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Propensity Rules for the Stability of Odd-Numbered Fullerenes: A Semiempirical Proposal

E. Albertazzi[†] **and Francesco Zerbetto***[,‡]

Contribution from Lamel, Consiglio Nazionale delle Ricerche, Via Gobetti 108,
40129 Bologna, Italy, and Dipartimento di Chimica "G. Ciamician", Università di Bologna,
V. F. Selmi 2, 40126 Bologna, Italy

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Abstract: The structures of C_{119} and C_{129}, the two lowest odd-numbered fullerenes, are investigated by semiempirical quantum chemical calculations. In the process, the use of a recently proposed parametrization for a tight-binding Extended-Hückel model is validated to study the relative stability of fullerenes. Three general routes for the generation of the structures of odd-numbered fullerenes are described and used to generate systems that can be loosely characterized as having either a four-membered ring or a patch of adjacent pentagons, or a set of multiple connections between the cages of the pristine fullerenes. The structures of the six isomers of C_{119} obtained in this manner are optimized and it is confirmed that the most stable isomer of C_{119} has C_2 symmetry and forms three bonds between the C_{59} and the C_{60} moieties. By analogy with C_{119}, 56 structures of C_{129} are generated and their geometries are optimized. As in the case of C_{119}, it is found that the most stable isomer of C_{129} can be formed both from the reaction of C_{59} with C_{70} and from the reaction of C_{60} with C_{69}. On the basis of the calculation, five propensity rules for the stability of odd-numbered carbon clusters are proposed and a source of exception is discussed.

I. Introduction

If one defines fullerenes as molecules whose frames describe close polyhedra, the simple Euler rule predicts that the number of their atoms, *n*, must be even and that they bind to share 12 pentagons and ($n/2 - 10$) hexagons. In recent years, this rule has been followed by others that account in more detail for the physical chemistry of carbon and by powerful algorithms that can generate all the possible structures of these species.[1] Despite the stringent requirement that fullerenes have an even number of atoms, McElvany et al. reported the detection of $C_{11}{}^{9}$, C_{129}, and small quantities of C_{139}.[2] This result implies that a class of odd-numbered fullerenes exists which can be described as the coalescence of any two fullerenes minus one carbon atom. To account for the experimental observations, the authors proposed that these species are produced through an oxidative process which yields CO (or CO_2) plus an open carbon cage with a missing atom which, in turn, reacts with another fullerene to produce an odd-numbered fullerenic aggregate. This suggestion has since found experimental support.[2b] Cautiously, they suggested that a possible scheme for attaching C_{59} to a fullerene would join the three nearest neighbors of the "missing" carbon to three atoms of another intact fullerene. To the best of our knowledge, no further detail was provided. Subsequently[3] came the proposal that, after removal of the carbon atom, two of its former nearest neighbors would react with one another to form a four-membered ring located in the C_{59} fragment. Such a ring, together with its environment, would endow the molecule with an additional source of stability since it bears resemblance to the stable molecule of biphenylene. The remaining carbene would then react with another fullerene to form a spirane. This structure should be stable and satisfies the basic requirement that each of the two fullerenic moieties has an even number of π carbon atoms. In further work,[4] Adams et al. used molecular dynamics based on the Harris functional to propose that C_{119} has C_2 symmetry, three four-coordinated atoms, and two seven-membered rings.[4] To date, no direct comparison has been provided between the energy of these two structures.

In this work, we investigate the structures of C_{119} and C_{129}, two prototypical odd-numbered fullerenes. We select these molecules both because they were observed experimentally and because they can be thought of as the smallest homoderived and heteroderived odd-numbered fullerenes. Our purpose is 3-fold: first, we would like to lend further support to either one of the two previously proposed structures of C_{119} or, if possible, obtain a novel one; second, we would like to obtain the most stable structure of C_{129}; finally, through a systematic exploration of the isomers of C_{119} and C_{129}, we try to develop a set of propensity rules that should be of assistance in the determination of the structures of any odd-numbered fullerene.

Because of the size of the molecules and the number of isomers studied, it is not practical to use ab initio methods for full geometry optimization of the several possible structures of C_{119} and C_{129} that one may devise. We therefore decided to proceed in steps: in section II, we briefly show that a recently proposed tight binding model can be used to study the relative stability of fullerenes. In section III, we present the procedure by which the isomers were generated and the results obtained by our study of C_{119} and C_{129}. We back up the tight binding results with MNDO calculations for C_{119}. In section IV, we conclude our work proposing a set of propensity rules for the formation of odd-numbered fullerenes.

II. Computational Background

In this work, we use two unrelated semiempirical quantum chemical models. The first, which has been used to distraction in fullerene theoretical studies[5] is the MNDO method.[6] The second is a tight-binding Extended-Hückel model whose parametrization has been

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Table 1. Tight-Binding Relative Energies of the 24 Isomers of C_{84} Which Satisfy the Isolated Pentagon Rule

isomer	energy (eV)	isomer	energy (eV)	isomer	energy (eV)
1	1.668	2	1.051	3	0.753
4	0.489	5	0.441	6	0.484
7	0.570	8	0.474	9	0.611
10	0.495	11	0.259	12	0.281
13	0.573	14	0.503	15	0.262
16	0.294	17	0.634	18	0.583
19	0.317	20	1.135	21	0.327
22	0.000	23	0.007	24	0.310

recently proposed for accurate and fast geometry optimization.[7] The rationale for its use in the present context is 3-fold: first, and most practical, our implementation makes it about ten times as fast as the MNDO method and therefore allows us to explore a large number of isomers of C_{119} and C_{129}. Second, one cannot expect an accurate geometry optimization without a reasonable potential energy surface, at least in the neighborhood of the minima. The implication that the relative positions of such minima are accurate requires a modicum of testing. Third, the present tight binding model is more general than most models of this type whose main use is geometry optimization or molecular dynamics in that it is based on Slater atomic orbitals and is already parametrized also for hydrogen, nitrogen, oxygen, and fluorine.[7]

Before using the tight-binding model to assess the relative stability of odd-numbered fullerenes, however, we thought it necessary to devise a few tests to validate the method for this particular purpose. The tests we selected were the following: (1) comparison of the energies of the 24 isomers of C_{84} that satisfy the isolated pentagon rule, (2) comparison of the energies of I_h C_{60}, i.e., the experimentally observed isomer, and its closest energetic neighbor, and (3) comparison of the energies of the four isomers of $C_{60}O$.

The tests were contrived to fully cover all the aspects of the possible structures of odd-numbered fullerenes. The first test verifies the ability of the model to assess correctly the interplay of the energetics of pentagons and hexagons within the isolated pentagon rule. The second test extends the validation outside such rule. The third test brings in the role of sp^3 carbon atoms in the case, more extreme than the present one, of the presence of a heteroatom.

The tight-binding Extended-Hückel model passed the three tests. In the first test, in agreement with experiment[8] and with other calculations,[9] it found that the isomers of C_{84} known as 22 and 23[10] are the most stable (in the forthcoming IUPAC nomenclature, these isomers are respectively [84-D_2(IV)]fullerene and [84-D_{2d}[II)]fullerene). Remarkably and in accord with other calculations, the two isomers were also calculated to be quasidegenerate. In Table 1, we list the energies of the 24 isomers of C_{84} (the numbering is the same as that used in ref 10). Interestingly, the energy spanned by the isomers is very similar to that obtained in another tight-binding calculation by Ho et al.: 1.668 vs 1.908 eV.[9a] These results indicate that the present model is adequate for treating fullerenes that satisfy the isolated pentagon rule.

In the second test, the energy difference between the two C_{60} isomers with the lowest energies was calculated to be 27.5 kcal/mol. Obviously enough, I_h C_{60}, or isomer 1812,[1,12] was calculated as the most stable isomer. Although no experimental value is available, the energy difference can be compared with Density Functional Theory results that gave 36.8 kcal/mol[11] and with QCFF/PI results that gave 38.7 kcal/mol.[12] It appears that the model can treat fullerenes when pentagon−pentagon adjacencies are present. In particular, isomer 1809 has two such adjacencies.[12] Upon consideration of the results of the first two tests and in the wider context of other calculations, one can conclude that, if anything, the tight-binding Extended-Hückel model tends to underestimate the energy differences between the various isomers.

The third and final test concerned $C_{60}O$. In this molecule, an oxygen atom binds two carbons of C_{60}. In principle, there are four possible isomers of this molecule. Two of them arise from the presence, in C_{60}, of two types of CC bonds: the short, or double, hexagon−hexagon edge and the long, or single, pentagon−hexagon edge. Upon insertion of the oxygen atom, the bond may snap. This yields two further possibilities that bring the count to four isomers. High-level ab initio calculations[13] showed that there are only two isomers and that they are quasidegenerate. The two stable isomers are the true epoxide formed by reacting the short CC bond, which elongates but remains intact, and the isomer in which the oxygen bridges over the long CC bond which is severed. In particular, HF/6-31G* gave an energy difference between the two isomers of 2.2 kcal/mol, Density Functional Theory calculations with DZP basis set yielded an energy difference of 1.1 kcal/mol, while the inclusion of the nonlocal corrections reverted the energy ordering and obtained a 0.5-kcal/mol difference in stability. The tight-binding model yielded an energy difference of 0.4 kcal/mol in favor of the "open" isomer. It therefore appears that the present model can be used to study the relative stability of fullerenes.

III. C_{119} and C_{129}: The Generation of the Isomers

C_{119}. In the previous section, we showed that the use of the tight-binding Extended-Hückel model to study the stability of fullerenes is soundly based. To lend further support to the conclusion, we decided to complement our calculations with some MNDO geometry optimizations. The agreement between these two unrelated models should both put on a firmer basis our results and dispel doubts about the use of the tight-binding method to study odd-numbered fullerenes.

As a first step, we devised three routes for the generation of the isomers. One such route is offered by the structure proposed in ref 3. The gist of that proposal is that removal of a carbon atom leads to three carbenes, two of which react with one another to form a four-membered ring, while the remaining carbene atom reacts with another C_{60} molecule. The process can be made more general. Removal of the carbon atom leads to the "disappearance" of three bonds: one hexagon−hexagon bond and two pentagon−hexagon bonds. The two former hexagon−pentagon bonds can be substituted by a new bond that makes a four-membered ring, alternatively, one of the former hexagon−pentagon and the former hexagon−hexagon bond can be replaced by a bond that forms a five-membered ring (see Figure 1). Notice that in the case of C_{60} and C_{70} the newly formed pentagon will always be adjacent to at least one, but usually two, other pentagons (only removal of one of the twenty carbons above and below the belt of C_{70} and closure to form a pentagon with a carbon of the belt can generate a doublet of pentagons). The pentagon−pentagon adjacency entails a penalty in terms of energy.[12] It is difficult to predict a priori if, in odd-numbered fullerenes, the pentagon−pentagon adjacency penalty is lower than the energy penalty for the formation of a four-membered ring. Both of the new structures have a further carbene atom that can react with a pentagon−hexagon bond or a hexagon−hexagon bond that belong to another C_{60} ball. In this way, one can therefore generate four isomers of C_{119}.

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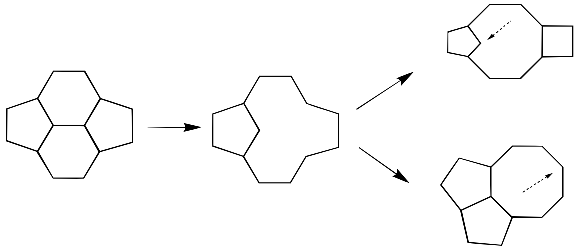

Figure 1. Removal of a carbon atom from a generic fullerene patch destroys three bonds and creates three atoms with dangling valences. Two carbenes can react to form either a square or a pentagon. The remaining carbene is indicated by the dashed arrow.

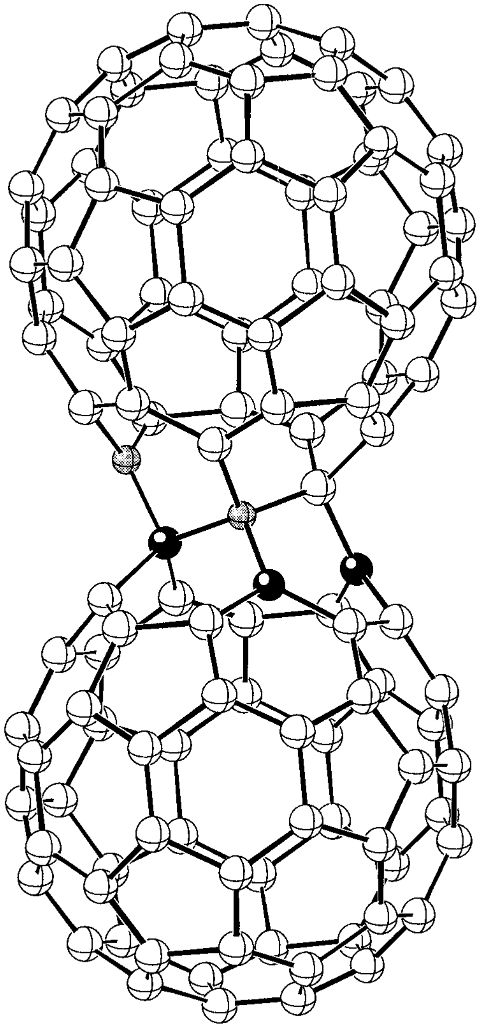

Figure 2. The most stable isomer of C_{119}. The three carbene atoms of C_{59} are represented in black in the lower half, and the two C_{60} atoms whose bond reacts with one of the carbenes are in gray in the upper half.

In ref 4, it was shown that another possibility exists, namely that each of the three carbenes react with another C_{60}. Before comparing the energy of the isomers generated via the formation of the square or the pentagon, one should try and find a general way to obtain the structure of ref 4 and to generate other related structures. As a starting point, we describe a similar isomer obtained by us (vide infra) in some detail. In Figure 2, the isomer is shown: to facilitate the inspection, the three carbene atoms of the C_{59} fragment appear, in black, in the lower half. The two C_{60} atoms, whose bond reacts with a carbene atom, are given, in gray, in the upper half. As in the case of ref 4, the molecule has C_2 symmetry, with one of the former carbenes sitting on the symmetry axis. It is convenient to start the description of the route to this isomer with the addition of one of the carbenes to C_{60}. As usual, there are two possibilities: addition to a pentagon−hexagon edge or to a hexagon−hexagon edge. In the isomer of Figure 2, the reaction goes to the pentagon−hexagon bond—i.e., the single bond—and severs it. This makes the two atoms of the C_{60} moiety trivalent again. The topological arrangement of bonds allows the two remaining carbenes of C_{59} to react with the short—i.e., double—C_{60} bond formed by one of the two formerly bound atoms and by another carbon. The net result is that there are two tetravalent carbons in the C_{60} fragment and one in the C_{59} one. Neither sphere has unpaired electrons and one can no longer recognize which "half" was C_{59} and which C_{60}. The largest ring is seven-membered and the π electron framework is interrupted by a set of three sp^3-hybridized carbon atoms. Along this route, there is a second isomer (also obtained by us) in which one of the carbenes reacts with a hexagon−hexagon edge. This bond does not break and the species therefore contains an inner three-membered ring. The hypothetical process that we are using to describe the isomer formation then goes on. The topological arrangement of the bonds of the two cages allows the fulvene moiety of C_{60}, i.e., the pentagon with the radial C−C bond reacted with the carbene, to further react in the 2,2′ positions with the two remaining carbenes of C_{59}. Two additional bonds are formed in this way. The net result is that there are four tetravalent carbon atoms in the C_{60} fragment and three in the C_{59} fragment. Neither sphere has therefore an odd number of π atoms. We would like to emphasize that for both isomers, the real dynamics of the formation of C_{119} can actually proceed along different lines. For instance, the second step may precede the first or the two steps may be concerted. It must also be mentioned that the isomer shown in Figure 2 fits well the present understanding of fullerene chemistry: In fact, it agrees with the tendency of C_{60} to form multiple connections between the spheres as in the case of its polymerization which may occur both photochemically[14] and via its radical anion,[15] and also with the propensity of the single bonds of C_{60} to break when they react.[13,16]

The three routes generate six C_{119} isomers. Notice that in the course of our work, we did consider other possibilities, these species, however, are those that gave the lowest energies. Before providing further details, it is probably best to introduce a simple scheme to name the isomers: 4m stands for four-membered ring and indicates the structures obtained according to ref 3; 5m stands for five-membered ring and indicates the structures obtained modifying the prescription of ref 3 and forming the pentagon with adjacent pentagons; D stands for diversely connected, that is the structures obtained generalizing the structure of ref 4 according to what was discussed above. The subscript 56 indicates that the intersphere reaction goes onto a long pentagon−hexagon bond, while the subscript 66 indicates that the intersphere reaction goes onto a short hexagon−hexagon bond. In Table 2, we show the MNDO and the tight-binding energies of the six optimized structures obtained using the three routes outlined above. Interestingly,

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Table 2. Energies (eV) of the Six Isomers of C_{119} Relative to Isomer D_{56} Generated According to the Three Schemes Described in the Text

	MNDO	tight binding
$4m_{56}$	4.535	*a*
$4m_{66}$	3.690	*a*
D_{56}	0.000	0.000
D_{66}	1.514	1.073
$5m_{56}$	1.952	1.149
$5m_{66}$	4.615	3.427

[a] No stationary point with this connectivity was found: the optimization led to the D structures.

while MNDO gives $4m_{56}$ and $4m_{66}$ as stable molecules, admittedly rather high in energy, the tight-binding model cannot locate any stationary points with these characteristics and rearranges the bonds to form D_{56} and D_{66}. Of the two isomers with a triplet of adjacent pentagons, namely $5m_{56}$ and $5m_{66}$, only the isomer formed by reacting the spare carbene with the pentagon−hexagon edge is low in energy. Although the relative stability could not have been anticipated quantitatively one would have expected that $5m_{66}$ would be rather strained in energy both because of the pentagon triplet and because of the three-membered ring present in the molecule. The diversely connected isomers are the most stable in energy with D_{56} the more stable. Encouragingly, these two unrelated quantum chemical procedures furnish a rather similar trend in stability. As already noticed above, the tight-binding model tends to predict smaller energy differences than other models and this applies also to the comparison with the MNDO calculations given here. Finally, the large energy gaps calculated by both models make quite certain that the ground state of C_{119} is D_{56}.

C_{129}. We should notice, however, that the three routes that have generated six isomers for C_{119} now yield many more molecules. To simplify matters, we were therefore forced to use only the tight-binding model. Overall 56 structures were obtained: 32 for the reaction $C_{59} + C_{70} \rightarrow C_{129}$ (as counted by steps 1 to 3 below) and 24 for the reaction $C_{69} + C_{60} \rightarrow C_{129}$ (as counted by steps 1 and 4 below). In the following, we try to explain the isomer count in four steps:

(1) Since tight-binding optimization of $4m_{56}$ and $4m_{66}$ for C_{119} yielded D_{56} and D_{66}, we started considering only structures of the type $4m_{xy}$ and $5m_{xy}$; the implicit assumption, verified by the calculations, was that the structures containing the four-

Table 3. Relative Energies (eV) of the Isomers of C_{129}[a]

	C_{59} (4-m ring → multiple connectivity) + C_{70} (p-h edge)	
bond a	0.000 (0.000)[b]	
b	0.073[c] (0.157)	
c	0.282 (3.471)	
d	0.502 (0.502)	
	C_{59} (4-m ring closure → multiple connectivity) + C_{70} (h-h edge)	
A	0.984 (1.012)	
B	1.048 (1.048)	
C	1.257 (3.686)	
D	0.641 (1.114)	
	C_{59} (5-m ring closure) + C_{70} (p-h edge)	
a	0.585 (1.142)	
b	0.748 (1.260)	
c	1.215 (1.315)	
d	2.213 (2.285)	
	C_{59} (5-m ring closure) + C_{70} (h-h edge)	
A	2.749 (2.749)	
B	2.829 (2.852)	
C	1.730 (3.028)	
D	1.201 (2.843)	
atom 1	C_{60} (h-h edge) + C_{69} (4-m ring closure → multiple connectivity)	1.042
	C_{60} (p-h edge) + C_{69} (4-m ring closure → multiple connectivity)	0.000[b]
	C_{60} (h-h edge) + C_{69} (5-m ring closure)	2.711
	C_{60} (p-h edge) + C_{69} (5-m ring closure)	1.141
2	C_{60} (h-h edge) + C_{69} (4-m ring closure → multiple connectivity)	1.197
	C_{60} (p-h edge) + C_{69} (4-m ring closure → multiple connectivity)	0.073[c]
	C_{60} (h-h edge) + C_{69} (5-m ring closure)	2.797
	C_{60} (p-h edge) + C_{69} (5-m ring closure)	0.703
3	C_{60} (h-h edge) + C_{69} (4-m ring closure → multiple connectivity)	1.363
	C_{60} (p-h edge) + C_{69} (4-m ring closure → multiple connectivity)	0.157
	C_{60} (h-h edge) + C_{69} (5-m, u,[d] ring closure)	2.519
	C_{60} (p-h edge) + C_{69} (5-m, u, ring closure)	0.757
	C_{60} (h-h edge) + C_{69} (5-m, l,[d] ring closure)	1.547
	C_{60} (p-h edge) + C_{69} (5-m, l, ring closure)	1.072
4	C_{60} (h-h edge) + C_{69} (4-m ring closure → multiple connectivity)	1.585
	C_{60} (p-h edge) + C_{69} (4-m ring closure → multiple connectivity)	0.722
	C_{60} (h-h edge) + C_{69} (5-m, u, ring closure)	2.227
	C_{60} (p-h edge) + C_{69} (5-m, u, ring closure)	2.495
	C_{60} (h-h edge) + C_{69} (5-m, l, ring closure)	1.933
	C_{60} (p-h edge) + C_{69} (5-m, l, ring closure)	0.688
5	C_{60} (h-h edge) + C_{69} (5-m, u, ring closure)	2.822
	C_{60} (p-h edge) + C_{69} (5-m, u, ring closure)	2.885
	C_{60} (h-h edge) + C_{69} (5-m, l, ring closure)	1.613
	C_{60} (p-h edge) + C_{69} (5-m, l, ring closure)	1.011

[a] The isomers were generated with rules i) to iv) of the text. For the isomers containing the C_{59} moiety, in bracket, the less stable isomer generated applying rule ii), that is by rotating C_{70} by 180°. [b],[c] The same isomer is obtained by more than one route. [d] u stands for upper closure, l stands for lower closure, see text.

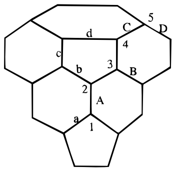

Figure 3. C_{70} fragment with the atom and bond labeling used in Table 3 (see text).

membered rings would evolve into the multiply connected ones, if the incoming fullerene had the right setup of bonds available.

(2) If the spare carbene belongs to the C_{59} fragment, then it can react with 8 symmetry inequivalent C_{70} bonds (4 pentagon−hexagon edges and 4 hexagon−hexagon edges). This generates $2 \times 8 = 16$ isomers, where the factor of 2 comes from 1).

(3) As additional factor of 2 in the count of the isomers generated by the encounter of C_{59} with C_{70} comes from the fact that the approaching bond of C_{70} can rotate by 180°. At odds with the case of C_{60}, the rotation of C_{70} may generate a different isomer. Overall, there are therefore 32 molecules to study.

(4) If the bond undergoing reaction belongs to the C_{60} fragment, then the spare carbene of C_{69} can be generated in five different ways (there are 5 symmetry inequivalent carbons in C_{70}). At first, one would then think that the number of isomers is 2 (rule 1) × 2 (two types of bonds of C_{60}) × 5 = 20 isomers. To complicate things, however, removal of one of these 5 atoms and subsequent ring closure to either a 4-membered or a 5-membered ring does not always lead to the formation of a single isomer. To illustrate this point, let us start by orienting C_{70} vertically along its long axis. If one starts from the top, removal of the first atom and subsequent ring closure can give either a 4-membered or a 5-membered ring. The same applies to the removal of the second atom. The third atom from the top, however, can generate a 4-membered ring and two different 5-membered rings that we label u (for upper) and l (for lower) where the label indicates the position of the ring with respect to the long molecular axis. The fourth atom is in the same situation as the third. Finally removal of the fifth atom can only give two 5-membered rings. This generates $(2 + 2 + 3 + 3 + 2) \times 2 = 24$ isomers.

A couple of words of caution about this procedure should be given: It may happen that some of the isomers of C_{129} generated in this way coincide (and they do). Moreover, one could find other schemes by which the present list of isomers could be extended. However, our experimenting with C_{119} leads us to believe that they will all be higher in energy. In any event, we feel that we have found three fairly general mechanisms that ought to yield both the lowest energy isomer of C_{129} and a set of propensity rules that could be of assistance in the study of the structure of odd-numbered fullerenes.

In Table 3, we show the relative energies of the optimized geometries of the 56 C_{129}. The nomenclature of the isomers has been partially introduced above to distinguish the upper, u, and lower, l, ring closures of the C_{69} fragment. The position of the C_{70} atom removed from the sphere is numbered 1 to 5 from top to bottom. In Figure 3, such numbering is illustrated on a fragment of C_{70} in which the pentagon sitting at the top of the long axis is at the bottom of the figure. The fragment is terminated by an hexagon part of the C_{70} belt. Reaction of C_{59} with C_{70} requires distinguishing the eight symmetry inequivalent bonds. In Figure 3, the four pentagon−hexagon bonds are labeled with lower-case letters, a to d, while the hexagon−hexagon bonds are labeled with upper-case letters, A to D. With these prescriptions, inspection of Table 3 should be made easier. As one can gather from the table, the most stable isomer, see Figure 4, can be generated in more than one way. In our procedure, we started forming C_{59} with the four-membered ring and attached it to the topmost pentagon−hexagon bond of C_{70}. Geometry optimization led to the usual ring opening and multiple bonds between the fullerenic moieties. The molecule is invariant to rule 2, which is rotation of C_{70} by 180°. The same structure can be obtained by removing the topmost atom of C_{70}, forming the transient four-membered ring and attaching C_{69} to a pentagon−hexagon bond of C_{60}. Because of the dual parentage from both C_{59} and C_{69}, one can think that C_{129} is reminiscent of the C_2 symmetry of C_{119}. In fact, as in the case of C_{119}, the central atom may belong to either cage.

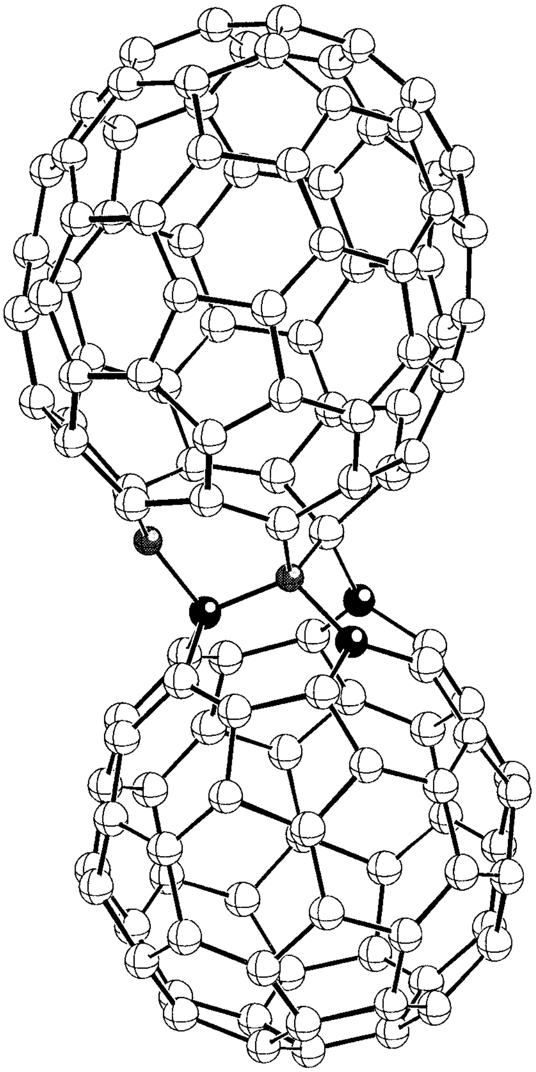

Figure 4. The most stable isomer of C_{129}. The three carbene atoms of C_{59} are represented in black in the lower half, and the two C_{70} atoms whose bond reacts with one of the carbenes are in gray in the upper half. Notice that the same isomer can be obtained combining a C_{69} fragment with C_{60}.

IV. Propensity Rules for the Stability of Odd-Numbered Fullerenes

In this section, we present a distilled discussion and summary of the calculations that we have performed. The intent is to provide a few simple guidelines, or propensity rules, for the stability of odd-numbered fullerenes. The five rules that came out of the calculations are the following:

Rule 1 is carried out both by chemical intuition and by our calculations and allows only an even number of unsaturated atoms on both moieties.

Rule 2 affirms that the inter-ball reaction of the carbene atoms

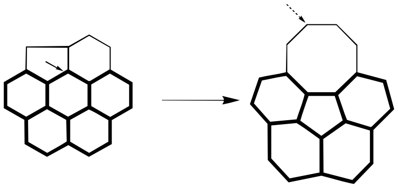

Figure 5. Removal of the carbon atom shown by the solid arrow may lead the benzo[*cd*]pyrenyl patch (thick line) to close to a pentagon without any other abutting pentagons. The dashed arrow indicates the position of the remaining carbon with dangling valences.

is favored over the pentagon formation route and even more over the square formation route.

Rule 3 minimizes the number of sp^3-sp^3 bonds between the two frames once rule 2 is obeyed.

Rule 4 states that the favored attachment site of a carbene atom is to a pentagon−hexagon edge.

Rule 5 predicts that the environment of the pentagon−hexagon edge must have the largest curvature as in C_{60} or in the top parts of C_{70}.

Interestingly, the present set of rules together with previous work[12] point toward a possible "corollary", namely that the pentagon closure may actually become favored when it does not create adjacent pentagons. For this event to occur, one needs a fullerene with a benzo[*cd*]pyrenyl patch, see Figure 5, or in less formal words, a patch with a naphthalene abutted on the top of an anthracene. Removal of the central top-most atom of the anthracene moiety and subsequent ring closure to a pentagon leads to no abutting pentagons. A benzo[*cd*]pyrenyl structural motif occurs in higher fullerenes such as the C_{78} isomer of C_{2v} symmetry with 21 inequivalent atoms,[17] a fullerene that has already been isolated.[18] If C_{137} ($C_{60} + C_{78} - 1C$) were found, it could well differ from other odd-numbered fullerenes.

V. Conclusion

The structures and the stability of several isomers of the two prototypical odd-numbered fullerenes have been studied by two unrelated quantum chemical procedures. C_{119} is the smallest homoderived odd-numbered fullerene while C_{129} is the smallest heteroderived odd-numbered fullerene. By generalizing work already present in the literature,[3,4] three routes to the generation of the connectivity of odd-numbered fullerenes have been proposed. They can be referred to as the square route, the pentagon route, and the multiple connectivity route. It is found that the isomers produced in the square formation are always higher in energy, if they exist, than those produced by the other two routes. The multiply connected isomers are the most stable. If a benzo[*cd*]pyrenyl patch (see Figure 5) is present, some isomers generated by the pentagon route may be further stabilized by the absence of abutting pentagons. The results of the calculations have been summarized in terms of five propensity rules that should help narrow down the number of isomers that one has to consider when trying to determine the structure of larger odd-numbered fullerenes.

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