

Computing enthalpy-entropy interplay for isomeric fullerenes: C₉₄ IPR set

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Abstract

The complete set of 134 isolated-pentagon-rule (IPR) isomers of C₉₄ has been studied by SAM1, PM3, AM1, MNDO quantum chemical methods, MM3 method, and their energetics is also checked by *ab initio* SCF calculation at HF/4-31G level and density functional theory calculations at the B3LYP/6-31G* level. All the methods point out a C₂ species as the system ground state. As energetics itself cannot predict relative stabilities at elevated temperatures, entropy contributions are also computed in terms of the Gibbs function. Further stability interchanges in the system are found and a good agreement of the computations with available observed data is achieved.

Keywords: *ab initio* calculations, IPR fullerene, relative stabilities, enthalpy- entropy interplay.

Introduction

Higher fullerenes C_n have represented [1] an interesting and constantly expanding family of nano-carbon materials, at present comprising over twenty observed and characterized members (with n at least till 94, or even beyond). A coexistence of two or more isomers is a rather typical feature of higher fullerenes. Indeed, several mixtures of fullerene isomers (from C₇₈ to C₉₂) [2-5] have extensively been studied both experimentally and theoretically, though some information fragments are already available for even higher number [6].

The computations demonstrated [5] that, at the theoretical end, the higher fullerenes couldn't be really understood without an inclusion of entropy contributions. This requirement is rather natural, given the high temperatures needed for fullerene synthesis.

Clearly enough, C₉₄ is the next system in the row to be subjected to the high-temperature computational analysis. In this preliminary report the C₉₄ IPR structures are investigated at various theoretical levels. The vibrational analyses and entropy calculations are carried out at the SAM1 semi-empirical level, and the relative stabilities at higher temperatures are evaluated. Based on the results of the enthalpy-entropy interplay, the thermodynamically stable isomers are discussed and compared with available experimental observations [7-10].

Calculations

The geometry optimizations of all 134 IPR fullerene cages were first performed at the MM3 molecular mechanics level, and then reoptimized at the SAM1, PM3, AM1, and MNDO semi empirical MO levels respectively, implemented in the AMPAC [11] and MOPAC [12] program packages. The geometry optimizations were performed with no symmetry constraints in Cartesian coordinates and with analytically constructed energy gradient. Based on the SAM1 optimized geometries, the harmonic vibrational analyses have been carried out by a numerical

differentiation of the analytical energy gradient, and have confirmed that all the localized stationary points are indeed local energy minima as there was no imaginary frequency. For selected cases the inter-isomeric energetics was further computed with *ab initio* SCF method at HF/4-31G level and also with density-functional theory method at B3LYP/6-31G* level, using the G98 suit of programs [13]. The *ab initio* calculations were however performed in the fixed, SAM1 optimized geometries: HF/4-31G//SAM1 and B3LYP/6-31G*//SAM1 approaches.

Rotational-vibrational partition functions were constructed from the SAM1 computed structural and vibrational data (though, only of the rigid rotator and harmonic oscillator quality, and with no frequency scaling). Relative concentrations (mole fractions) w_i of m isomers can be expressed through the partition functions q_i and the ground-state energy $\Delta H_{0,i}^\circ$ by the following formula [14]:

$$w_i = \frac{q_i \exp[-\Delta H_{0,i}^\circ / (RT)]}{\sum_{j=1}^m q_j \exp[-\Delta H_{0,j}^\circ / (RT)]} \quad (1)$$

where R is the gas constant and T the absolute temperature. The conventional heats of formation at room temperature $\Delta H_{f,298}^\circ$ by semi-empirical methods have to be converted to the heats of formation at the absolute zero temperature $\Delta H_{f,0}^\circ$. Chirality's contributions, frequently ignored, must also be considered in Eq. (1); too.

Results and Discussion

The computations start from topologically generated structures with correct connectivity. All such 134 C_{94} IPR topologies possible have been submitted to the fully geometry optimizations with SAM1, PM3, AM1, MNDO, and also MM3 models, in describing the primary classifications of energetic and stability. Out of the 134 cages, a structure with a C_2 symmetry and coded [15] by

133: C_2 is predicted as the lowest energy isomer of the IPR set, at five different levels of theory. The highest energy species in this system is located about 96.1 kcal/mol (SAM1) above the ground state structure. We have also preformed *ab initio* calculations at HF/4-31G and B3LYP/6-31G* levels (in the fixed SAM1 optimized geometries) for the best 20 low-energy isomers sorted by SAM1 energetics. All results have indicated that seven levels of theory agree well in predicting 133: C_2 as the ground state of the C_{94} IPR system. But the second lowest energy isomer differs somewhat with different methods: (3: C_2 by SAM1, PM3, AM1, MM3), (42: C_s by HF/4-31G and B3LYP/6-31G*) and 92: C_1 by MNDO. It is clear that further progress in this sophisticated case is particularly necessary.

Energetics itself cannot predict relative stabilities in an isomeric system at high temperatures. As this situation is particularly pertinent to isomeric fullerenes, we have included entropy effects and evaluated the relative concentrations. Figure 1 presents the temperature evolution of the relative concentrations under the conditions of the inter-isomeric thermodynamic equilibrium. It turns out that only five structures exhibit substantial populations at least in some parts of the wide temperature interval. In addition to three structures relatively low in the SAM1 energy: 133: C_2 , 42: C_s , and 44: C_s , there are also two significant structures with relatively high SAM1 energy, 34: C_1 and 37: C_1 . Although the ground-state structure (133: C_2) has of course to be prevailing at very low temperatures, its stability order is reversed already since 950 K. Then, the 42: C_s species (the third lowest SAM1 energy isomer) increases its relative fraction to very high temperatures at about 1390 K with a yield of some 49.5 %. At some higher temperatures beyond 1550 K, the structure 37: C_1 becomes quite significant. Around a temperature range of 700-2000 K, the SAM1 calculations point out three structures with a comparable stability. There are also some small but non-negligible populations for two minor isomers (44: C_s and

34: C_1). Interestingly enough, the second SAM1 lowest energy isomer (3: C_2) remains rather less populated with its maximum yield of about 1 %.

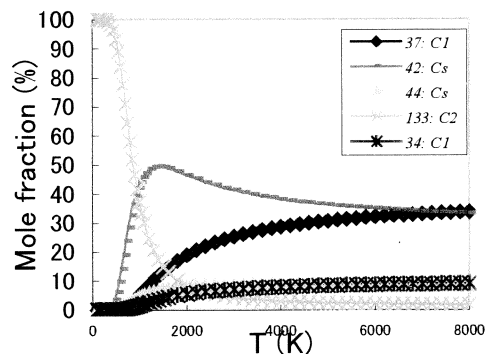


Fig. 1 Relative concentrations of C_{94}

Achiba *et al.* reported [1,7] preliminary notes on their ^{13}C NMR investigations of C_{94} fullerenes. They have listed just two structures [1] with the same symmetry of C_2 , though no concentration ratio is given and a further development [8] is possible. On the other hand, Howard *et al.* reported their observation [8,9] of extractable fullerenes up to C_{116} generated in flames and measurements of UV-vis spectra for some higher fullerenes including C_{94} , where the presence of *three different* HPLC peaks could be observed in the case of C_{94} [9]. They concluded that two distinct C_{94} isomers could be discerned based on the obviously different spectra, and the spectrum of the third C_{94} isomer was too noisy to distinguish for sufficient reliability. Clearly enough, discrepancy of distinct experimental observations from two different groups needs a further effort of more accurate experimental investigations.

We do not know how ^{13}C NMR spectrum of C_{94} in solution had originally been interpreted by Achiba *et al.* [1,7], even previous experience had shown that synergy between theory and experiment played quite well (e.g. in C_{90} [16]). However, in figure 1 there are just three *different* structures (133: C_2 , 42: C_5 , and 37: C_1) that control the higher temperature region related to fullerene formation. The thermodynamic evaluations have

indicated the highest relative population of 42: C_5 isomer (with the *largest* HOMO-LUMO gap at both Hückel MO and B3LYP/6-31G* levels) at high temperatures, considerably higher than the population of the second most abundant isomer 133: C_2 . Our results predicted that the two most thermodynamically stable species are indeed the different structures - 133: C_2 with 47 NMR lines and 42: C_5 with 49 NMR lines (four of them with a half intensity). This finding agrees well with the experimental observations [8,9] of Howard *et al.* In fact, the further result of molecular electronic circular dichroism (CD) and UV spectra by an improved VESCF-CI(full-CIS)-DV Molecular Mechanical calculations [17] matches the observed data [9] by Howard's group quite well and is reported elsewhere [18]. Moreover, a third stable isomer (37: C_1), at very high temperatures, is predicted with some relative stability if the amounts of HPLC-isolated sample are enough to examine. Clearly enough, Fig. 1 also suggests some small but non-negligible population of about 6.8% and 4.0% around 1500 K (at SAM1 level) for other two lower structures (44: C_5 and 34: C_1) respectively, even though 44: C_5 possesses a distinct NMR pattern (48 lines, two of them with a half intensity) rather than 42: C_5 .

Conclusions

In this report, the complete IPR set of C_{94} fullerene has been systematically described using various quantum chemical approaches. Seven different levels of theory agree in predicting 133: C_2 structure as the lowest energy isomer in the IPR set. The relative stability under the inter-isomeric thermodynamic equilibrium has been evaluated by a *combined quantum-chemical and statistical-mechanical treatment*. The result of entropy effect suggests that two distinct structures (42: C_5 and 133: C_2) remain as the most thermodynamically stable isomers and exist as equilibrium mixtures of fullerene C_{94} . The present study indicates that the two most abundant isomers should be assigned in the experiment and

gives a very good agreement with the current experimental observation [8,9].

The reported considerable thermal effects on the relative concentrations in the C₉₄ IPR set, which belongs to the family of isomeric fullerenes with a substantial role of entropy, result from a complex interplay between rotational, vibrational, potential-energy terms, and chirality factors. Such effects can never be seen if only energetics is considered while entropy terms are neglected. The entropy contribution actually gives a reasonable explanation why some particular species, which is not the structure lowest in potential energy, still represents the most abundant isomer and could be first isolated experimentally [5,19-20]. The whole scheme however based on the presumption of the inter-isomeric thermodynamic equilibrium. At present, it is still difficult to check this presumption under the real experimental conditions (as well as it is hardly to measure some synthetic temperatures accurately). Anyhow, our results indeed present a good relative-stability prediction of the IPR set and have already produced a reasonable theory-experiment agreement. This relatively strong evidence clearly supports our belief in a good applicability of the combined quantum chemical and statistical mechanical treatment, and further application in materials science and nano-technology.

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