium isomeric mixture, respectively. The FEM treatment reduces the temperature for the reproduction of the observed ratio [10] to about 1200 K with 96.1, 3.2, and 0.7 % for the $1/\text{C}_{2v}$, $4/\text{C}_1$, and $103/\text{C}_1$ isomer, respectively. It should be however realized that the observed relative populations are just roughly estimated from chromatography peak areas. The ratios at 1500 K would be changed to 88.4, 8.8, 2.8 % in the FEM treatment. Thus, the computations support the experimental finding [10] of two Yb@C_{74} isomers and point out that the major species should have the IPR cage while the minor one should contain one pentagon-pentagon junction in the carbon cage. A similar situation should be met with Ca@C_{74} but rather not with Ba@C_{74} .

There is a more general stability problem [49-52] related to fullerenes and metallofullerenes, viz. the absolute stability of the species or the relative stabilities of clusters with different stoichiometries. Let us consider

formation of a metallofullerene:



Under equilibrium conditions we shall deal with the encapsulation equilibrium constant $K_{@,p}$:

$$K_{@,p} = \frac{p_{X@C_n}}{p_X p_{C_n}}, \quad (2)$$

expressed in the terms of partial pressures of the components. Temperature dependency of the encapsulation equilibrium constant $K_{@,p}$ is described by the van't Hoff equation, $\frac{d \ln K_{@,p}}{dT} = \frac{\Delta H_{@}^{\circ}}{RT^2}$, where $\Delta H_{@}^{\circ}$ stands for the (negative) standard change of enthalpy upon encapsulation. Let us further suppose that the metal pressure is close to the saturated pressure $p_{sat}(X)$. With this presumption, we shall deal with a special case of clustering under saturation conditions [53,54]. While the saturated pressures $p_{sat}(X)$ for various metals are known from observations [55], the partial pressure of C_n is less clear as it is obviously influenced by a larger set of processes (though, p_{C_n} should exhibit a temperature maximum and then vanish). Therefore, we avoid the latter pressure in our considerations at this stage. The computed equilibrium constants $K_{@,p}$ show a temperature decrease as it must be the case with respect to the van't Hoff equation for the negative encapsulation enthalpy. However, if we consider the combined term $p_{sat}(X)K_{@,p}$, that directly controls the partial pressure of the endohedral species formed, we get a different picture. The critical term increases with temperature which is the basic scenario of the metallofullerene formation in the electric-arc technique. An optimal production temperature could be evaluated in a more complex model that also includes temperature development of the fullerene partial pressure. If we however want to evaluate production abundancies for two metallofullerenes like $Ba@C_{74}$ and $Yb@C_{74}$, the combined $p_{sat}(X)K_{@,p}$ term can straightforwardly be used. Let us consider a temperature of 1500 K as the observations [43] suggest that fullerene synthesis should happen in the temperature region. Our computations for 1500 K show that the $p_{sat}(Ba)K_{@,p}$ quotient is about three times smaller than the $p_{sat}(Yb)K_{@,p}$ term. This new stability criterion suggests that, as $Yb@C_{74}$ should come in higher yields than $Ba@C_{74}$, the conditions for the isolation of a minor isomer are more convenient in the $Yb@C_{74}$ case (in addition to the computed higher fraction of the non-IPR species in the Yb encapsulation).

Various endohedral cage compounds have been suggested as possible candidate species for molecular memories and other future nanotechnological applications. One approach is built on endohedral species with two possible location sites of the encapsulated atom [56] while another concept of quantum computing aims at a usage of spin states of $N@C_{60}$ [57] or fullerene-based molecular transistors [58]. In the connection, low potential barriers for a three-dimensional rotational motion of encapsulates in the cages [14,16,40,59-61] or at least large amplitude oscillations [62,63] can be a significant factor. The low barriers are responsible for simplifications of the NMR patterns at room temperature. This simplification is made possible by a fast,

isotropic endohedral motions inside the cages that yield a time-averaged, equalizing environment [59,60] on the NMR timescale. The internal motion can however be restricted by a cage derivatization [41] thus in principle allowing for a versatile control of the endohedral positions needed for memory applications. In overall, a still deeper knowledge of various molecular aspects of the endohedral compounds is at present needed before their tailoring to nanotechnology applications is possible.

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