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Relative Stabilities of C_{92} IPR Fullerenes

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Abstract The complete set of 86 isolated-pentagon-rule (IPR) isomers of C_{92} has been described by the SAM1 quantum-chemical method, and their energetics checked by density functional theory at the B3LYP/6-31G* level. Although the lowest-energy cage is not identical in both approaches, it still exhibits D_2 symmetry in both cases. As energetics themselves cannot produce reliable relative stabilities at high temperatures, entropy terms are also computed and the relative-stability problem is treated entirely in terms of the Gibbs function. The lowest-energy structure is not the most populated isomer at higher temperatures - it is replaced by a D_3 structure. Further stability interchanges are possible at very high temperatures, when C_3 and C_1 structures are also important. There is a partial agreement of the computations with available observed data.

Keywords Higher fullerenes, IPR structures, Jahn-Teller effect, SAM1 method

Introduction

Fullerene science has constantly been supported [1] by computations, this being also true for higher fullerenes. At present over thirty higher fullerenes C_n with n from 76 to 94 have been identified,[2-6] typically through ^{13}C NMR in solution. Their molecular symmetries have been assigned from the spectra, although this does not always mean that their molecular topologies are known. Elucidation of the symmetries and structures has been based entirely on the isolated-pentagon-rule (IPR) conjecture.[7,8]

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Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70th birthday

The coexistence of two or more isomers is a rather typical feature of higher fullerenes. In fact, several mixtures of fullerene isomers have already been studied, viz.: C_{78} (e.g.[9-12]), C_{80} (e.g.[13-16]), C_{82} (e.g.[17-21]), C_{84} (e.g.[22-26]), C_{86} (e.g.[2,27]), C_{88} (e.g.[2,28]), C_{90} (e.g.[2,29]). Some preliminary results are even available [3,6,30] for C_{92} and for still higher members.[5,6,31,32] Overall, the computations have demonstrated [33,34] that, from the theoretical point of view, the higher fullerenes cannot really be understood without the inclusion of temperature effects, i.e., without entropy contributions. This requirement is rather natural, given the high temperatures needed for fullerene synthesis.

C_{92} is the next IPR system that should be studied computationally in this comprehensive way. There are 86 topologically different C_{92} cage structures [8] that obey the isolated-pentagon rule. In this paper we refer to the numbering system suggested previously.[8] In this report the C_{92}

IPR structures are computed at the semiempirical SAM1 level [35] and also using density functional theory. The C_{92} relative concentrations are evaluated and compared with available observations.[3,6]

Computations

The geometry optimizations were primarily performed with the new semiempirical method SAM1 constructed [35] in order to overcome some drawbacks of previous methods.[36,37] The computations were carried out primarily with the AMPAC program package [38] (some preliminary computations at the AM1 and PM3 levels were also performed with the MOPAC program [39]). The geometry optimizations were performed with no symmetry constraints in Cartesian coordinates and with analytical energy gradients. In the SAM1 optimized geometries, the harmonic vibrational analysis was carried out by a numerical differentiation of the analytical energy gradient.

For selected cases the relative energies of isomers were further computed at two *ab initio* levels, using the Gaussian94 program package.[40] First, Hartree-Fock (HF) SCF calculations were performed with the standard 4-31G basis set in the fixed optimized SAM1 geometries, HF/4-31G//SAM1. At the HF/4-31G computational level the stability of the SCF solution was checked (i.e., if it is really a local minimum in wave-function space). After this step, density-functional computations at the B3LYP/6-31G* level followed, using the HF/4-31G SCF solution as the starting guess, again in the fixed optimized SAM1 geometries, i.e., the B3LYP/6-31G*//SAM1 approach.

The geometrical symmetries of the optimized cages represent an important issue and they were determined not only by the AMPAC built-in procedure,[38] but primarily by a new procedure [16] which treats precision of the computed coordinates as a variable parameter. While changing the parameter, we get a string of symmetries and the relevant point group comes from the region corresponding to the supposed computed coordinate accuracy. Rotational-vibrational partition functions were constructed from the computed structural and vibrational data (although only of 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 $\Delta H^o_{0,i}$ by a master formula:[41]

$$w_i = \frac{q_i \exp\left[-\Delta H^o_{0,i} \big/ (RT)\right]}{\sum_{j=1}^{m} q_j \exp\left[-\Delta H^o_{0,j} \big/ (RT)\right]} \qquad (1)$$

where R is the gas constant and T the absolute temperature. Clearly enough, with the semiempirical quantum-chemical methods the conventional heats of formation at room temperature $\Delta H^o_{f,298}$ must be converted to heats of formation at the absolute zero temperature $\Delta H^o_{f,0}$. Chirality contributions, frequently ignored, must also be considered in Eq. (1), as the partition function q_i is doubled for an enantiomeric pair.

Results and discussion

The computations start from topologically generated structures [42,43] with correct connectivity. All such 86 C_{92} IPR topologies possible were submitted to the SAM1 geometry optimizations. Table 1 surveys energetics and symmetries of the fourteen structures lowest in the SAM1 energy. Out of those 86 cages, a structure with D_2 symmetry and coded [8] by ***82*** emerges as the lowest energy isomer at the SAM1 level (Figure 1).

The symmetries resulting from quantum-chemical optimizations can be different from those found in molecular-mechanical or topological treatments. In quantum chemical calculations the symmetry can in particular be lowered by the Jahn-Teller effect, pseudo Jahn-Teller effect, or simply owing to general energy reasons. It is known that Jahn-Teller conditioned distortions are rather common for higher fullerenes.[1] In the C_{92} IPR set we observe several cases where the topological symmetry is higher than the symmetry extracted after the SAM1 geometry optimizations. Some of the symmetry reductions cannot be related to Jahn-Teller effect, because the starting topological symmetry is not sufficiently high to allow for degenerate representations (for example, if a C_2 symmetry is relaxed to C_1). Moreover, there is no symmetry relaxation among the low-energy structures of

Table 1 *The relative energies [a] of low-energy IPR structures of C_{92} (kJ mol^{-1})*

Label [b]	Symmetry	SAM1	B3LYP/6-31G* //SAM1
82	D_2	0.0	0.0
81	D_2	10.44	49.77
38	C_1	14.82	-33.81
84	D_2	15.39	-84.93
28	D_3	29.57	-33.51
9	C_2	41.03	18.05
26	C_2	46.98	17.69
50	C_1	48.24	23.21
46	C_2	53.54	29.79
73	C_1	54.85	26.77
72	C_1	60.05	12.21
39	C_1	66.89	69.16
43	C_1	68.84	12.31
4	C_2	69.74	44.52

[a] $\Delta H^o_{f,298,r}$ *(SAM1) or* ΔE_r *(DFT)*
[b] Numbering convention recommended in Ref. [8]

Table 1. There is one structure, placed relatively high in energy, that nevertheless counts in the relative-stability evaluations and that exhibits a substantial symmetry lowering. This interesting structure is labeled by ***71***, it has a topological symmetry D_3 that is reduced at the SAM1 geometry optimizations to C_3.

Although the original tests on smaller compounds produced [35] quite satisfactory results, improved over the performance of the previous semiempirical methods,[36,37] there is still not enough computational experience with the SAM1 method. Hence, we also performed computations with a density functional theory, namely at the B3LYP/6-31G* level, i.e., about the best approach technically feasible at present. The B3LYP/6-31G* computations were performed in the fixed SAM1 geometries. In fact, it is known [1] that the semiempirical geometries for fullerenes are quite close to experiment and to results from higher levels of theory. Moreover, the SAM1, PM3 and AM1 results also usually agree. In order

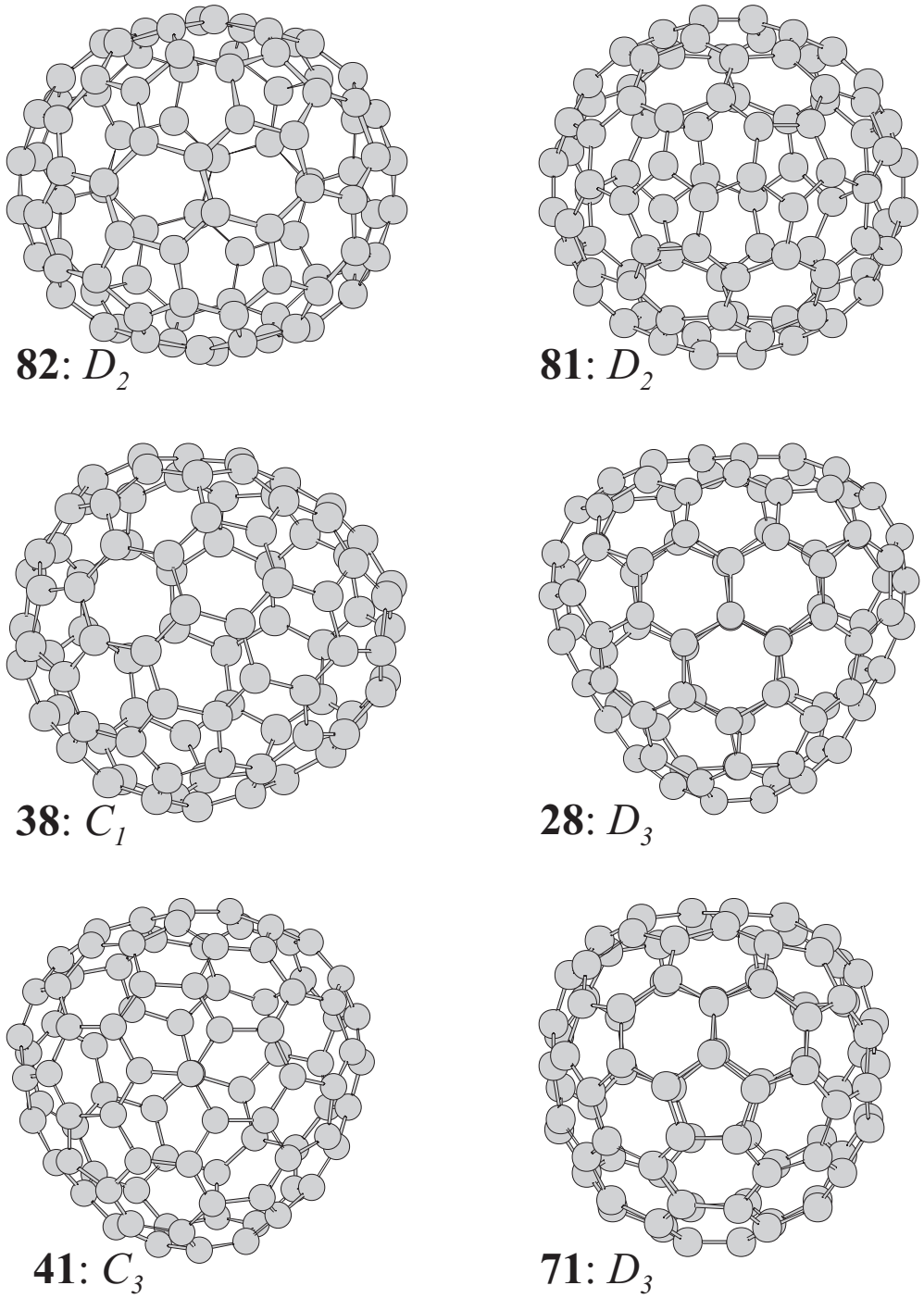

Figure 1 *Six SAM1 optimized structures of C_{92} fullerenes*

Table 2 *B3LYP/6-31G* mole fractions* w_i *for the selected* C_{92} *isomers [a]*

Label [a]	Symmetry	w_i (%) 1000 K	2500 K
82	D_2	1×10^{-3}	0.04
81	D_2	4×10^{-6}	4×10^{-3}
38	C_1	0.58	1.53
84	D_2	51.72	3.40
28	D_3	47.63	89.88
9	C_2	6×10^{-4}	0.07
26	C_2	3×10^{-3}	0.33
50	C_1	5×10^{-4}	0.09
46	C_2	2×10^{-4}	0.05
73	C_1	3×10^{-3}	0.53
72	C_1	9×10^{-3}	0.61
39	C_1	1×10^{-6}	7×10^{-3}
43	C_1	0.06	3.47
4	C_2	9×10^{-6}	7×10^{-3}

[a] See Table 1, numbering according to Ref. [8].

to check at least partly the stability of the SCF solutions obtained, we first ran HF/4-31G computations with the available option [40] for stability checking. The HF/4-31G solutions properly tested for SCF stability were then used as the starting guess in the following B3LYP/6-31G* approach. It was not feasible to perform a similar stability test at this final level of our computations.

It turns out that the relative energies of isomers are somewhat different at the SAM1 and B3LYP/6-31G* levels of theory (Table 1). It is actually one of the first cases of such a disagreement - for other fullerene system agreement is usually better.[34] We cannot automatically conclude that the B3LYP/6-31G* data should be preferred. Schaefer *et al.* recently reported [44] some interesting cases of the B3LYP method failing, although not for fullerenes but for an annulene. As computations of an MP2 type are still impossible for higher fullerenes, we plan to check the C_{92} energetics at least with some other standard approaches of density functional theory. In particular, the ground state structure at the B3LYP/6-31G* level is different from that in the SAM1 approach. However, if we perform the BLYP/6-31G*//SAM1 computations for the three low-energy isomers with D_2 symmetries (***82***, ***81***, and ***84***) we obtain values of 0.0, 10.6, -21.6 kJ mol^{-1}, *i.e.*, still supporting the B3LYP ground state. In the B3LYP/6-31G* treatment the structure labeled by ***84*** is also the lowest in energy (Table 1).

Energetics themselves cannot predict relative stabilities in an isomeric system at high temperatures. As this situation is particularly pertinent to fullerenes, we included entropy effects and evaluated the relative concentrations of all 86 C_{92} IPR cages. Figures 2 and 3 show their development over a wide temperature interval when all input data are based on SAM1 results. 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: ***82*** D_2, ***38*** C_1, and ***28*** D_3, there are also two significant structures with relatively high SAM1 energies, ***41*** C_3 and ***71*** D_3/C_3. At very low temperatures, the ground-state structure must of course prevail, however, at higher temperatures the structure is less and less significant. Around a temperature of 2000 K, the SAM1 calculations point out three structures with a comparable stability.

Table 2 shows that the B3LYP/6-31G* energetics combined with the SAM1 entropy gives somewhat simpler picture at higher temperatures (although at this stage only the fourteen IPR cages from Table 1 have been considered). At a temperature of 1000 K, the D_2 and D_3 structures labeled by ***84*** and ***28***, respectively, are almost comparable, sharing about 50% each. At a temperature of 2500 K the D_3 structure is a major isomer with two quite minor structures of D_2 and C_1 symmetry.

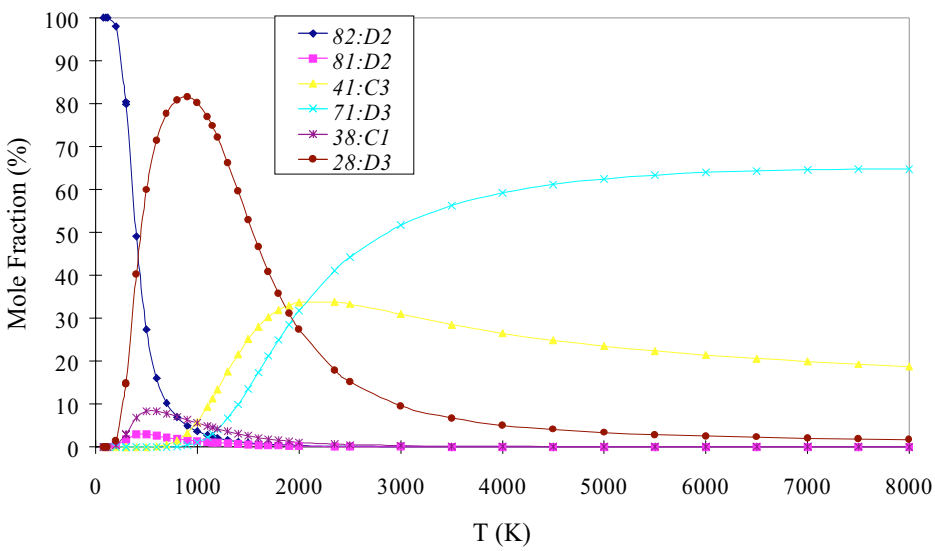

Figure 2 *The SAM1 computed relative concentrations of* C_{92}*, numbering according to Ref. [8]*

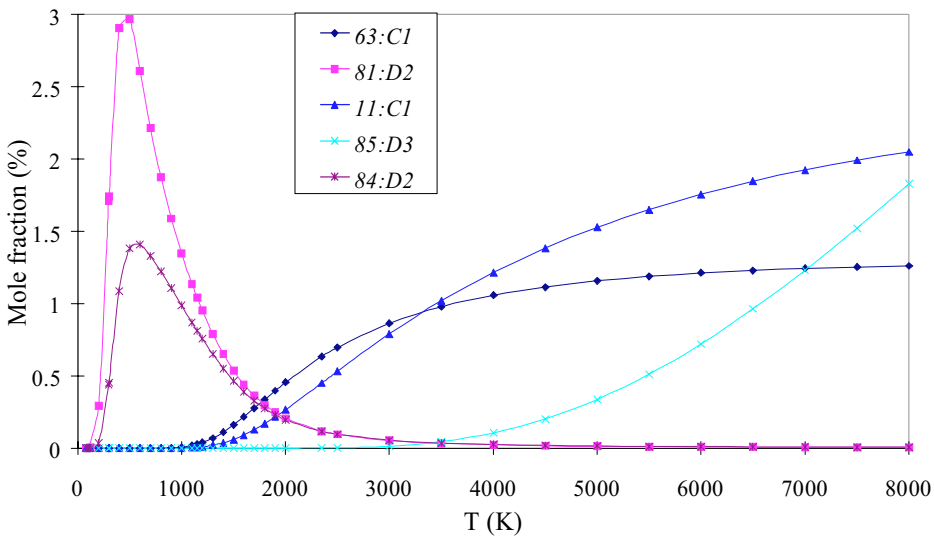

Figure 3 *Some less-populated isomers of C_{92}; numbering according to Ref. [8]*

Achiba *et al.* reported [3] preliminary notes on their ^{13}C NMR investigations of C_{92} fullerenes. They have listed [3] four structures with symmetries of D_2, D_2, C_2, C_2, though no concentration ratio is given and a further development is possible.[6] Neither the SAM1 nor the B3LYP/6-31G* computed relative concentrations match the observed data very well. Both agree in a significance of one D_2 species. In principle, one NMR pattern can sometimes be interpreted in several ways, especially if we deal with a mixture of two isomers.[29] Moreover, we should certainly not consider the IPR conjecture as a rule without exceptions. It has already been reported [45] for $Ca@C_{72}$ that the rule did not work always. Even for the pristine C_{72}, the SAM1 computations[46] have shown an entropy enhancement of a non-IPR structure. However, the number of non-IPR structures that should be checked for C_{92} is considerable. The possible presence of heptagons represents another issue of a more general nature. These points can be clarified only after further computations and their juxtaposition with experiments.

The reported considerable thermal effects on the relative concentrations in the C_{92} IPR set result from a complex interplay between rotational, vibrational, potential-energy terms, and chirality factors. Such effects can never be seen if only energetics are considered (i.e., simple Boltzmann factors instead of Eq. (1)) while entropy terms are neglected. Our treatment, however, deals with thermodynamic equilibria, although in fact only with respect to the inter-isomeric equilibrium. It is difficult to guess a degree to which this presumption is satisfied in the experiment. However, the thermodynamic-equilibrium treatment has already given reasonable agreement between theory and experiment in eight isomeric systems (C_{76}, C_{78}, C_{80}, C_{82}, C_{84}, C_{86}, C_{88}, and C_{90}). As for the C_{92} case, a third computational method is to be applied in order to clarify the disagreement between two methods that usually work reasonably well for fullerene isomeric sets.

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