

Stabilities of Fullerenes: Illustration on C₈₀ ♣

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Abstract. Theoretical studies of fullerenes, metallofullerenes, and their derivatives have employed a wide spectrum of techniques, in particular graph-theoretical (like the Wiener index), quantum-chemical, and statistical-mechanical treatments, in order to evaluate and rationalize stability, reactivity, and properties of the unique cage species. The theoretical stability measures of various types are analyzed, compared and illustrated on C₈₀ cages satisfying the isolated-pentagon rule.

♣ *Dedicated to Professor Nenad Trinajstić on the occasion of his 70th birthday.*

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Introduction

Fullerenes and metallofullerenes were for the first time observed [1] in the gas phase about twenty years ago and then prepared [2] in crystalline form about fifteen years ago. An enormous amount of observed and computed data has been obtained since the discovery. Approaches of theoretical chemistry have systematically been applied to various aspects of fullerene science including rich cage and positional isomerism, stability and reactivity, or the enthalpy-entropy interplay in fullerene and metallofullerene formations. Fullerenes themselves are cage compounds built exclusively from carbon atoms. In addition to spheroidal fullerene cages, fullerene science also deals with other objects like elongated cylindrical bodies known as nanotubes, prepared by Iijima [3] soon after mastering the fullerene synthesis, nanocones or peapods. All the species exhibit a substantial application potential, especially for molecular electronics.

Exhaustive topological enumerations and generations of fullerene cages represent a crucial step, systematically studied from early days of fullerene science - see, e.g., refs. [4,5]. Several concepts are useful in the treatments, e.g., Goldberg polyhedra, leapfrog transformation, topological duals, etc. Stone and Wales [6] introduced a formal transformation processes for pentagon/hexagon rearrangements in fullerene cages. The topological treatments can further be generalized [7] by inclusion of additional types of rings. Of other graph-theoretical tools, the Wiener index (and also Harary index) [8-10] was considered [11] a possible measure of the relative-stability order for the isolated-pentagon-rule (IPR) isomers of higher fullerenes. The Wiener index, defined as the sum of topological distances between all pairs of vertices in a molecular graph, is a rather natural choice for such stability studies. The carbon atoms in fullerenes are always distorted from an ideal sp^2 hybridization; this distortion can be measured by the surface curvature. The buckminsterfullerene itself exhibits a constant curvature. Other stable fullerenes exhibit quasi-spheroidal shapes. On the other hand, structures with abrupt changes of the curvature (which happens for example if two pentagons are connected) are likely to have a high energy, i.e. low stability. The abrupt changes in the curvature cause an elongated rather than spheroidal shape. Instead of treating terms of curvature or quasi-spheroidality, one can use a measure of the structural compactness, and the Wiener index in particular.

The Wiener index as a stability measure was studied [11] on seven possible IPR isomers of C_{80} . The relative potential-energy changes were that time derived from the SAM1 (Semi-Ab-Initio Model 1) semiempirical calculations. Although a rather poor correlation was found between the SAM1 relative potential energies and the topological Hückel HOMO-LUMO gaps for the IPR set, the Wiener numbers correlated much better with the relative energies. In the meantime, the relative energies and even Gibbs free energies can be evaluated at more advanced levels of theory so that the fullerene stability topics can be treated with a higher reliability.

Moreover, other aspects have become topical for C_{80} . Very high temperatures of fullerene synthesis produce significant populations of excited electronic states with some significant consequences for fullerene thermodynamics or kinetics. At present, the excited electronic states can be evaluated by means of configuration interaction (CI) approach or time-dependent (TD) density functional theory (DFT) response theory [12]. Moreover, for still larger systems the semiempirical (CI based) ZINDO (Zerner Intermediate Neglect of Differential Overlap) method [13-15] represents a more practical option. In the present report, initial numerical illustrations [16-19] continue with the C_{80} IPR system. There are seven [10] topologically possible IPR structures. The IPR structures were several times computed in the past [21-27], and two of them were also isolated [28,29]. Moreover, C_{80} is well known from some metallofullerenes [30-33]. In the literature, the C_{80} IPR isomers have been conventionally coded by letters [22,23,34] **A - G** or by serial numbers [20] (FM code). Recently, Furché and Ahlrichs [27] carried out DFT calculations and in particular pointed out existence of low-lying triplet states for the C_{80} isomers. Their interesting finding represents a further impetus for re-evaluations of the C_{80} system.

Calculations

Seven C_{80} IPR structures were optimized using DFT methods implemented in the Gaussian package [35,36], namely Becke's [37] three parameter exchange functional combined with the non-local Lee-Yang-Parr [38] correlation functional (B3LYP) with the standard 3-21G and 6-31G* basis sets, i.e. the B3LYP/3-21G and B3LYP/6-31G* treatments, with the analytical first derivatives of energy. The ultrafine grid in numerical in-

tegrations of the DFT functional and the tight SCF convergency criterion were used. In the optimized B3LYP/3-21G geometries the harmonic vibrational analysis was carried out, using the analytical force-constant matrix. For the same B3LYP/3-21G optimized structures TD B3LYP/3-21G electronic excitation energies were computed for first 10 singlet and 10 triplet excited states. In the B3LYP/6-31G* geometries, the second order Møller-Plesset (MP2) perturbation treatment [39,40] with frozen core (FC) option, in which inner-shells are excluded from the correlation calculation, was also performed with the same basis set (MP2=FC/6-31G*), however, only for two structures.

The computed energy, structural, vibrational, and electronic data are further employed in the construction of isomeric partition functions, and evaluations of the relative Gibbs free energies. The rotational-vibrational-electronic partition functions q_i are of the rigid rotor and harmonic oscillator quality, and no frequency scaling is considered. Relative concentrations (mole fractions) x_i of m isomers can be expressed through their partition functions q_i and the ground-state energy $\Delta H_{0,i}^o$ by a compact formula [41]:

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

where R is the gas constant and T the absolute temperature. The geometrical symmetries of the optimized cages represent an important issue and they were determined by a new procedure which treats precision of the computed coordinates as a variable parameter [23]. Chirality contribution [42] is also considered in Eq. (1) - for an enantiomeric pair its partition function q_i is doubled. Finally, the electronic partition function was constructed by a direct summation over twenty lowest electronic levels.

Let us mention that Eq. (1) is an exact formula that can be directly derived [41] from the standard Gibbs energies of the isomers, supposing the conditions of the inter-isomeric thermodynamic equilibrium. In principle, every excited electronic state could be treated as an individual isomer with its own rotational-vibrational partition function. This approach would however drastically increase the computational demands. Consequently, in numerical evaluations we have to follow the conventional approach in which the rotational and vibrational levels of any excited electronic state are identified with those of the respective electronic ground state. For relatively rigid fullerenes the approximation seems, generally speaking, to be reasonable.

Table 1. Selected characteristics of the IPR isomers of C_{80}

Species ^a	FM code ^a	Symmetry	W-index	ΔE_{rel} ^b (kcal/mol)
A	2	D_2	17352	0.0
B	7	D_{3d}	17600	27.27
C	1	D_{5d}	17340	2.08
D	6	C_{2v}	17500	10.65
E	3	C_{2v}	17412	6.66
F	4	D_3	17368	8.86
G	5	C_{2v}	17454	8.09

^a The letter and number code are taken from Refs. [22, 23] and [20], respectively.

^b The B3LYP/6-31G* relative potential energy based on the B3LYP/6-31G* optimized structures.

Results and discussion

Let us start with symmetries of the IPR isomers of C_{80} presented in Table 1. Two classes of symmetry can be distinguished - topological symmetries and the actual symmetries from the geometry optimizations obtained at a particular level of computations (which in Table 1 is the B3LYP/6-31G* approach). Obviously, the actual computed symmetries are either equal or lower than the topological ones. A symmetry reduction can follow from general energy reasons or from the Jahn-Teller distortions. There are two cages in the C_{80} IPR set that allow for the Jahn-Teller effect, namely **B** and **D**. The **B** structure has topologically icosahedral symmetry which is at the B3LYP/6-31G* level reduced to D_{3d} . The **D** cage is relaxed from D_{5h} to C_{2v} .

In contrast to the previous semiempirical SAM1 calculations [11], the ground state structure at the B3LYP/6-31G* level is not the **C** species of D_{5d} symmetry but the **A** cage with D_2 point group. Moreover, the still higher MP2=FC/6-31G* treatment for

Table 2. The lowest triplet and singlet electronic excited states computed at the TD B3LYP/3-21G level

Species ^a	FM code ^a	Symmetry	1-st triplet (cm ⁻¹)	1-st singlet (cm ⁻¹)
A	2	<i>D</i> ₂	4777	7096
B	7	<i>D</i> _{3d}	383	1981
C	1	<i>D</i> _{5d}	1601	4353
D	6	<i>C</i> _{2v}	-1660	1729
E	3	<i>C</i> _{2v}	-1908	2619
F	4	<i>D</i> ₃	-1952	2898
G	5	<i>C</i> _{2v}	-1754	1963

^a The letter and number code are taken from Refs. [22, 23] and [20], respectively.

just the two critical species confirms this finding, giving a separation energy of 2.79 kcal/mol - almost identical with 2.08 kcal/mol found at the B3LYP/6-31G* level. Although the correlation between the B3LYP/6-31G* relative potential energies and the Wiener numbers (Table 1) is influenced by the interchange, it still remains true that isomers low in potential energy also show relatively small values of the Wiener index and the cages with the highest potential energies exhibit the largest Wiener numbers.

Table 2 surveys the lowest triplet and singlet electronic excited states computed at the TD B3LYP/3-21G level. It turns out that in four cases (**D**, **E**, **F**, **G**) the lowest triplet is actually located below the lowest singlet state. The basis-set influence is small as at the TD B3LYP/6-31G* level the first triplet in the **E** case is placed at -1859 cm⁻¹ and for the **F** isomer at -1908 cm⁻¹. In the **B** case the two lowest states are very close in energy. Only the **A** and **B** cages exhibit a usual pattern of the first excited electronic states relatively high above the ground state (so that only in these two cases the MP2=FC/6-31G* treatment is really plausible).

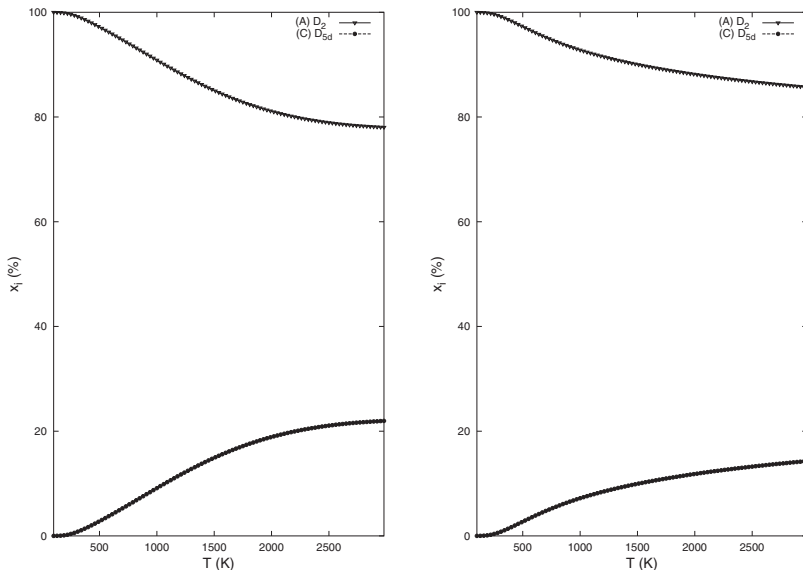


Figure 1. Computed mole fractions x_i for the two observed IPR isomers of C_{80} , **A** (D_2) and **C** (D_{5d}), based on the B3LYP/6-31G* energy and B3LYP/3-21G entropy, using the singlet and triplet (left) and singlet (right) electronic excitation energies.

These findings of so low triplet states suggest a question how to deal with them in the electronic partition function, q_{el} . Two cases can be considered - q_{el} based on both singlet and triplet electronic excited states, or q_{el} based just on singlet electronic excited states. It can be argued [34] that the latter approach could produce more realistic results. The basic reason is that it can be expected that the fullerene triplet species, after condensation, will in the end polymerize and form insoluble solids (supposing that the triplet states will have sufficiently long life time). This physical feature can be shown to be respected by the treatment with q_{el} built from the singlet electronic excited states only.

In experiment, Henrich *et al.* [28] first isolated a major species, ^{13}C NMR spectra of which were consistent with the **A**/ D_2 isomer. Later on, Wang *et al.* [29] separated also a minor C_{80} isomer - the **C**/ D_{5d} cage. Fig. 1 presents the computed temperature development of the mole fractions for the two experimentally known C_{80} isomers, evalua-

Table 3. Two C₈₀ isomers^a (α , β) with the same cage topology - C/D_{5d}

Term	isomer α	isomer β
$\Delta E_{pot,rel}$ (kcal/mol)	0.0	3.938
the lowest vibr. frequency (cm ⁻¹)	191.8	187.3
the shortest CC bond (Å)	1.393	1.379
the longest CC bond (Å)	1.467	1.459
the longest C-C distance (Å)	9.446	9.576
the highest rot. constant (GHz)	0.05599	0.05691
the ¹³ C NMR span ^b (ppm)	89-161	104-167

^aSee Fig. 2; computed at the B3LYP/3-21G level.

^b Computed at the B3LYP/6-311G**//MPW1B95/6-31G* level; the observed [29] ¹³C NMR span is 129-164 ppm.

ted according to Eq. (1) based on the B3LYP/6-31G* energy and B3LYP/3-21G entropy, for both approaches to the electronic partition function q_{el} . In the two approaches the **A**/D₂ isomer prevails throughout, being relatively more populated in the treatment with q_{el} built from the singlet electronic excited states only.

Results in Fig. 1 can actually be used in a kind of estimation of the **C**/D_{5d} - **A**/D₂ energy difference as the experiment [29] suggests a concentration ratio $x_{D_2}:x_{D_{5d}}=30:1$ (though no synthetic temperature is assigned to the ratio). In Fig. 1 the ratio would be achieved at a temperature of about 550 K. We can also postulate that a true synthetic temperature is, say [43], 1500 K, for which temperature Fig. 1 gives a ratio 90:10. Incidentally, if any entropic contributions are neglected in the treatment (so that we drop to the level of the simple Boltzmann factors [41]), the concentration ratio at 1500 K would be changed considerably - to about 67:33. This profound difference also illustrates the importance of the enthalpy-entropy interplay. We can also try to guess the separation energy from the inverse thermodynamic problem [44,45]. The inverse treatment applied to the situation in Fig. 1 requires the **A** cage to be located some 5.65 kcal/mol below

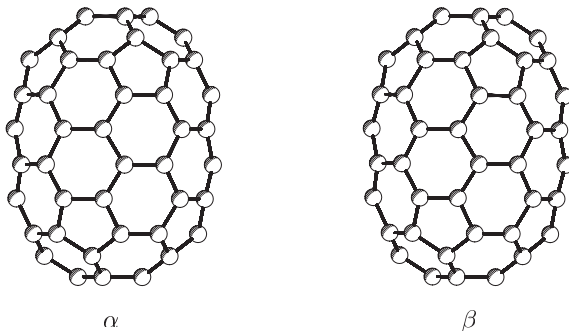


Figure 2. B3LYP/3-21G optimized structures of the α and β isomers of C/D_{5d} C_{80} .

the **C** isomer in order to have the 30:1 concentration ratio.

During the course of geometry optimizations, we experienced some instabilities with jumps. The cross-jumps could be just because of accidental interchanges of orbitals facilitated by low lying excited states. In the C/D_{5d} case, however, we could really locate two different energy-minimum structures, about 4 kcal/mol apart at the B3LYP/3-21G level (Table 3). The vibrational analysis confirms that both are the true minima as all the frequencies are real, none imaginary. Various geometry parameters differ though the differences are modest (Fig. 2). Of the two isomers, α and β , just the α species - lower in energy - is considered for the above-mentioned computations, especially in Fig. 1. The event could be viewed as a type of rotational isomerism though it is not clear if it really has some experimental significance, it can also be considered as a case of bond-stretch isomerism [46]. For one thing, it could mean a kind of structural flexibility if the related kinetic factors are fast. Even if it is just an artifact of the particular functional, it still requires the lower of the two isomers to be found before a comparison with experiment is carried out. The event influences not only energetics but also, for example, comparison with the computed NMR lines (the computed ^{13}C NMR lines in Table 3 are scaled to the C_{60} line [47,48]). In order to clarify the issue further, related calculations at other levels of theory would be useful.

In conclusion, it is obvious that theoretical tools different in nature can all play productive complementary roles in observation-computation interplay in fullerene science. Given the complexity of the systems, their treatment by just one parameter [49,50] can

facilitate understanding though their complete description still remains [51] a somewhat distant target. In particular, the fullerene/nanotube formation mechanism is likely to employ processes from virtually any major physico-chemical sub-field.

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