C₉₀ AND C₉₂ - TEMPERATURE AND RELATIVE STABILITIES OF THE IPR ISOMERS

Zdeněk Slanina, Xiang Zhao, Shyi-Long Lee, and Eiji Ōsawa

Department of Knowledge-Based Information Engineering
Toyohashi University of Technology, Toyohashi 441, Japan

Department of Chemistry
National Chung-Cheng University, Chia-Yi 621, Taiwan

The complete set of 46 isolated-pentagon-rule (IPR) isomers of C₉₀ is described by the SAM1 quantum-chemical method, and their energetics is also checked by ab initio SCF computations (HF/3-21G, HF/4-31G), and by the AM1 and PM3 semiempirical methods. All the methods point out a C₂ species as the system ground state (with an exception at the HF/3-21G level). However, the energetics itself is not able to produce a good agreement with observations. Achiba et al. (Mater. Res. Soc. Symp. Proc. 359 (1995) 3) reported five C₉₀ species: one C₂₉, three C₂, and one C₁ (separated into three HPLC fractions). A more elaborated computational treatment (inclusion of entropy effects) is to be applied in order to reach a full agreement between computations and observations. A similar type of computations is also reported for the complete set of 86 IPR isomers of C₉₂.

INTRODUCTION

Our knowledge of higher fullerenes has expanded considerably: over twenty stable fullerenes Cₙ have presently been characterized (1) (n from 60 to 94). A coexistence of several isomers is a typical feature in the region beyond n = 76. In fact, several mixtures of fullerene isomers have extensively been studied, namely C₇₈ (e.g., (2-5)), C₈₀ (e.g., (6-9)), C₈₂ (e.g., (10-14)), C₈₄ (e.g., (15-19)), C₈₆ (1,20), C₈₈ (1,21). The computations demonstrated (22) that the higher isomers cannot be really understood without considering temperature effects, i.e., entropy contributions. This requirement comes directly from the fact that fullerenes are synthesized at high temperatures.
C_{90} and C_{92} are the next systems in the row (1,23,24). There are forty six topologically different C_{90} structures (25) which obey the isolated-pentagon rule (IPR structures), and eighty six IPR structures for C_{92}. In this paper we refer to the two previously introduced coding systems: either the numbering used in Ref. 26, or in Ref. 25 (FM system), though the FM system is more common (in Fig. 1 the FM code numbers are given in the second position, Fig. 3 refers to the FM numbers only, and Fig. 4 gives the FM code numbers in the first position). In this our preliminary report the C_{90} and C_{92} IPR structures are computed at semiempirical (SAM1 (27) and others) and SCF ab initio levels, their relative concentrations are evaluated and related to observations (1,23,28).

COMPUTATIONS

The geometry optimizations were first performed at the MM3 molecular mechanics level (26), then reoptimized with the the semiempirical SAM1 method (27), and also with the older methods AM1 (29) and PM3 (30). The computations were carried out with the AMPAC (31) and MOPAC (32) program packages. The geometry optimizations were performed with no symmetry constraints in Cartesian coordinates and with analytically constructed energy gradient. In the SAM1 optimized geometries, the harmonic vibrational analysis was carried out by a numerical differentiation of the analytical energy gradient. The inter-isomeric energetics was computed at two ab initio Hartree-Fock (HF) SCF levels - HF/3 21G and HF/4 31G, using the G94 program package (33). The ab initio computations were however performed in the fixed optimized SAM1 geometries.

Relative concentrations (mole fractions) \( w_i \) of \( m \) isomers can be computed using their partition functions \( q_i \) (the rigid-rotor and harmonic-oscillator approximation). In the terms of \( q_i \) and the ground-state energy \( \Delta H_{0,i}^g \) the mole fractions are given (34):

\[
w_i = \frac{q_i e^{\Delta H_{0,i}^g/(RT)}}{\sum_{j=1}^m q_j e^{\Delta H_{0,j}^g/(RT)}} ,
\]

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 \( \Delta H_{f,298}^g \) have to be converted to the heats of formation at the absolute zero temperature \( \Delta H_{f,0}^g \). Chirality contribution, mostly ignored, have to be considered in Eq. (1), too, as for an enantiomeric pair its partition function \( q_i \) is doubled. The symmetries of the optimized structures were determined by a procedure (9).

---

Electrochemical Society Proceedings Volume 97-14 681
Fig. 1. The five IPR structures of C_{90} significant at higher temperatures.
RESULTS AND DISCUSSION

The computations point out the structure with a $C_2$ symmetry (labeled 38 and 45 according to Ref. (26) and (25), respectively) as the $C_{90}$ ground state - 38/45 in Fig. 1. However, there is an exception in the HF/3-21G treatment as a $D_{5h}$ structure (only one such high-symmetry species in the set) is practically isoenergetic with the 38/45 structure; this singularity we can take as a numerical artifact. This is in agreement with the previous computations of Murry and Scusereia (35) and Okada and Saito (36). Fig. 2 demonstrates that the SAM1, AM1, PM3, HF/3-21G, and HF/4-31G relative inter-isomeric energetics are mutually well consistent.

In experiment of Achiba et al. (1,28) altogether five $C_{90}$ species were identified from $^{13}$C NMR spectra (distributed in three HPLC fractions): one $C_{2v}$, three $C_2$, and one $C_1$. The symmetries of the five SAM1 lowest-energy structures are: $C_2$ (38/45), $C_{2v}$ (29/46), $C_4$ (43/35), $D_{5h}$ (19/1), $C_1$ (22/30), i.e., at least two structures do not appear in the experiment. The computation-observation agreement however becomes even worse if we look into the NMR pattern (25) of the computed $C_{2v}$ structure - 24 lines, 3 of them weaker. The $C_{2v}$ species considered (1) in the experiment exhibits 25 lines, 5 of them weaker.

Let us note that the symmetries resulting from quantum-chemical optimizations can be different from those found in molecular-mechanics or topological treatments. In quantum chemical calculations the symmetry can in particular be lowered owing to Jahn-Teller or pseudo Jahn-Teller effect or simply owing to general energy reasons. The Jahn-Teller conditioned distortions are rather common for higher fullerenes (37). In the $C_{90}$ set however we could observe only one such case of symmetry lowering, the structure coded 8/23. Its topological symmetry is (25) $C_2$ but after the SAM1 optimizations we get $C_1$. As the $C_2$ symmetry does not allow for degenerate representations it cannot be the exact Jahn-Teller case.

In the view of the above poor agreement with the experiment we have to investigate possible temperature effects on the relative stabilities. First, we have to decide which energetics is to be applied. As the SAM1 method is the newest item in the semiempirical field, supposedly superior (27) to the AM1 approach (incidentally, the SAM1 heat of formation of $C_{90}$ is closer to experiment). Thus, we based our relative-stability calculations primarily on the SAM1 computed data. We however recomputed the relative concentrations with the HF/4-31G energetics (though keeping the SAM1 vibrational and geometrical data).

It turns out that there are just five structures which exhibit a significant population in a high-temperature region. In addition to the three structures lowest in energy ($C_2$ 38/45, $C_{2v}$ 29/46, $C_4$ 43/35), two high-energy species are relevant: $C_2$ 16/18 ($\Delta E_r = 130 \text{ kJ/mol}$) and $C_1$ 12/9 ($\Delta E_r = 202 \text{ kJ/mol}$) - see Fig. 3. At
Fig. 2. The relative energetics (kJ/mol) of C₉₀ by various methods.
Fig. 3. Temperature dependency of the relative concentrations of C₉₀;
Top: structures from Fig. 1, bottom: some less-populated species.
very low temperatures the ground-state structure has of course to be the dominant species, however, its decrease of stability with increasing temperature is considerable (Fig. 3). According to the SAM1 computations the ground-state isomer exhibits equimolarity with the 16/18 structure of C\textsubscript{2} symmetry at a temperature of 2012 K. Two other structures, C\textsubscript{4}, 43/35 and C\textsubscript{2v}, 29/46, show moderate maxima close to 1500 K. The last structure of Fig. 1, C\textsubscript{1}, 12/9, becomes quite important at very high temperatures though its population is still too low around 1000 K. The second part of Fig. 3 samples several less-populated structures (N.B., the concentration scale is reduced by one order of magnitude there) - it is of interest that the species with the highest temperature maximum in the second group, 22/30, also has again a C\textsubscript{1} symmetry, and the same is true for the second most populated species in the lower part of Fig. 3, 32/32. Results with the HF/4-31G energetics are not particularly different. The equimolarity point is reached sooner and the C\textsubscript{1} 12/9 species is more pronounced in the HF/4-31G energetics.

We do not know what was a temperature interval in which the C\textsubscript{90} sample used in the observations was actually synthesized, we may guess the temperatures somewhere beyond 800 K (though we hardly know how much beyond the point). Our computations predict (Fig. 3) that at elevated temperatures we primarily deal with the five structures of the symmetries: two times C\textsubscript{2}, C\textsubscript{\textast}, C\textsubscript{2v}, C\textsubscript{1}. This SAM1 high-temperature set compares now better with the conclusion (1) from the \textsuperscript{13}C NMR spectra: C\textsubscript{2v}, three times C\textsubscript{2}, C\textsubscript{1}. However, we should remember that in the computations and experiment we in fact deal with the C\textsubscript{2v} species of different NMR pattern. The experimental conclusion is based on an NMR spectrum consisting (1) of exactly 70 lines, five of them weaker. Any IPR C\textsubscript{90} isomer of C\textsubscript{2} symmetry exhibits (25) always 45 lines (none weaker). There are C\textsubscript{2v}, C\textsubscript{90} structures with exactly 25 lines (5 of them weaker). This is the essence of the experimental interpretation. However, in the computations, we deal with a different C\textsubscript{2v} structure - only 24 lines (3 of them weaker). Moreover, we have still another species not mentioned in the experiment interpretation, a C\textsubscript{\textast} structure with 46 lines (2 of them weaker). If we now combine together the NMR patterns of the two structures predicted by theory, C\textsubscript{2v} and C\textsubscript{\textast}, we also get 70 lines (5 of them weaker). With this alternative interpretation of the NMR spectrum (1) we reach a complete agreement of the computations with the observations. Let us note finally that the C\textsubscript{\textast} species is somewhat more populated than C\textsubscript{2v} (Fig. 2, Table 2) which actually helps to equalize intensities of their NMR lines.

We have repeated the combined energy-entropy treatment with the C\textsubscript{92} IPR set, too. Out of its 86 members six structures depicted in Fig. 4 have emerged as particularly stable species in a high temperature interval. Although the SAM1, AM1, PM3, HF/3-21G, and HF/4-31G relative inter-isomeric energetics are again essentially consistent (Fig. 5), there is an important difference between the SAM1
Fig. 4. The six IPR structures of C_{62} significant at higher temperatures.
Fig. 5. The relative energetics (kJ/mol) of C₉₂ by various methods.
and HF/4-31G treatments. The C92 ground-state structure is represented by the 82/38 species (Fig. 4) in the SAM1 method. However, in the HF/4-31G computations it is replaced by the 38/65 structure (Fig. 4). This change, together with some other minor energy shifts, produces the relative-concentration development which is somewhat different from that yielded by the SAM1 method. Here we meet a situation different from the C90 case where the SAM1 and HF/4-31G predictions are in a mutual agreement. We cannot say which of the two energetics is closer to the C92 reality unless we perform additional computations at a third, still more advanced methodological level.

Achiba et al. (38,39) published preliminary notes on their 13C NMR investigations of C92. They list four structures, symmetries D2, D2, C2, C2, though no concentration ratio is given. In our SAM1 evaluations of the C92 mole fractions we can clearly see one or even two D2 structures. There is also a significant C1 structure and with still higher temperatures also a D3 isomer. Clearly enough, similarly to the C90 case, two different breakdowns of an isomeric-mixture NMR spectrum are not excluded. This point can be clarified only after further computations and their juxtaposition with the observed NMR spectra. Still, already at this preliminary stage of the computations and observations we can notice encouraging pieces of an agreement.

The reported considerable thermal effects on the relative concentrations in the C90 and C92 IPR sets 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 (i.e., simple Boltzmann factors instead of Eq. (1)) while entropy terms are neglected. Our treatment however deals with thermodynamic equilibrium, though 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 already produced a reasonable theory-experiment agreement in eight isomeric systems (C76, C78, C80, C82, C84, C86, C88, and C90), with no serious failure. This relatively large set strengthens our believe in a still wider applicability of the equilibrium treatment, and its further testing on C92, C94, and C96 is in progress in our lab.

ACKNOWLEDGEMENT

The reported research was supported by the Ministry of Education, Science and Culture in Japan, and by the National Science Council, Taiwan, Republic of China.
REFERENCES


(32) J. J. P. Stewart, MOPAC 5.0, QCPE 455, Indiana University, 1990.