C$_{94}$ IPR isomeric set: large-scale computations of relative stabilities based on the Gibbs function

Zdeněk Slanina[a,b,*], Xiang Zhao[c], Filip Uhlík[d], Shyi-Long Lee[e]

[a]*Institute of Chemistry, Academia Scinica, 128 Yen-Chiu-Yuan Rd., Sec. 2, Nankang, Taipei 11529, Taiwan, ROC*

[b]*Department of Theoretical Studies, Institute for Molecular Science, 38 Nishigo-Naka Myodaiji, Okazaki, Aichi 444-8585, Japan*

[c]*Laboratory of Computational Chemistry, Department of Knowledge-Based Information Engineering, Toyohashi University of Technology, Toyohashi, Aichi 441-8580 Japan*

[d]*Department of Physical and Macromolecular Chemistry, School of Science, Charles University, Albertov 6, CZ-128-43 Prague 2, Czech Republic*

[e]*Department of Chemistry, National Chung-Cheng University, Ming-Hsiung, Chia-Yi 621, Taiwan, ROC*

Abstract

At present C$_{94}$ is one of the highest sets of isomeric fullerenes that has been characterized by ^{13}C NMR spectra. This contribution reports quantum-chemical computations on the C$_{94}$ system. The complete set of 134 isolated-pentagon-rule isomers of C$_{94}$ is described by four semiempirical quantum-chemical methods (MNDO, AM1, PM3, and SAM1). The C$_{94}$ energetics is also checked with Hartree–Fock SCF calculations in the standard 4-31G basis set (HF/4-31G). The calculations point out a C_2 structure as the system ground state. As energetics itself cannot produce reliable relative stabilities at high temperatures, entropy terms are also computed and the relative-stability problem is entirely treated in terms of the Gibbs function. The lowest-energy structure remains the most populated isomer at higher temperatures. However, several other structures show significant populations at higher temperatures. The six most populated species at the AM1 computational level read: C_2, C_2, C_1, C_1, C_s, and C_2. This selected six-membered isomeric set indeed contains the four symmetries observed in the available experiment (C_2, C_s, C_2, and C_2). This incidence represents a good agreement with the experiment and can be viewed as another evidence that the supposed inter-isomeric thermodynamic equilibrium does exist in experiments.
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1. Introduction

Fullerene science has constantly been supported [1] by computations, this being also true for higher fullerenes. At present already over 30 higher fullerenes C$_n$ with n from 76 to 94 have been identified [2–6], typically through ^{13}C NMR in solution. Their

* Corresponding author. Address: Department of Theoretical Studies, Institute for Molecular Science, 38 Nishigo-Naka Myodaiji, Okazaki, Aichi 444-8585, Japan. Tel.: +81-564-55-7222; fax: +81-564-4660.

E-mail address: zdenek@ims.ac.jp (Z. Slanina).

molecular symmetries have been assigned from the spectra though it does not always mean that their molecular topologies are really known. Elucidation of the symmetries and structures has entirely been based on the isolated-pentagon-rule (IPR) conjecture [7,8].

A 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], C_{92} [3,6, 30–33], and even some still higher families [5,6,34, 35]. In overall, the computations have demonstrated [36,37] that, from the theoretical point of view, the higher fullerenes cannot be really understood without an inclusion of temperature effects, i.e. without entropy contributions. This requirement is rather natural, given the high temperatures needed for fullerene synthesis.

C_{94} is the next IPR system that should be studied computationally in this comprehensive way. There are 134 topologically different C_{94} cage structures [8] which obey the IPR requirement. Throughout the study we refer to their previously suggested [8] numbering system (FM). In this report the C_{94} IPR structures are computed at various semiempirical levels, and to some extent also using ab initio Hartree–Fock (HF) SCF approach. The C_{94} relative concentrations are evaluated and compared with the newest available observations of Achiba et al. [33]— in their experiment four species have been recognized: C_2, C_s, C_2, and C_2.

2. Computations

The geometry optimizations were performed not only with the new semiempirical method [38] SAM1, but also with the older methods [39,40] AM1, PM3, and MNDO. The computations were carried out primarily with the AMPAC [41] program package (some preliminary computations at the AM1 and PM3 levels were also performed with the MOPAC [42] program). The geometry optimizations were performed with no symmetry constraints in Cartesian coordinates and with analytically constructed energy gradient. In the optimized geometries, the harmonic vibrational

analysis was carried out by a numerical differentiation of the analytical energy gradient.

For selected cases the inter-isomeric energetics was further computed at a simple ab initio level, using the G94 program package [43]. Namely, the Hartree–Fock SCF computation was performed with the standard 4-31G basis 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 wavefunction space).

The geometrical symmetries of the optimized cages represent an important issue and they were determined not only by the AMPAC built-in procedure [41], 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 calculated 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 energies $\Delta H^{\circ}_{0,i}$ by a master formula [44]:

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

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 $\Delta H^{\circ}_{f,298}$ have to be converted to the heats of formation at the absolute zero temperature $\Delta H^{\circ}_{f,0}$. Chirality contribution, frequently ignored, have to be considered in Eq. (1), too, as for an enantiomeric pair its partition function q_i is doubled.

Although there is no explicit reference to the Gibbs function in Eq. (1), let us mention that the (essentially) exact formula is in fact based entirely on the function. The master equation can be derived [44] from a presumption that there is an inter-isomeric thermodynamic equilibrium in the isomeric mixture. The partial thermodynamic

Table 1
Computed energetics for the C_{94} IPR set

Rank (SAM 1)	FM:Sym.	HF/4-31G//SAM1 ΔE (kJ/mol)	SAM1 $\Delta\Delta H_f$ (kJ/mol)	AM1 $\Delta\Delta H_f$ (kJ/mol)	PM3 $\Delta\Delta H_f$ (kJ/mol)	MNDO $\Delta\Delta H_f$ (kJ/mol)
1	133 : $C2$	0.00	0.00	0.00	0.00	0.00
2	3 : $C2$	37.60	26.71	17.32	20.33	51.64
3	42 : Cs	28.17	28.36	33.52	37.98	51.50
4	43 : $C2$	28.27	29.91	36.51	40.33	46.80
5	15 : $C1$	40.01	32.27	30.55	32.62	42.99
6	92 : $C1$	39.93	32.82	31.96	31.75	33.52
7	44 : Cs	37.75	37.26	39.93	40.70	49.12
8	31 : Cs	55.02	45.34	41.10	41.26	51.55
9	34 : $C1$	53.90	46.24	47.43	49.42	54.00
10	18 : Cs	60.26	47.36	46.41	49.49	53.62
11	16 : $C1$	56.18	48.39	46.84	46.31	55.53
12	37 : $C1$	53.37	48.46	51.05	53.13	69.24
13	105 : $C1$	52.56	49.50	47.30	42.44	49.58
14	122 : $C1$	70.91	59.20	56.42	54.08	47.65
15	83 : $C1$	61.48	61.04	59.50	51.75	60.99
16	39 : Cs	67.11	61.95	60.46	56.46	65.64
17	79 : $C1$	68.30	62.01	59.01	53.61	59.35
18	78 : $C1$	65.96	62.82	61.34	54.66	59.40
19	61 : $C2$	68.17	64.75	68.26	69.64	77.90
20	129 : $C1$	83.21	65.54	60.82	59.33	52.11
21	94 : $C2$		68.46	66.08	67.35	73.06
22	35 : $C1$		69.34	69.00	67.85	80.79
23	128 : $C1$		69.48	66.25	63.29	55.88
24	63 : $C1$		71.41	68.86	61.51	75.32
25	93 : $C1$		72.14	70.51	66.80	77.51
26	36 : $C1$		77.15	74.04	75.29	75.68
27	9 : $C2$		79.57	73.61	70.47	98.48
28	127 : $C1$		80.37	77.25	72.36	69.15
29	91 : $C1$		81.65	82.16	81.72	78.32
30	80 : $C1$		81.87	76.24	70.96	71.85
31	17 : Cs		83.41	80.89	72.00	92.23
32	86 : $C2$		83.57	80.77	71.69	85.03
33	107 : $C2$		84.62	82.36	73.84	89.53
34	65 : $C1$		86.30	86.42	84.12	84.51
35	62 : $C1$		89.54	85.92	83.75	83.56
36	84 : $C1$		89.80	86.02	74.87	91.49
37	56 : $C1$		95.72	91.01	89.28	86.77
38	97 : $C1$		95.99	93.64	89.38	86.87
39	98 : $C1$		97.96	93.56	89.94	86.53
40	32 : $C1$		98.80	89.81	89.14	104.08
41	77 : $C1$		100.54	95.02	89.17	89.77
42	45 : Cs		101.57	96.57	98.31	103.52
43	115 : $C1$		102.41	94.80	92.19	80.84
44	119 : $C1$		102.44	95.16	92.42	83.32
45	126 : $C2$		103.48	98.15	98.23	86.15
46	87 : $C1$		104.02	99.07	92.73	93.81
47	103 : $C1$		104.19	99.66	92.63	92.63
48	73 : $C2$		104.45	96.95	92.93	94.31
49	113 : $C1$		108.99	103.32	94.95	97.59
50	68 : $C1$		110.39	109.81	103.04	104.83

Table 1 (*continued*)

Rank (SAM 1)	FM:Sym.	HF/4-31G//SAM1 ΔE (kJ/mol)	SAM1 $\Delta\Delta H_f$ (kJ/mol)	AM1 $\Delta\Delta H_f$ (kJ/mol)	PM3 $\Delta\Delta H_f$ (kJ/mol)	MNDO $\Delta\Delta H_f$ (kJ/mol)
51	12 : $C1$		110.75	105.09	103.34	108.35
52	124 : $C2$		111.61	106.35	102.61	88.45
53	51 : $C2$		113.05	106.88	110.22	105.29
54	130 : $C2$		113.79	107.31	104.99	92.61
55	59 : $C1$		116.11	109.10	108.69	105.03
56	69 : $C1$		116.32	112.92	107.33	108.50
57	95 : $C1$		117.17	110.29	107.87	100.98
58	85 : $C1$		119.21	114.69	104.58	107.97
59	125 : $C1$		119.74	114.53	111.02	97.30
60	40 : Cs		120.28	116.98	104.58	128.67
61	5 : $C1$		120.57	110.54	106.30	128.05
62	66 : $C1$		122.78	119.09	113.10	118.38
63	20 : $C2$		123.24	124.99	130.26	135.32
64	81 : $C1$		123.52	119.33	110.70	110.32
65	72 : $C1$		126.19	118.06	114.10	107.23
66	123 : $C1$		129.86	124.34	118.18	107.89
67	132 : $C1$		130.61	121.37	117.67	103.32
68	55 : $C1$		134.76	129.74	125.06	132.51
69	41 : $C1$		135.44	129.01	119.86	142.68
70	111 : $C1$		135.58	126.12	119.44	116.34
71	57 : $C1$		136.15	130.53	128.23	120.47
72	50 : $C1$		136.24	128.94	120.47	129.58
73	70 : $C1$		138.50	130.48	120.56	127.65
74	75 : $C1$		139.47	142.99	129.33	143.48
75	49 : $C1$		143.95	135.38	131.53	127.28
76	134 : $C3v$		148.70	140.34	133.23	119.14
77	102 : $C1$		150.45	140.30	134.40	122.26
78	101 : $C1$		150.49	145.42	140.44	131.88
79	10 : $C1$		150.71	144.72	135.05	146.07
80	19 : $C1$		151.16	146.46	140.21	149.23
81	118 : $C1$		151.95	142.20	138.33	121.22
82	121 : $C2$		152.11	141.58	140.79	125.40
83	23 : Cs		152.48	145.01	136.94	147.11
84	74 : $C1$		154.33	147.24	142.11	134.97
85	21 : $C1$		155.57	148.93	144.01	149.81
86	96 : $C3$		156.17	149.85	145.84	138.41
87	6 : $C1$		156.81	148.29	137.49	170.45
88	47 : $C2$		157.18	151.98	150.12	149.06
89	76 : $C1$		159.21	148.91	142.82	139.37
90	131 : $C1$		159.74	150.44	143.64	133.71
91	2 : $C1$		160.18	151.25	139.67	177.81
92	99 : $C1$		160.73	150.78	146.50	138.70
93	112 : $C1$		160.76	149.31	145.55	134.93
94	67 : $C1$		161.08	157.13	149.06	147.64
95	60 : $C1$		162.48	150.09	144.22	149.46
96	11 : $C1$		164.22	156.67	151.28	148.38
97	4 : $C2$		165.33	158.28	144.91	182.74
98	8 : $C1$		168.24	159.05	152.02	158.52
99	82 : $C1$		169.03	162.98	154.18	148.50
100	89 : $C2$		169.08	163.42	150.29	164.79
101	22 : $C2$		169.62	164.62	157.61	164.02
102	54 : $C1$		170.16	158.98	154.47	142.09

Table 1 (*continued*)

Rank (SAM 1)	FM:Sym.	HF/4-31G//SAM1 ΔE (kJ/mol)	SAM1 $\Delta\Delta H_f$ (kJ/mol)	AM1 $\Delta\Delta H_f$ (kJ/mol)	PM3 $\Delta\Delta H_f$ (kJ/mol)	MNDO $\Delta\Delta H_f$ (kJ/mol)
103	7 : *C2*		171.51	167.04	150.80	173.20
104	48 : *C1*		172.59	162.07	154.26	161.19
105	106 : *C1*		175.16	166.88	154.69	162.96
106	33 : *C2*		177.44	171.47	168.48	159.93
107	53 : *C1*		177.44	175.84	170.48	180.85
108	64 : *C1*		179.27	175.25	165.95	169.10
109	71 : *C1*		180.14	171.85	159.91	160.95
110	120 : *Cs*		183.20	171.13	166.31	148.44
111	116 : *C1*		184.68	176.57	169.17	156.55
112	100 : *C1*		187.09	179.07	170.44	169.71
113	104 : *C1*		188.59	177.39	168.30	163.02
114	58 : *C1*		189.06	180.61	172.60	183.76
115	90 : *C1*		195.71	182.83	176.98	172.03
116	117 : *C2*		204.23	193.89	189.87	168.58
117	30 : *C1*		204.25	194.90	177.28	217.67
118	29 : *C1*		205.37	191.41	180.99	189.61
119	28 : *C1*		205.96	198.24	180.70	206.38
120	1 : *C2*		212.12	199.19	185.08	227.31
121	109 : *C2*		216.19	211.90	196.94	204.59
122	24 : *C2v*		218.15	215.44	212.46	222.67
123	108 : *C2*		219.41	210.84	197.73	205.87
124	114 : *C3*		219.90	208.62	193.54	192.66
125	88 : *C1*		220.22	211.93	199.12	207.71
126	110 : *C3*		232.24	227.34	224.90	213.41
127	27 : *C1*		241.38	229.74	212.00	232.34
128	25 : *C1*		241.70	226.66	212.51	230.02
129	26 : *C2*		243.25	233.16	211.91	249.20
130	13 : *Cs*		256.44	250.28	231.32	244.10
131	14 : *Cs*		265.80	262.38	245.97	261.28
132	38 : *C1*		278.86	267.28	249.00	276.38
133	52 : *C2v*		280.61	270.48	252.81	268.11
134	46 : *Cs*		402.20	386.87	357.36	390.51

equilibrium is described by a set of equilibrium constants so that both enthalpy and entropy terms are considered accordingly. Then, all the terms are expressed through partition functions and Eq. (1) is obtained. Consequently, this computational study is principally different from customary treatments based on the potential energy (heats of formation) only. Here, a due respect is paid to temperature and entropy effects. The procedure allows, inter alia, for relative stability interchanges with a temperature change, an important physico-chemical event that cannot be concluded from the potential energy terms only.

3. Results and discussion

The computations start from topologically generated structures [45,46] with correct bond connectivities. All such 134 C_{94} IPR topologies possible were submitted to the MNDO, PM3, AM1, and SAM1 geometry optimizations. Table 1 surveys their computed energetics, and also symmetries from the flexible procedure [16]. Out of those 134 cages, a structure with a C_2 symmetry and FM coded [8] by 133 emerges as the isomeric-system ground state in all the treatments considered (for graphical representations of all the C_{94} IPR structures, see Ref. [8]).
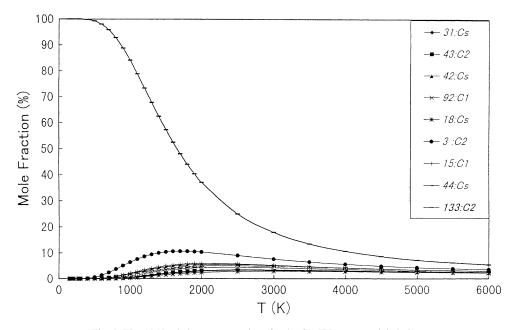
Fig. 1. The AM1 relative concentrations for the C_{94} IPR cages—global view.

Let us note that the symmetries resulting from the full quantum-chemical geometry optimizations can be different from those found in molecular-mechanical or topological treatments. In quantum chemical calculations the symmetry can in particular be lowered owing to Jahn–Teller effect, pseudo Jahn–Teller effect, or simply owing to general energy reasons (all the events are also covered by a general term of electronic effects). It has been known that Jahn–Teller conditioned distortions are rather
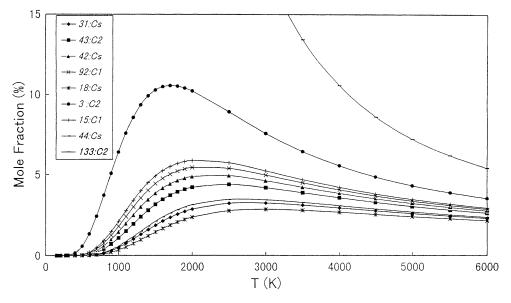
Fig. 2. The AM1 relative concentrations for C_{94} IPR cages—local view.

common for higher fullerenes [1]. Some of the symmetry reductions cannot however be related to Jahn–Teller effect as 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).

There is still not enough computational experience with the SAM1 method though the original tests on smaller compounds produced [38] quite satisfactory results, improved over the performance of the previous semiempirical methods [30,40]. Hence, we performed also computations at the Hartree–Fock SCF level with the standard 4-31G basis in the fixed optimized SAM1 geometries, HF/4-31G//SAM1. In fact, it has been known [1] that the semiempirical geometries for fullerenes are quite close to both experiment and results from higher levels of theory. It

turns out that the inter-isomeric separation energies in all five methods are also rather close (Table 1) and it is difficult to select the best method out of them. As computations of an MP2 type are still impossible for higher fullerenes, we plan to check the C_{94} energetics at least with some approaches of density functional theory.

Energetics itself cannot predict relative stabilities in an isomeric system at high temperatures. As this situation is in particular pertinent to fullerenes, we included entropic effects and evaluated the relative concentrations. Figs. 1 and 2 present their development in a wide temperature interval when all input data are of the AM1 origin. The AM1 results are selected for presentation as the method is at present most commonly used among the semiempirical methods. It turns out that there are at least six
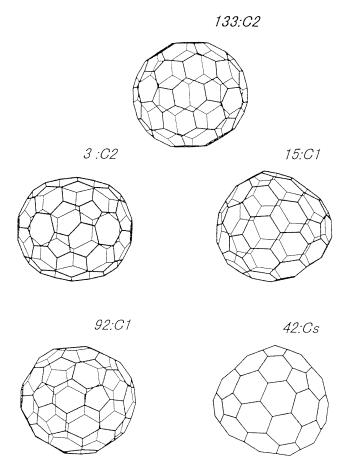

Fig. 3. The five C_{94} IPR cages most populated at higher temperatures (numbering according to Ref. [8]).

structures that exhibit substantial populations in some parts of the wide but still relevant temperature interval. The six most populated species at the AM1 computational level read: C_2, C_2, C_1, C_1, C_s, and C_2 (cf. Fig. 3).

Achiba et al. have released [6,33] preliminary notes on their ^{13}C NMR investigations of C_{94}. They list [6,33] four structures with the symmetries: C_2, C_s, C_2, and C_2, though no concentration ratio is given and a further development is, in principle, possible. Clearly enough, the AM1 computed relative concentrations match the observed data quite well as the above computational six-membered set of especially populated species contains the four symmetries observed in the experiment. However, there are obviously several degrees of freedom to check and to improve further the quality of the computed terms. In principle, such developments are only question of available computing power.

This computational study represents another evidence that the supposed inter-isomeric thermodynamic equilibrium does exist in experiment. However, there may also be other interpretation, viz. that although the inter-isomeric equilibrium is not yet reached, the relative non-equilibrium and equilibrium isomeric concentrations do not differ significantly. The computational treatment of isomeric mixtures has several interesting and convenient features: the results depend on temperature but not on pressure, only the relative and not the absolute values of the heats of formation are needed, the form of the master Eq. (1) allows for an ample cancellation of terms in the partition functions.

A subsequent, more general (and more important) task—relative stabilities of carbon cages with different dimensions or sizes, i.e. non-isomeric fullerenes with different stoichiometries, is discussed only very rarely [47–51]. Interestingly enough, the problem was, probably for the first time, touched by Schultz [52]. Clearly enough, further exploration of the rules behind the relative stabilities of isomeric and non-isomeric fullerenes is to be expected.

Acknowledgements

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