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Competition between Even and Odd Fullerenes: C_{118}, C_{119}, and C_{120}

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Calculations of the relative stability of C_{118}, C_{119}, and C_{120}, pure carbon species with both trivalent and tetravalent atoms, show the interplay between the various forms of molecular carbon and under which conditions they are thermodynamically accessible. The analysis is performed by quantum chemical screening of all the classical fullerenes with isolated pentagons (8148 isomers for C_{118} and 10774 isomers for C_{120}) for comparison with the most stable structure of C_{119} and C_{60} dimer. While fullerenes show similar trends of stability over a range of temperatures, introduction of sp^3 carbons profoundly affects them. It is concluded that very high synthetic temperatures may favor formation of clusters with tetravalent atoms.

Introduction

Pure carbon molecules exist in a variety of structures whose atoms have hybridizations that range from sp,[1] to sp^2,[2] and even, in some cases, to sp^3.[3] The sp hybridization appears in the low nuclearity regime, while sp^2 hybrids are formed when more than 20 atoms are present[4] and, initially, take the form of bi- and poly-cyclic rings to turn into fullerenes for larger numbers of atoms. These small clusters do not show marked preference toward even or odd numbers of atoms and appear in the interstellar media and the electric arcs used in the preparation of fullerenes. In the case of fullerenes, production is achieved at ∼2100 K in flames.[5] Somewhat higher temperatures are used in experiments in which carbon cylinders in a He atmosphere at 150 kPa are subjected to inductive heating leading to sublimation of carbon at 2800 K.[6] The standard electric arc production of fullerene reaches temperatures well above 4300 K.[7] Different temperature regimes may lead to thermodynamic distributions of isomeric carbon species that are very different from the relative stabilities of the carbon forms at either 0 K or room temperature. At high temperatures, atomic, diatomic, and tri-atomic carbon are the most abundant species. The details of the aggregation and possibly equilibration between lighter and heavier isomers are not known. It is certain, however, that the clusters start with little or no preference in terms of even or odd numbers of sp hybridized carbon atoms since nearly all the isomers from C_4 to C_{13} have been detected experimentally.[1] The abundance of the isomers is governed by the high-temperature free energies, ΔG, of the molecules rather than their electronic energy.[1,8] In the fullerene region,[1,4] even-numbered species with sp^2-like hybridization, dominate. From C_{60} to C_{84}, the arc discharge generates the thermodynamically most stable species for each number of atoms. At higher masses, the assembly occurs in the kinetic regime and generates nanotubes. To find odd-numbered carbon species with sp^3 carbons, such as C_{119}, it was necessary to resort to an indirect pathway of production in which two fullerenes coalesce after removal of a single atom. This assembly may be triggered when C_{60} first forms $C_{60}O$, then expels the stable CO molecule, and finally reacts with another C_{60}.[9] The relative stability of the tri- and tetra-valent systems, i.e., in this context even- and odd-numbered clusters, has not been investigated theoretically before. One reason is that the competition between these species occurs around 120 atoms and the structures of the basic fullerenes C_{118} and C_{120} are not known. The issue of the relative stability in the conditions of assembly of odd- and even-numbered carbon clusters bears on the actual mechanism of assembly. Since only even-numbered species are detected in the fullerene region, a similar stability of both types of clusters would implicitly require that (a) no equilibration occurs (despite the high temperatures) and (b) the structural differences leading to one or the other type of system are the driving force for the growth. It is therefore the purpose of this work to provide chemical insight into the temperature-dependent stability of carbon species in the critical area of cluster sizes about twice that of Buckminsterfullerene. To accomplish this, it was necessary to locate the most stable structures of all-carbon molecules between 118 and 120 atoms. The electronic energy calculations presented here are supplemented with further calculations of the temperature-dependent free energy of the most stable systems.

Background

The Isomers. A fully unconstrained search of all the carbon isomers with 118, 119, and 120 atoms is impossible because of the very large number of possible structures. Filtering principles must therefore be used. One can start with the even-numbered clusters and safely assume that the most stable structures correspond to classical isolated-pentagon-rule (IPR) fullerenes. These cages contain 12 isolated pentagons and $n/2-10$ hexagons, where n is the number of atoms. Complete sets of these isomers were generated using the spiral algorithm.[10] It is not claimed that the set of N IPR fullerenes with isolated pentagons coincide with the N most stable isomers. Overlap in energy between the least stable IPR fullerenes and the best cages with abutting pentagons is to be expected. Previous work, however,[11] suggests that the structures within 70−150 kJ mol^{-1} of the global minimum should all fall within the isolated-pentagon set as this is the estimated energetic cost of a single pentagon

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TABLE 1: Summary of the Distribution of the IPR Isomers of C_{118} and C_{120}[a]

	C_{118}	C_{120}
N	8148	10774
ΔE_{1n}	799	999
N_{10}	1	3
N_{100}	507	590
H	22.98−23.84	23.2−24.4
A	0.176−4.151	0.112−6.988

[a] N is the total number of IPR isomers generated with the spiral algorithm, ΔE_{1n} is the range of DFTB energies, kJ mol^{-1}, spanned by the isomers N_{10} (N_{100}) is the number of isomers in the first 10 (100) kJ mol^{-1} of the range. H and A are the ranges of the second moment of hexagon adjacency (eq 1) and the asphericity (eq 2), respectively.

adjacency. A total of 8148 and 10774 isomers were generated by the spiral algorithm and optimized for C_{118} and C_{120}, respectively. They are identified in what follows by their position in the spiral lexicographic order as xxx:yyyy, with xxx the number of carbon atoms. Other structures considered for comparison were the C_{60} dimer and the optimal structure of C_{119} as found in previous studies.[3] Thus, nearly 20000 molecules are involved in this study of the interplay between tri- and tetra-valent carbon.

The Computational Model. Initial Cartesian coordinates for the fullerenes were generated for each of the IPR isomers from the topological coordinates.[12] A full geometry optimization was carried out for each isomer using a tight binding model based on density functional theory parameters.[13] As one of the referees pointed out, the acronym for this model, DFTB, is a somewhat of a misnomer but its use has been so general that we do not modify it to avoid further confusion. The model makes use of general, two-particle, short-range repulsive potentials that are derived in an almost parameter-free manner using ab initio results for small reference systems. It was designed to reproduce the results of local density approximation calculations and has been used for hydrocarbon molecules, small carbon clusters, C_{60}, and bulk systems.[13] Extensive testing and comparison with other models is reported in ref 11b. In the case of the C_{60} dimer, the DFTB model was found to give a reasonable binding energy of 0.3 eV compatible with experiment and higher-level methods as HF and GGA-DFT,[3c] whereas semiempirical MNDO-type methods fail to describe the [2 + 2] cycloaddition bridge correctly and LDA gives poor binding energies due to its overbinding [see Table 1 in ref 3i] For C_{119}, DFTB relative energies agree with those of other methods and its calculated ^{13}C NMR spectrum is in excellent agreement with experiment.[3h] Importantly, at the end of the optimization runs, the identity of the isomers was checked through their bond connectivity.

Results and Discussion

Fullerene and fullerene derivatives can coexist with number of atoms 118, 119, and 120 and can contain tri- and tetra-valent atoms. Of the tetravalent carbon-containing species, C_{119} is built from the coalescence of two C_{60} units minus an atom removed chemically in the form of a stable CO molecule, while the C_{60} dimer results from the 2 + 2 addition of two hexagon−hexagon bonds. To make a comparison between the various forms of carbon, the most stable structures of C_{118} and C_{120} are required. Table 1 gives a summary of the calculations. The optimized IPR structures cover 799 (999) kJ mol^{-1} for C_{118} (C_{120}) and in the first 10 kJ mol^{-1} above the minimum energy fullerene only 1 (3) isomers are found. Widening this window to 100 kJ mol^{-1} brings in more than 500 isomers for both nuclearities. Figures 1 and 2 show histograms of the energy distributions of the isomers and their typical Poisson-like shape.

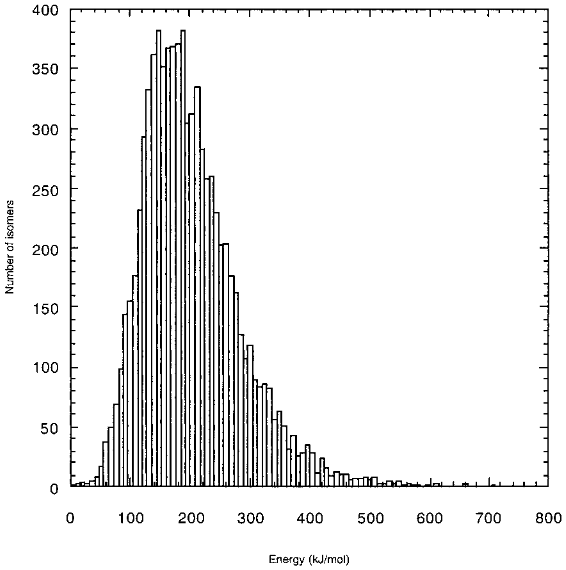


Figure 1. Histogram of the relative energies of the C_{118} IPR isomers.

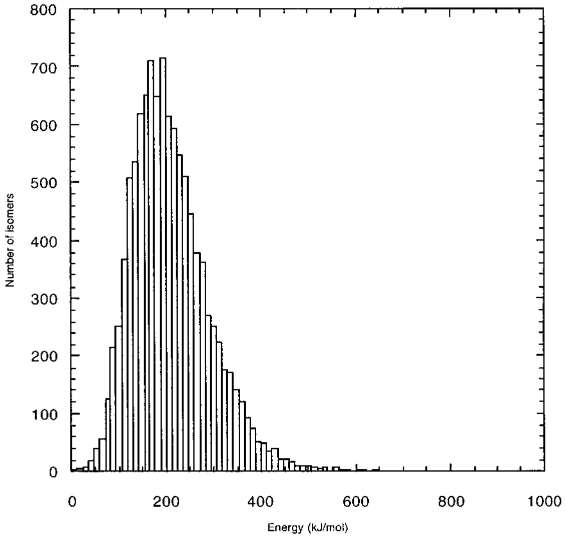


Figure 2. Histogram of the relative energies of the C_{118} IPR isomers.

Necessity for a Full Computational Screening of All the Isomers. The need to screen quantum chemically the entire sets of the classical C_{118} and C_{120} fullerene isomers becomes evident if one realizes the difficulty of identifying reliably the most stable species using simple graph theoretical and geometrical arguments. Two gauges of stability have been tried. The first is a graph model of strain, the second is general. Specifically, the first approach is connected with the hexagon-neighbor rule, HNR, which emerged from calculations on the set of 24 IPR C_{84} fullerenes performed by Raghavachari.[14] The idea behind the HNR is that in a stable fullerene the hexagons should have environments that are as similar as possible, to spread the steric strain evenly. If h_k is the number of hexagons with k hexagonal neighbors, the HNR then requires minimal spread in $\{h_k\}$, the hexagon-neighbor signature, which is equivalent to minimization of a function:

$$H = \frac{\sum_{k=0}^{6} k^2 h_k}{\sum_{k=0}^{6} h_k} \tag{1}$$

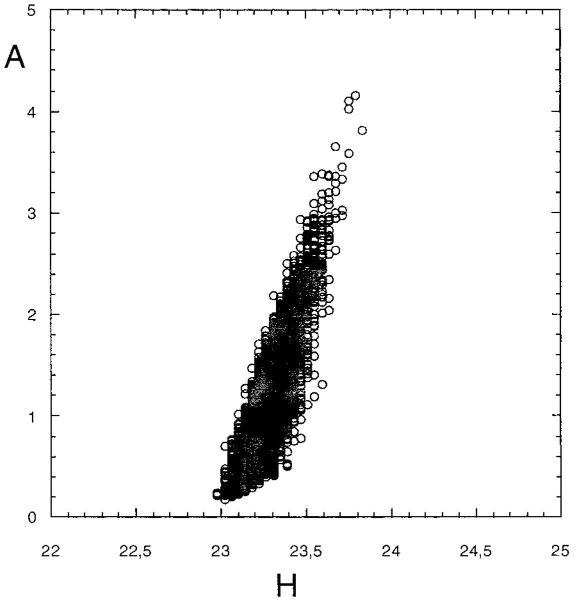


Figure 3. *H* vs *A* for C_{118}. The correlation coefficient for the linear regression is $r = 0.834$.

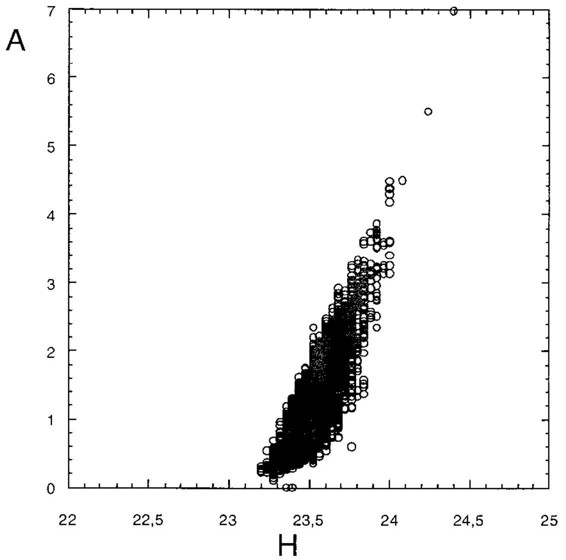


Figure 4. *H* vs *A* for C_{120}. The correlation coefficient for the linear regression is $r = 0.831$.

the normalized second moment of the signature which represents a mean square coordination number for the hexagons. Decrease in this quantity has been found to correlate roughly linearly with relative stability for the 1812 non-IPR C_{60} isomers[15a] and to pick out the best few IPR isomers of C_{116}.[15b] A more geometrical approach used to assess the stability of the cages is through their asphericity, *A*,

$$A = \sum_i \frac{(r_i - r_0)^2}{r_0^{\,2}} \tag{2}$$

where r_i is the radius distance of atom *i* from the cage center of mass, and r_0 is the average radius. In previous work, $(BN)_x$ clusters showed some trend to higher stability for smaller values of A.[16] The range of asphericity for the C_{118} and C_{120} isomers is given in Table 1. Figures 3 and 4 show the quasi-linear relation between *H* and *A*. The correlation coefficients, *r*, are sufficiently close to unity to imply a similarity between the two parameters.

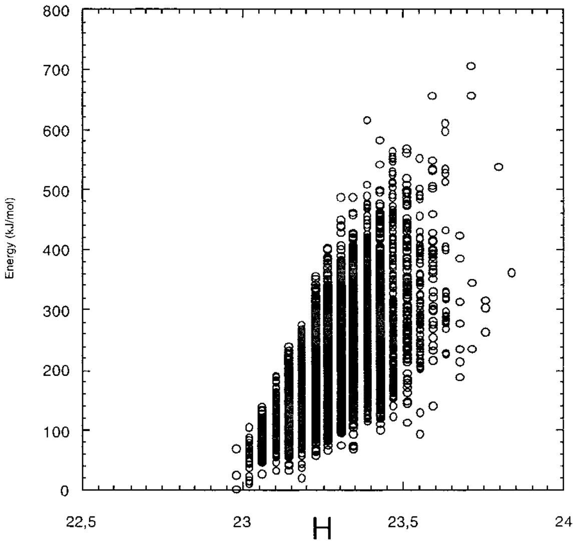


Figure 5. Electronic energies as a function of *H* for C_{118}. The relation is non linear, the correlation coefficient for the linear regression is $r = 0.659$.

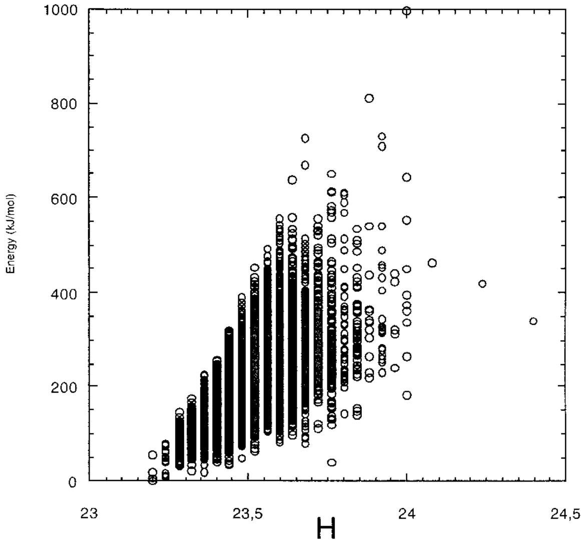


Figure 6. Electronic energies as a function of *H* for C_{120}. The relation is non linear, the correlation coefficient for the linear regression is $r = 0.644$.

The trends of energy versus *H* or *A* are shown in Figures 5−8. The relations deviate markedly from linearity with correlation factors never reaching 0.7. Importantly, *H* successfully predicts the most stable C_{118} and C_{120} isomers, as it did for C_{116}.[15b] To prove further the efficacy and predictive power of either quantity for fullerene stability, a systematic comparison of the calculated energies with the *H* and *A* values is required. First one must set a bracket for the structures of interest: 50 kJ mol^{-1} appears to be a fair range, likely to be twice the accuracy of the computational model. Inspection of the *H* values for the C_{118} (C_{120}) isomers within this set bracket gives a largest value of *H* equal to 23.183674 (23.76). It is unfortunate for predictive purposes that 2502 (10627) cages fall inside this value. Analogously, inspection of *A* in the same initial energy range gives a largest value of 0.733923 (0.897991) which include 2280 (4332) cages. The trends of energy and *H* or *A* make these two parameters of partial predictive value to identify the most stable fullerenes, and they should always be accompanied by a quantum chemical calculation.

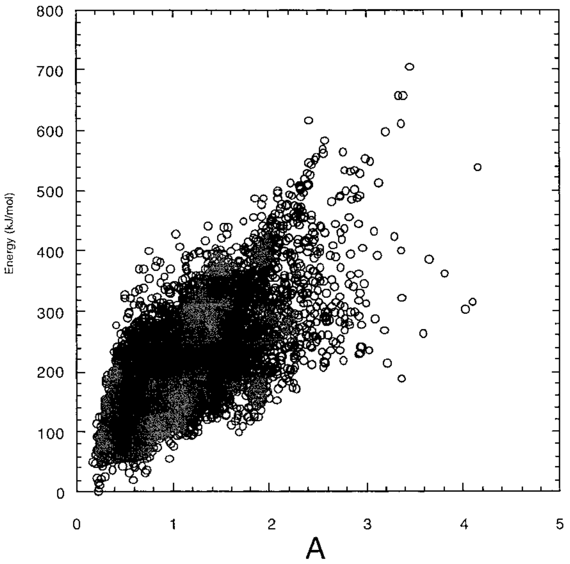


Figure 7. Electronic energies as a function of *A* for C_{118}. The relation is non linear, the correlation coefficient for the linear regression is $r = 0.692$.

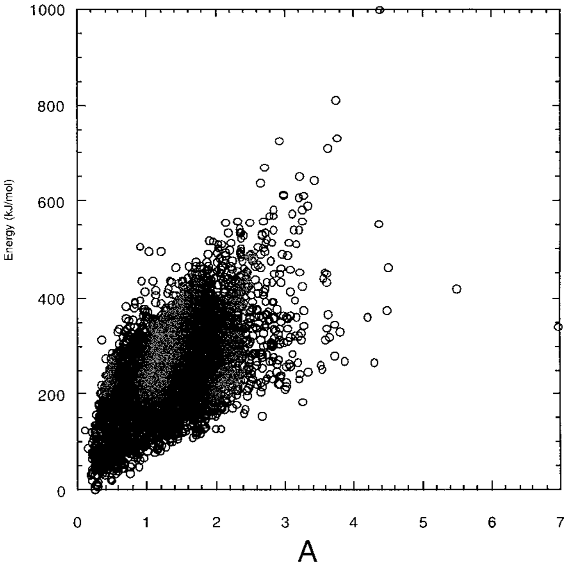
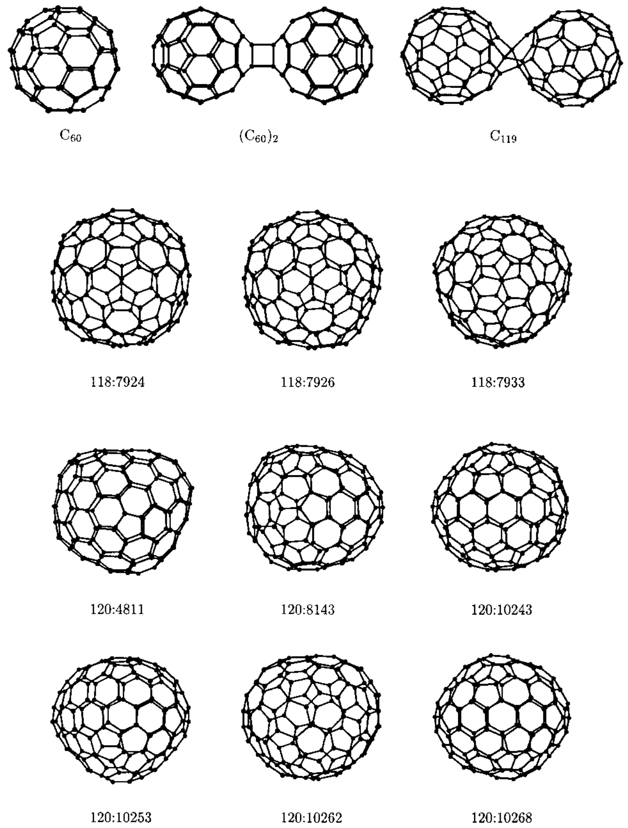


Figure 8. Electronic energies as a function of *A* for C_{120}. The relation is non linear, the correlation coefficient for the linear regression is $r = 0.685$.

The Stability. Table 2 shows the binding energies per atom of the most stable C_{118}, C_{120}, C_{119} and $(C_{60})_2$, see also Figure 9.


C_{60} $(C_{60})_2$ C_{119}

118:7924 118:7926 118:7933

120:4811 120:8143 120:10243

120:10253 120:10262 120:10268

Figure 9. Most stable structures of C_{118}, C_{119}, and C_{120}.

In terms of electronic energy, C_{60} is less stable than the higher fullerenes because of the higher curvature of its cage. Upon doubling the size of classical fullerenes, the increase in stability is ~14 kJ mol^{-1} per atom. C_{119} and $(C_{60})_2$ are nearly as stable, or unstable, as C_{60} itself. Zero-point energies do not modify the picture.

However, inclusion of the temperature-dependent vibrational contributions to the free energy does modify the trends. In the harmonic approximation, such contributions are obtained as $\Delta G_T = -k_BT \ln Q$, with Q the product of the vibrational partition functions of the individual normal modes, as such they refer to gaseous carbon. In agreement with previous calculations,[17] on increasing the temperature, small variations in stability are observed for the various fullerenes, but these are probably within the error bars of the computational model. As the temperature approaches the region of fullerene production, the gap in stability between C_{60} and higher isomers widens and the larger fullerenes increase in relative stability (and in a thermodynamic regime,

TABLE 2: Energetics of the Fullerenes and Other Carbon Clusters[a]

	S	E_b	ΔG_{298}	ΔG_{1000}	ΔG_{3000}	ΔG_{5000}	ΔE	ZPE	ν
C_{118}:7933	C_2	−14.00	3.58	−5.39	−75.88	−180.73	0.57	17.86	173
C_{118}:7924	C_1	−13.91	3.68	−5.27	−75.72	−180.53	0.66	17.87	174
C_{118}:7926	C_1	−13.88	3.71	−5.25	−75.74	−180.59	0.59	17.86	173
C_{120}:10253	C_2	−14.32	3.26	−5.73	−76.31	−181.26	0.46	17.86	169
C_{120}:4811	C_s	−14.15	3.45	−5.52	−76.03	−180.89	0.43	17.88	162
C_{120}:8143	C_1	−14.17	3.40	−5.58	−76.14	−181.06	0.39	17.86	166
C_{120}:10243	C_1	−14.24	3.35	−5.64	−76.19	−181.11	0.58	17.87	170
C_{120}:10262	C_2	−14.16	3.40	−5.60	−76.21	−181.19	0.35	17.85	170
C_{120}:10268	C_2	−14.22	3.36	−5.63	−76.20	−181.13	0.44	17.86	168
C_{119}	C_2	0.10	17.47	8.43	−62.46	−167.76	1.63	17.69	38
$(C_{60})_2$	D_{2h}	−0.24	17.10	7.97	−63.17	−168.71	1.64	17.71	20
C_{60}	I_h	0.00	17.62	9.59	−57.45	−158.28	1.93	17.71	273

[a] The quantities tabulated for the most stable fullerene isomers at C_{118} and C_{120}, the odd-numbered species C_{119}, the bridged dimer $(C_{60})_2$ and C_{60} itself are: the symmetry group, S, electronic binding energy per atom, E_b, temperature-dependent free energy ΔG, HOMO−LUMO gap ΔE (in eV), zero-point energy, and lowest vibrational wavenumber ν. Energy data are in kJ mol^{-1}, T is in kelvin, and ν in cm^{-1}.

abundance) which is ultimately an entropic effect of the presence of lower frequencies in the larger cages. For both C_{119} and $(C_{60})_2$, the ΔG's parallel those of the classical fullerenes despite never reaching them. Since both $(C_{60})_2$ and C_{119} can be obtained by small reaction pathway deviations in the last steps of assembly of C_{60}, in conditions that do not favor the formation of larger cages, C_{60} could be displaced by these two derivatives ($(C_{60})_2$ is probably not very stable at high temperatures because of the weak intercage bonds). Importantly, the calculated frequencies may be overestimated and, as a consequence, the onset of the higher stability of C_{119} will actually occur at lower temperatures.

Conclusion

Factors in the competition between fullerene structures and related carbon clusters in the midrange of cluster size have been assessed in the calculations of the electronic energy and free energy for the most stable isomers of C_{118}, C_{119}, and C_{120}. The size range is the first where both types of structures may be concurrently present. While the C_{119} structure has been determined, little previous information was available on C_{118} and C_{120}. Screening of all 8148 C_{118} and 10774 C_{120} classical fullerenes yielded their most stable structures. As expected, higher fullerenes are intrinsically more stable than C_{60}, regardless of temperature. However, structures derived from clustering of C_{60} also become more stable than C_{60} itself as the temperature increases and may provide a pathway for depletion of Buckminsterfullerene yields. Absence of these in the soot produced by arc discharge would be unsurprising for $(C_{60})_2$ in view of the low energy barrier to dissociation. Absence of C_{119} would be more significant in view of the stronger binding of this species. If C_{119} is not found, it would imply that even at high temperature, evaporation or addition of a single carbon from an almost complete C_{60} cage does not occur. This, in turn would lend further, general support to the growth mechanisms that have been proposed in the past for fullerenes[18] and, in particular, to the C_2 insertion and extrusion mechanism.

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