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Theoretical Studies of Derivatized Buckyballs and Buckytubes

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Abstract: Computational studies of patterns of addition to fullerenes have been extended (1) from $C_{60}H_2$ and $C_{60}H_4$ to $C_{60}H_6$, (2) from $C_{60}H_2$ and $C_{70}H_2$ to models of buckytubes-H_2, and (3) from the products of the reaction of $:CH_2$ with C_{60} to the corresponding products with buckytubes. A paradigm of multiple addition has appeared: as the number of H_2 addends increases, 1,4 addition becomes competitive with 1,2-addition. A significant chemical difference between singly- (buckytube) and doubly- (C_{60}) curved carbon is revealed by the energetics of H_2 addition to the sidewalls vs. end-caps of a buckytube model. Remarkably, $:CH_2$ insertion into either sidewalls or endcaps of buckytubes yields structures with similar heats of formation. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

The pattern of multiple addition to fullerenes has become increasingly important as research into fullerene derivatives moves toward applications in materials science and pharmaceuticals. Recent studies have shown the utility of both kinetic control and templated synthesis for the preparation of complex derivatives of fullerenes.[1,2] Experimentally validated computational studies have also provided useful information on the thermodynamics of isomeric addended fullerenes. The thermodynamics of isomeric addended fullerenes are often more easily studied computationally than experimentally, not necessarily because of instability or reactivity, but rather because the synthetic or analytical tools needed for the synthesis and/or separation of such isomers have not yet been perfected.

This work is an extension of computational studies of hydrogenated fullerenes as models of more complex derivatives.[3,4a,5,6] The relative energies of eighteen $C_{60}H_6$ isomers have been evaluated using ab initio computational techniques previously validated for $C_{60}H_2$, $C_{60}H_4$ and $C_{70}H_2$. Hydrogenation of buckytubes has been examined using approximate semiempirical methods via heuristic models of single-walled buckytubes composed of 120 atoms. Finally, the study of fulleroids and methanofullerenes has similarly been extended to addition of $:CH_2$ to the endcaps and sidewalls of such buckytube models.

RESULTS AND DISCUSSION

$C_{60}H_2$, $C_{60}H_4$ and $C_{60}H_6$

The results of geometry-optimized Hartree-Fock (HF) calculations are listed in Table 1 for isomers of $C_{60}H_2$, $C_{60}H_4$ and $C_{60}H_6$ (Figure 1). All calculations were performed using direct SCF methods within the GAUSSIAN-92 series of programs[7] on either a Cray YMP or an IBM RS/6000-390 desktop computer. Previous work[4a,6] has shown that semiempirical methods often fail to reproduce the relative energies of isomeric hydrogenated fullerenes. Energies calculated with HF/3-21G methods reproduce trends in isomer stabilities when compared with experiment, but are not quantitative (the estimated reliability for relative total energies with these methods is 3 kcal/mol). For 1,9- and 7,8-$C_{70}H_2$, for which an experimental equilibrium constant has been measured, quantitative agreement with HF/6-31G* methods was observed. The calculated difference in total energies between the isomers (1.3 kcal/mol) agrees with the 1.4 ± 0.2 kcal/mol value obtained from the equilibrium constant. We estimate the reliability of HF/6-31G* methods for hydrogenated fullerenes to be similar to the experimental uncertainty.

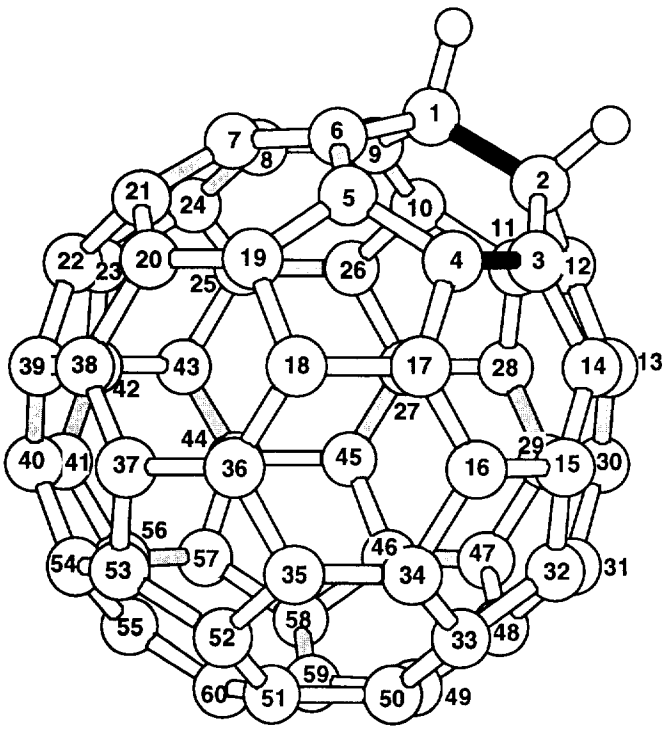

Figure 1. The numbering system used in this work.[8] $C_{60}H_2$ is depicted; deeply shaded bonds correspond to 1,2,3,4-$C_{60}H_4$. Lightly shaded bonds correspond to unique 6,6-ring fusions used to generate $C_{60}H_6$ isomers from 1,2,3,4-$C_{60}H_4$.

Results for $C_{60}H_2$ are listed in Table 1 for 4 of 23 possible isomers of this compound in the order of increasing isomer energy: (1) 1,2-addition to a 6,6 ring fusion, (2) 1,4-addition to a 6-ring, (3) 2,7-addition to a naphthalene subunit, and (4) 1,2-addition to a 6,5 ring fusion. These are not necessarily the 4 lowest energy isomers, but provide data for comparison with data on isomers of $C_{60}H_4$ and $C_{60}H_6$. Almost 8 kcal/mol separates isomers resulting from 1,2 and 1,4-addition (Figure 2), while 24 kcal/mol separates addition to 6,6 vs. 6,5 ring fusions. Qualitative agreement with experiment is observed -- only 1,2-$C_{60}H_2$ has been isolated,[9] although there is some NMR evidence for the existence of a second, presumably 1,4-addended, isomer.

Table 1. Ab Initio Hartree-Fock Results for $C_{60}H_2$,[1] $C_{60}H_4$,[2] and $C_{60}H_6$ [this work].[10]

$C_{60}H_2$	Nomenclature	Relative Energy (kcal/mol) HF/3-21G	Relative Energy (kcal/mol) HF/6-31G*
1	1,2	**0.0**	**0.0**
2	1,4	**7.8**	**7.6**
3	1,16	23.1	20.9
4	1,6	26.4	24.0
$C_{60}H_4$			
1	1,2,3,4	**0.0**	**0.0**
2	1,2,7,21	6.1	6.6
3	1,2,16,17	8.1	8.5
4	1,2,18,36	3.2	4.0
5	1,2,34,35	4.1	4.9
6	1,2,33,50	3.5	4.2
7	1,2,51,52	3.9	4.8
8	1,2,55,60	3.9	4.8
9	1,2,4,15	**2.8**	**3.9**
$C_{60}H_6$			
1	1,2,3,4,5,6	16.4	
2	1,2,3,4,7,21	10.5	
3	1,2,3,4,8,24	8.9	
4	1,2,3,4,9,10	**2.3**	**0.0**
5	1,2,3,4,11,12	5.5	
6	1,2,3,4,13,30	16.2	
7	1,2,3,4,22,23	7.2	
8	1,2,3,4,25,26	11.1	
9	1,2,3,4,27,45	6.1	
10	1,2,3,4,28,29	11.4	
11	1,2,3,4,39,40	7.1	
12	1,2,3,4,41,42	7.0	
13	1,2,3,4,43,44	7.0	
14	1,2,3,4,46,47	7.1	
15	1,2,3,4,56,57	7.6	
16	1,2,3,4,58,59	7.9	
17	1,2,3,4,7,19	19.4	
18	1,2,4,11,15,30	**0.0**	**0.4**

Of 4190 possible $C_{60}H_4$ isomers,[11] 9 were selected on the basis of the $C_{60}H_2$ results for further study. In the order presented in Table 1, the first eight correspond to H_2 addition to two 6,6 ring fusions, and are listed in the order of increasing distance between the hydrogenated double bonds. The ninth isomer results from 1,2-addition followed by 1,4-addition as shown in Figure 3. The 7.6 kcal/mol (HF/6-31G*) that separates 1,2- from 1,4-$C_{60}H_2$ drops to 3.9 kcal/mol in 1,2,3,4- (1,2 followed by 1,2-addition) vs. 1,2,5,15-$C_{60}H_4$ (1,2 followed by 1,4-addition). This is a chemically significant change in the relative energetics of 1,2 vs. 1,4 H_2 addition.

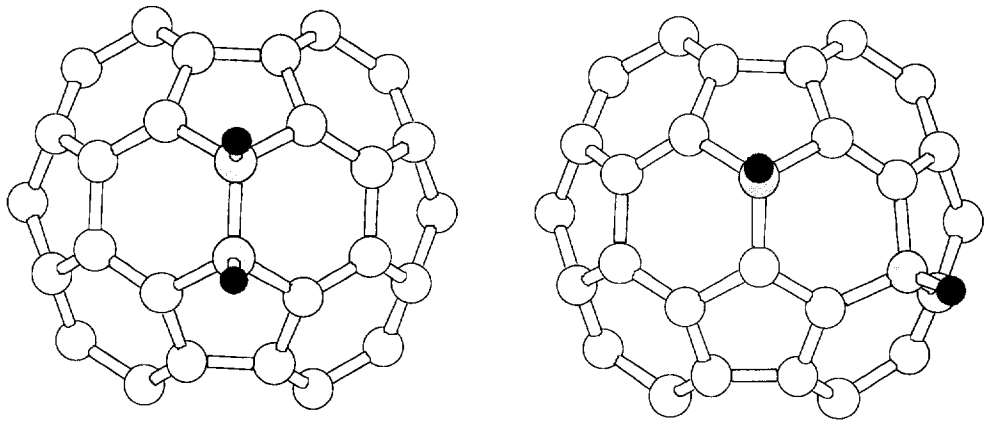

Figure 2. Of 23 possible $C_{60}H_2$ isomers, 1,2-$C_{60}H_2$ (left) and 1,4-$C_{60}H_2$ (right) have the lowest total energies at all levels of theory applied (semiempirical, HF/3-21G and HF/6-31G*). The most reliable estimate of the difference in free energy between these two structures is 7.6 kcal/mol (HF/6-31G* result). For clarity, only part of the molecule is shown.

Multiple isomers of $C_{60}H_6$ are formed in the presence of excess reducing agent, but the structure of these products is not known.[11] By adding to the lowest energy isomer of $C_{60}H_4$ by predominantly 1,2-addition to 6,6 ring fusions, 18 of the possible 418,470 isomers[12] of $C_{60}H_6$ were considered at the HF/3-21G level (Table 1). The range in calculated energies in this case greatly exceeds that observed for $C_{60}H_4$, but an exhaustive search of other geometries was not attempted; therefore, other $C_{60}H_6$ isomers may exist with energies within the span calculated here.

The HF/3-21G energies of 7 of the 18 $C_{60}H_6$ isomers (**7**, **11**, **12**, **13**, **14**, **15**, and **16**) cluster between 7 and 8 kcal/mol above the lowest energy isomer (**18**, at this level of theory). As in the case of $C_{60}H_4$ isomers **5-8**, this may be interpreted as a lack of electronic or geometric interaction between the one set of addended hydrogens and the remotely located, saturated 6,6 ring fusion. Therefore $C_{60}H_6$ isomers with lower isomer energies (**4**, **5**, **9** and **18**) may be viewed as having favorable electronic or geometric factors, and those with higher energies (isomers **1**, **2**, **3**, **6**, **8**, **10**, and **17**) as having unfavorable interactions. At the HF/3-21G level isomer **4** lies only 2.3 kcal/mol above the most stable isomer, **18**. The

highest lying isomers **1** and **17** are 16.4 and 19.4 kcal/mol less stable, respectively. Isomer **18** corresponds to the experimentally observed geometry of $C_{60}Cl_6$ (or $C_{60}Br_6$):[13] 1,2-addition followed by two 1,4-additions to a corannulene cap of C_{60}.

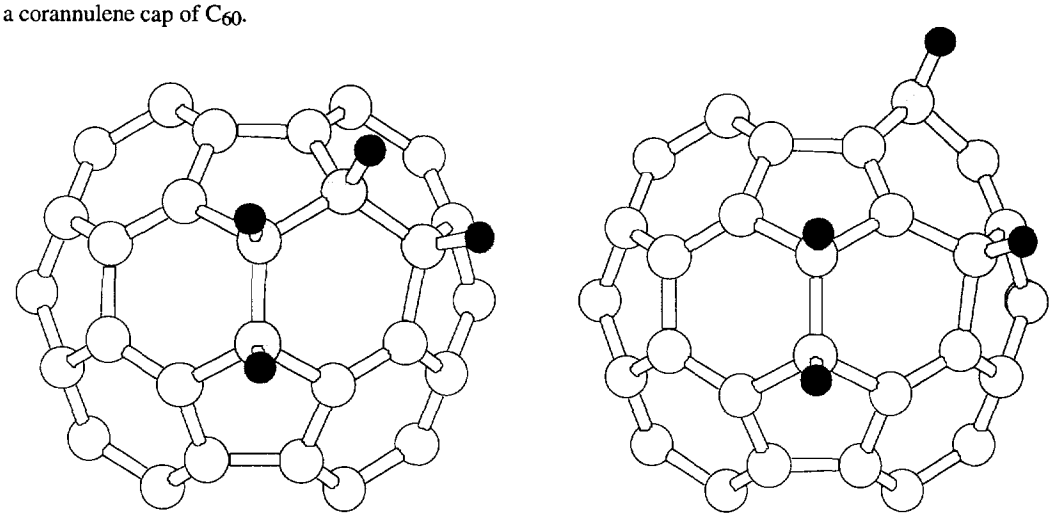

Figure 3. Of 4190 possible $C_{60}H_4$ isomers, nine were examined with ab initio computational techniques. 1,2,3,4-$C_{60}H_4$ (left: a product of exclusive 1,2 additions) lies 3.9 kcal/mol below 1,2,4,15-$C_{60}H_4$, the product with the next lowest total energy (right: 1,2- followed by 1,4-addition) at the HF/6-31G* level. All other geometries constructed from two successive 1,2-H_2 additions to 6,6 ring fusions showed higher total energies. The structure on the right places one double bond into a 6,5 ring fusion.

HF/6-31G* calculations were limited to $C_{60}H_6$-**4** and **18** (Figure 4), the two lowest-lying isomers that are well separated in energy from the other isomers examined. With this polarized basis set, the energy ordering is reversed from HF/3-21G, with isomer **18** lying only 0.4 kcal/mol above isomer **4**. These results indicate that isomers **4** and **18** are likely to exist at room temperature in an equilibrated mixture of $C_{60}H_6$ isomers. Statistical (entropic) factors do not favor either isomer, therefore when combined with the estimated reliability of ± 0.2 kcal/mol for this energy difference, the observed ratio of **4** to **18** at room temperature is predicted to be between 1.4 and 2.8. Measurement of this ratio would provide an excellent test of the computational approach because zero-point and solvation energies differences between these isomers are arguably small.

Although a simple interpretation of the pattern and spacing of the isomer energies is not obvious, the energy difference between isomers formed exclusively with 1,2-additions and those formed with a combination of 1,2 and 1,4 additions decreases to 0.4 kcal/mol for $C_{60}H_6$ from 7.6 kcal/mol ($C_{60}H_2$) and 3.9 kcal/mol ($C_{60}H_4$). [This trend suggests that for $C_{60}H_8$, the 1,4-addition structures may be significantly more stable than those resulting from exclusively 1,2 additions, but the number of isomers to be examined is prohibitive at this time.] Steric effects probably do not play the definitive role because of the small hydrogen atom radius. If

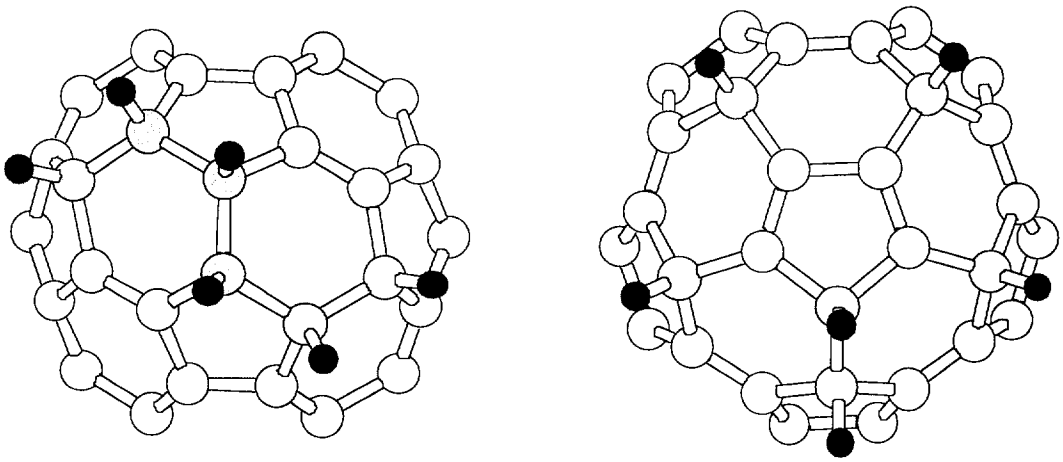

Figure 4. Of over 400,000 possible $C_{60}H_6$ isomers, 18 were investigated with ab initio techniques. The isomers 1,2,3,4,9,10-$C_{60}H_6$ (**4**, left) and 1,2,4,11,15,30-$C_{60}H_4$ (**18**, right) have the lowest total energies. In this case, the 1,4-addition product (right) lies only 0.4 kcal/mol above the most stable 1,2-addition product and places two double bonds into 6,5 ring fusions.

geometric (strain) effects were the source of the energy ordering, semiempirical calculations would likely provide a reliable energy ordering. However, semiempirical calculations on $C_{60}H_4$ yield an incorrect energy ordering (relative to both ab initio calculations and experiment).[4a] Subtle electronic effects that are adequately modeled only with polarized basis sets may be the determining factor in the energy ordering. For isomer $C_{60}H_6$-**18**, these electronic effects may reflect the stability of the cyclopentadiene ring system present in this $C_{60}Br_6$-like structure. Such an interpretation further suggests that **18** may be among the strongest carbon acids known.

$C_{120}H_2$

The chemistry of single-walled nanotubes is largely unexplored, in part because of the difficulties associated with purification of these materials. Traditional ab initio computational approaches to their chemistry are also limited because of their relatively large size. However, semiempirical calculations can be used on these larger systems to yield semi-quantitative information about the differences between doubly-curved carbon, e.g., C_{60}, and singly curved carbon, e.g., the sidewalls of nanotubes. Doubly curved carbons incorporate pentagons whereas singly curved and planar (graphite) carbons can be constructed entirely of hexagons even though both are composed entirely of trigonal carbon. The initial approach is through a model of a single wall nanotube, such as the C_{120} structure shown in Figure 5, that includes elements of both C_{60} (at the endcaps) and nanotubes. This approach is limited here to one tube radius and to zero helicity .

Thirteen $C_{120}H_2$ isomers, each resulting from 1,2-addition to a 6,6 or 6,5 ring fusion of C_{120}, were studied with full geometry optimization at the MNDO/PM3 level.[14] The carbons are labeled alphabetically in

layers, beginning with an apical pentagon (layer A). Sites for H_2 addition are denoted by two letter codes: AB for addition to a 6,6 ring fusion that connects carbons in layers A and B, or CC for the 6,6 ring fusion in layer C, etc. Energies of these isomers, relative to addition to the AB layer that corresponds to 1,2-$C_{60}H_2$, are depicted in Figure 5. Addition to the CC layer yields a structure with a relative heat of formation of only 2.9 kcal/mol, which is reasonable for an addition to a 6,6 ring fusion near the poles of a fullerene. Addition to a BC bond, which is a 6,5 ring fusion, is 20.1 kcal/mol higher than addition to the AB bond, which is also consistent with previous work. These values establish that the end-cap bonds of this C_{120} structure are similar to those in C_{60} or C_{70}.

Addition to the sidewall of C_{120} is 30-50 kcal/mol less favorable than addition to the end-caps. If the heat of reaction of H_2 with C_{60} is taken as 40 kcal/mol, H_2 addition to the sidewall of a nanotube is predicted to be nearly thermoneutral. These results suggest that functionalization of the sidewalls of nanotubes by addition chemistry will require highly reactive reagents.

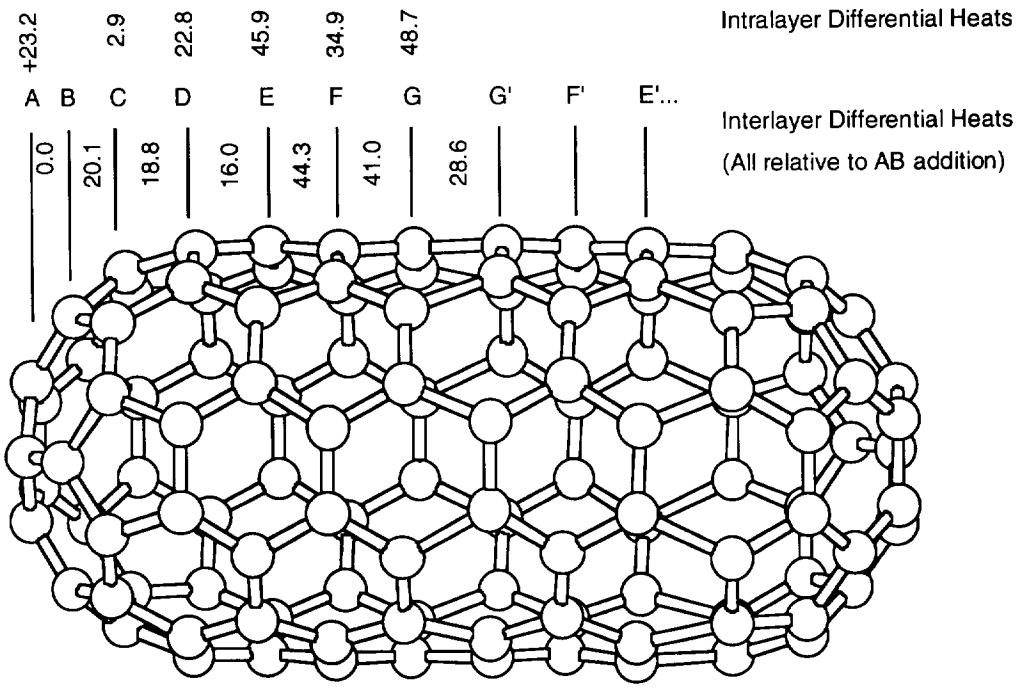

Figure 5. Structure of the C_{120} nanotube model with C_{60}-like end-caps. The heats of formation of twelve $C_{120}H_2$ isomers, relative to AB-$C_{120}H_2$, are given in kcal/mol.

$C_{90}CH_2$

Methanofullerenes (cyclopropanes that result from :CR_2 insertion into 6,6 ring fusions) and fulleroids (annulene-like compounds that result from :CR_2 insertion into 6,5 ring fusions) are among the most important fullerene derivatives because a wide range functional groups can be attached to fullerenes via formal carbene addition. In many cases both methanofullerenes and fulleroids form under reaction conditions, and in some cases, these isomers equilibrate. The high relative energies for H_2 addition to the sidewall of C_{120} (above) suggest that, for nanotube functionalization, a method other than simple addition may be required. The results of carbene insertion into C_{90}, a smaller nanotube model, suggest that some products are remarkably stable.

Table 2. Relative heats of formation for products of :CH_2 insertion to C_{90}. See also Figure 6. The calculated heats of formation (PM3) for C_{90} and EE-$C_{90}CH_2$ are 1013.5 and 1006.2 kcal/mol, respectively.

Reaction Site	Type of Product	Relative Heat of Formation (PM3, kcal/mol)	Bond Length (Å)	Ring Fusion
AA	fulleroid	2.0	2.216	6,5
AB	methanofullerene	2.5	1.563	6,6
BC	fulleroid	4.6	2.202	6,5
CC	methanofullerene	6.1	1.543	6,6
CD	methanofullerene	25.4	1.604	6,5
DD	fulleroid	6.5	2.195	6,5
DE	methanofullerene	14.9	1.551	6,6
EE	fulleroid	0.0	2.278	6,6
EF	methanofullerene	40.4	1.565	6,6
FF	fulleroid	9.0	2.249	6,6

Semiempirical calculations on the 10 possible carbene insertion structures are summarized in Table 2 and the most stable $C_{90}CH_2$ isomer is shown in Figure 6. The contrast in relative heats of formation between the EF and FF isomers indicates that the relief of strain energy associated with expanding the radius of the nanotube may be a stabilizing effect for :CH_2 insertion into circumferential nanotube bonds. The EE-$C_{90}H_2$ isomer results from insertion into a 6,6 ring fusion and requires opening of the structure as observed for only 6,5 ring fusions in C_{60} and C_{70}. These results suggest that nanotubes may react readily with the carbenes, but only to form fulleroids with structures that relieve the strain associated with the small nanotube radius.

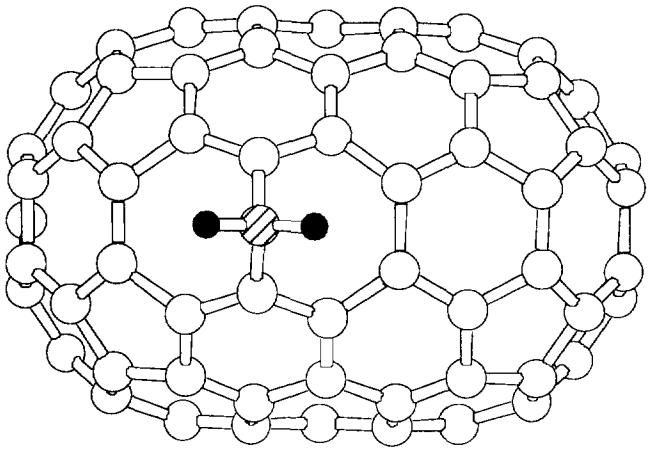

Figure 6. The structure of the most stable of 6 isomers resulting from the formal insertion of $:CH_2$ into a C_{90} buckytube model as determined by MNDO/PM3 calculations.

CONCLUSIONS

Experimentally validated ab initio calculations on hydrogenated C_{60} indicate that, relative to products of exclusive 1,2-addition, the stability of derivatized fullerenes that incorporate 1,4-additions increases with an increasing number of addends. This addition pattern places "double" bonds into 6,5 ring fusions, a consequence which previously has been thought unfavorable (as in $C_{60}R_2$), but which for $C_{60}H_6$, leads to a product, **18**, that is only 0.4 kcal/mol less stable than the product, **4**, that results from exclusive addition to 6,6 ring fusions.

For addition to buckytubes, semiempirical calculations on a model $C_{120}H_2$ cluster suggest that H_2-addition to the sidewall of a nanotube is nearly thermoneutral. The difference between H_2 addition to doubly-curved (C_{60}) carbon and singly-curved (nanotube) carbon is 30-50 kcal/bond and is a further demonstration of the unique nature of C_{60}. In contrast, similar calculations suggest that the thermodynamics of $:CH_2$ insertion is equally favorable to both buckyballs and buckytubes.

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