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DFT Study on the Stabilities of the Heterofullerenes $Sc_3N@C_{67}B$, $Sc_3N@C_{67}N$, and $Sc_3N@C_{66}BN$

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On the basis of calculations using density functional theory, we investigated the relative stabilities of all isomers of $Sc_3N@C_{67}B$ and $Sc_3N@C_{67}N$ as well as those of stable isomers of $Sc_3N@C_{66}BN$. As a result, we predict that $Sc_3N@C_{68}$ can be doped substitutionally with a boron atom much better than C_{60}. This effect can be ascribed to the favorable electrostatic attraction between the encased Sc_3N cluster and the polar C−B bonds of the fullerene cage, which show the important role played by the encapsulated atoms in stabilizing the fullerene. A difference in the interaction also determines the regiospecificity of $Sc_3N@C_{67}B$. On the contrary, N-doping of the fullerenes forming $Sc_3N@C_{67}N$ is much less favorable than that in C_{60} or C_{70}. A judicious choice of stable isomers of $Sc_3N@C_{66}BN$ among a vast number of possible isomers indicates that $Sc_3N@C_{68}$ can also be doped with a pair of B and N atoms better than C_{60} under the simultaneous existence of B and N sources. Relative stabilities of various isomers of the BN-substituted fullerenes can be understood in terms of the combined electrostatic effects in the B- and N-substitutions of $Sc_3N@C_{68}$ complemented by a specific local preference in the N-substitution and the formation of a B−N bond.

Introduction

Recently, the introduction of heteroatoms into a fullerene cage has been an interesting subject in fullerene science. For example, microscopic amounts of $C_{60-n}B_n$ ($n = 1, 3$), in which C_{60} was substitutionally doped with several boron atoms, were identified by the laser vaporization technique.[1] Later, arc evaporation of graphite rods doped with boron nitride, boron carbide, and boron produced $C_{59}B$ and $C_{69}B$ in macroscopic amounts.[2] A number of methods exist for the production of C_nN_m, which are based on either arc discharge or the laser vaporization technique.[3] The production of a macroscopic amount of $C_{59}N$ was made possible by the chemical modifications of C_{60} at the postsynthetic stage of the fullerene.[4] In addition, $C_{58}BN$ was produced by high-temperature laser ablation of BC_2N-graphite rods.[5] Even the existence of $C_{48}N_{12}$ has been proposed.[6]

Meanwhile, Dorn and co-workers reported the production of a family of encapsulated trimetallic nitride clusters inside fullerenes in macroscopic quantities by introducing a small amount of N_2 gas during the fullerene synthesis.[7] For example, they were able to produce $Sc_3N@C_{80}$ in a yield that exceeded that of C_{84},[8] which is the third most abundant fullerene after C_{60} and C_{70}. $Sc_3N@C_{68}$ was also produced as a byproduct of $Sc_3N@C_{80}$ synthesis. The fullerene violates the isolated-pentagon rule (IPR) in such a way that three pentagon pairs are fused together.[9] It was assigned to the isomer $Sc_3N@C_{68}$:6140 (D_3) on the basis of the relative energies of the isomers and the ^{13}C NMR pattern.[10] The stability of those endohedral fullerenes, which is significantly enhanced over that of the bare fullerenes, can be ascribed to the transfer of six electrons from the Sc_3N moiety to the fullerene cage.[11] A negative surface charge greatly affects the chemical reactivity of the system. One of the remarkable consequences of this charge effect is the resulting regiospecificity in organic functionalizations. For example, a Diels−Alder reaction[12] and 1,3-dipolar cycloaddition[13] occur exclusively at [5,6] double bonds, the reasons for which have not yet been completely understood.

These observations raise the interesting question of whether or not B- and/or N-doping to $Sc_3N@C_n$ ($n = 68$ and 80) are also possible. Also, another question can be raised as to whether there is a regiospecificity in the substitutional doping of those atoms. Answering these questions may lead to understanding the origin of the specificity in terms of the role of the encased atoms. In turn, those investigations will contribute significantly to our understanding of the chemistry of endohedral fullerenes. In this work, we will first investigate $Sc_3N@C_{68}$, since it has fewer substitutional isomers than $Sc_3N@C_{80}$. From this study, factors governing the relative stabilities of various isomers of the substituted fullerenes will be extracted. On the basis of the findings, we will also select several candidates for stable isomers of $Sc_3N@C_{66}BN$ among a vast number of possible isomers.

Theoretical Methods

All total energy calculations were performed using the Vienna ab initio simulation package (VASP).[14] Electron−ion interactions were described by the projected augmented wave (PAW) method,[15] which is basically a frozen-core all-electron calculation. Exchange-correlation effects were treated within the generalized gradient approximation presented by Perdew, Burke, and Ernzerhof (PBE).[16] The solution of the Kohn−Sham (KS) equation was obtained using the Davison blocked iteration scheme followed by the residual vector minimization method. All valence electrons of chemical elements were explicitly considered in the KS equation. We adopted a supercell geometry in which the k-space sampling was done with Γ-point. In doing this, we used large supercells that guaranteed that interatomic

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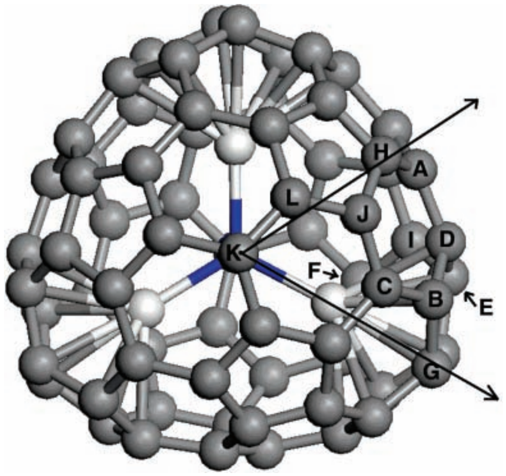

Figure 1. Optimized structure of $Sc_3N@C_{68}$, where A−L denote the different sites for boron or nitrogen substitution. The irreducible region is surrounded by arrows.

TABLE 1: Parameters for $C_{59}B$ and Various Isomers of $Sc_3N@C_{67}B$

	isomer	ΔE_B (eV)	S_B[a]	E_{es}[b] (eV)
$C_{59}B$		2.38	665	
$C_{69}B$	A	2.44	665	
	B	2.54	666	
$Sc_3N@C_{67}B$	A	1.32	666	−3.60
	B	1.49	665	−3.02
	C	1.60	666	
	D	1.61	665	
	E	1.62	665	−3.02
	F	1.82	665	
	G	1.89	655	−2.45
	H	1.97	665	−2.74
	I	1.98	665	
	J	1.98	665	
	K	2.05	666	−1.73
	L	2.27	665	−1.58

[a] Local environment around the boron substitution site. For example, 665 denotes a site is abutted by two six-membered rings and one five-membered ring. [b] Electrostatic energy between the Sc_3N cluster and the C_3B moiety of the fullerene cage. See the text for more details.

distances between neighboring cells were greater than 7.00 Å. The cutoff energy was set high enough (400 eV) to ensure accurate results, and the conjugate gradient method was employed to optimize the geometry until the Hellmann−Feynman force exerted on each atom was less than 0.03 eV/Å. For systems with an odd number of electrons, explicit spin-polarized calculations were performed. The reliability of the PBE calculations using the PAW method has been confirmed in our recent calculations of the electronic and chemical properties of various systems ranging from metal−aromatic sandwich complexes to nanotubes.[17]

Results

First, we begin with the substitutional B-doping of the endohedral fullerene. To describe this process, we define the energy change of doping, $\Delta E_B(Sc_3N@C_{68})$, by that of the process $Sc_3N@C_{68} + B \rightarrow Sc_3N@C_{67}B + C$. As shown in Figure 1, the symmetry of the system allows 12 different sites for the possible boron substitution in $Sc_3N@C_{68}$. Table 1 shows that the substitution at site A results in the most stable isomer. Surprisingly, a comparison of its value (1.32 eV) of $\Delta E_B(Sc_3N@C_{68})$ with those (2.38 and 2.44 eV) for the B-substitution of C_{60} and C_{70} shows that it is much more feasible to make a substitutional doping of a boron atom in $Sc_3N@C_{68}$ than in C_{60} or C_{70}. Even the least stable isomer of $Sc_3N@C_{67}B$, represented by doping at site L, can be formed as easily as $C_{59}B$. This leads to the conjecture that the presence of a boron source in the synthesis of $Sc_3N@C_{68}$ will result in the production of B-doped derivatives in an amount that is even greater than that of C_{60}, which is known to be produced in a macroscopic amount.

Table 1 shows that the substitutions at [666] sites are generally more favorable than at [665] sites, where a [666] site denotes the site shared by three six-membered rings. In fact, two of the three most stable isomers belong to this case. {Other than those sites, Table 1 shows that there is one [655] site. We will use the subscripts $i = 1-3$ for [666], [665], and [655] sites, respectively, and this labeling system will be used throughout this work. For later use, we define the [666] or [665] group by a set of isomers in which the substitution occurs at a [666] or [665] site.} To investigate whether [666] sites are “locally” more favorable for B-substitution than [665] sites, we have also calculated ΔE_B for $C_{69}B$. Table 1 shows that there is one [666] site (site B) in the equatorial region of C_{70} at which B-substitution is rather slightly (by 0.1 eV) less favorable than that at a nearby [665] site (site A). What is also worth mentioning is that $C_{59}B$ exclusively belongs to the [665] group.

In relation to the observation in Table 1, natural questions which arise are as follows: (1) Why is the B-substitution in $Sc_3N@C_{68}$ much more favorable than that in C_{60} or C_{70}? (2) Why is the substitution at a specific site more favorable than those at other sites? A related question is the following: Will the endohedral group affect the stability of isomers of $Sc_3N@C_{67}B$? To answer these questions, we have calculated the electrostatic energy between the Sc_3N cluster and the $C_{B3}N$ moiety, where C_B is a carbon atom bonded to the boron atom. Our analysis of the natural bond orbitals[18] (NBOs) with the GAUSSIAN03 program[19] using the 6-311(d,p) basis set shows that average charges on Sc and N_C atoms are 1.35 and −1.47, respectively, indicating the transfer of 2.58 electrons from the Sc_3N_C cluster to the cage. The average charges on B and each of the three C_B atoms are 0.50 and −0.30, indicating that the total charge of the $C_{B3}B$ moiety is −0.40. Therefore, the better electrostatic attraction is expected when the moiety is located closer to one of the Sc atoms. To be more quantitative, Table 1 lists the values of the electrostatic energy for each isomer defined by the relation $E_{es} = \sum_i \sum_\alpha (Q_i Q'_\alpha / r_{i\alpha})$. Here, Q_i ($i = 1, 3$) represents the NBO charge on each of the three atoms in the Sc_3N cluster other than the Sc atom, which is the farthest from the boron atom among the three Sc atoms, Q'_α ($\alpha = 1, 4$) denotes the charge on either the boron or one of the three C_B atoms, and $r_{i\alpha}$ is the distance between atoms i and α. The table shows that the values of E_{es} correlate nicely with the relative stabilities of the isomers, showing a crucial effect of the encased cluster on the regiospecificity of the B-substitution. For example, isomer A, which is the most stable, has the most favorable electrostatic interaction among all isomers for which the interaction was calculated. On the other hand, isomer L, which is the least stable among all isomers investigated, has the least favorable electrostatic interaction. Considering that (1) there is no such interaction in $C_{59}B$ and $C_{69}B$ and (2) even E_b of the least stable isomer (isomer L) is comparable to that of $C_{59}B$, it is reasonable to conjecture that the pronounced stability of isomer A of $Sc_3N@C_{67}B$ with respect to $C_{59}B$ or $C_{69}B$ is mostly due to the favorable electrostatic stabilization involving the Sc_3N

TABLE 2: Parameters for $C_{59}N$ and the Various Isomers of $Sc_3N@C_{67}N$

	isomer	ΔE_N (eV)	S_N[a]	E_{es}[b] (eV)
$C_{59}N$		3.24	665	
$C_{69}N$	A	3.25	665	
	B	3.85	666	
$Sc_3N@C_{67}N$	J	3.66	665	1.15
	L	3.66	665	1.30
	H	3.67	665	
	I	3.71	665	
	F	3.80	665	0.86
	G	3.97	655	0.86
	K	3.99	666	1.10
	E	4.09	665	
	B	4.10	665	
	A	4.10	666	0.58
	C	4.20	666	
	D	4.31	665	0.72

[a] Local environment around the nitrogen substitution site. See footnote *a* of Table 1 for more details. [b] Electrostatic energy between the Sc_3N cluster and the C_3N moiety of the fullerene cage. See the text for more details

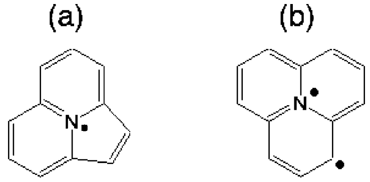

Figure 2. "Isolated" molecular structures composed of three aromatic rings in $C_{59}N$ or $Sc_3N@C_{67}N$: [665] (a) and [666] (b) sites.

cluster. In addition, differences in the stability of different isomers also seem to originate from the different electrostatic interactions.

We now discuss nitrogen substitution in $Sc_3N@C_{68}$. Considering that there was no report regarding the identification of $Sc_3N@C_{67}N$ in the synthesis of the former, we make a conjecture that the derivative is unstable. To determine whether the conjecture can be confirmed by our calculations, Table 2 lists $\Delta E_N(Sc_3N@C_{68})$ values for the process $Sc_3N@C_{68} + N_S \rightarrow Sc_3N@C_{67}N_S + C$. [When necessary, we denote the substitutional nitrogen atom by N_S to distinguish it from the other nitrogen atom (N_C) in the Sc_3N cluster.] In strong contrast to the case of B-substitution, ΔE_N (=3.66 eV) for the most stable isomer (J) shows that the reaction is much more endothermic than that ($\Delta E_N = 1.32$ eV) for B-substitution, indicating that the N-doping tendency of $Sc_3N@C_{68}$ is much weaker than its B-doping tendency. Comparison of $\Delta E_B(C_{60})$ (=2.38 eV) in Table 1 and $\Delta E_N(C_{60})$ (=3.24 eV) in Table 2 shows that a similar argument holds for B- and N-substitutions in C_{60}, although it is less pronounced. This is consistent with experimental observations which show that the simultaneous existence of B and N sources in the form of boron nitride crystals produces $C_{59}B$ but not $C_{59}N$.[1a,2] Our observations described above indicate that it would be even more difficult to achieve N-substitution in $Sc_3N@C_{68}$ than in C_{60} or C_{70}.

Table 2 shows that N-substitution on site A of C_{70}, which is a [665] site, is more favorable than that on a nearby [666] site (site B) by 0.6 eV. Comparison of this value with the corresponding difference (0.1 eV) for the B-substitution in C_{70} indicates that the preference for [665] sites is much stronger in N-substitution, which can be denoted by the "[665]N" rule. This observation is further supported by our calculation of the relative stability of "local" molecular structures shown in Figure 2. It shows "isolated" molecular structures representing the local environments around a [665] or [666] site. For each of them, we have calculated the energy change (ΔE_S) of the process $M_i + N \rightarrow M_{N,i} + C$, where $M_{N,i}$ represents an isolated molecule or radical shown in parts b and a of Figure 2 for $i = 1$ and 2, respectively. Our calculations show that the changes are 3.28 and 2.83 eV for $i = 1$ and 2, respectively. It is worth stressing that the N-doping process at a [665] site, which produced the isolated molecular species shown in Figure 2a, is more favorable than that which produced the species shown in Figure 2b, even though the process is accompanied by the production of a radical from a spin-paired molecule. These observations indicate that the different stabilities of various isomers of N-substituted fullerene can be ascribed to a combined effect of different local structures around the substitution site and the different degrees of electrostatic stabilization. This is different from the case of B-substitution in which the relative stabilities are mostly determined by the latter factor alone.

In Table 2, also shown are the values of E_{es} similarly defined as in the B-substitution, except for the introduction of an N atom instead of a B atom. It is worth mentioning that $E_{es} > 0$ for all isomers, which is in strong contrast with the case of B-substitution for which $E_{es} < 0$. Our separate NBO analysis shows that the average charges on N_C and Sc atoms are similar to those in $Sc_3N@C_{67}B$, thus indicating that the net charge on the fullerene cage is similar in the two cases. However, charges on the N_S and C_N atoms in the $C_{N3}N_S$ moiety are -0.33 and 0.18, respectively. Therefore, the total charge (0.21) on the moiety is even positive, while that (-0.40) on the $C_{B3}B$ moiety is negative in $Sc_3N@C_{67}B$. As a result, charges on the remaining part of the cages are -2.18 and -2.71 in $Sc_3N@C_{67}B$ and $Sc_3N@C_{67}N$, indicating that the electrostatic interaction between the Sc_3N cluster and the remaining part is much more important in the latter case. In short, a reasonable estimation of the electrostatic energy between the Sc_3N_C cluster and the cage cannot be made unless more atoms of the fullerene cage adjacent to the cluster are included in the calculation properly. If we include one more shell around N_S, the total local charge of the moiety $N_S(C_NC_2)_3$ now becomes negative ($q = -0.17$). Therefore, it is not surprising that we do not find a linear relationship between the stability of isomers and our crude estimate of E_{es}. Rather, the relative stability of each isomer is opposite that in B-substitution. For example, isomers of $Sc_3N@C_{67}N$ generated from N-substitution at sites J and L are the most stable among all its isomers belonging to a [665] group, while those of $Sc_3N@C_{67}B$ generated from B-substitution at the same sites are the least stable. In short, sites unfavorable for B-substitution are favorable for N-substitution as long as they belong to [665] sites.

Finally, we focus on the formation of $Sc_3N@C_{66}BN$ from $Sc_3N@C_{68}$ by a simultaneous doping of B and N atoms. Although an enormous number of isomers exist, we can select some of them that are potentially more stable than others on the basis of what we have learned about the relative stability of isomers of $Sc_3N@C_{67}B$ and $Sc_3N@C_{67}N$. In this work, four sets of isomers were investigated. The first set is based on boron substitution (B_A) at site A, which was known to produce the most stable isomer of $Sc_3N@C_{67}B$. After B-substitution, we chose two different sites for N-substitution. In the first subset, substitution is allowed at one of three sites bonded to site A, and the resulting three isomers are denoted by $B_AN_{A+1}^{(1)}$, $B_AN_{A+1}^{(2)}$, and $B_AN_{A+1}^{(3)}$. In the second subset, N-substitution (N_J) occurs at site J, which was shown to give the most stable isomer of $Sc_3N@C_{67}N$. Due to the symmetry breaking caused by the preintroduction of a boron atom in $Sc_3N@C_{68}$, six J sites

TABLE 3: Parameters for Various Isomers of $C_{58}BN$, $C_{68}BN$ and $Sc_3N@C_{66}BN$

	isomer	ΔE_{BN} (eV)	ΔE_B[a] (eV)	$\Delta E_N^{(1)}$[b] (eV)	L_B[c]	L_N[d]	S_B[e]	S_N[f]	l_{B-N}[g]
$C_{58}BN$	$B_BN_{B+1}^{(1)}$	3.33	2.38	0.95			665	665	1.45 (1.40)
	$B_BN_{B+1}^{(2)}$	3.71	2.38	1.33			665	665	1.50 (1.45)
	$B_BN_J^{(1)}$	5.13	2.38	2.75			665	665	
$C_{68}BN$[h]	$B_AN_{A+1}^{(1)}$	3.29	2.54	0.75	A	B	666	665	1.47 (1.42)
	$B_BN_{B+1}^{(1)}$	3.55	2.44	1.11	B	C	665	665	1.49 (1.44)
	$B_BN_{B+1}^{(2)}$	3.79	2.44	1.35	B	A	665	666	1.47 (1.42)
$Sc_3N@C_{66}BN$	$B_AN_{A+1}^{(1)}$	2.99	1.32	1.67	A	H	666	665	1.49 (1.44)
	$B_{J+1}N_J^{(1)}$	3.03	1.60	1.43	C	J	666	665	1.48 (1.43)
	$B_BN_{B+1}^{(1)}$	3.17	1.49	1.68	B	G	665	655	1.52 (1.45)
	$B_{J+1}N_J^{(2)}$	3.43	1.97	1.46	H	J	665	665	1.50 (1.45)
	$B_BN_{B+1}^{(2)}$	3.46	1.49	1.97	B	D	665	665	1.54 (1.47)
	$B_AN_J^{(1)}$	3.48	1.32	2.16	A	J	666	665	
	$B_AN_{A+1}^{(2)}$	3.56	1.32	2.24	A	D	666	665	1.51 (1.46)
	$B_BN_{B+1}^{(3)}$	3.62	1.49	2.13	B	C	665	666	1.49 (1.44)
	$B_{J+1}N_J^{(3)}$	3.69	2.27	1.42	L	J	665	665	1.49 (1.44)
	$B_AN_J^{(2)}$	3.88	1.32	2.56	A	J	666	665	
	$B_BN_J^{(1)}$	3.90	1.49	2.41	B	J	666	665	
	$B_AN_J^{(3)}$	3.94	1.32	2.62	A	J	666	665	
	$B_AN_{A+1}^{(3)}$	4.04	1.32	2.72	A	A	666	666	1.52 (1.46)
	$B_BN_J^{(2)}$	4.04	1.49	2.55	B	J	665	665	
	$B_AN_J^{(4)}$	4.05	1.32	2.73	A	J	665	665	
	$B_BN_J^{(3)}$	4.05	1.49	2.56	B	J	665	665	
	$B_BN_J^{(4)}$	4.06	1.49	2.57	B	J	665	665	
	$B_AN_J^{(5)}$	4.08	1.32	2.76	A	J	665	665	
	$B_AN_J^{(6)}$	4.10	1.32	2.78	A	J	665	665	
	$B_BN_J^{(5)}$	4.13	1.49	2.64	B	J	665	665	
	$B_BN_J^{(6)}$	4.13	1.49	2.64	B	J	665	665	

[a] Energy change for the process $C_{60} + B \rightarrow C_{59}B + C$ or $Sc_3N@C_{68} + B \rightarrow Sc_3N@C_{67}B + C$. [b] Energy change for the process $C_{59}B + N \rightarrow C_{59}BN + C$ or $Sc_3N@C_{67}B + N \rightarrow Sc_3N@C_{66}BN + C$. [c] Label for the site for the substituted boron atom in Figure 1. [d] Label for the site for the substituted nitrogen atom in Figure 1. [e] Local environment around the boron substitution site. See footnote *a* of Table 1 for more details. [f] Local environment around the nitrogen substitution site. See footnote *a* of Table 1 for more details. [g] B−N bond lengths when the two atoms are adjacent to each other. Numbers in parentheses denote the corresponding C−C bond lengths before substitution. This quantity is not defined when there is no B−N bond. [h] The three most stable isomers for which the B−N substitution occurs in the equatorial region are shown. Other isomers are not shown.

are now no longer equivalent to one another. Each of the six isomers thus generated is denoted by $B_AN_J^{(1)}$−$B_AN_J^{(6)}$. The second set of isomers can be obtained from an N-substitution at site J. Its first subset can be constructed if B-substitution is done at one of three carbon sites bonded to the N-substitution site, each of which is denoted by $B_{J+1}N_J^{(1)}$, $B_{J+1}N_J^{(2)}$, and $B_{J+1}N_J^{(3)}$. The second subset can be built if a B-substitution occurs at each of the six B sites. Again, breaking of the molecular symmetry causes those six sites for B-substitution to be inequivalent. Therefore, there are six isomers in the subset, and each of them is denoted by $B_BN_J^{(1)}$−$B_BN_J^{(6)}$. The fourth set of isomers can be built if B-substitution occurs at site B followed by N-substitution at one of three sites bonded to the boron atom. They are denoted by $B_BN_{B+1}^{(1)}$−$B_BN_{B+1}^{(3)}$. Table 3 and Figure 3a show that the most stable isomer is $B_AN_{A+1}^{(1)}$, in which B-substitution occurs at site A and the atom N_S is bonded to it. Its value of ΔE_{BN} is 2.99 eV, where ΔE_{BN} is the energy change of the process $Sc_3N@C_{68} + B + N \rightarrow Sc_3N@C_{66}BN_S + 2C$. For the isomer, the table also shows that the label "A+1" designates site H in Figure 1. As shown in Table 2, it is the most favorable N-substitution site among all sites which results in a B−N bond. The table and Figure 3b show that the next most stable isomer is $B_{J+1}N_J^{(1)}$, which has N-substitution at site J. As shown in Table 2, it is the most favorable N-substitution site, and the B atom is bonded to it. [The label "J+1" designates site C in Figure 1. See Table 3.] Again, site C is the most favorable site for B-substitution, which results in a B−N bond. Isomers $B_BN_{B+1}^{(1)}$ and $B_{J+1}N_J^{(2)}$ are slightly less stable. Isomers with B and N atoms more than one bond apart are even less stable. For example, see ΔE_{BN} (=3.48 eV) for $B_AN_J^{(1)}$ in Table 3. Isomer $B_BN_J^{(6)}$ is the least stable among all the isomers considered. For comparison, the table also shows the values of ΔE_{BN} of $C_{58}BN$ obtained from our separate calculations for three isomers [$B_BN_{B+1}^{(1)}$, $B_BN_{B+1}^{(2)}$, and $B_BN_J^{(1)}$].

Comparison of the values (2.99 and 3.03 eV) of ΔE_{BN} for the two most stable isomers of $Sc_3N@C_{66}BN_S$ shown in Figure 3a,b with the corresponding value (3.33 eV) for the most stable isomer of $C_{58}BN$ [$B_BN_{B+1}^{(1)}$] shown in Figure 3c leads us to expect the experimental identification of $Sc_3N@C_{66}BN$ by an amount which exceeds that of $C_{58}BN$ under the simultaneous existence of B and N sources in the fullerene synthesis. In the synthesis, we should also expect the production of $Sc_3N@C_{67}B$. [We recall that $C_{59}B$ and $C_{58}BN$ were experimentally identified, while $C_{59}N$ was rarely done, when the B and N sources were simultaneously present in the synthesis of C_{60}.[1a,2,5] For example, no evidence was found for the existence of $C_{59}N$ in the arc vaporization of graphite and boron nitride.[20] In most cases, $C_{59}N$ is prepared at the postsynthetic stage of C_{60}.[4]]

Table 3 also shows that the value of $\Delta E_N^{(1)}$ (=1.67 eV) for the most stable isomer is defined by the energy change of the process $Sc_3N@C_{67}B + N \rightarrow Sc_3N@C_{66}BN + C$. The value is much smaller than ΔE_N (=3.66 eV) for the most stable isomer of $Sc_3N@C_{67}N_S$ shown in Table 2. This implies that it is much easier to simultaneously introduce a pair of B and N atoms in $Sc_3N@C_{68}$ than to introduce only a N atom. The table also shows that this tendency is more pronounced in C_{60}. In addition, the table indicates that there is only a small (0.05 Å) elongation in B−N bonds with respect to C−C bonds after BN-substitution.

Comparison of ΔE_{BN} (=2.99 eV) for the most stable isomer [$B_AN_{A+1}^{(1)}$] of $Sc_3N@C_{66}BN$ with that (=3.33 eV) of isomer $B_AN_{A+1}^{(1)}$ of $C_{58}BN$ suggests that the extra contribution of the

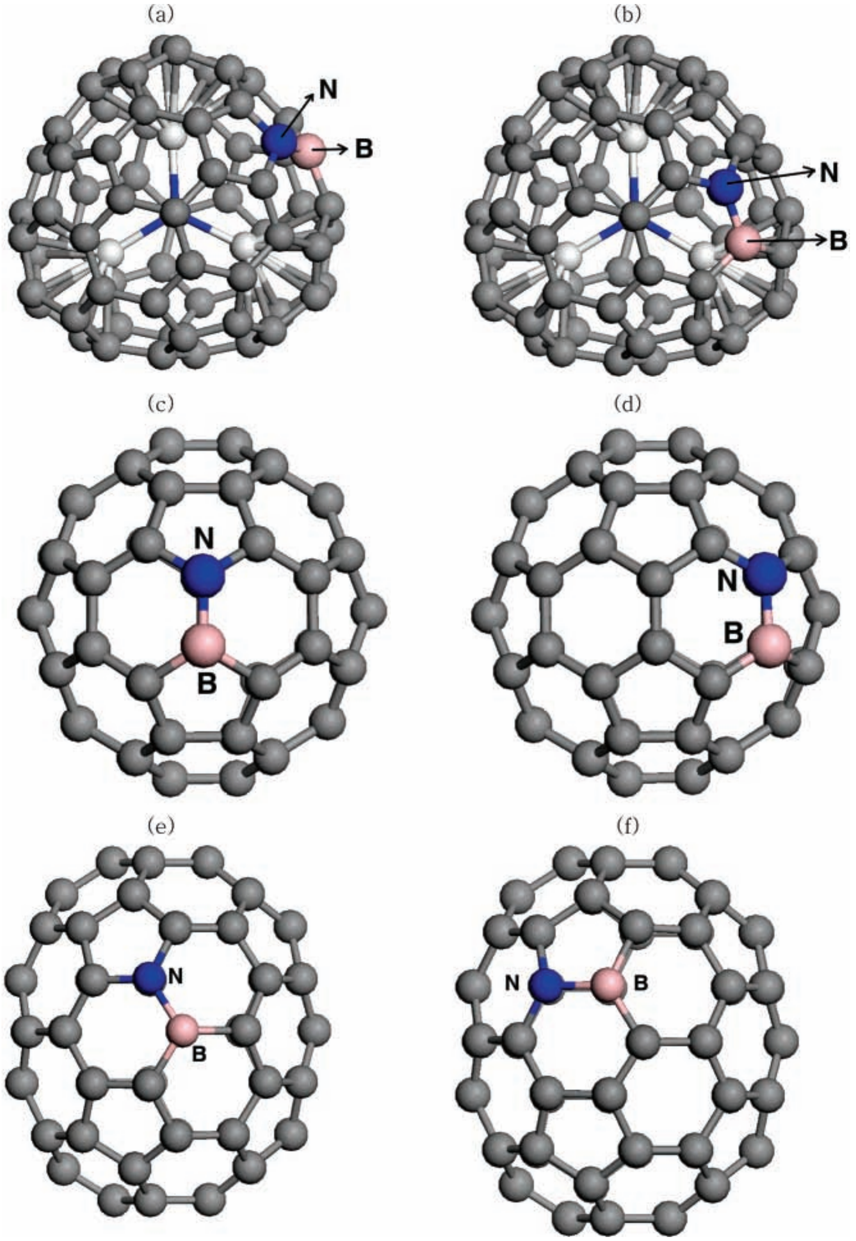

Figure 3. Optimized structures of isomers $B_AN_{A+1}^{(1)}$ (a) and $B_{J+1}N_J^{(1)}$ (b) of $Sc_3N@C_{66}BN$. Also shown are isomers $B_BN_{B+1}^{(1)}$ (c) and $B_BN_{B+1}^{(2)}$ (d) of $C_{58}BN$ and $B_AN_{A+1}^{(1)}$ (e) and $B_BN_{B+1}^{(1)}$ (f) of $C_{68}BN$.

electrostatic interaction involving the Sc_3N cluster to the stabilization of $Sc_3N@C_{66}BN$ should be weaker than that in $Sc_3N@C_{67}B$. However, the interaction seems to affect the relative stabilities of various isomers among themselves significantly, noting that the difference (0.70 eV) in ΔE_{BN} for isomers $B_AN_{A+1}^{(1)}$ and $B_{J+1}N_J^{(3)}$ is comparable to that (0.95 eV) in ΔE_B for isomers A and L in Table 1. In summary, relative stabilities of various isomers in Table 3 can be easily understood in terms of the combined effect of the relative stabilities in B- and N-substitutions. Namely, the most stable isomer, $B_AN_{A+1}^{(1)}$, is characterized by the most favorable B- and N-substitutions subject to the formation of a B−N bond. In addition, Table 3 shows that the seven most stable isomers have N-substitution at [665] sites in accordance with the [665]N rule aforementioned, indicating that the rule complements the electrostatic effect.

Conclusion

On the basis of calculations using density functional theory, we investigated the relative stabilities of all isomers of $Sc_3N@C_{67}B$ and $Sc_3N@C_{67}N$ in comparison with those of $C_{59}B$ and $C_{59}N$. In addition, candidates for the most stable isomers of $Sc_3N@C_{66}BN$ were also investigated, for which a judicious choice was made among an enormous number of isomers.

We predict that $Sc_3N@C_{68}$ can be substituted with a boron atom much more favorable than C_{60}, suggesting that it could be produced in macroscopic amounts required for applications in molecular electronics. The pronounced stability of $Sc_3N@C_{67}B$ can be ascribed to the favorable electrostatic interaction between the encased Sc_3N cluster and the polar C−B bonds of the fullerene cages. The interaction is “attractive” in the B-doped fullerenes, indicating that the encasement of the cluster favors B-substitution. On the other hand, a N-doping to the fullerenes to form $Sc_3N@C_{67}N$ is much less favorable than B-doping, which leads us to expect that the N-doped derivatives will not be easily identified experimentally. [666] sites are much more favored than in B-substitution. Our calculations show that the fullerenes can also be substituted with a pair of B and N atoms under the simultaneous presence of B and N sources. Stabilities of various isomers of $Sc_3N@C_{66}BN$ can be explained in terms of the combined effect of B- and N-substitutions in $Sc_3N@C_{68}$, which is basically the electrostatic effect between the Sc_3N cluster and the polar B−N bonds. The local preference of [665] sites in N-substitution to [666] sites also plays an important role. Our findings demonstrate the important role of encased atoms in the chemistry of endohedral fullerenes, which works through the electrostatic interactions. We expect that this finding will give insight into the principles governing the diverse chemical reactions of endohedral fullerenes.

As far as the authors' knowledge is concerned, this work is the first report on endohedral heterofullerenes. These fullerenes can be potentially much more useful in semiconductors and molecular electronics than nonendohedral heterofullerenes, since their chemical and electronic properties can be modulated by encased atoms in various ways. We expect that this work will stimulate experimental investigations of endohedral heterofullerenes including those theoretically investigated in this work.

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