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Theoretical Studies on the Substitution Patterns in Heterofullerenes $C_{70-x}N_x$ and $C_{70-x}B_x$ ($x = 2-10$)

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A systematic investigation on possible structures of heterofullerenes $C_{70-x}N_x$ and $C_{70-x}B_x$ ($x = 2-10$) has been performed, and their electronic properties have been calculated employing semiempirical AM1, PM3, MNDO, and ab initio methods. It was found that the heterofullerenes $C_{70-n}X_n$ are less stable than their all-carbon analogues and the N-doped fullerenes are thermodynamically more stable than their B-doped analogues. The stabilities decrease with increasing number of heteroatoms. The structures whose carbon atoms are substituted in the para pattern across the equatorial hexagons correspond to the most stable isomers of $C_{70-x}N_x$ and $C_{70-x}B_x$, and the redox characteristics can be fine-tuned by doping. Our previously proposed correlation between the isomerism of the fullerene adducts $C_{60}X_n$ and that of the heterofullerenes $C_{60-n}N_n$ or $C_{60-n}B_n$ holds true for C_{70} adducts and doped C_{70} systems, which allows us to deduce the isomerism of the doped C_{70} fullerenes on the basis of the relatively well studied regioselectivity of [70]fullerene adducts. The aromaticity of the most stable structures of heterofullerenes decreases with increasing number of the heteroatoms in the system, and N-doped structures are slightly more aromatic than their B-doped analogues.

1. Introduction

Heterofullerenes are fullerenes in which one or more carbon atoms of the cage are substituted by heteroatoms such as boron or nitrogen. Apart from exohedral and endohedral fullerene derivatives, heterofullerenes represent the third fundamental group of modified fullerenes and are a new and fascinating discovery in the class of fullerene-based materials. The successful incorporation of heteroatoms into the fullerene skeleton opened up the possibility of fine-tuning the electronic properties of the cage structures. Heterofullerenes are new trends in material development, and they are expected to have many potential applications. In general, there are two ways to generate heterofullerenes. One way is to use isocyclic fullerenes as starting materials. In this field, great progress has already been achieved, especially with nitrogen heterofullerenes, as summarized in recent reviews.[1−3] The other one is the laser ablation technique or the contact-arc method, which is similar to the one used for the production of all-carbon cage frameworks.[4] Up to now, boron- and nitrogen-doped $C_{60-n}X_n$ and $C_{70-n}X_n$ ($X = N, B$),[5−7] oxygen-doped $C_{59}O$,[8] silicon-doped C_nSi ($n = 3-69$),[9] arsenic- and germanium-doped $C_{59}X$ (X=As, Ge) and $C_{69}As$,[10] BN-doped $C_{58}BN$,[11] phosphorus-doped fullerenes $C_{59}P$ and $C_{69}P$,[12] and metal-doped $C_{59}M^+$ (M = Pt, Ir)[13] have already been generated successfully.

The contact-arc method may be the most convenient way to obtain macroscopic amounts of heterofullerenes. The chemistry of heterofullerenes will develop only if macroscopic amounts of materials are available. However, there are many experimental problems with respect to purification and characterization of heterofullerenes generated by this method, and their structures have not been clarified so far.

On the theoretical side, the enormous number of possible isomers also makes it difficult to determine the most stable molecular structures of these doped fullerenes. For doped C_{70} systems, there are 143 structurally distinct isomers for $C_{68}X_2$, 46 275 for $C_{66}X_4$, and 6 553 764 for $C_{64}X_6$.[14] Given these huge numbers, it is impractical, if not impossible, to calculate every single isomer by quantum-chemical methods, even at the semiempirical levels. A prescreening by classical force-field methods is not feasible due to the lack of suitable heteroatom parameters, apart from the fact that these methods do not predict relative stabilities with sufficient accuracy even for pure fullerenes. Likewise, simple topological approaches are not accurate enough for such purposes.[15] For pure fullerenes, a reliable prescreening scheme has recently been proposed,[16] which evaluates relative stabilities from increments for structural motifs and an overall curvature correction. However, since such increments are not yet available for heterofullerenes, we are forced to select the systems to be studied without systematic prescreening and to rely in this regard on previous experience and qualitative considerations.

Our previous work showed that the 1,4-substitution pattern is thermodynamically preferred for $C_{68}X_2$ ($X = N, B$)[17] and that there is a fair correlation between the regioisomers of heterofullerenes and fullerene adducts with sterically demanding and seggregated addends.[17−20] These findings build a bridge to connect these two groups and allow us to deduce the most stable isomers on the basis of the knowledge of the relatively well studied fullerene adducts. Assuming that the reaction products obtained in the contact-arc method are thermodynamically controlled, the computationally lowest energy isomers would be the experimentally observed structures when the contact-arc method is used.

In our recent studies, the most stable isomers of $C_{58}X_2$ ($X = N, B, P$),[18,19] $C_{68}X_2$ ($X = N, B$),[17] $C_{60-x}N_x$, and $C_{60-x}B_x$ ($x = 2-8$)[20] have been calculated. Here, an extended investigation

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on the molecular structures of 46 possible isomers of $C_{70-x}N_x$ and $C_{70-x}B_x$ ($x = 2-10$) will be presented using semiempirical (AM1, PM3, MNDO) and ab initio methods. The equilibrium geometrical structures, heats of formation, heats of atomization, ionization potentials, and affinity energies were determined. The correlation between the isomerism of the fullerene adducts $C_{60}X_n$ and that of heterofullerenes $C_{60-n}N_n$ or $C_{60-n}B_n$ holds true for the corresponding clusters containing 70 atoms. The relative energies of $C_{70}X_n$ systems correlate with those of the regioisomeric heterofullerenes $C_{70-n}X_n$. Moreover, the degree of electron delocalization is evaluated by using the computed NICS (nucleus independent chemical shifts)[21] at the cage centers of the most stable isomers of $C_{70-n}X_n$. NICS has been demonstrated to be a useful criterion for aromaticity or antiaromaticity.[21,22] The NICS at the cage center has essentially the same value as that of the ^3He endohedral shift, which is a valuable experimental tool for characterizing fullerenes and their derivatives.[23,24]

2. Computational Details

Given the large number and the size of the studied isomers, we have mostly applied semiempirical MNDO-type methods to assess the relative stability of the heterofullerenes. These methods generally provide reasonable results for pure fullerenes and their derivatives (see ref 25 for a brief review). Among these methods, MNDO has been most widely used in fullerene chemistry and physics for a variety of applications, ranging from superconductivity to stability and reactivity.[26] When compared with high-level ab initio or density functional approaches, MNDO has often been found to provide realistic relative stabilities (e.g., for the isomers of C_{84},[16,27] giant fullerenes such as C_{180} or C_{240},[28] and derivatives such as $C_{60}H_2$ and $C_{70}H_2$[29]), although there are noticeable exceptions (e.g., the overbinding of the C_{60} dimer[30,31]). For heteroatom-doped systems, the performance of MNDO for the relative stabilities is consistently better than that of AM1 for heteroatom substituted buckybowls.[32] The same has been found in our previous studies of B-doped C_{60} systems.[18] In the present work, the MNDO, AM1 and PM3 methods have been utilized together in order to assess the consistency of the semiempirical methods. We believe that common trends obtained at the semiempirical level are unlikely to change at higher levels.

Full geometry optimizations were carried out at the MNDO,[33] AM1,[34] and PM3[35] semiempirical levels utilizing the VAMP 7.0 program.[36] Eigenvector following was used to locate the minima. The optimizations were carried out without any symmetry constraints in Cartesian coordinates, and initial input geometries were based on the optimized C_{70} structure with specific carbon atoms replaced by B and N. For the key structures, single-point ab initio Hartree−Fock (HF) energy calculations were performed at the MNDO-optimized geometries employing the 3-21G basis set (HF/3-21G//MNDO) using the Gaussian-98 program.[37] Nucleus independent chemical shifts (NICS)[21] were computed at the cage centers of interest at the GIAO-SCF/3-21G level with the MNDO geometries utilizing the Gaussian-98 suite of program.[37]

3. Results and Discussion

The numbering system used in this work (Figure 1) conforms to the definition of Taylor.[38] Similar to previous studies,[20] the isomers of the fullerene adducts $C_{70}X_n$ and the isomers of the heterofullerenes $C_{70-n}X_n$, in which the heteroatoms substitute the carbon atoms at those positions where the addends of $C_{70}X_n$ are bound, are defined to have the same isomer pattern. As a consequence, the isomers chosen for this work have the same addition pattern as the $C_{70}X_n$ adducts calculated by Clare and Kepert.[39]

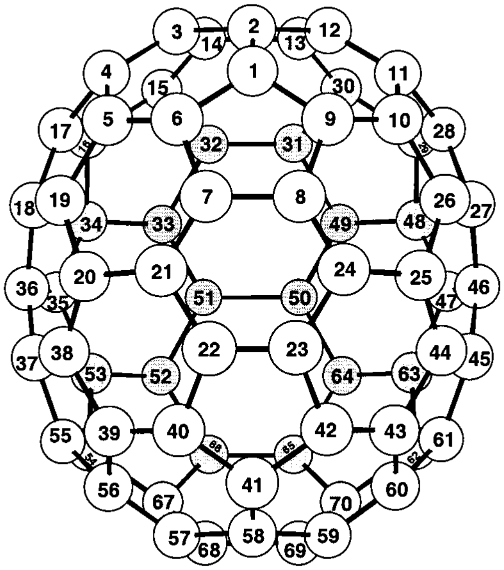

Figure 1. Numbering of atoms in C_{70}.

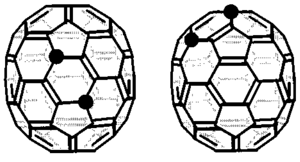
1, 3 **2, 4**

Figure 2. The two most stable isomers of $C_{68}X_2$ (X = N, B).

TABLE 1: Heats of Formation, Relative Heats of Formation, and Relative Total Energies (kcal/mol) of the Most Possible Stable Isomers of $C_{68}X_2$ (X = N, B)

	MNDO		AM1		PM3		HF/3-21G //MNDO
species	ΔH_f	E_{rel}	ΔH_f	E_{rel}	ΔH_f	E_{rel}	E_{rel}
$C_{68}N_2$ **1** (7,23)	941.56	0.00	1085.86	0.00	871.96	0.00	0.00
$C_{68}N_2$ **2** (2,5)	941.76	0.20	1086.16	0.30	873.67	1.71	6.26
$C_{68}B_2$ **3** (7,23)	911.97	0.00	1074.05	0.00			0.00
$C_{68}B_2$ **4** (2,5)	919.12	7.15	1083.74	9.69			12.94

Isomerism of Heterofullerenes. *$C_{68}N_2$ and $C_{68}B_2$.* The systematic theoretical studies on the heterofullerenes $C_{68}X_2$ (X = B, N)[17] indicated that $C_{68}X_2$ (7,23), which corresponds to 1,4-substitution of a cyclohexatriene unit in the equator of C_{70}, is the lowest-energy isomer. The energy data for the most stable isomers of $C_{68}X_2$ are summarized in Table 1, and their structures are shown in Figure 2.

In our previous studies,[17−20] a correlation between the isomerism of heterofullerenes and that of fullerene adducts, especially with large addends such as bromine atoms, has been established and used to predict the most stable structures of heterofullerenes successfully. Very recently, Clare and Kepert[39] have studied the isomers of $C_{70}Br_n$ ($n = 2-12$) systematically, finding those with addends situated obliquely across the para position of an equatorial C_6 ring to be most stable. The reason for the preference of 1,4-addition above 1,2-addition can be explained as sterical crowding in the case of 1,2-adducts. This is also true for $C_{70-x}N_x$, since 1,2-substituted isomers would exhibit a lone-pair/lone-pair repulsion between the nitrogen atoms. The analogous effect for $C_{70-x}B_x$, however, is of an electronic origin: In 1,4-adducts, there are more (i.e., three)

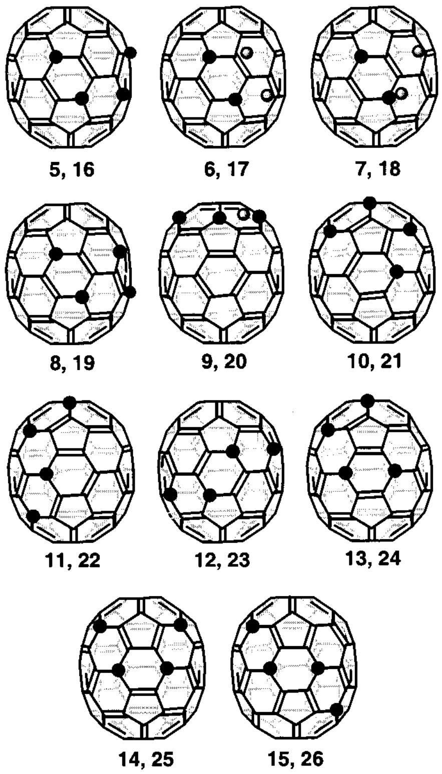

Figure 3. Calculated isomers of $C_{66}X_4$ (X = N, B).

possibilities for $p\pi/p\pi$-like interactions to carbon, which enable a better compensation of the electron deficiency of boron, as compared to 1,2-substitution. Furthermore, it is of importance in which region of C_{70} the substitution with heteroatoms takes place: C_{70} contains two strongly curved polar caps and a comparatively "planar" equatorial belt. The degree of curvature determines the reactivity of the corresponding double bonds toward addition reactions.[40] Introduction of boron preferably takes place in the equatorial region, since in this case a more planar surrounding is favorable. Although in the case of nitrogen the strain release caused by addition to the polar caps would be bigger, substitution also takes place preferably in the equatorial region. The prevailing 1,4-addition is responsible for this effect, as it provides for the removal of formal [5,6] double bonds present in the equatorial belt of C_{70} (see Figure 2, structure a). It has been shown that this effect has an experimental consequence: The addition of benzyne to C_{70} leads, among others, to the hitherto unknown C7−C8 isomer, where one of the five formal [5,6] double bonds is removed by the addition.[41] Apart from this, 1,4-substitution in the polar caps would lead to the introduction of [5,6] double bonds which are strongly unfavorable here.[40]

$C_{66}N_4$ and $C_{66}B_4$. The computational results for $C_{68}X_2$ above indicate that the isomers with 1,4-substitution, i.e., substitution across the para positions of a six-membered ring, are favorable, and the isomer obtained by substituting carbon atoms across the equatorial hexagon is the lowest-energy structure. If further substitution follows the same pattern of this most stable isomer of $C_{68}X_2$, i.e., with para substitution only across two equatorial C_6 rings, four possible isomers **5**−**8**, **16**−**19** for $C_{66}X_4$ would result as shown in Figure 3. There are also seven other possible structures **9**−**15**, **20**−**26** with para-para-para substitutions as shown in Figure 3. All these isomers and their energies are summarized in Table 2 and Table 3.

Both the semiempirical and ab initio calculations indicate that the isomer (7,23;44,27) is the most stable structure of $C_{66}X_4$.

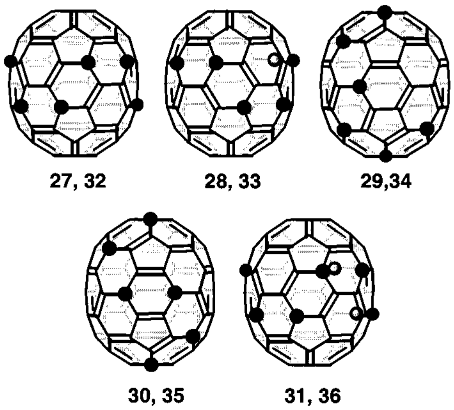

Figure 4. Calculated isomers of $C_{64}X_6$ and the most stable structure of $C_{62}X_8$ (X = N, B).

TABLE 2: Heats of Formation, Relative Heats of Formation, and Relative Total Energies (kcal/mol) of Various Possible Stable Isomers of $C_{66}N_4$

	MNDO		AM1		PM3		HF/3-21G //MNDO
$C_{66}N_4$	ΔH_f	E_{rel}	ΔH_f	E_{rel}	ΔH_f	E_{rel}	E_{rel}
5 (7,23;44,27)	939.03	0.00	1104.90	0.00	855.62	0.00	0.00
6 (7,23;63,49)	942.71	3.68	1108.51	3.61	858.37	2.75	0.61
7 (7,23;48,64)	945.26	6.23	1111.14	6.24	861.13	5.51	
8 (7,23;26,45)	949.40	10.37	1116.04	11.14	866.80	11.18	
9 (1,4;15,30)	947.51	8.48	1113.52	8.62	868.41	12.79	
10 (5,2;10,24)	953.90	14.87	1114.56	9.66	869.14	13.52	
11 (2,5;21,39)	960.02	20.99	1121.98	17.08	877.52	21.90	
12 (7,19;37,53)	961.01	21.98	1130.78	25.88	879.77	24.15	
13 (2,5;21,24)	972.13	33.10	1129.38	24.48	886.01	30.39	
14 (5,21;24,10)	969.29	30.26	1126.59	21.69	883.49	27.87	
15 (5,21;24,43)	994.38	55.35	1150.43	45.53	903.75	48.13	

TABLE 3: Heats of Formation, Relative Heats of Formation, and Relative Total Energies (kcal/mol) of Various Possible Stable Isomers of $C_{66}B_4$

	MNDO		AM1		HF/3-21G//MNDO
$C_{66}B_4$	ΔH_f	E_{rel}	ΔH_f	E_{rel}	E_{rel}
16 (7,23;44,27)	879.75	0.00	1080.14	0.00	0.00
17 (7,23;63,49)	883.06	3.31	1084.62	4.48	3.46
18 (7,23;48,64)	885.85	6.10	1087.48	7.34	
19 (7,23;26,45)	889.62	9.87	1092.33	12.19	
20 (1,4;15,30)	900.78	21.03	1106.55	26.41	
21 (5,2;10,24)	902.08	22.33	1113.10	32.96	
22 (2,5;21,39)	901.55	21.80	1111.96	31.82	
23 (7,19;37,53)	905.32	25.57	1110.25	31.11	
24 (2,5;21,24)	898.21	18.46	1109.54	29.40	
25 (5,21;24,10)	899.56	19.81	1112.01	31.87	
26 (5,21;24,43)	924.65	44.90	1130.70	50.56	

This structure corresponds to the para-para-para substitution pattern across the equatorial area. As discussed above, this is thermodynamically favorable since no [5,6] double bonds have to be introduced in the polar region and [5,6] double bonds in the equator are removed. On the other hand, the energy difference between this best structure and the second lowest-energy isomer (7,23;63,49) is very small; thus, we can expect that these two isomers may coexist in the reaction products.

$C_{64}X_6$ and $C_{62}X_8$. For $C_{64}X_6$, four possible para-para-para-para-para structures **27**−**30**, **32**−**35** exist as shown in Figure 4. All the semiempirical methods here indicate that the most stable structure has oblique para substitution across three connected equatorial six-membered rings. Further substitution in the same way yields $C_{62}X_8$ **31** and **36**. The structures and energy data of $C_{64}X_6$ and $C_{62}X_8$ are summarized in Tables 4 and 5.

$C_{60}N_{10}$ and $C_{60}B_{10}$. Further substitution with the same addition pattern does not lead to a continuous para equatorial belt in all

TABLE 4: Heats of Formation, Relative Heats of Formation, and Relative Total Energies (kcal/mol) of Possible Stable Isomers of $C_{64}N_6$ and $C_{62}N_8$

species	MNDO		AM1		PM3	
	ΔH_f	E_{rel}	ΔH_f	E_{rel}	ΔH_f	E_{rel}
$C_{64}N_6$ **27** (7,23;44,27;48,64)	936.70	0.00	1124.08	0.00	839.26	0.00
$C_{64}N_6$ **28** (7,19;37,53;33,49)	947.60	10.90	1137.86	13.78	851.56	12.30
$C_{64}N_6$ **29** (2,5;21,39;58,43)	955.69	18.99	1138.30	14.22	859.56	20.30
$C_{64}N_6$ **30** (2,5;21,24;43,58)	971.05	34.35	1149.69	25.61	872.12	32.86
$C_{62}N_8$ **31** (7,23;44,27;48,64;52,34)	932.80		1141.64		820.96	

TABLE 5: Heats of Formation, Relative Heats of Formation, and Relative Total Energies (kcal/mol) of Possible Stable Isomers of $C_{64}B_6$ and $C_{62}B_8$

species	MNDO		AM1	
	ΔH_f	E_{rel}	ΔH_f	E_{rel}
$C_{64}B_6$ **32** (7,23;44,27;48,64)	847.79	0.00	1086.47	0.00
$C_{64}B_6$ **33** (7,19;37,53;33,49)	862.29	14.50	1103.81	17.34
$C_{64}B_6$ **34** (2,5;21,39;58,43)	878.05	30.26	1130.67	44.34
$C_{64}B_6$ **35** (2,5;21,24;43,58)	874.97	27.18	1128.23	41.76
$C_{62}B_8$ **36** (7,23;44,27;48,64;52,34)	814.02		1091.10	

five equatorial six-membered rings; only the structures **37** and **42** shown in Figure 5 can be obtained (namely, para[9] or series IIA, following Clare's definition[39]). On the other hand, a complete belt can be obtained if one or more ortho equatorial rings are introduced. Thus, we can get four such isomers, **38**−**41** and **43**−**46**, as also summarized in Figure 5 and Table 6, among which the isomers **38** and **43** (7,23;44,27;48,64;52,34;18,19) correspond to the experimental structure of $C_{70}Cl_{10}$.[42] For $C_{60}N_{10}$, all the semiempirical methods used give the same stability order of the isomers, indicating that isomer **37** is the lowest-energy structure, which is expected to be more than 10 kcal/mol more stable than the second most stable isomer. However, there are some discrepancies for $C_{60}B_{10}$. According to MNDO, isomer **42** is most stable, ca. 11 kcal/mol lower in energy than isomer **43**, while these two isomers are almost isoenergetic according to AM1, with a slight preference for isomer **43**. The ab initio data support the MNDO energy order and favor isomer **42** without adjacent B−B bond by ca. 14 kcal/mol over isomer **43**.

For clarity, all the most stable isomers for the heterofullerenes studied are shown in Figure 6. Evidently N−N and B−B bonds should be avoided in heterofullerenes. Requiring that there is no adjacent N−N or B−B bond in doped C_{70}, the maximum number of heteroatoms in the C_{70} cage is 26, i.e., the same as the maximum number of bromine atoms in C_{70} adducts without adjacent Br atoms.[43] Thus, it is reasonable to assume that there is an upper limit of heteroatom substitution, and the possibility of syntheses for the so-called "fully inorganic fullerenes" such as N_{70} and B_{70} is very low.

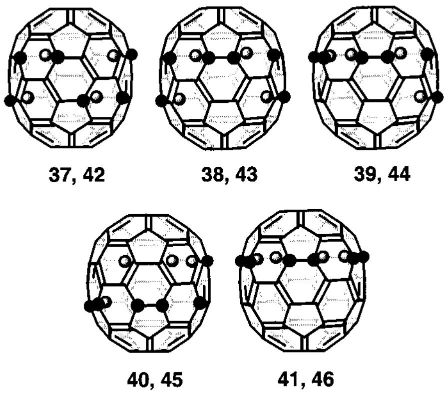

Figure 5. Calculated isomers of $C_{60}X_{10}$ (X = N, B).

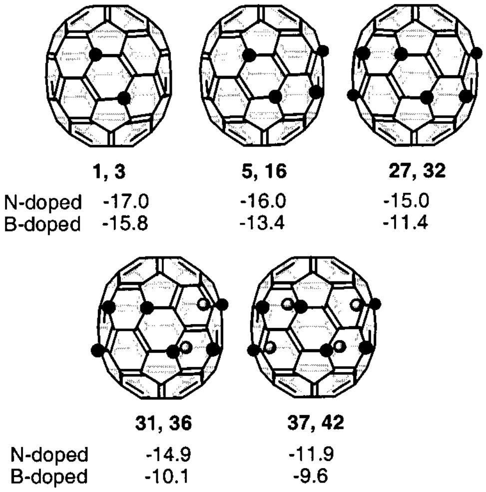

Figure 6. The most stable isomers of $C_{70-n}X_n$ (X = N, B) $C_{68}X_2$ **1**, **3**; $C_{66}X_4$ **5**, **16**; $C_{64}X_6$ **27**, **32**; $C_{62}X_8$ **31**, **36**; $C_{60}X_{10}$ **37**, **42** and their endohedral chemical shifts (ppm).

The most stable structures of doped [70]fullerenes $C_{70-n}X_n$ follow the same regioisomerism as that of the fullerene adducts $C_{70}Br_n$, or the regioisomerism of $C_{70}H_n$ when only para additions across six-membered rings are considered. Thus, the correlation between the isomerism of the fullerene adducts $C_{60}X_n$ and that of the heterofullerenes $C_{60-n}N_n$ or $C_{60-n}B_n$ can be extended to C_{70} adducts and doped C_{70} systems. As an example, the correlation between the heats of formation of the heterofullerenes $C_{66}X_4$ and those of $C_{70}H_4$ with the same isomerism is shown in Figure 7.

Heats of Atomization of Heterofullerenes and Their All-Carbon Analogue C_{70}. The heat of atomization (H_{at}) is a good index for the stability of heterofullerenes, and a more negative value of H_{at} indicates higher stability of a species. The heats of atomization for the most stable isomers of the heterofullerenes studied herein and their all-carbon analogue C_{70} are summarized in Figure 8. Similar to the doped C_{60} systems,[20] C_{70} cannot be stabilized by doping with nitrogen or boron atoms, and the N-doped fullerenes are more stable than their B-doped analogues. Since B-doped $C_{70-n}B_n$ have already been synthesized by a DC arc-burning method,[6] it is reasonable to expect the successful synthesis of nitrogen-doped $C_{70-n}N_n$ if suitable synthetic protocols can be achieved. However, it can also be found that the stabilities are lower with increasing number of heteroatoms, which suggests that it is getting more and more difficult to synthesize doped fullerenes with a higher number of heteroatoms.

Ionization Potentials and Affinity Energies of Heterofullerenes. The MNDO calculated ionization potentials (IP) and affinity energies (AE) from Koopmans' theorem for the most stable heterofullerene isomers studied in this paper are summarized in Figure 9. For the most stable species, both N-doped and B-doped fullerenes have bigger affinity energies than their all carbon analogue C_{70}, indicating that these heterofullerenes

TABLE 6: Heats of Formation and Relative Heats of Formation (kcal/mol) of Possible Stable Isomers of $C_{60}N_{10}$ and $C_{60}B_{10}$

	MNDO		AM1		PM3	
$C_{60}N_{10}$	ΔH_f	E_{rel}	ΔH_f	E_{rel}	ΔH_f	E_{rel}
37 (7,23;44,27;48,64;52,34;18,38)	937.29	0.00	1168.40	0.00	813.09	0.00
38 (7,23;44,27;48,64;52,34;18,19)	947.19	9.90	1180.15	11.75	826.11	13.02
39 (7,23;44,27;48,49;33,34;18,19)	987.94	50.65	1226.30	57.90	875.22	62.13
40 (7,23;44,45;63,64;52,34;18,19)	988.27	50.98	1226.42	58.02	875.76	62.67
41 (7,8;26,27;48,49;33,34;18,19)	1028.37	91.08	1272.35	103.95	923.86	110.77

	MNDO		AM1		HF/3-21G//MNDO
$C_{60}B_{10}$	ΔH_f	E_{rel}	ΔH_f	E_{rel}	E_{rel}
42 (7,23;44,27;48,64;52,34;18,38)	788.03	0.00	1104.91	0.00	0.00
43 (7,23;44,27;48,64;52,34;18,19)	799.32	11.29	1103.65	−1.26	13.97
44 (7,23;44,27;48,49;33,34;18,19)	842.96	54.93	1127.39	22.48	
45 (7,23;44,45;63,64;52,34;18,19)	842.88	54.85	1127.11	22.20	
46 (7,8;26,27;48,49;33,34;18,19)	886.78	98.75	1151.47	46.56	

add electrons more easily to form anions; thus, it is somewhat easier to reduce them as compared to C_{70}. As far as the sequence of ionization potentials is considered, the sequence is N-doped $< C_{70} <$ B-doped, which indicates that N-doped fullerenes lose electrons more readily than C_{70} to form positive ions; thus, they are somewhat easier to oxidize, while the B-doped analogues lose electrons less easily. Compared with the doping effects on IPs and AEs of C_{60} systems,[20] the doped C_{70} systems show somewhat lower ionization potentials and higher affinity energies; thus, it is much easier to oxidize and reduce $C_{70-n}X_n$ relative to $C_{60-n}X_n$. Therefore it can be concluded that doping may have different effects on the redox characteristics for substituted C_{60} and C_{70} systems.

Symmetry lowering with respect to C_{70} is responsible for the existence of permanent dipole moments in heterofullerenes, and the dipole difference is very important in HPLC or other column separations. The dipoles of the most stable isomers of $C_{70-n}X_n$ are shown in Figure 10. The significant differences between the most stable isomers of heterofullerenes with a different number of doped atoms suggest that these species may be separated if appropriate protocols can be achieved.

Aromaticity of Heterofullerenes. Containing a conjugated π-system, fullerenes form a unique class of spherical molecules. It is interesting to ask the question how the heteroatom substitution will affect its aromaticity or electron delocalization. For this purpose, nucleus-independent chemical shifts (NICS)[21] calculated at the cage centers have been employed to evaluate the mobility of electrons on the cage surfaces.

The endohedral chemical shifts of the most stable isomers of heterofullerenes studied in this paper are summarized in Figure 6. Compared with the endohedral chemical shift of C_{70} at the same level, −20.9 ppm (exp. −28.8 ppm[23]), the aromaticity decreases with increasing number of heteroatoms in the system, and N-doped structures are slightly more aromatic

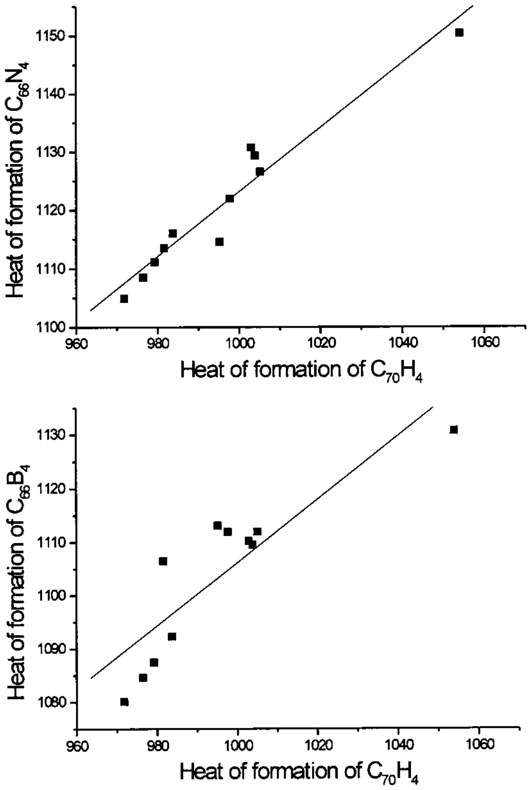

Figure 7. Correlation between the heats of formation (kcal/mol) of $C_{66}X_4$ and those of $C_{70}H_4$ with the same isomerism (upper X = N; lower X = B).

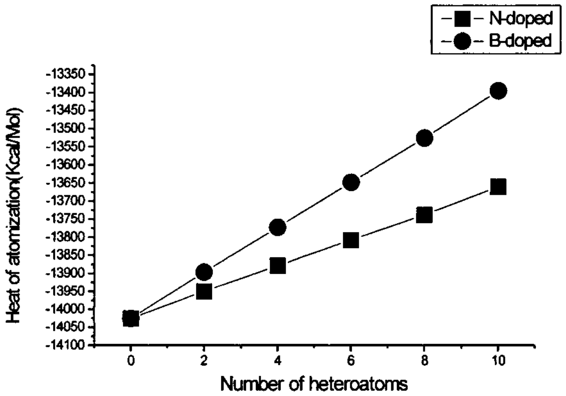

Figure 8. Dependence of H_{at} of $C_{70-n}X_n$ (X = B, N) vs the number of heteroatoms in the doped fullerenes (most stable isomers).

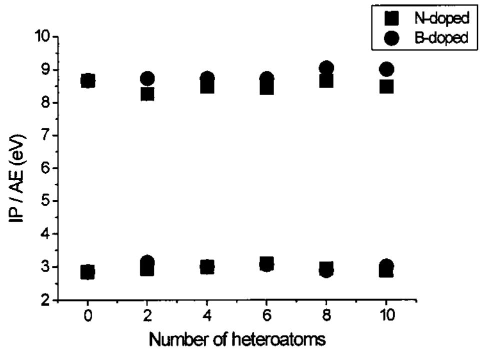

Figure 9. Ionization potentials and affinity energies of the most stable isomers of $C_{70-n}X_n$ (X = N, B).

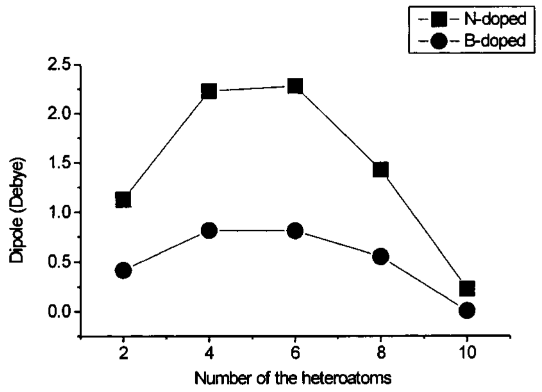

Figure 10. Dipole moments of the most stable isomers of $C_{70-x}N_x$ and $C_{70-x}B_x$ ($x = 2-10$).

than their B-doped analogues. Since NICSs at the cage centers have essentially the same values as the endohedral helium chemical shifts, these computed values also provide a basis for the possible characterization of these heterofullerenes.

4. Conclusions

The most stable structures of the heterofullerenes $C_{70-x}N_x$ and $C_{70-x}B_x$ have been calculated and their electronic properties have been studied using both semiempirical (MNDO, AM1, PM3) and ab initio methods. Similar to doped C_{60} systems, the heterofullerenes $C_{70-n}X_n$ are less stable than their all-carbon analogues, and the N-doped fullerenes are thermodynamically more stable than their B-doped analogues, while the stabilities decrease with increasing number of heteroatoms. Our previously proposed correlation between the isomerism of the fullerene adducts $C_{60}X_n$ and that of the heterofullerenes $C_{60-n}N_n$ or $C_{60-n}B_n$ holds true for C_{70} adducts and doped C_{70} systems; thus, we can correlate the stability of the doped C_{70} fullerenes on the basis of the regioselectivity of [70]fullerene adducts. Since N−N and B−B bonds should be avoided in heterofullerenes and the stabilities of heterofullerenes decrease with increasing number of heteroatoms, there should exist some limit to the maximum heteroatom number in the fullerene framework. By doping with heteroatoms such as nitrogen and boron, the redox characteristics of C_{70} can be tuned. Moreover, the endohedral chemical shifts of the most stable isomers of $C_{70-n}X_n$ have been computed to assess the aromaticity and provide a basis for further characterization of these doped fullerenes. The aromaticity of heterofullerenes studied in this paper decreases with increasing number of the hoteroatoms in the system, and N-doped structures are slightly more aromatic than their B-doped analogues.

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