The Electronic Structure and Stability of the Heterofullerene : C$_{(60-2x)}$(BN)$_x$

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The transition from aromatics to heteroaromatics is very attractive since it provides an extremely large structural variety, the chemical functionality as well as the possibilities for electronic tuning of the fullerene properties. A synthesis of heterofullerenes in macroscopic quantities is unknown however the spectrometric detection of C$_{59}$B has been reported. The electronic structures of C$_{(60-2x)}$(BN)$_x$ systems, isoelectronic with C$_{60}$ have been explored by Extended Hückel, AM1 and *ab initio* methods. The polyhedral assembly energy are 7.7 kcal greater than C$_{60}$ when one B-N unit is substituted with C-C unit. The assembly energies are getting bigger if more B-N unit is introduced. We focus on HOMO-LUMO energy gap and the stability effects in C$_{(60-2x)}$(BN)$_x$ with different compositions of (BN)$_x$ moiety. The bonding properties of the substituent atoms were investigated in detail.

Key Words : Heterofullerene, Electronic structure, MO calculation

Introduction

Recently the fullerenes have been intensively studied. In the beginning, interests in these compounds were twofold. These were totally new allotropic form of the carbon element. And secondly the closed polyhedral framework was originally recognized before born of genius mathematician Euler. Nowadays, it enthralled many chemists and physicists for being new materials. For example, Rb$_3$C$_{60}$ shows superconducting property with a transition temperature of 28 K.[1] Another astonishing material, C$_{60}$(TDAE)$_{0.86}$, has been known as a new organic ferromagnet with higher Curie temperature than any other known organic ferromagnet.[2] And C$_{60}$ doped in the polyvinyl-carbazole shows outstanding photo- conductive materials which was tested as equal or better than those of industry standard thiapyrillium dyes.[3] Also, C$_{70}$ has shown to nucleate for diamond growth[4] and many applications have been reported.[5]

After initial proof of the special stability of C$_{60}$, the substitutions of the carbon cage by heteroatoms are designed and realized by Smalley and coworkers.[6a,b] They have been successful in replacing at least one to six carbon atoms for boron. This is interesting because "doped bucky" is totally new material and expected to have enhanced chemical reactivity of carbon cage. Also, a useful procedure for production of macroscopic amounts of the boron hetero-fullerenes using a modified Kratschmer-Huffman process has been reported.[7] The electronic effects in the metal complexation of C$_{60}$, C$_{60}$N, and C$_{59}$B have been studied theoretically by Jansen *et al.*[8] Tanaka investigated the electronic structures of the transition metal (M)-C$_{60}$ dumbell polymers (η^6-C$_{60}$)$_n$M$_n$ have been examined with the one

dimensional tight-binding crystal orbital method at the extended Hückel approximation level.[9] Experimentally, C$_{59}$B is known and C$_{59}$B-NH$_3$ a Lewis acid/base adduct is also stable.[10] C$_{59}$N is a reactive free radical and in its bulk form dimerizes to form (C$_{59}$N)$_2$.[11-13] However, in recent work, it has been shown that C$_{59}$N sublimes in the monomer form.[14] The electronic structure of C$_{58}$BN heterofullerenes has been calculated by Esfarjani *et al.*[15] Two different orientation of the C$_{58}$BN molecule of which N and B neighbors in the unit cell and the molecule N and B apart by *ab-initio* calculations using an all-electron mixed-basis approach and within the local density approximation.

We have investigated the electronic structures of C$_{(60-2x)}$-(BN)$_x$ systems and compared with those of known boron or nitrogen doped systems. Doped material is usually kinetically stable like *n*- or *p*-type impurity doped bulk silicon semiconductors. Thus, in order to make doped bucky inert, it is necessary to have high enough energy barrier to prevent the separation of the dopant. Also, the sizes of constituent atoms appear to be important not to distort the ball much as pointed out elsewhere.[16] From these points of view, boron and nitrogen are regarded as good candidates for guests. Furthermore, both dopants are typical atoms known as a trivalent.

In reality, many carbon compounds have analogous compounds in which C-C moieties are substituted for B-N to the extended systems; for instance, borazine *vs.* benzene, hexagonal modification of boron nitride *vs.* graphite, etc. The known B=N bond distances are 145 pm in boron nitride, 142 pm for 4-membered cyclic system, and 144 pm for borazine.[17] These bond distances are within the range of C-C bond distances of the fullerene (140 and 146 pm).[18]

Table 1. Atomic orbital parameters used in the EH calculations: Principal quantum number n, Slater exponent (au), ionization potentials (H_{ii})

Atom	Orbital	H_{ii}, eV	Exponent (au)
B	2s	−15.20	1.30
B	2p	−8.50	1.30
C	2s	−21.40	1.63
C	2p	−11.40	1.63
N	2s	−26.00	1.95
N	2p	−13.40	1.95

Computational Methods and Models

The Extended Hükel (EH) methodology is utilized for evaluation and comparison of doped C_{60} analogues, which has shown to be great in the analysis of systems involving carbon, boron and nitrogen atoms.[19] The parameters[20] used are listed in Table 1.

The geometries are optimized by AM1 and *ab initio* with STO-3G basis sets. The *ab initio* calculations are carried out with the GAUSSIAN 98 [21] on a Cray Y-MP C916.

The delocalized and localized model geometries are used for EH calculations and compared, since the amount of distortion are about 3 pm at AM1 and 7 pm at *ab initio* levels. For the localized model, the experimental C-C bond distances of 140 and 146 pm are used[18] and averaged 143 pm for the delocalized model. Although the localized model are energetically more stable, the delocalized model might be more realistic because the observed physical properties revealed to be averaged ones. However, the results are not varied much for both models. Therefore, we limit our discussion only to the localized model, unless specified.

For the multiply substituted fullerenes with heteroatoms, numerous isomers are possible. Extended Hükel method was reliable to predict the stable isomer in this study. The same kinds of dopants prefer to stay as far as possible. The energy differences are not ignorable between the isomers in which two heteroatoms are the nearest and furthest. The energy difference is calculated to be 1.09 eV for $C_{58}B_2$ system, however only 0.22 eV is obtained for $C_{58}N_2$ system. The B-B bond is not energetically preferable because each boron has only electrons to form single bond. Furthermore, bonding electrons should be dripped into the carbon atoms of the cage after doping which induce net destabilization. Therefore, the isomers with B atoms on the opposite side of the cage are energetically more preferable.

It can be explained with similar reason for the small energy difference of dinitrogen doped systems, where dripped electrons from the carbon would be filled into the dinitrogen antibonding level somewhat to destabilize the N-N bonding in the carbon cage due to the electronegativity difference. Although the weakening of the N-N bond causes destabilization of the cage, this is compensated by the stabilizing effect of the filled N-N bonding levels which are supposed to be more stabilized than the atomic N-level. Two heteroatoms preferred to stay in the opposite side of the

inversion center, but gained less energy than $C_{58}B_2$ system.

In fact, the energy differences by EH method is quite contrast to Kurita's report where only 0.02 eV difference, possibly too small, was calculated for both $C_{58}N_2$ and $C_{58}B_2$ systems.[22] Experimentally the boron atoms are well separated form each other in $C_{58}B_2$ system.[6a]

Nitrogen and boron atoms preferred to be closer as possible in the co-doped system. For example, B and N atoms at the edge between 5- and 6- membered rings are condensed due to the induced polar character of B and N atoms. The B-N unit is isoelectronic to C-C. The electron loss at boron site is compromised by the electron gain at nitrogen. The isomer of the nearest B and N is more stable by 1.55 eV than the other isomers. The same rationale is applied to the systems, more than one C-C units are replaced by B-N units. The B and N atoms were found to be stay as close as possible to each other.

Results and Discussion

Experimentally, $C_{(60-x)}B_x$ with $x = 0$ to 6 are known and the Lewis acids-base adducts. $C_{(60-x)}B_x$-xNH_3, are also known as inert.[6a,b] The nitrogen doped C_{60} has been reported by Rao et al. with a mixture of $C_{59}N_2$ and other nitrogen derivatives.[23] First of all, these heteroatom doped fullerenes are especially attractive in order to improve the chemical reactivity of fullerenes. For instance, boron doped fullerene immediately forms NH_3 adducts under 1×10^{-6} torr of ammonia pressure for 2 seconds.[6a] This noticeable reactivity is understood as originated from the small HOMO-LUMO energy gap of doped fullerene and polar nature of boron atom in the cage.

Secondly, one might expect to have broad range of new semiconductors because various gaps are formed with respect to the substituents and the range of substitution. For example, impurity doped silicon is proven to be better semiconductor than the intrinsic one. In addition, both *n*- and *p*- type co-doped fullerenes are expected to be a new material with hole/electron junction inside the molecule. Thus much applications can be designed, if it is synthesized.

We have carried out AM1 and *ab initio* calculations for the isomers of heteroatom doped fullerenes which are the most stable forms by EH calculations. As noted in Figure 1, there is not much of geometric distortions as the system changes from C_{60} to $C_{58}BN$, which means "maintenance of the polyhedral cage" after doping. The carbon-carbon distances for C_{60} (Figure 1(a)) are optimized to the value of 138-146 pm with AM1 and 137-153 pm with *ab initio* level, which are pretty close to the experimental values of 140-146 pm.

The B-N bond distances of $C_{58}BN$ system (Figure 1(b)) are 139 pm and 143 pm at AM1 and STO-3G levels, respectively. These are quite close to the sum of B and N atom covalent radii (B-; 82 pm and N=; 61 pm)[24] which indicates some degree of multiple bonding character. The B-C, N-C, and C-C bond distances for this system are in the range of 139-149 pm at AM1 and 137-153 pm at STO-3G level.

In addition, our computed results are close to those of self

(a)

(b)
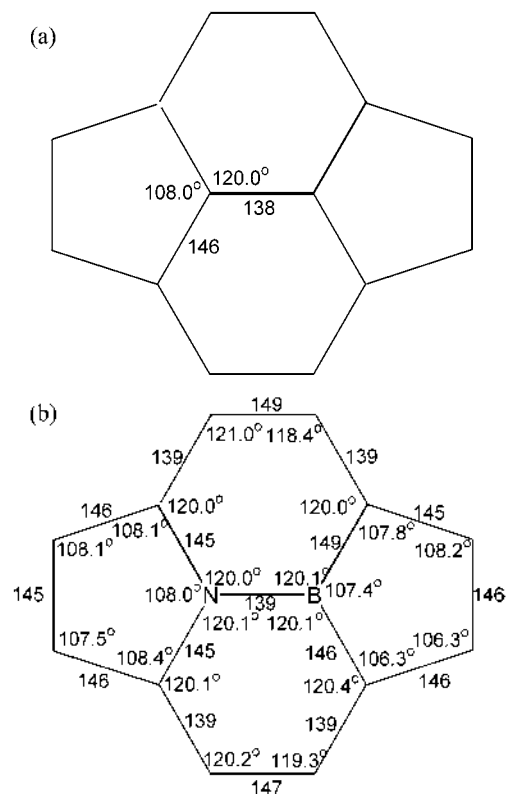
Figure 1. (a) The optimized bond distances and angles for C_{60} by AM1 method. 139-146 pm range of C-C distance with AM1 and 137-153 pm with Gaussian 98, HF/STO-3G calculations which are close to those of experimental values (140-146 pm). (b) The optimized bond distances and angles for $C_{58}BN$ by AM1. 139 pm of B-N distance with AM1 and 143 pm with HF/STO-3G calculations are close to the sum of known covalent radii (B-: 82 pm and N-: 61 pm) indicating some degree of multiple bonding character. And 139-149 pm with AM1 and 137-153 pm with HF/STO-3G calculations are obtained for the B-C, N-C and C-C bond distances.

consistent field (SCF) optimization of C_{60} using Harris approximation.[25] where 143 and 149 pm were obtained. For

boron substituted C_{60} and nitrogen substituted C_{60} by Kurita *et al.*,[22] the maximum atomic distortions were between 6 pm and 13 pm for $C_{59}N$, $C_{58}N_2$, $C_{59}B$, $C_{58}B_2$ systems.

HOMO-LUMO energy level, energy gap, assembly energy (A.E.), Mulliken's charges, and overlap populations (O.P.) by the extended Hükel calculation are given in Table 2.

The HOMO-LUMO energy gaps indicate that these are indeed new family semiconducting systems in terms of various gaps. The energy levels for C_{60}, $C_{58}BN$, $C_{58}B_2$, and $C_{58}N_2$ systems are displayed in Figure 2.

The dark squares are filled levels and the blank squares are empty levels. Right-side brackets are the size of energy gaps. The gaps for nitrogen-doped systems are small because one or two electrons are put in an antibonding level which is derived from T_{1u}'s of C_{60}. T_{1u} set are splitted by 0.19 eV for $C_{59}N$ and 0.27 eV for $C_{59}N_2$ systems. Those for boron doped systems are explained by taking out electrons from the filled H_u bonding level of C_{60}. Also the gaps are not splitted much. The gaps are 0.28 and 0.37 eV for $C_{59}B$ and $C_{58}B_2$ systems. respectively. This is ameliorated in the isoelectronic $C_{(60-2x)}$ $(BN)_x$ system where the gaps get close to that of C_{60}. but narrower. The narrower gaps are due to the second order interaction resulted by lowering symmetry from I_h to C_s.

The assembly energies for mono-substituted and di-substituted systems are quite different. These results may explain the unique C_2 unit fragmentation behavior observed by the FT-ICR (Fourier Transform Ion Cyclotron Resonance) mass spectrum because the C_2 unit is the most fragile fragment compared to the other units.[6c-e]

Even the nitrogen doped fullerene is questionable,[23] our calculations show that there is no obvious reason for their labilities. Our results are inconsistent with the previous reports. where the nitrogen doped system is less favorable than boron doped systems.[8,22a] The assembly energies in our calculations are certainly smaller than that of C_{60} itself due to filling two extra electrons in the level derived from the cage antibonding T_{1u}. Therefore, $C_{58}N_2^{2-}$ is better formulation for dinitrogen-doped fullerene. And the assembly energies

Table 2. HOMO-LUMO energy levels, Gaps, Assembly energies (A.E.), Charges, Overlap Populations (O.P) for B and/or N doped fullerenes

Systems	HOMO[a]	LUMO[a]	Gap[a]	A. E.[a]	Charge[b]	O.P.[c]
C_{60}	−11.47	−9.90	1.57	307.83(304.32)[d]	0.00	
$C_{59}N$	−10.09	−9.90	0.19	296.81(293.40)	−0.14	0.822
$C_{59}B$	−11.42	−11.14	0.28	295.13(291.70)	+0.71	0.883
$C_{58}N_2$	−10.18	−9.91	0.27	306.16(303.07)	−1.21	0.846
$C_{58}B_2$	−11.40	−11.02	0.38	304.94(301.45)	+0.61	0.889
$C_{58}BN$	−11.31	−9.92	1.39	307.92(304.41)	+0.78(B) −0.13(N)	0.831
$C_{56}(BN)_2$[e]	−11.26	−9.98	1.28	308.86(305.39)	+0.86(B)[f] −0.68(N)[f]	0.821
$C_{54}(BN)_3$[e]	−11.37	−9.92	1.45	311.37(307.91)	+0.97(B) −0.86(N)	0.827

[a]Units are in eV scale. [b]Charges are resulted from Mulliken's analysis. [c]The Overlap Population (O.P.) number for only heteroatom to nearest neighbor carbon. The values are averaged for symmetry in equivalent ones. [d]Numbers in parenthesis are for delocalized models. [e]These values are for the isomer with one 6-membered ring of N, B, N, B, C, C atom sequence. [f]These are averaged charge between two unequivalent B's and N's. [g]The most stable isomer is that 3 C-C units are substituted for B-N units in one hexagon where B and N's are alternating.
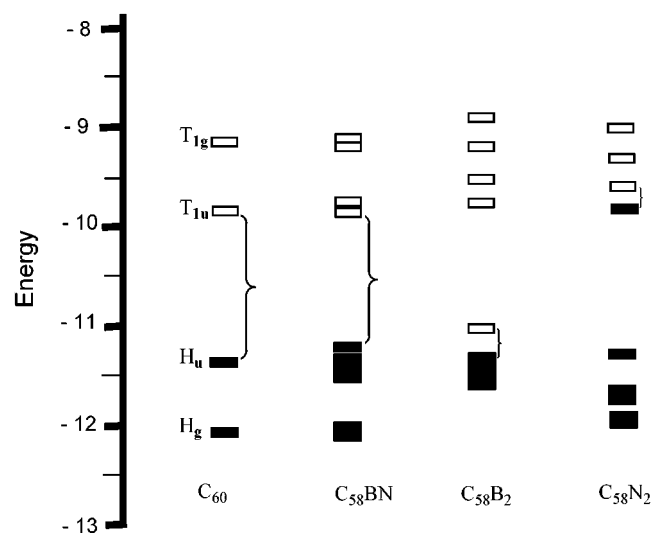
Figure 2. The energy levels for various heteroatom doped systems. Notice HOMO (H_u)-LUMO (T_{1u}) gap for C_{60} and small changes after doping. Gaps in heteroatom doped fullerenes are indeed controlled by the number of electrons available. Dark squares are filled levels and blank squares indicate empty levels.

are bigger than those of $C_{58}B_2$ or $C_{59}B$. The stability of nitrogen-doped systems comes from electron filling in nitrogen based orbitals which are more electronegative than boron level. On the other hand, boron-doped fullerenes have an opposite effect owing to many bonding levels, perturbed by the electropositive boron level. Noticed in Figure 2, the filled M.O. levels of $C_{58}B_2$ system are at higher energy than those of $C_{58}N_2$.

These situations are compromised in boron and nitrogen co-doped system. The molecular levels are perturbed by both electronegative N and electropositive B atoms. The B-N bonding levels are at work rather than N or B atomic levels themselves because of the B-N bond formation in $C_{58}BN$ cage. This is different from $C_{58}B_2$ and $C_{58}N_2$ systems where B-B or N-N bond does not exist in our concerning isomers. The filled B-N levels have more nitrogen character. Thus the assembly energy of $C_{58}BN$ system is bigger than that of C_{60}. Much improvement is made if one more C-C unit is substituted for B-N units with the same protocol.

It is also possible to think that nitrogen doped system may be stable, at least better than boron doped system as assembly energy indicates. But the nitrogen atoms may interact themselves to produce a stable N_2 molecule which has 9.76 eV of the experimental formation enthalpy as pointed out elsewhere.[23] Therefore one needs rather inert compounds with high enough energy barrier to preclude the separation of constituent atom N. In that sense, the B-N co-doped fullerenes are energetically better formulations than $C_{58}N_2$ or $C_{58}B_2$ system. And it is better to increase the number of B-N substitution, x. However, much more extent of x would create an opposite result as we have pointed out earlier, for B-B or N-N bumping is unavoidable that is energetically unfavorable.

The atomic charges are computed to be +0.71 in $C_{59}B$ and

+0.61 in $C_{58}B_2$ systems on B atoms and −0.14 in $C_{59}N$ and −0.21 in $C_{58}N_2$ systems on N atoms. These are consistent with the order of atomic electronegativity. B < C < N. The electrons are polarized from electropositive atom to electronegative atom. This is also the case when boron and nitrogen atoms are doped together. As given in Table 2, the charges of B and N atoms in $C_{58}BN$ system are calculated to be +0.78 and −0.53, respectively. And at *ab initio* level, +0.28 for B and −0.21 for N atoms are observed.

The averaged overlap populations of the heteroatom-carbon bondings where the carbon is the nearest neighboring one from heteroatom are 0.889 for $C_{58}B_2$, 0.830 for $C_{58}BN$, and 0.846 for $C_{58}N_2$ systems. The calculated values are quite close to each other. This indicates the preservation of similar bonding character throughout the concerned systems.

Conclusions

In order to investigate the electronic effects for heteroatom doped fullerenes, we have utilized EH, AM1, and *ab initio* methods. Especially we have concentrated on the stability factors for the possible systems with electron/hole junctions and compared with known systems. The polyhedral assembly energy are 0.09 eV (7.7 kcal) greater than C_{60} when one B-N unit is substituted with C-C unit. The assembly energies increased if more B-N units are introduced. However, this energy is totally static one. The energy barrier for the constituent atoms to be separated out is getting higher for B and N co-doped fullerenes than for only borons or nitrogens doped systems.

In addition, the optimum geometries at AM1 and *ab initio* levels show not much geometrical distortions after introduction of the heteroatoms. This is a good indicator to judge the molecular stability of cage together with assembly energy. These materials are very interesting, since it is possible to have series of hole or/and electron doped semiconductors. Not surprisingly, the calculated gaps are extended over wide ranges from 0.19 to 1.48 eV.

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