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Theoretical Studies on the Relative Stabilities of C_{96} IPR Fullerenes

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The complete set of 187 isolated-pentagon-rule (IPR) isomers of C_{96} has been systematically investigated by full geometry optimizations with various quantum chemical semiempirical methods as well as molecular mechanics, and their energetics are also computed at the ab initio HF/4-31G level. Some lower-energy isomers are further optimized at the B3LYP/6-31G level. All of the applied methods point out a D_2 species as the system ground state. Since the energetics alone cannot predict relative stabilities at elevated temperatures, entropy contributions are also taken into account, and the relative-stability problem is entirely treated in terms of the Gibbs function. Considerable temperature effects on the stability interchanges in the isomeric set are found, and good agreement of the computations with available observed data is achieved.

Introduction

Evaluations of relative stabilities of carbon cage clusters have been the subject of intensive studies[1−3] over the last few decades and have been speeded up especially since the discovery of the large-scale preparation of C_{60} fullerene.[4] Until now, there has been only one type of relative stability, namely, the relative stability of isomeric cages, that has been reasonably well understood. At present, already well over 30 higher fullerene isomers C_n with n from 76 to 96 have been identified,[5−9] typically through ^{13}C NMR spectra in solution. The elucidation of the symmetries and structures has been entirely based on the well-known isolated-pentagon-rule (IPR) conjecture.[10,11] Although the cage molecular symmetries have been assigned from the NMR spectra, this does not always mean that their molecular topologies are really known. Owing to the multiplicity of cages among higher fullerenes with the same point group of symmetry, theoretical calculations constantly represent a substantial complementary tool in fullerene research.

Moreover, a coexistence of two or more isomers is a common feature of higher fullerenes. In fact, several mixtures of fullerene isomers have already been studied extensively by equilibrium-thermodynamic computations,[3,12,13] and reasonable agreement with experiment has been found for C_{76} to C_{94}.[14] Overall, the computations have demonstrated[12−14] that temperature effects are indeed significant in understanding higher fullerenes. Clearly enough, from the theoretical point of view, the formation of higher fullerenes cannot be completely interpreted without the inclusion of temperature effects (i.e., without entropy contributions). This requirement is natural and reasonable because the temperatures needed for fullerene syntheses are the highest ever used in a chemical synthesis process. Recent experimental work[15] indicated that the temperature in the fullerene-forming zone represents one of the most important physical parameters for fullerene formation.

C_{96} is the next IPR system in the row that should be studied computationally in this comprehensive thermodynamic way. There are 187 topologically different C_{96} cage structures[11] that obey the isolated-pentagon rule. So far, only a few preliminary theoretical studies have been devoted to this fullerene system. Ho et al.[16,17] reported the tight-binding energetics as well as the local density approximation (LDA) results of some C_{96} isomers and predicted a low-symmetry C_2 isomer as the ground-state structure. Later, Murry and Scuseria[18] employed MM3 and MNDO calculations on the C_{96} IPR system and indicated that two D_2 structures remain the lowest in energy. Obviously, no convincing results from theoretical aspects are yet given with respect to available experimental observation; therefore, further study of the C_{96} IPR set is certainly necessary. In the reported research, all C_{96} IPR structures are systematically computed with four semiempirical quantum chemical approaches, a molecular mechanics (MM3)[19] scheme, and an ab initio Hartree−Fock method. To confirm and enhance the separation-energy accuracy, some lower-energy isomers from the semiempirical results are further optimized using hybrid density functional theory[20] at the B3LYP/6-31G level. Throughout the study, we refer to the numbering system of the IPR isomers previously introduced by Fowler and Manolopoulos.[11] Finally, the C_{96} equilibrium relative concentrations are evaluated and compared with the newest available experimental result by Achiba et al.[21]

Computations

The geometry optimizations were performed not only with the new semiempirical method SAM1[22] but also with the older MNDO,[23] AM1,[24] and PM3[25] methods to confirm the essential energetic classifications. The SAM1 computations were carried out primarily with the AMPAC program package[26] and calculations at the AM1, PM3, and MNDO levels were also performed with the updated MOPAC program.[27] The geometry optimizations were carried out with no symmetry constraints in Cartesian coordinates and with an analytically constructed energy gradient. The MM3 geometry optimizations of all C_{96} IPR isomers have also been employed for comparisons with previous work.[18] In

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the SAM1 optimized geometries of 187 C_{96} cages, the harmonic vibrational analyses were carried out by a numerical differentiation of the analytical energy gradient, respectively. The inter-isomeric energies of all IPR isomers were also computed at the ab initio level with the standard 4-31G basis set in the fixed SAM1 optimized geometries (HF/4-31G//SAM1) using the G94 program.[28] In the HF/4-31G calculations, the stability of the SCF solution has been examined by a built-in option[29] whether it really reached a local minimum in the wave function space. For 30 selected lower-energy isomers' cases out of the semiempirical results, the hybrid density-functional theory calculations were combined with full geometry optimizations at the B3LYP/6-31G level of theory using the G98 program.[30]

The geometrical symmetries of the optimized cages represent an important issue, and they were determined not only by the AMPAC or MOPAC built-in procedures[26,27] but also by a new topological procedure[31] that treats the 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 (though only of rigid rotator and harmonic oscillator quality and with no frequency scaling). As a key outcome for comparisons with available experiments, temperature-dependent relative concentrations (mole fractions) have been evaluated,[32] where the partial thermodynamic equilibrium is described by a set of equilibrium constants so that both enthalpy and entropy terms are considered accordingly.

Results and Discussion

The computations start from topologically generated structures[33,34] with correct bond connectivity and the VESCF optimizations with the MM3 method. Thus, all 187 C_{96} IPR possible topologies were submitted to the MNDO, AM1, PM3, and SAM1 geometry optimizations and further refined by the HF/4-31G SCF calculations to produce the primary classifications of energetics and stability. Table 1 surveys their computed energetics and topological symmetries that represent just an upper bound and in some case are higher than those found by quantum chemical optimizations. As a kind of kinetic-stability measure, the calculated HOMO−LUMO gaps from the simple Hückel MO level, which are consistent with the values of ref 11, are also listed for comparison in Table 1. Out of those 187 cages, a structure with a D_2 symmetry (FM code 183) emerges as the lowest-energy isomer in all of the treatments considered (as shown in Figure 1). It also turns out in Table 1 that the MM3 prediction generally agrees with other quantum chemical results even with some trends in underestimating the relative energy differences. Similar to C_{84} and C_{92} fullerenes with a plentiful type of point-group symmetry, there are 13 kinds of symmetry (C_1(108), C_s(14), C_2(43), C_{2v}(3), C_{3v}(1), D_2(8), D_{2d}(1), D_{2h}(1), D_3(3), D_{3d}(1), D_{3h}(1), D_{6d}(2), D_{6h}(1)) distributively available in the C_{96} IPR set. Clearly, nonsymmetry structures are predominantly leading in number among C_{96} IPR isomers. The species richest in energy is located more than 500 kJ/mol (SAM1) above the system's ground state.

As already mentioned, the symmetries resulting from the full 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 owing to the Jahn−Teller effect, the pseudo-Jahn−Teller effect, or general energy reasons (all of these events are also covered by a frequently used general term of electronic effects, which are unknown in molecular mechanics or topology). It has been known that Jahn−Teller conditioned distortions are rather common for higher fullerenes.[2] In the C_{96} IPR set, we could observe several cases when the topological symmetry is higher than the symmetry extracted after the semiempirical geometry optimizations. Some of the symmetry reductions cannot, however, be related to the Jahn−Teller effect because the starting topological symmetry is not high enough to allow for degenerate representations (e.g., if 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[22] quite satisfactory results, which showed improvement over the performance of the previous semiempirical methods.[23−25] Hence, we also performed computations at the Hartree−Fock SCF level with the standard 4-31G basis in the fixed SAM1 optimized geometries. In fact, it has been known[2] that the semiempirical geometries of fullerenes are quite close to both experiment and results from higher levels of theory. Moreover, the SAM1, PM3, AM1, and MNDO results in Table 1 usually agree well, though there are also some interesting differences existing among them. Because thermochemical data on higher fullerenes are quite limited (and there are of course no observed thermochemical data for C_{96}, cf. refs 8, 35−37), it is difficult to recommend the best method out of them. To check at least the stability of the obtained SCF solutions, we first run the HF/4-31G calculations with the available option[29] for a stability check. Finally, for 30 lower-energy structures, full geometry optimizations were performed at the B3LYP/6-31G level (with rigorous convergence criteria) to determine the stable isomeric structures and separation energetics. The B3LYP/6-31G energetics and HOMO−LUMO properties are summarized in Table 2 in combination with the potential energies derived from the HF/4-31G and SAM1 methods.

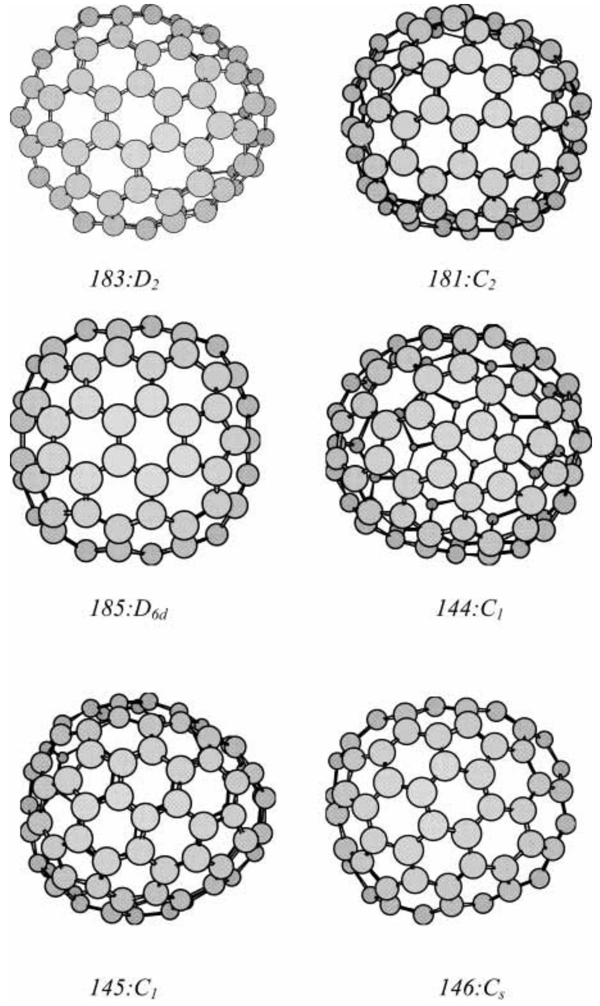
Energetics alone cannot predict relative stabilities in an isomeric system at high temperatures. Because this situation is particularly pertinent to fullerenes, we included entropy effects and evaluated the relative concentrations of all 187 C_{96} IPR cages. Figures 2 and 3 present the relative concentrations under the condition of the inter-isomeric thermodynamic equilibrium in the C_{96} IPR set evaluated from the HF/4-31G (or HF/4-31G//SAM1) separation energies and the SAM1 entropy contributions. It turns out that the inter-isomeric thermodynamic equilibrium behaves rather selectively, and Figure 2 shows that only four major structures exhibit substantial populations in the wide temperature interval. Clearly enough, at lower temperatures the ground state 183:D_2 must prevail. However, at higher temperatures the vibrational partition functions gradually become more important, and the importance of the ground-state terms decreases. It is such an enthalpy−entropy interplay that produces the final temperature development upon the relative stability. The species 181:C_2 (ranked the 16th lowest in energy at the SAM1 level or the 27th lowest in energy at the PM3 level) exhibits a fast increase in its relative fraction with a maximum yield of about 40.6% at a temperature of around 2200 K and becomes the most thermodynamically abundant structure at higher temperatures. Its equimolarity with the system ground-state 183:D_2 is reached in the temperature region around 1400 K. Interestingly enough, the further full geometry optimization at the B3LYP/6-31G level of theory predicts 181:C_2 as the second-lowest-energy structure among C_{96} IPR isomers. The third populated isomer 144:C_1 also exhibits a temperature profile with its maximum fraction of about 19%, and its stability order with respect to the ground state 183:D_2 is reversed since 1800

TABLE 1: Computed Energetics for the C_{96} IPR Set

rank sorting (SAM1)	FM:sym	HF/4-31G ΔE kJ/mol	SAM1 $\Delta\Delta H_f$ kJ/mol	PM3 $\Delta\Delta H_f$ kJ/mol	AM1 $\Delta\Delta H_f$ kJ/mol	MNDO $\Delta\Delta H_f$ kJ/mol	MM $\Delta\Delta H_f$ kJ/mol	HMO band$\lvert\beta\rvert$	rank sorting (SAM1)	FM:sym	HF/4-31G ΔE kJ/mol	SAM1 $\Delta\Delta H_f$ kJ/mol	PM3 $\Delta\Delta H_f$ kJ/mol	AM1 $\Delta\Delta H_f$ kJ/mol	MNDO $\Delta\Delta H_f$ kJ/mol	MM $\Delta\Delta H_f$ kJ/mol	HMO band$\lvert\beta\rvert$
1	183:D_2	0.0	0.0	0.0	0.0	0.0	0.0	0.193	70	34:C_1	112.9	118.8	104.1	108.7	109.8	80.6	0.028
2	185:D_{6d}	34.9	22.5	12.6	17.2	11.7	28.4	0.073	71	134:C_1	119.9	119.6	103.8	119.6	112.1	63.6	0.357
3	176:C_2	41.2	47.2	44.7	48.2	39.9	33.7	0.2	72	100:C_1	101.7	119.9	105.0	112.9	109.4	65.6	0.218
4	145:C_1	31.4	49.0	50.4	51.9	49.2	39.9	0.271	73	156:C_s	124.7	120.7	109.8	115.7	103.6	76.4	0.04
5	109:D_2	44.0	49.1	43.1	42.3	64.2	26.6	0.253	74	31:C_2	102.8	121.4	102.0	115.4	124.7	48.5	0.339
6	127:C_2	38.9	50.7	44.2	47.7	47.4	34.6	0.238	75	10:C_s	121.0	122.3	106.7	108.5	117.0	76.5	0.122
7	14:C_2	38.9	51.3	46.3	44.3	62.5	35.0	0.054	76	129:C_1	114.9	124.0	107.1	122.5	120.5	64.3	0.394
8	43:C_1	45.9	52.5	44.3	46.6	54.7	37.8	0.259	77	27:C_1	105.5	124.9	107.0	119.6	125.4	56.8	0.347
9	130:C_1	39.8	58.3	55.4	59.2	52.5	42.0	0.258	78	159:C_1	133.4	126.7	116.3	121.0	101.4	88.4	0.117
10	144:C_1	38.9	58.9	62.2	64.3	61.3	45.4	0.334	79	70:C_1	100.0	127.5	121.0	124.2	109.4	101.4	0.231
11	47:C_1	62.4	62.2	61.0	62.1	70.3	54.0	0.312	80	41:C_2	112.9	127.6	111.4	123.3	125.4	65.6	0.296
12	116:C_1	62.7	62.5	58.4	61.8	56.4	46.4	0.186	81	135:C_1	127.0	131.3	111.9	130.1	124.5	63.3	0.309
13	128:C_1	46.9	65.0	57.8	64.5	60.9	40.0	0.305	82	162:C_{2v}	136.7	131.9	125.4	131.8	113.2	89.7	0.048
14	132:C_2	53.4	65.0	62.2	66.3	66.0	45.1	0.301	83	92:C_1	128.7	132.5	120.0	123.0	111.4	104.0	0.208
15	107:C_1	54.2	65.8	55.8	63.0	66.5	28.4	0.269	84	15:C_2	141.0	132.9	125.5	129.5	133.5	93.4	0.033
16	181:C_2	54.9	66.2	71.7	72.6	63.7	51.0	0.291	85	106:C_1	123.7	133.1	112.4	126.7	137.2	58.5	0.294
17	142:C_2	56.5	67.2	68.1	69.5	71.9	51.7	0.301	86	29:C_1	118.7	133.3	113.6	124.4	126.1	71.6	0.209
18	102:C_1	56.6	70.1	61.2	67.3	67.4	36.3	0.31	87	66:C_1	122.5	134.0	118.2	127.1	121.4	88.4	0.194
19	182:C_2	71.4	70.2	71.6	74.3	61.0	51.9	0.246	88	12:C_1	126.8	134.0	124.0	129.7	131.1	94.6	0.147
20	146:C_s	50.8	71.0	71.5	77.0	71.8	49.7	0.29	89	74:C_1	131.9	134.2	116.4	132.3	130.6	71.0	0.321
21	96:C_2	58.4	71.3	59.2	66.5	68.7	46.7	0.158	90	165:C_2	126.1	134.3	134.0	137.1	117.7	91.0	0.14
22	143:C_1	69.0	75.3	71.9	76.7	74.1	49.0	0.206	91	51:C_1	121.6	136.2	123.3	129.1	129.6	82.4	0.177
23	179:C_2	86.7	75.9	75.2	77.7	64.7	53.7	0.175	92	118:C_2	121.6	136.3	134.9	139.6	132.1	127.4	0.229
24	175:C_1	79.7	76.1	72.9	78.4	68.0	49.1	0.184	93	23:C_1	128.7	137.4	119.5	127.4	130.7	74.5	0.187
25	131:C_1	67.2	77.6	71.5	78.5	73.1	47.2	0.244	94	91:C_1	131.2	138.0	133.7	136.6	124.9	111.0	0.093
26	82:C_2	81.8	77.7	68.0	72.8	69.0	57.9	0.127	95	11:C_s	132.5	138.4	119.4	127.2	147.3	72.1	0.143
27	5:C_1	61.0	78.0	65.2	70.4	94.7	41.1	0.305	96	28:C_1	124.9	139.6	118.6	132.3	145.8	59.0	0.293
28	125:C_1	69.2	79.6	72.7	79.8	75.3	49.8	0.231	97	184:D_{6h}	135.8	140.1	122.4	138.9	136.8	84.2	0.129
29	172:C_1	88.8	79.6	74.9	80.4	71.3	49.7	0.156	98	137:C_{3v}	142.9	140.4	122.3	142.4	132.4	73.7	0.42
30	177:C_1	75.4	80.2	73.7	81.3	68.7	50.3	0.216	99	163:D_2d	168.2	140.5	127.9	135.3	107.8	102.8	0.183
31	1:D_2	83.4	80.2	64.3	66.7	112.1	38.5	0.537	100	121:D_3	148.8	142.4	129.5	137.0	126.3	81.9	0.03
32	104:C_1	64.7	82.2	71.2	75.8	71.1	50.5	0.197	101	112:C_1	130.2	142.6	131.7	136.5	121.6	105.9	0.185
33	3:D_{3d}	93.5	82.8	66.0	68.9	110.4	45.4	0.517	102	139:C_1	144.8	142.6	130.9	140.3	130.8	85.5	0.067
34	94:C_1	62.2	85.3	85.8	87.3	88.3	73.3	0.27	103	38:C_1	129.0	143.0	125.0	135.5	134.2	82.3	0.268
35	147:C_s	90.3	85.8	81.8	83.5	77.1	65.6	0.169	104	167:C_2	152.9	143.5	128.2	131.6	111.3	96.6	0.019
36	6:C_2	75.3	86.2	73.4	76.1	108.3	43.1	0.263	105	13:C_2	145.3	143.6	130.2	140.4	149.2	91.2	0.199
37	174:C_2	85.6	86.8	77.5	87.8	76.9	48.5	0.184	106	64:C_1	146.0	144.0	129.0	138.7	130.4	90.5	0.155
38	158:C_2	74.1	86.9	76.8	78.1	63.6	59.9	0.147	107	44:C_1	147.6	144.2	124.0	128.7	125.1	94.7	0.1
39	171:C_2	96.0	87.3	79.0	86.8	79.4	48.7	0.083	108	60:C_1	142.3	144.8	133.1	137.0	122.8	100.6	0.083
40	173:C_2	90.4	88.5	77.8	88.3	79.6	48.0	0.3	109	72:C_1	146.0	145.6	130.2	140.1	126.1	81.6	0.067
41	49:C_1	83.1	89.1	82.4	85.4	100.3	60.2	0.259	110	76:C_1	145.6	148.4	131.0	145.1	131.8	82.8	0.193
42	151:C_2	88.9	89.1	76.8	85.6	91.1	42.3	0.195	111	54:C_1	133.7	148.9	131.5	141.4	138.1	90.1	0.133
43	164:C_1	80.8	90.6	88.0	91.2	76.9	62.2	0.199	112	53:C_1	141.4	150.4	135.4	142.0	129.8	96.0	0.1
44	105:C_2	86.7	91.1	78.4	85.9	95.1	42.1	0.293	113	119:C_1	130.5	150.9	143.2	147.1	129.2	99.1	0.146
45	90:C_1	81.5	91.1	88.7	90.4	86.5	76.2	0.194	114	68:C_1	146.4	151.2	141.1	145.6	136.5	106.5	0.121
46	180:C_s	93.3	97.8	99.1	104.0	89.6	64.4	0.131	115	83:C_2	143.7	151.5	131.6	145.4	142.2	81.6	0.245
47	88:C_1	85.0	97.9	84.6	95.5	94.5	58.9	0.333	116	154:D_2	173.2	152.4	140.4	143.9	125.3	105.6	0.006
48	114:C_1	58.1	100.8	103.0	105.7	97.6	69.8	0.302	117	108:C_1	153.6	153.0	136.4	146.4	153.3	82.6	0.173
49	115:C_2	117.7	102.3	97.9	99.8	98.1	72.6	0.044	118	73:C_2	153.1	153.0	134.7	148.9	143.4	80.0	0.117
50	178:C_s	108.5	102.5	96.1	105.7	92.4	60.7	0.123	119	19:C_1	142.6	153.5	135.5	144.3	151.7	99.0	0.14
61	155:C_1	111.3	109.9	104.7	107.5	92.4	78.7	0.116	120	67:C_1	129.9	153.8	151.6	152.9	138.8	117.0	0.117
62	101:C_1	110.7	112.1	99.4	103.4	91.6	78.4	0.142	121	69:C_1	125.6	156.1	149.8	155.9	142.0	115.4	0.224
63	169:C_1	123.0	114.6	105.1	111.2	97.8	67.4	0.058	122	59:C_1	140.0	156.2	152.8	157.6	145.6	126.4	0.085
64	93:C_1	106.3	115.4	106.8	112.2	110.4	84.1	0.129	123	87:C_1	143.8	156.2	135.4	150.7	151.4	77.5	0.325
65	40:C_2	100.4	115.8	101.4	110.0	118.1	53.9	0.234	124	99:C_2	147.8	158.2	136.9	153.3	158.2	72.3	0.35
66	153:C_1	121.3	116.2	105.5	113.4	96.5	75.8	0.106	125	36:C_1	126.8	158.2	152.0	158.5	153.6	117.6	0.122
67	55:C_2	122.2	116.7	107.4	104.9	100.8	88.4	0.061	126	140:C_1	159.1	159.3	145.0	153.3	137.6	106.2	0.139
68	46:C_2	107.8	117.6	117.4	121.6	118.8	95.1	0.189	127	97:C_1	129.8	160.2	147.8	155.2	144.3	111.8	0.09
69	138:C_1	97.1	118.6	114.6	121.1	112.3	79.3	0.214	128	166:C_1	171.8	161.9	148.1	156.4	134.4	94.4	0.04
60	113:C_1	82.7	109.2	102.8	107.6	99.4	76.1	0.164	129	133:C_s	167.2	162.0	140.7	157.2	144.8	90.1	0.192
61	155:C_1	111.3	109.9	104.7	107.5	92.4	78.7	0.116	130	45:C_1	173.7	163.1	153.5	163.1	160.7	110.5	0.134
62	101:C_1	110.7	112.1	99.4	103.4	91.6	78.4	0.142	131	57:C_1	141.4	163.3	161.1	165.6	152.4	132.3	0.085
63	169:C_1	123.0	114.6	105.1	111.2	97.8	67.4	0.058	132	61:C_1	173.0	164.6	151.7	161.3	147.9	108.2	0.162
64	93:C_1	106.3	115.4	106.8	112.2	110.4	84.1	0.129	133	30:C_2	148.8	164.9	137.1	155.8	174.4	66.4	0.622
65	40:C_2	100.4	115.8	101.4	110.0	118.1	53.9	0.234	134	80:C_2	159.1	165.1	141.4	161.9	159.0	78.8	0.272
66	153:C_1	121.3	116.2	105.5	113.4	96.5	75.8	0.106	135	85:C_1	174.3	165.7	147.7	159.9	145.8	101.5	0.095
67	55:C_2	122.2	116.7	107.4	104.9	100.8	88.4	0.061	136	98:C_1	171.9	166.0	147.3	157.9	142.2	109.3	0.048
68	46:C_2	107.8	117.6	117.4	121.6	118.8	95.1	0.189	137	150:D_2	165.0	169.1	147.1	163.6	176.8	84.2	0.342
69	138:C_1	97.1	118.6	114.6	121.1	112.3	79.3	0.214	138	9:C_2	177.5	171.2	158.7	165.2	182.2	122.5	0.034
139	78:C_1	167.8	171.9	150.1	167.0	153.9	88.4	0.118	164	50:C_s	190.8	211.5	182.8	193.0	205.6	133.9	0.095
140	18:C_1	161.3	173.2	171.5	169.9	174.9	131.5	0.043	165	86:C_1	224.6	211.8	189.8	204.0	198.5	130.4	0.119
141	35:C_1	151.1	173.2	162.4	169.0	163.2	121.5	0.072	166	20:C_1	205.1	214.3	194.4	207.8	200.1	157.3	0.006
142	63:C_1	164.3	173.4	161.8	168.5	163.9	126.0	0.153	167	157:C_2	247.3	216.6	197.2	202.2	174.5	145.5	0.028
143	42:C_2	180.3	175.8	157.5	167.1	161.5	111.0	0.124	168	65:C_1	208.7	219.1	199.5	209.8	193.3	146.2	0.061
144	24:C_1	168.8	176.1	152.2	167.8	174.8	84.6	0.207	169	39:C_1	223.7	223.6	197.0	213.2	216.7	111.6	0.153
145	22:C_1	167.9	176.3	152.2	168.2	180.0	79.2	0.377	170	25:C_1	229.9	227.3	202.5	214.5	213.9	129.2	0.071
146	160:C_1	187.2	176.4	164.2	168.8	143.8	118.4	0.128	171	21:D_2	236.6	229.1	199.5	217.4	232.0	106.1	0.187
147	124:C_2	160.6	178.8	170.8	175.7	161.5	133.7	0.063	172	7:C_1	232.3	230.9	206.5	220.9	226.2	139.8	0.039
148	136:D_3	177.1	178.8	149.9	175.9	173.4	79.2	0.642	173	123:C_1	228.0	233.8	214.7	226.4	212.2	151.7	0.069
149	2:D_3	191.0	179.9	158.9	168.4	200.5	110.9	0.21	174	152:C_1	253.5	238.3	214.5	224.2	201.3	149.6	0.115
150	16:C_1	198.9	180.7	160.0	169.3	166.0	110.1	0.02	175	120:C_1	239.4	240.2	215.7	233.2	228.0	153.6	0.159
151	89:C_s	186.2	180.7	166.7	170.6	151.2	135.4	0.024	176	8:C_s	235.1	241.2	209.8	232.4	247.0	128.4	0.345
152	168:C_2	181.6	182.0	161.2	174.6	151.5	97.2	0.063	177	56:C_1	255.8	255.0	234.4	246.6	222.7	174.2	0.101
153	77:C_1	191.8	183.8	165.3	179.3	168.1	102.8	0.081	178	17:C_1	274.8	257.8	231.5	241.9	225.0	158.1	0.063
154	75:C_1	181.4	184.0	162.0	175.6	159.3	108.2	0.152	179	149:C_{2v}	261.6	263.0	228.0	256.6	260.0	135.5	0.201
155	26:C_1	187.7	185.9	162.5	174.6	166.6	109.8	0.134	180	186:D_2	327.1	283.3	256.0	262.6	226.4	188.2	0.028
156	32:C_1	178.9	188.7	163.5	180.3	196.0	88.4	0.392	181	170:C_s	350.7	310.0	304.8	319.2	283.4	196.6	0.041

TABLE 1 (Continued)

rank sorting (SAM1)	FM:sym	HF/4-31G ΔE kJ/mol	SAM1 $\Delta\Delta H_f$ kJ/mol	PM3 $\Delta\Delta H_f$ kJ/mol	AM1 $\Delta\Delta H_f$ kJ/mol	MNDO $\Delta\Delta H_f$ kJ/mol	MM $\Delta\Delta H_f$ kJ/mol	HMO band|β|
157	*122:*C_2	214.1	189.8	180.0	188.9	187.9	142.3	0.095
158	*62:*C_1	203.8	193.2	175.5	188.6	178.5	123.1	0.115
159	*37:*C_1	188.6	193.3	176.1	185.3	176.2	122.2	0.187
160	*71:*C_1	203.9	197.0	174.5	189.3	178.7	125.1	0.032
161	*58:*C_1	191.7	200.1	196.3	198.3	188.0	128.7	0.082
162	*52:*C_2	205.4	203.3	186.5	197.4	189.6	129.8	0.127
163	*81:*C_s	215.5	206.0	183.2	194.6	173.8	125.1	0.02
182	*111:*D_2	365.1	339.2	298.3	323.4	330.3	187.4	0.109
183	*48:*C_2	387.1	365.7	327.7	356.1	355.0	210.1	0.215
184	*110:*C_{2v}	378.1	388.5	334.8	375.8	385.0	181.0	0.302
185	*148:*D_2h	393.5	393.1	340.5	380.9	391.4	188.7	0.347
186	*187:*D_{6d}	488.8	424.3	370.6	395.8	357.6	218.6	0
187	*33:*D_{3h}	495.7	520.6	446.5	501.3	516.6	222.3	0.632



183:D_2 *181:*C_2

185:D_{6d} *144:*C_1

145:C_1 *146:*C_s

Figure 1. Six selected cage structures of C_{96} IPR isomers.

TABLE 2: Relative Energies and HOMO−LUMO Gaps[a] for Low-Energy C_{96} IPR Isomers

FM:sym	B3LYP/6-31G	HOMO−LUMO	HF/4-31G	SAM1
183:D_2	0.0	1.62	0.0	0.0
181:C_2	4.8	1.43	54.9	73.6
144:C_1	5.8	1.60	38.9	63.6
145:C_1	9.8	1.46	31.4	51.3
182:C_2	13.7	1.38	71.4	73.2
146:C_s	19.5	1.58	50.8	73.7
142:C_2	26.3	1.52	56.5	68.4
176:C_2	28.4	1.53	41.2	47.7
130:C_1	30.6	1.54	67.2	58.2
47:C_1	35.6	1.56	62.4	61.8
116:C_1	36.1	1.38	62.7	63.8
132:C_2	36.4	1.61	53.4	65.3
175:C_1	36.5	1.35	79.7	78.9
185:D_{6d}	42.7	1.03	34.9	18.3
143:C_1	42.7	1.39	69.0	77.9
127:C_2	42.9	1.51	38.9	49.1
128:C_1	50.1	1.81	46.9	63.7
43:C_1	51.5	1.45	45.9	50.2
131:C_1	54.4	1.58	67.2	78.5
125:C_1	55.6	1.55	72.7	79.4
14:C_2	55.9	1.15	38.9	49.2
109:D_2	57.7	1.67	44.0	46.1
102:C_1	61.0	1.78	56.6	69.3
107:C_1	64.1	1.80	54.2	64.0
82:C_2	66.8	1.29	81.8	77.2
104:C_1	70.2	1.40	64.7	81.9
96:C_2	79.3	1.31	58.4	67.9
5:C_1	93.8	1.88	61.0	73.5
1:D_2	120.2	2.24	83.4	73.2
3:D_{3d}	122.1	2.17	93.5	75.5

[a] Relative potential energy (0 K) ΔE (kJ/mol) (B3LYP/6-31G, HF/4-31G, and SAM1); HOMO−LUMO gap (eV) at the B3LYP/6-31G level of theory.

K. There is, however, a structure 145:C_1 with a steady increase (though rather modest) that eventually overcomes 183:D_2 from 2200 K. As shown in Figure 2, there are also some small but nonnegligible relative populations for two C_1 structures (143:C_1 and 175:C_1). Figure 3 indicates some relative concentrations for lots of minor isomers. Next to 143:C_1 and 175:C_1, the local relative populations related to fullerene-formation temperatures in Figure 3 can be read as such a sequence: 146:C_s, 176:C_2, 172:C_1, 182:C_2, and so on. Clearly enough, two higher-symmetry species 185:D_{6d} (ranked the second-lowest energy at both SAM1 and PM3 levels) and 109:D_2 (the third-lowest-energy isomer at both SAM1 and PM3 levels) remain very small fractions (each having a maximum of ~0.2%), and another higher-symmetry species 3:D_{3d}, which is located relatively high in energy above the system's ground state (122 (B3LYP); 94 (HF); 83 (SAM1) in kJ/mol, respectively), is completely unfavorable and negligible at all temperatures.

Achiba et al. have recently reported their ^{13}C NMR observations[21] for C_{96} fullerenes. According to their results, the isomeric abundance should decrease along a sequence for the top 10 species: C_1 (four isomers), C_2 (three isomers), C_s, D_2, and D_{3d} (though no concentration ratio is yet given and further development is, in principle, possible). As shown in Figures 2 and 3, the HF/4-31G evaluations of the equilibrium isomeric composition at some moderate temperatures related to fullerene formation predict the 10 most-populated species in a comparable stability sequence: C_2, C_1, D_2, C_1(× 3), C_s, C_2, C_1, and C_2. It is obvious that the computed data match the observed data quite well (only with one exception of D_{3d}). Although no method can really reproduce the complete 10-membered observed set, the achieved theory−experiment correspondence on such a large IPR fullerene system, C_{96}, is nontrivial and encouraging. Actually, it is turned out that the 181:C_2 structure becomes the second lowest in energy in the B3LYP/6-31G treatment (as shown in Table 2); other species (144:C_1, 145:C_1, 175:C_1) also have lower B3LYP/6-31G separation energy over that of the ground state 183:D_2. Overall, the B3LYP/6-31G energetics does not favor the 3:D_{3d} isomer. Generally, the remaining discrepancy between experiment and computation can be resolved by the further improvement of computations and their juxtaposition with a refined experimental finding if possible. There are obviously several degrees of freedom to examine that may

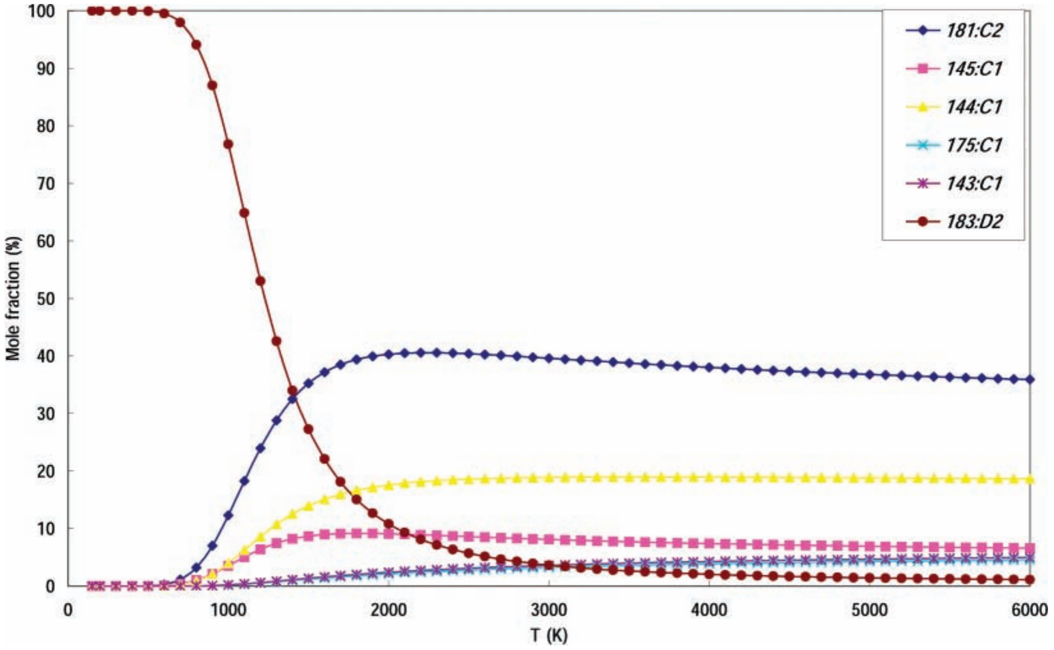


Figure 2. Relative concentrations of the most important C_{96} IPR isomers—global view.

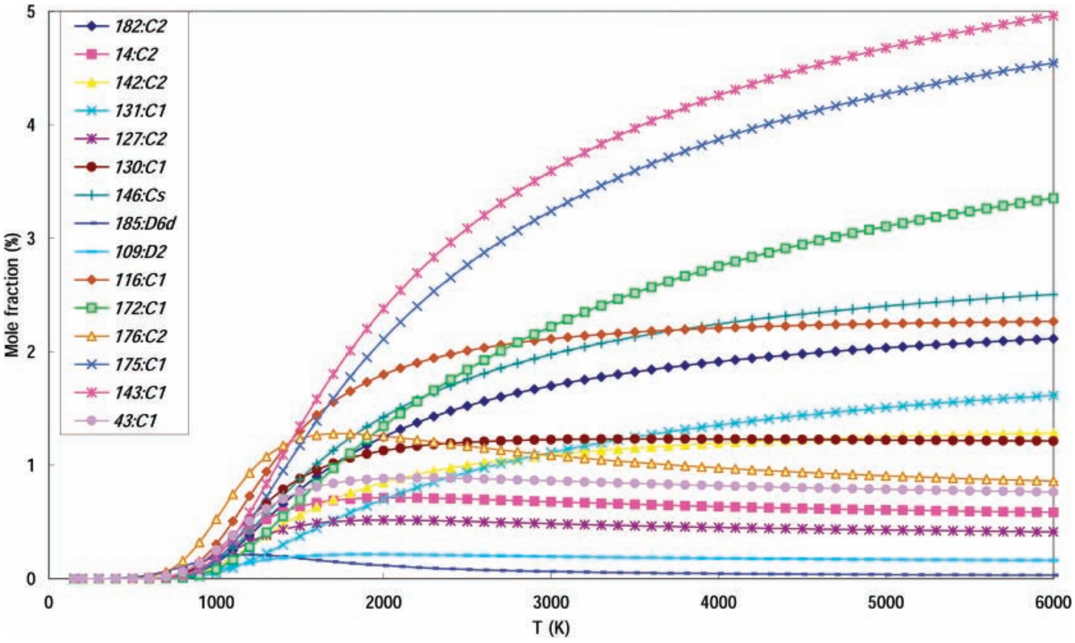


Figure 3. Relative concentrations of some less-populated C_{96} IPR isomers—local view.

enhance the quality of the computed terms. In principle, such developments are only a question of available computing power.

Conclusions

In this paper, the complete IPR set[38] of fullerene C_{96} has been, for the first time, investigated systematically by various theoretical chemistry approaches. Seven different levels of theory agree in predicting the 183:D_2 structure as the lowest-energy species among 187 IPR isomers. Our study indicates that the isomeric separation energies can in some cases be quite method-sensitive and vary dramatically with different methods in relative energy ordering. The HF/4-31G evaluations of the equilibrium isomeric composition predict some lower-symmetry species (181:C_2 and 144:C_1) to be more thermodynamically stable than 183:D_2 at higher temperatures. The computational results of entropy effects suggest that at least the four major abundant isomers (C_2, C_1, D_2, and C_1) should be assigned preferentially in the experiment if sufficient amounts of pure fullerene samples are available and agree reasonably with the preliminary experimental observation.[21]

Our results provide more evidence that C_{96} belongs to the family of isomeric fullerenes with a substantial entropy-contribution role. As entropy effects in the isomeric fullerene system are taken into account, the stability behavior of the entropy—enthalpy interplay can be explored, and myriad thermodynamically favored isomers are preferentially shown. The reported considerable thermal effects on the C_{96} IPR relative stabilities result from the complex interplay between rotational, vibrational, and potential energy terms and chirality factors. Our treatment, however, deals with the inter-isomeric thermodynamic equilibrium that may exist in experiment. There may also be another interpretation, viz., that although the inter-isomeric equilibrium is not yet reached the relative nonequilibrium isomeric concentrations do not differ significantly from the equilibrium concentration. It is still difficult to clarify the degree to which this presumption is satisfied in each particular experiment. Some experiments[39,40] indicate that such equilibrium requires sufficiently high He pressures and high temperatures in the process of fullerene formation. Moreover, there may be some as-yet unexplored catalytic effects[41] involved.

There is a subsequent, more general (and also more important) task: relative stabilities of carbon cages with different dimensions or sizes (i.e., nonisomeric fullerenes with distinct stoichiometries). In the most general form, this relative-stability problem can be treated as a complex kinetic scheme described by a very large number of kinetic differential equations. Obviously, further exploration of the general rules behind the relative stabilities of isomeric and nonisomeric fullerenes is to be expected.

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