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Theoretical Studies of the Substitution Patterns in Heterofullerenes $C_{60-x}N_x$ and $C_{60-x}B_x$ ($x = 2-8$)

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Possible structures of heterofullerenes $C_{60-x}N_x$ and $C_{60-x}B_x$ ($x = 2-8$) have been calculated using semiempirical MNDO, AM1, PM3, and ab initio methods in order to determine the most stable structures, to investigate the underlying cause of their stabilities, and to predict their electronic properties. The calculation results indicate that the N-doped fullerenes are more stable than their B-doped analogues, but both are less stable than C_{60} thermodynamically, and the stabilities decrease with increasing number of the heteroatoms. The most likely structures of the heterofullerenes investigated in this paper are determined; it is found that there is a fair correlation between the regioisomerism of N- or B-doped fullerenes and that of fullerene adducts. It is proposed that the changes of hybridization from sp^2 to sp^3 are the predominant factors of the regiochemistry for both heterofullerenes and fullerene adducts, which leads to the existence of this unexpected correlation. This regioisomerism correlation makes it possible to deduce the most stable structures of heterofullerenes on the basis of the relatively well studied fullerene adducts. The redox characteristics of fullerene C_{60} can be enhanced by doping; heterofullerenes under investigation have somewhat smaller ionization potentials and bigger affinity energies relative to their all-carbon analogue C_{60} , which suggests it is easier to oxidize and reduce these doped fullerenes relative to C_{60} . There should be significant electron transfer when the dimeric fullerenes are formed, and these electron-transfer directions are predicted.

1. Introduction

Heterofullerenes, which have one or more of the carbon atoms substituted by other elements such as boron and nitrogen, are a new and fascinating discovery in the class of fullerene-based materials. Since the incorporation of heteroatoms into the fullerene skeleton is expected to modify its structural and electronic properties, such heterofullerenes are expected to have applications in superconductivity, photoinduced electron transfer (photoelectronic device), and organic ferromagnetism and may be used as semiconductors and building materials for nanometer electronics; furthermore, the doping enhances the chemical reactivity of the fullerene and opens new pathways to the synthesis of new compounds. The production of the first substituted fullerenes $C_{60-x}B_x$ ($x = 1-6$)¹ in 1991 opened new avenues in materials science and organic chemistry, revealed another inspiring world for scientists to explore, and raised many new fundamental questions about their stability, morphology, electronic behavior, and the basic features of the chemical bondings waiting for us to solve.

The experimental work on the heterofullerenes have achieved great progress, especially on the nitrogen heterofullerenes.²⁻¹¹ Soon after the successful production of the boron-doped fullerenes, a number of C_nN_m fullerenes were produced by Rao et al.² in the same year. In 1995, the mass spectrometric detection of $C_{59}N^+$ and $C_{69}N^+$ formed by fragmentation of iminofullerene derivatives was reported by Hirsch et al.,³ the detection of $C_{59}NH^+$ and $C_{59}NH_2^+$ was reported by Mattay et al.,⁴ and the synthesis and characterization of $C_{59}N$ were reported by R. Yu et al.⁵ In the same year, the $C_{59}N$ dimer ($C_{59}N$)₂ was

isolated from a cluster-opened ketolactame precursor by Hummelen et al.⁶ In 1996, the synthesis and isolation of heterofullerenes ($C_{59}N$)₂ and ($C_{69}N$)₂ and their adducts $RC_{59}N$ and $RC_{69}N$ were achieved by Nuber and Hirsch,⁷ and the intercalation compound of the heterofullerene salt $K_6C_{59}N$ was prepared and structurally characterized by Prassides et al.⁸ with ($C_{59}N$)₂ as the precursor. In 1997, the successful derivatization of $C_{59}N$ from ($C_{59}N$)₂ and $C_{59}NH$ was reported by Wudl et al.⁹ and the hydrogenated azafullerene $C_{59}NH$, which can be a suitable source of $C_{59}N$ radical when it is deprotonated, was isolated and fully characterized by F. Wudl et al.¹⁰ Most recently, the Hirsch's group¹¹ reported the successful synthesis of arylated heterofullerenes $ArC_{59}N$ with ($C_{59}N$)₂ as precursor. The experimental work on boron-substituted fullerenes will also make great progress with the macroquantitative synthesis of $C_{60-n}B_n$ and $C_{70-n}B_n$.¹²

On the theoretical side, studies of electronic properties, band structures, and the third-order polarizability of the heterohedral fullerenes have also been carried out,¹³⁻³⁸ and some intriguing properties different from the all-carbon fullerenes are predicted. These heterofullerenes include not only single-atom-doped fullerenes such as $C_{59}B$,¹⁴⁻²⁰ $C_{59}N$,¹⁷⁻²¹ $C_{59}S$,¹⁵ and $C_{59}O$ ²² but also double-atom-doped $C_{58}X_2$ ($X = N, B$)^{15,19,23-25,33,35} and $C_{58}BN$ ^{23,26,35,38} and the doped C_{28} system $C_{24}X_4$ ($X = N, B$).²⁷⁻³⁰ However, theoretical studies of the molecular properties, including all the static properties and most kinetic properties, largely depend on the accuracy and reliability of the equilibrium geometries. Since we know that if more than one carbon atom in the fullerene cage are substituted by heteroatoms, an

enormous number of theoretically possible isomers will emerge.³⁹ Hence, it is necessary for us to make it clear which structures are the most possible isomers to predict their properties. In fact, Kurita et al.²⁴ have already pointed out that the electronic properties of $C_{58}X_2$ ($X = B, N$) largely depend on the relative positions of the substituted fullerenes. Unfortunately, the properties of the heterofullerenes doped with diatoms predicted so far are mostly based on the arbitrarily assigned geometries, which often give ambiguous and contradictory results. The enormous number³⁹ of theoretically possible isomers and the experimental problems of purification and characterization of these doped fullerenes make it an urgent task for us to determine the structure–energy relationship and calculate the stable molecular structures of the doped fullerenes theoretically.

To calculate the most stable structures of heterofullerenes, Wang et al.¹⁹ have studied the stabilities of $C_{60-x}N_x$ and $C_{60-x}B_x$ ($x = 1$ and 2) using extended Huckel method and molecular modeling at the MM2 level. Chen et al.^{31,32} studied all the possible isomers of $C_{58}X_2$ at the CNDO/2 level and extended their studies to $C_{57}X_3$ and $C_{56}X_4$ ($X = N, B, P$) system. We have calculated all the possible structures of $C_{58}X_2$ ($X = N, B$)^{33,35} and $C_{58}BN$ ^{35,38} using MNDO, AM1, and PM3 methods in order to find the structure–energy relationship and extended our studies to $C_{68}X_2$ ($X = N, B$),³⁴ $C_{60-2x}(BN)_x$ ($x = 2, 3$)³⁶ and $C_{70-x}(BN)_x$ ($x = 1-3$)³⁷ systems. However, a series of systematic calculations on doped fullerenes with more than two N or B heteroatoms have not been reported.

The difficulty confronted in determining the stable molecular structures is that there are too many isomers for the heterofullerenes. From true geometric considerations, for $C_{58}X_2$, there are a total of 23 possible isomers, while $C_{56}X_4$, $C_{54}X_6$, and $C_{52}X_8$ should have thousands of isomers according to Balasubramanian's enumeration.³⁹ These isomers differ in the relative positions of the heteroatoms and therefore in energy. Thus, not all of them can be synthesized. Therefore, the relative stability of regioisomers of the doped fullerenes is being studied theoretically in this work.

In the present work, both the semiempirical methods AM1, PM3, and MNDO and the ab initio method were used to perform a systematic and extended investigation of the molecular structures of the possible isomers of $C_{60-x}N_x$ and $C_{60-x}B_x$ ($x = 2-8$). The equilibrium geometrical structures, heats of formation, heats of atomization, ionization potentials, affinity energies, and absolute electronegativities will be predicted theoretically. The correlation between the heats of formation of $C_{60}X_n$ and the $C_{60-n}N_n$ or $C_{60-n}B_n$ isomers, in which the heteroatoms substituted the carbon where the addends are added, is determined, which builds a bridge to connect the regiochemistry of fullerene adducts and heterofullerenes and makes it possible to deduce the regioselectivity of the doped fullerenes in light of the knowledge of the fullerene adducts.

2. Computational Details

The size of the systems studied prevents the use of ab initio molecular quantum mechanical methods to perform optimizations. Therefore, full geometry optimization in the present paper were carried out at the MNDO, AM1, and PM3 semiempirical levels utilizing the Mopac quantum chemical program packages (QCPE455). The Broyden–Fletcher–Goldfarb–Shanno function minimizer (BFGS)⁴⁰ was used in the full geometry optimization, and the PRECISE option was used in order to increase the criteria for terminating the optimization by a factor of 100. The optimization was carried out without any symmetry constraints in Cartesian coordinates, and initial input

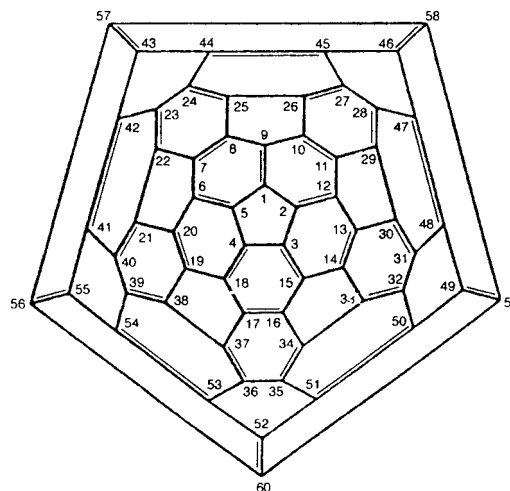


Figure 1. Numbering system for C_{60} .

geometries were based on the optimized C_{60} with specific carbon atoms displaced by other elements such as B and N. For the key structures, single-point ab initio Hartree–Fock (HF) energy calculations have been performed at the MNDO-optimized geometries employing the 3-21G basis set⁴¹ (HF/3-21G//MNDO) using the Gaussian 94 program.⁴²

3. Results and Discussion

The numbering system for the carbon atoms in C_{60} is shown in Figure 1. For simplicity, the isomer of the fullerene adducts $C_{60}X_n$ and the isomer of the heterofullerenes $C_{60-n}X_n$, in which the heteroatoms substituted the carbon atoms where the addends were added, are thought to have the same regioselectivity pattern.

Regioisomerism of Heterofullerenes. $C_{58}N_2$ and $C_{58}B_2$. We have performed systematic theoretical studies of the heterofullerenes $C_{58}X_2$ ³³ and $C_{68}X_2$ ³⁴ ($X = B, N$). For $C_{58}X_2$ ($X = N, B$), the isomer corresponding to 1,4-substitution to the cyclohexatriene unit is the most stable isomer among 23 possible isomers, and the stabilities decrease with increasing distance between the heteroatoms. The energy data for the most stable isomers of $C_{58}X_2$ ($X = N, B$) are summarized in Table 1.

Since currently available structural data for fullerene adducts $C_{60}X_2$ show that the arrangement of the addends on the fullerene surface is independent of the nature of the X group, it appears that the regioisomerism of such systems is predominantly determined by the interactions within the carbon clusters and to some small extent by the properties of the addends. We know that the driving force for addition reactions of fullerene is the relief of strain in the fullerene cage, and reactions lead sp^2 -hybridized C atoms in the fullerene framework to saturated tetrahedrally hybridized sp^3 C atoms. Thus, the changes of hybridization from sp^2 to sp^3 of the carbon atoms where the addends are added may be the underlying factors for determining the regioisomerism of the fullerene adducts.³³ Because B and N substituted atoms in doped fullerenes also have the same hybridization changes and because the hybridized lone electron pair on the N atom and the hybridized empty orbital on the B atom can be seen as the “addends” to some extent, they have similar angle strain in fullerene cages that can be relieved and similar deformation occurs upon either substitution or addition; the changes of hybridization from sp^2 to sp^3 may also be an underlying factor that controls the regiochemistry of doped fullerenes. If it is the case, there should be some connection between the addition pattern in fullerene adducts and the

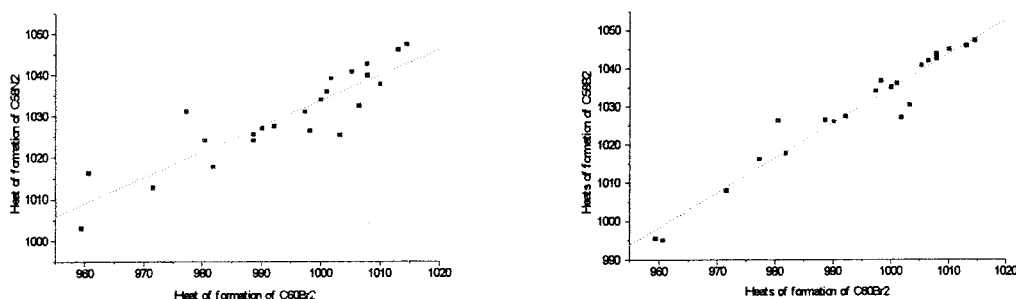


Figure 2. Heats of formation (kcal/mol) of 23 isomers of C₆₀Br₂ and the same isomers of C₅₈X₂ (left, X = N; right, X = B).

TABLE 1: Heats of Formation, Relative Heats of Formation, and Relative Total Energies (kcal/mol) of the Most Stable Isomers of C₅₈X₂ (X = N, B)^a

species	MNDO		AM1		PM3		HF/3-21G//MNDO RTE
	HF	RHF	HF	RHF	HF	RHF	
C ₅₈ N ₂ (1,7)	877.73	0.00	1003.05	0.00	806.46	0.00	0.00
C ₅₈ N ₂ (1,23)	886.28	8.55	1012.73	9.68	814.49	8.03	23.68
C ₅₈ N ₂ (1,9)	888.43	10.70	1016.24	13.19	821.81	15.35	16.56
C ₅₈ B ₂ (1,7)	849.54	0.00	995.54	0.00			0.00
C ₅₈ B ₂ (1,23)	858.80	9.26	1007.98	12.44			33.64
C ₅₈ B ₂ (1,9)	865.62	16.08	995.05	-0.49			20.70

substitution pattern in heterofullerenes. In fact, this connection has already been used to find the most stable C₆₈X₂ isomers successfully.³⁴ Considering that the N–N and B–B bonds will tend to destabilize the structures of the heterofullerenes (thus, the 1,2-C₅₈X₂ isomer should be avoided) while the fullerene adducts with bulky groups also disfavor the sterically demanding 1,2-isomer, there should be some fair correlation between the stabilities of the fullerene adducts with bulky addends such as C₆₀Br_n and those of the heterofullerenes.

The correlation between the heats of formation of C₆₀Br₂⁴³ and those of the same isomers of C₅₈X₂ shown in Figure 2, which reveals that most points lie on a straight line, confirmed our above discussion. From Figure 2 it can be found that two points corresponding to C₅₈N₂ (1,2) and C₅₈N₂ (1,9), which have neighboring nitrogen atoms, obviously have higher heats of formation than those given by the straight line, which indicates that the C₅₈N₂ isomers having adjacent nitrogen atoms have smaller possibilities in the product mixture than the corresponding C₆₀Br₂ isomers if the reaction is controlled thermodynamically. The correlation between the stability order of C₅₈B₂ and that of C₆₀Br₂ is much better; the isomer (1,2) and (1,9) also lie on the straight line, which indicates that the isomers having a B–B bond have similar possibilities in the product mixtures with the same isomers of C₆₀Br₂. The bond strength of B–B and N–N bonds has been examined by Kurita²⁴ in terms of bond orders. Their result indicated that the B–B bond is much stronger than the N–N bond in C₅₈X₂ with two heteroatoms in the junction of 6/5 ring. The bond orders of X–X calculated by the MNDO method are 0.9079 for C₅₈N₂ (1,9), 0.9070 for C₅₈B₂ (1,9), 0.8735 for C₅₈N₂ (1,2), and 0.9075 for C₅₈B₂ (1,2). The results obtained by the AM1 method are 0.9128 for C₅₈N₂ (1,9), 0.8637 for C₅₈B₂ (1,9), 0.7578 for C₅₈N₂ (1,2), and 0.8574 for C₅₈B₂ (1,2). It is indicated that the N–N bond is somewhat stronger than the B–B bond in C₅₈X₂ (1,9) while the B–B bond is stronger than N–N bond in C₅₈X₂ (1,2); i.e., in the junction of the 6/6 ring, N atoms are somewhat strongly bonded relative to B atoms, whereas in the junction of the 6/5 ring N atoms are somewhat weakly bonded to each other compared with B atoms.

Now let us discuss the effects of oxidation and reduction introduced by heteroatoms in doped fullerenes C₅₈X₂ (X = N, B). In C₅₈B₂, replacing two carbons by boron atoms makes C₅₈B₂ two-electron deficient and provides two holes in the

5-fold-degenerate HOMO of C₆₀. The splitting of these energy levels results in the LUMO of C₅₈B₂ in which the coefficients in B and their neighboring carbon atoms are enhanced. The B atom substitution produces an electronic deficient site on the fullerene cage; boron atoms donate electronic charges to neighboring carbons and act as donors. Thus, the electronic population indicates a slight oxidation for boron atoms. In C₅₈N₂, the N atom substitution causes C₅₈N₂ to have an excess of two electrons. Two electrons are doped in the 3-fold-degenerate LUMO of C₆₀, which results in three nondegenerated levels. One of these levels is occupied by two electrons and becomes the HOMO of C₅₈N₂, which has the highest coefficients at N and neighboring carbon atoms. In N-doped fullerenes, nitrogen atoms accept electronic charges and exist as acceptors. Thus, the electronic population indicates a slight oxidation for N atoms in C₅₈N₂. The oxidation and reduction introduced by doping heteroatoms in a fullerene cage lead to unbalanced charge dispersion in heterofullerene systems. There are positive charges for B atoms and negative charges for their neighboring carbon atoms in C₅₈B₂, while the N atoms carry negative charges and positive charges are carried by their adjacent carbon atoms in C₅₈N₂. It is known that an electrophilic attack should preferably take place at the positions where the negative charges are centered, while a nucleophile attack should preferably happen at where the positive charges are centered. All carbon atoms in C₆₀ are equivalent, and the net charges are essentially zero. Thus, the reactivity of the carbon atoms toward electrophilic or nucleophilic attack is identical. The net charges on doped atoms and their neighboring atoms indicate that these positions can be attacked by electrophilic or nucleophilic reagents more readily; hence, the reactivity of fullerene can be enhanced by doping.

C₅₆N₄ and C₅₆B₄. The results obtained above permit a reliable search for the most likely structures of the other title compounds with little effort. When the 1,4-substitution pattern is considered, there are a total of 18 possible 1,4-/1,4 isomers for C₅₆X₄ (excluding the isomers with unfavorable X–X bond). The heats of formation are listed in Tables 2 and 3. Both the semiempirical and ab initio calculations indicate that the isomers (1,7,11,27) and (1,7,10,28) are the most stable isomers for C₅₆N₄ and that (1,7,11,27) is slightly preferred. For C₅₆B₄, the semiempirical calculations indicate that the isomers (1,7,10,28), (1,7,11,27), and (1,7,4,20) are among the best isomeric forms. However,

TABLE 2: Heats of Formation, Relative Heats of Formation, and Relative Total Energies (kcal/mol) of Various Possible Stable Isomers of C₅₆N₄

C ₅₆ N ₄	MNDO		AM1		PM3		HF/3-21G// MNDO RTE
	HF	RHF	HF	RHF	HF	RHF	
1,7,4,20	890.54	11.13	1040.56	14.30	809.11	14.02	26.6
1,7,46,49	885.83	6.42	1032.99	6.73	801.56	6.47	
1,7,48,58	887.01	7.60	1034.09	7.83	802.77	7.68	
1,7,50,60	887.22	7.81	1034.34	8.08	802.76	7.67	
1,7,49,52	886.14	6.73	1033.48	7.22	801.79	6.70	
1,7,11,27	879.41	0.00	1026.26	0.00	795.09	0.00	0.00
1,7,10,28	881.43	2.02	1029.06	2.80	796.09	1.00	0.20
1,7,3,13	891.10	11.69	1038.55	12.29	806.65	11.56	
1,7,4,16	889.07	9.66	1037.87	11.61	806.94	11.85	
1,7,3,17	887.77	8.36	1035.31	9.05	806.49	11.40	
1,7,15,18	888.82	9.41	1036.22	9.96	805.39	10.30	
1,7,16,36	885.71	6.30	1033.16	6.90	800.48	5.39	
1,7,17,35	885.84	6.43	1033.78	7.52	801.00	5.91	
1,7,34,37	887.00	7.59	1034.37	8.11	802.59	7.50	
1,7,32,35	886.33	6.92	1033.48	7.22	801.34	6.25	
1,7,34,50	887.08	7.67	1034.04	7.78	802.83	7.74	
1,7,33,51	886.82	7.41	1033.69	7.43	801.71	6.62	
1,7,14,31	887.74	8.33	1034.86	8.60	803.37	8.28	
1,7,13,32	891.44	12.03	1037.69	11.43	805.64	10.55	
1,7,30,33	886.36	6.95	1033.73	7.47	800.80	5.71	
1,7,28,31	886.98	7.57	1033.80	7.54	802.04	6.95	
1,7,29,48	887.56	8.15	1034.80	8.54	803.83	8.74	

TABLE 3: Heats of Formation, Relative Heats of Formation, and Relative Total Energies (kcal/mol) of Various Possible Stable Isomers of C₅₆B₄

C ₅₆ B ₄	MNDO		AM1		HF/3-21G// MNDO RTE
	HF	RHF	HF	RHF	
1,7,4,20	823.97	-0.53	1013.38	1.27	17.37
1,7,46,49	829.11	4.61	1016.65	4.54	
1,7,48,58	829.56	5.06	1017.59	5.48	
1,7,50,60	830.51	6.01	1017.94	5.83	
1,7,49,52	829.57	5.07	1017.05	4.94	
1,7,11,27	824.50	0.00	1012.11	0.00	0.00
1,7,10,28	823.86	-0.64	1011.29	-0.82	1.56
1,7,3,13	827.59	3.09	1016.54	4.43	
1,7,4,16	828.41	3.91	1017.15	5.04	11.82
1,7,3,17	827.26	2.76	1015.83	3.72	9.94
1,7,15,18	832.24	7.74	1020.49	8.38	
1,7,16,36	829.24	4.74	1017.13	5.02	
1,7,17,35	829.94	5.44	1017.97	5.86	
1,7,34,37	830.28	5.78	1018.11	6.00	
1,7,32,35	829.11	4.61	1016.73	4.62	
1,7,34,50	830.39	5.89	1017.93	5.82	
1,7,33,51	830.16	5.66	1017.45	5.34	
1,7,14,31	830.43	5.93	1018.65	6.54	
1,7,13,32	832.45	7.95	1020.48	8.37	
1,7,30,33	830.03	5.53	1017.89	5.78	
1,7,28,31	829.65	5.15	1017.28	5.17	
1,7,29,48	830.29	5.79	1018.55	6.44	

more rigorous ab initio calculations indicate that the isomers (1,7,11,27) and (1,7,10,28) are the two lowest energy structures, while the isomer (1,7,4,20) is unfavorable by 17 kcal/mol. Thus, we can draw the conclusion that the isomer (1,7,11,27) and (1,7,10,28) are also the most stable isomers for C₅₆B₄ with (1,7,11,27) preferred slightly. In fact, we can even deduce these two most stable isomers on the basis of the discussion above and the regioisomerism of fullerene adducts such as C₆₀Br₄.

Clare and Kepert⁴³ have decided that the isomers (1,7,11,27), (1,7,10,28), and (1,7,9,24) are the three most stable isomers for C₆₀Br₄. Considering the correlation between the fullerene adducts and heterofullerenes and the fact that the X-X bonds should be avoided in C₅₆X₄, we can draw the conclusion that the isomers (1,7,11,27) and (1,7,10,28) should be the most stable isomers for C₅₆X₄. This conclusion is consistent with our

calculations presented in this paper. As we can see from Figure 3, there is also a fair correlation between the stability order of C₆₀Br₄ isomers and the stability order of the same isomers of C₅₆X₄. Note that the points corresponding to (1,7,4,20), (1,7,4,16), and (1,7,3,17) isomers of C₅₆B₄ have strikingly lower heats of formation than those given by the straight line. This may be caused by the AM1 underestimated energy, since the ab initio method gives much higher energies for these isomers.

C₅₄N₆ and C₅₄B₆. Since there is a fair correlation between the stability order of the heterofullerenes and that of the fullerene adducts with bulky groups such as the bromofullerenes, the most stable stable isomers of the heterofullerenes C₅₄N₆ and C₅₄B₆ should be able to be determined on the basis of the relatively well studied fullerene adducts of C₆₀Br₆. Thus, the most stable, possible isomers of C₅₄X₆ (X = N, B) were built on the basis of the four most stable structures of C₆₀Br₆ in Kepert's work.⁴³ There are some inconsistencies in the calculated stability sequence of the isomers. For C₅₄N₆, the PM3 method give the same energy order as the ab initio results, which indicates that the isomer (1,7,23,40,10,28) has the lowest energy and that the isomer (1,7,10,28,48,58) is only slight unfavorable. The semiempirical AM1 and PM3 and ab initio methods suggest that the isomer (1,7,24,27,9,11), which has two adjacent nitrogen atoms, is the highest energy isomer and thus should be avoided, while the MNDO method suggests that the isomer (1,7,24,27,9,11) is the lowest energy isomer. Considering that it is wise to trust only those trends that are reproduced by several methods in working with semiempirical methods and that the N-N bond should be extremely avoided, as found in theoretical studies of C₅₈N₂, it is more reliable to conclude that the isomer (1,7,24,27,9,11) should be avoided and that the most stable isomers are (1,7,23,40,10,28) and (1,7,10,28,48,58). For C₅₄B₆, the AM1 gives the same stability order as the ab initio results, which indicates that the isomer (1,7,24,27,9,11) with two adjacent boron atoms is the lowest energy structure, while this isomer is the highest energy isomer according to the MNDO method. Considering that boron clusters (B_n, n = 2–52)⁴⁴ have been successfully produced by laser ablation, the most thermodynamically preferred structure should be the isomer (1,7,24,27,9,11). This regioisomer corresponds to the experimentally observed structures of C₆₀X₆ (X = Cl, Br),^{45,46} the computationally most stable structures of C₆₀Br₆⁴³ and C₆₀(OH)₆,⁴⁷ and the second computationally lowest energy structure of C₆₀H₆.⁴⁸

C₅₂N₈ and C₅₂B₈. In this section, some selected isomers of C₅₂N₈ and C₅₂B₈ are calculated. These structures are built on the basis of the regioisomerism correlation between the heterofullerenes and fullerene adducts as discussed above. These structures include computationally the five most stable isomers **a–e**⁴³ and the experimentally observed isomer **f**⁴⁵ of C₆₀Br₈ as shown in Figure 4. The calculation results are summarized in Tables 7 and 8. We can propose that structure **e** should be unfavorable for both C₅₂N₈ and C₅₂B₈ from chemical intuition, since there are two adjacent nitrogen or boron atoms in this structure. Our calculation results support this proposition. The best structures for C₅₂N₈ are isomers **a–d**, which computationally are among the five most stable isomers. The energy differences between these isomers are very small, less than 2 kcal/mol, and thus may be coexist in the product mixture. The structure corresponding to the experimentally observed isomer of C₆₀Br₈ is also not the lowest energy isomer for C₅₂N₈, which is expected to be several kcal/mol less stable than the best structure. However, this structure is the most stable isomer of C₅₂B₈, about 10–30 kcal/mol more stable than the other isomers, and thus should be dominant in the product mixture.

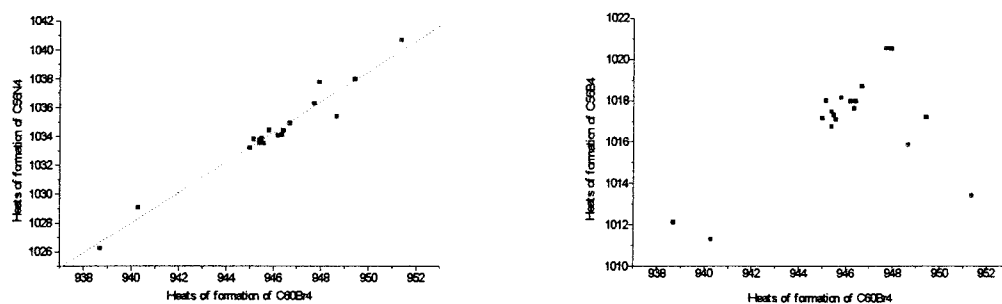


Figure 3. Correlation between the heats of formation (kcal/mol) of C₆₀Br₄ isomers and the same isomers of C₅₆X₄ (left, X = N; right, X = B).

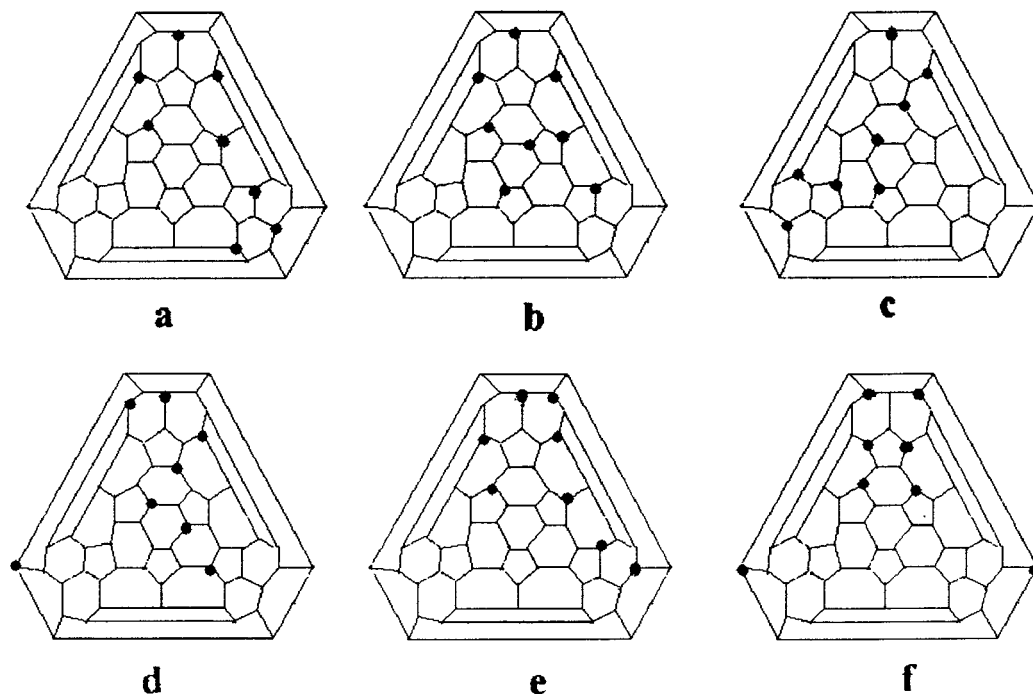


Figure 4. Possible structures of heterofullerenes C₅₂X₈ (X = N, B).

TABLE 4: Heats of Formation, Relative Heats of Formation, and Relative Total Energies (kcal/mol) of Possible Stable Isomers of C₅₄N₆

C ₅₄ N ₆	MNDO		AM1		PM3		HF/3-21G// MNDO RTE
	HF	RHF	HF	RHF	HF	RHF	
1,7,24,27,9,11	882.94	-1.52	1057.19	3.04	791.84	7.68	5.58
1,7,11,27,23,40	883.30	-1.16	1051.88	-2.27	784.94	0.78	2.37
1,7,23,40,10,28	884.46	0.00	1054.15	0.00	784.16	0.00	0.00
1,7,10,28,48,58	884.46	0.00	1053.23	-0.92	784.47	0.31	0.07

TABLE 5: Heats of Formation, Relative Heats of Formation, and Relative Total Energies (kcal/mol) of Possible Stable Isomers of C₅₄B₆

C ₅₄ B ₆	MNDO		AM1		HF/3-21G// MNDO RTE
	HF	RHF	HF	RHF	
1,7,24,27,9,11	803.91	0.00	1018.96	0.00	0.00
1,7,11,27,23,40	798.86	-5.05	1028.63	9.67	10.29
1,7,23,40,10,28	799.30	-4.61	1028.43	9.47	3.83
1,7,10,28,48,58	798.24	-5.67	1027.56	8.60	1.50

Now that up to six nitrogen or boron atoms have been incorporated into the carbon cage, are there some possibilities of substituting more fullerene carbon atoms with heteroatoms? If possible, are there some limitations on the number of heteroatoms in the fullerene framework? Can we substitute all the carbon atoms with heteroatoms to form the so-called “fully inorganic” fullerenes or “carbon-free” fullerenes⁴⁹ such as N₆₀ and B₆₀? Now let us discuss these problems on the basis of our above conclusions. It can be concluded that the weak N–N and

TABLE 6: Heats of Formation and Relative Heats of Formation (kcal/mol) of Possible Stable Isomers of C₅₂N₈

C ₅₂ N ₈	MNDO		AM1		PM3	
	HF	RHF	HF	RHF	HF	RHF
a	887.07	0.22	1077.63	0.00	773.77	2.08
b	886.85	0.00	1078.94	1.31	775.57	3.88
c	887.04	0.19	1078.67	1.04	771.69	0.00
d	888.46	1.61	1079.33	1.70	773.01	1.32
e	898.26	11.38	1089.91	12.28	790.41	18.72
f	893.58	6.73	1086.91	9.28	783.99	12.30

B–B bonds should be avoided in the heterofullerenes. To fulfill these requirements, at most 24 carbon atoms can be substituted with N or B atoms to form C₃₆N₂₄ and C₃₆B₂₄; i.e., two carbon atoms in each pentagon are substituted by heteroatoms. This structure corresponds to the experimentally observed C₆₀Br₂₄.⁵⁰ Fowler et al.⁵¹ have also deduced this structure on the basis of the assumption that the final product of bromination of C₆₀ should have no adjacent sp³ carbons, using the graph-theoretical

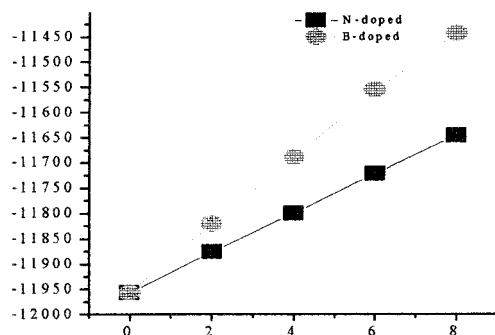


Figure 5. Dependence of H_{at} (kcal/mol) of $C_{60-n}X_n$ ($X = B, N$) on the number of heteroatoms in the doped fullerenes.

TABLE 7: Heats of Formation and Relative Heats of Formation (kcal/mol) of Possible Stable Isomers of $C_{52}B_8$

$C_{52}B_8$	MNDO		AM1	
	HF	RHF	HF	RHF
a	774.50	15.27	1046.10	14.25
b	770.60	11.37	1043.13	11.28
c	774.58	15.35	1045.79	13.94
d	775.44	16.21	1046.32	14.47
e	786.69	27.46	1049.40	17.55
f	759.23	0.00	1031.85	0.00

TABLE 8: Absolute Electronegativities of Heterofullerenes and Their All-Carbon Analogues

species	χ		species	χ	
	MNDO	AM1		MNDO	AM1
C_{60}	5.85	6.30			
$C_{58}N_2$	5.59	5.98	$C_{58}B_2$	6.05	6.32
$C_{56}N_4$	5.76	6.16	$C_{56}B_4$	6.06	6.31
$C_{54}N_6$	5.76	6.13	$C_{54}B_6$	5.94	6.06
$C_{52}N_8$	5.83	6.24	$C_{52}B_8$	5.97	6.07

concept of independence. Thus, there may be some limitation on the maximum heteroatom number in the fullerene framework; $C_{36}N_{24}$ and $C_{36}B_{24}$ may be the final N- and B-doped fullerenes. Although theoretically N_{60} is considerably stable⁵² and boron clusters B_n ($n = 2-52$) have already been produced by laser ablation,⁴⁴ which suggests that these carbon-free fullerenes may be synthesized under suitable conditions, the substituted fullerenes with more than 24 heteroatoms in the carbon framework are still unlikely to form.

Heats of Atomization of Heterofullerenes and Their All-Carbon Analogue C_{60} . As discussed in our previous studies,³³⁻³⁸ the stability of the heterofullerenes should be indicated by a greater negative value of the heat of atomization H_{at} . The heat of formation H_{at} can be calculated according to the gas-phase

reaction $nC + mX = C_nX_m$. This means that $H_{at}(C_nX_m) = H_f(C_nX_m) - nH_f(C) - mH_f(X)$. The heats of atomization of the most stable isomers of $C_{60-n}X_n$ ($X = B, N$) and C_{60} are summarized in Figure 5. The results presented in Figure 5 suggest that C_{60} cannot be stabilized by doping nitrogen or boron atoms and that the N-doped fullerenes are more stable than their B-doped analogues. This conclusion about the relative stability of $C_{58}N_2$ and $C_{58}B_2$ is consistent with Chen's result obtained by the CNDO/2 method³¹ while contrary to Wang's (EHMO method)¹⁹ and Kurita's (MO method with Harris functional and spin-restricted approximation)²⁴ results. It can also be found that the stabilities decrease with increasing number of heteroatoms, which suggests that it is increasingly more difficult to synthesize doped fullerenes with more doped atoms. This fact can also explain why the substituted fullerenes with more than six heteroatoms are not detected experimentally yet.

Ionization Potentials (IP) and Electron Affinity Potentials (EA) of Heterofullerenes. IP and EA are two well-known quantities and are of considerable interest from a theoretical viewpoint. The MNDO-calculated ionization potentials and affinity energies from Koopmans' theorem for the most stable heterofullerene isomers studied in this paper are summarized in Figure 6. The substitutional perturbation affects both HOMO and LUMO orbitals for the N- and B-doped fullerenes. The HOMO level of C_{60} is stabilized, and the LUMO level is destabilized compared to those of doped fullerenes. Thus, doped fullerenes have somewhat smaller ionization potentials and bigger affinity potentials compared with C_{60} , which suggests that heterofullerenes not only lose electrons somewhat more readily to form positive ions but also obtain electrons more easily to form anions; i.e., it is easier to oxidize and reduce $C_{60-n}X_n$ relative to C_{60} , and thus, the redox characteristics of C_{60} are enhanced by doping. It also can be found that both the ionization potential and affinity energies for B-doped fullerenes are bigger than their nitrogen analogues, which suggests that B-doped fullerenes obtain electrons more readily while loss of electrons is somewhat more difficult compared with their N-doped analogues. The AM1 calculation results, which are also summarized in Figure 6, give results that are similar to those obtained by MNDO methods.

In our previous work,³⁴ the absolute electronegativity (χ) has been used to predict the electron-transfer directions when the dimeric doped fullerenes are formed. The absolute electronegativities are also considered in this paper. The quantity of the absolute electronegativity (χ)⁵³ has been defined as $\chi = (\partial E / \partial N)$, where E is the energy and N is the number of electrons in the system considered. In a finite difference approximation using integer values for N , the expressions can be rewritten as $\chi = (IP + EA)/2$. The absolute electronegativity is a good measure

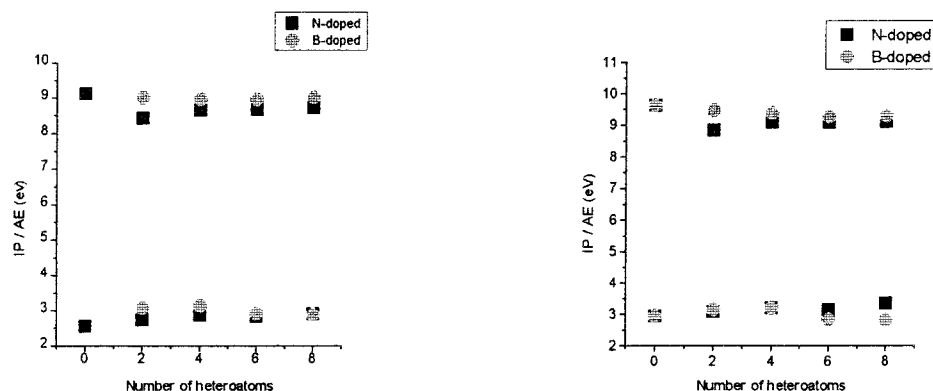


Figure 6. Ionization potentials and electron affinity energies of heterofullerenes $C_{60-n}X_n$ ($X = N, B$) (left, MNDO results; right, AM1 results).

of the ability of the molecule to attract electrons to itself. The calculated absolute electronegativities for the most stable heterofullerene isomers are summarized in Table 8. From Table 8 we found that there are remarkable differences between the absolute electronegativities of the doped fullerenes. These differences suggest that there should be significant electron transfer between all-carbon fullerene C₆₀ and B- or N-doped fullerenes or between the B-doped fullerenes and their nitrogen analogues; i.e. electrons should transfer from the N-doped fullerenes to all-carbon fullerene C₆₀ and B-doped fullerenes and from C₆₀ to B-doped fullerenes. This result is also consistent with the sequence of ionization potentials and affinity energies for the heterofullerenes under investigation as discussed above.

4. Conclusions

Semiempirical MNDO, AM1, and PM3 and ab initio calculations have been carried out on possible isomers of heterofullerenes C_{60-x}N_x and C_{60-x}B_x (x = 2–8) in order to determine the most stable structures and to investigate the underlying cause of their stabilities. The calculation results obtained by all these methods show that the heterofullerenes are less stable than C₆₀ and that the N-doped fullerenes are more stable than their B-doped analogues thermodynamically; the stabilities decrease with increasing number of heteroatoms. For C₅₈X₂, the isomer corresponding to 1,4-substitution to the cyclohexatriene unit is the most stable isomer among 23 possible structures. For C₅₆X₄, the isomers (1,7,11,27) and (1,7,10,28) are the two lowest energy structures among all the 1,4-/1,4-isomers with (1,7,11,27) preferred slightly. The most stable structures for C₅₄X₆ and C₅₂X₈ have also been calculated. Our previous proposition that the changes of hybridization from sp² to sp³ are the predominant factors of the regiochemistry for both C₆₀X₂ and C₅₈X₂ has been extended in this paper. It is found that there is a fair correlation between the stability order of the heterofullerenes and that of the fullerene adducts, especially those with bulky groups such as the bromofullerenes. According to the regioisomerism correlation between the heterofullerenes and fullerene adducts, the most stable isomers of heterofullerenes could be deduced on the basis of the relatively well studied fullerene adducts, which permits us investigate heterofullerenes with more doped atoms. Since N–N and B–B bonds should be avoided in heteroatoms, there may be some limitation on the maximum heteroatom number in the fullerene framework; C₃₆N₂₄ and C₃₆B₂₄ without adjacent N or B atoms may be the final N- and B-doped fullerenes. The redox characteristics of fullerene C₆₀ can be enhanced by doping. Heterofullerenes under investigation have somewhat smaller ionization potentials and bigger affinity energies compared with C₆₀, which suggests that it is easier to oxidize and reduce these doped fullerenes relative to C₆₀. On the basis of the absolute electronegativities, the electron-transfer directions in dimer fullerenes are predicted.

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