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Bonding and electronic properties of substituted fullerenes $C_{58}B_2$ and $C_{58}N_2$

Noriyuki Kurita, Kinya Kobayashi, Hiroki Kumahora, and Kazutami Tago
Energy Research Laboratory, Hitachi Ltd., 7-2-1 Omika-cho, Hitachi-shi, Ibaraki 319-12, Japan

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The binding energies and electronic properties of substituted fullerenes $C_{58}B_2$ and $C_{58}N_2$ have been calculated by a self-consistent-field molecular-orbital (MO) method; their structures are optimized by a MO method with Harris-functional and spin-restricted approximations. The most striking change by multiple substitutions is that the binding energies (5.90 and 5.92 eV/atom) of $C_{58}N_2$ isomers are much smaller than that (6.05 eV/atom) of C_{60}, while those (6.01 and 6.03 eV/atom) of $C_{58}B_2$ isomers are almost the same. The energy gaps between the highest-occupied MO and the lowest-unoccupied MO are also changed by multiple substitutions, being 0.49 and 0.54 eV ($C_{58}B_2$ isomers), 0.23 and 0.28 eV ($C_{58}N_2$ isomers), and these sizes are much smaller than that (1.50 eV) of C_{60}.

I. INTRODUCTION

Recently, Smalley and co-workers have carried out successful syntheses, replacing one or more carbon atoms of C_{60} with boron and/or nitrogen atoms, which have led to many kinds of modified C_{60} molecules:[1] $C_{60-n}B_n$, where n ranges from between 0 and at least 6, $C_{58}BN$, and so on. This success has opened up a potential new field of study on fullerenes from the viewpoint of semiconductor applications: $C_{60-2n}X_{2n}$ might be a useful component of semiconductors with various band gaps and electronic polarizations.

Regarding theoretical studies on stable structures of $C_{60-n}X_n$, quantum molecular-dynamics calculations for $C_{59}B$ and $C_{59}N$ (Ref. 2) and molecular cluster calculations for $C_{58}B_2$ and $C_{58}N_2$ (Ref. 3) have been performed. In our previous work,[4] by using a molecular-orbital method with Harris-functional and spin-restricted approximations, we calculated stable structures of $C_{59}X$ ($X=$B, N, and S) and found that there is no distinct difference in stable structure and binding energy between $C_{59}B$ and $C_{59}N$. However, the dependencies of bonding and electronic properties on the number and relative positions of substituted atoms have not been clarified yet. In this work, we obtained stable structures of two types of isomers for $C_{58}X_2$ ($X=$B and N) and calculated their binding energies and electronic properties self-consistently. Then, based on the present work and our previous results,[4] we considered how their bonding and electronic properties are changed by multiple substitutions.

II. COMPUTATIONAL METHOD

In this section, the Harris-functional approximation for the total energy and the energy gradient form in the approximation are briefly reviewed. Then, the structure optimization method is explained. Atomic units are used unless otherwise indicated. Details of molecular-orbital (MO) calculations are the same as those of our previous calculations:[4] the single-zeta basis set,[5] the integral method by Becke,[6] and the $X\alpha$ ($\alpha=0.7$) exchange-correlation potential are used.

A. Harris-functional approximation

In the Kohn-Sham density-functional theory, the total energy of an N-electron system with ν nuclei is

$$E=\sum_i n_i \int d\mathbf{r}\,\psi_i(\mathbf{r}) \left[-\tfrac{1}{2}\Delta - \sum_{a=1}^{\nu} Z_a/|\mathbf{r}-\mathbf{R}_a| \right] \psi_i(\mathbf{r}) + E_{\mathrm{xc}}(\rho)+E_c(\rho)+E_{NN} , \quad (1)$$

$$\rho(\mathbf{r})=\sum_i n_i \psi_i(\mathbf{r})\psi_i(\mathbf{r}) , \quad (2)$$

$$E_c=0.5\int d\mathbf{r} \int d\mathbf{x}\, \rho(\mathbf{r})\rho(\mathbf{x})/|\mathbf{r}-\mathbf{x}| , \quad (3)$$

where Z_a is the positive charge of the nucleus situated at the site R_a, ψ_i is the ith molecular orbital, and its electron occupation number is defined as n_i. E_c is the Coulomb self-interaction energy, E_{xc} is the exchange-correlation energy which depends on the electron density ρ, and E_{NN} is the nuclear repulsion energy.

Harris[7] has approximated E_c and E_{xc} using the following equations:

$$E_c^H=\int d\mathbf{r}\int d\mathbf{x}\frac{\rho(\mathbf{r})\rho^H(\mathbf{x})}{|\mathbf{r}-\mathbf{x}|}-0.5\int d\mathbf{r}\int d\mathbf{x}\frac{\rho^H(\mathbf{r})\rho^H(\mathbf{x})}{|\mathbf{r}-\mathbf{x}|} , \quad (4)$$

$$E_{\mathrm{xc}}^H=E_{\mathrm{xc}}(\rho^H)+\int d\mathbf{r}[\rho(\mathbf{r})-\rho^H(\mathbf{r})]\frac{\delta E_{\mathrm{xc}}(\rho^H)}{\delta\rho^H(\mathbf{r})} , \quad (5)$$

where ρ^H is a superposition of electron densities of atomic fragments. The first-order energy correction of the density error $[\rho(r)-\rho^H(r)]$ is exactly included in Eqs. (4) and (5), while other higher-order corrections are partially canceled and can be ignored. We used a superposition of spherical symmetric and spin-unpolarized electron densities of isolated ground-state atoms for ρ^H, in calculating the bond lengths and binding energies of the carbon clusters C_8, C_{24}, and C_{60}.[8]

The molecular-orbital ψ_i satisfies the equations

$$\left[-\tfrac{1}{2}\Delta-\sum_a Z_a/|\mathbf{r}-\mathbf{R}_a|+\int d\mathbf{x}\,\rho^H(\mathbf{x})/|\mathbf{r}-\mathbf{x}|+\mathbf{V}[\rho^H(\mathbf{r})]\right]\times\psi_i(\mathbf{r})=\varepsilon_i\psi_i(\mathbf{r})\ , \tag{6}$$

$$V[\rho^H(\mathbf{r})]=\frac{\delta E_{\mathrm{xc}}(\rho^H)}{\delta\rho^H(\mathbf{r})}\ . \tag{7}$$

In these equations, ρ^H does not depend on ψ_i, so that self-consistent iterations are not needed to obtain ψ_i.

B. Energy gradient form in the Harris-functional approximation

The force acting on the ath atom is given from the derivative of the total energy E with respect to a Cartesian nuclear coordinate R_a. In the Harris-functional approximation, it is given by[9]

$$\begin{aligned}\mathbf{F}_a&=-\partial E^H/\partial\mathbf{R}_a\\&=-\partial E_{NN}/\partial\mathbf{R}_a+\int d\mathbf{r}\,\rho(\mathbf{r})\frac{Z_a(\mathbf{r}-\mathbf{R}_a)}{|\mathbf{r}-\mathbf{R}_a|^3}-2\sum_i\sum_{p,q}C_{pi}C_{qi}n_i\int d\mathbf{r}\frac{\partial\chi_p(\mathbf{r})}{\partial\mathbf{R}_a}[H(\rho^H)-\varepsilon_i]\chi_q(\mathbf{r})\\&\quad-\int d\mathbf{r}\,\Delta\rho(\mathbf{r})\left[\int d\mathbf{x}\frac{\partial\rho^H(\mathbf{x})}{\partial\mathbf{R}_a}\frac{1}{|\mathbf{x}-\mathbf{r}|}+\frac{\partial\rho^H(\mathbf{x})}{\partial\mathbf{R}_a}\frac{\partial V[\rho^H(\mathbf{r})]}{\partial\rho^H(\mathbf{r})}\right]\ ,\end{aligned} \tag{8}$$

$$\Delta\rho(\mathbf{r})=\rho(\mathbf{r})-\rho^H(\mathbf{r})\ . \tag{9}$$

The first two terms on the right-hand side of Eq. (8) are the standard Hellmann-Feynman force terms. The one-electron Hamiltonian $H(\rho^H)$ is that of Eq. (6), and, in the following equation, C_{pi} and $\chi_p(r)$ are coefficients and atomic orbitals, respectively:

$$\psi_i(\mathbf{r})=\sum_p C_{pi}\chi_p(\mathbf{r})\ . \tag{10}$$

C. Method of structure optimization

In the optimization process, the atoms are allowed to move according to the forces acting on them and their velocities at a given moment,[10] in order not to search local energy-minimum structures. The velocity of an atom is approximated as the product of the inverse of the discrete time interval (δt) and the vector displacement since the previous step, $[r(t)-r(t-\delta t)]$. The molecular-dynamics algorithm by Verlet,[11]

$$r(t+\delta t)=r(t)+[r(t)-r(t-\delta t)]+\delta^2 tF(t)\ , \tag{11}$$

is used. In each coordinate updating step, if the x component of the force on atom i is positive, and that of the velocity is negative, the force acts to slow the atom down. In this case, the coordinate is updated by simply adding on $\delta^2 tF(t)$, i.e., the kinetic energy of atoms is systematically reduced. If the force has the same sign as the velocity component, the coordinate is updated as Eq. (11). This step is applied for the other two Cartesian coordinates, and for all atoms. The optimization process is iterated until the maximum atomic force becomes smaller than 0.01 hartree/a_0 (a_0 is the Bohr radius). For the optimized structure, its binding energy and electronic properties are calculated self-consistently by the MO method based on the local-density-functional formalism,[12] using ground-state atomic orbitals constructed by five (for s orbitals) and three (for p orbitals) Slater-type functions.

In order to justify the accuracy of the Harris-functional approximation, we calculated the stable structure of corannulene $C_{20}H_{10}$. The calculated result was almost the same as that calculated by the self-consistent-field (SCF) method with ground-state orbitals of atoms plus valence orbitals of $+2$ ions and two polarization $3d$ orbitals; there was only a 0.02 Å difference between the structures. From the binding energy versus bond-length curve obtained for some fullerenes in our previous study,[13] it was estimated that this difference in structure (0.02 Å) corresponds to about a 0.01 eV/atom difference in binding energy. Therefore, the present method is expected to be applicable to calculating stable structures of $C_{58}X_2$, and to comparing their binding energies.

III. RESULTS AND DISCUSSION

In our previous study,[4] we clarified that the stable structures and binding energies of $C_{59}B$ and $C_{59}N$ are almost the same as those of C_{60}, while those of $C_{59}S$ are very different. In the present study, we then considered $C_{58}B_2$ and $C_{58}N_2$ and calculated their stable structures, starting with the calculated stable structures of $C_{59}X$ ($X=$B or N). There are many isomers among $C_{58}X_2$ depending on the relative positions of substituted atoms X. In order to clarify their stability, we considered two types of isomers: (1) the two X's are in the nearest-neighbor sites of the pentagonal ring of the C_{60} cage, and (2) the two X's are on opposite sides of the cage. In this paper, the former is designated as $C_{58}X_2$(I), and the latter as $C_{58}X_2$(II). For C_{60}, $C_{58}B_2$, and $C_{58}N_2$, the optimized bond lengths, bond orders (the number of electrons contributing to the bonding), binding energies, energy gaps between the highest-occupied molecular orbitals (HOMO's) and lowest-unoccupied molecular orbitals (LUMO's), energy levels of HOMO, and Mulliken's charges are listed in Table I. Although Mulliken's analysis cannot estimate the atomic charge quantitatively, its sign can be predicted.[14] As for the numerical values of the HOMO-LUMO energy gaps, the $X\alpha$

TABLE I. Optimized bond lengths, bond orders (number of electrons contributing to bonding), binding energies, HOMO-LUMO energy gaps, HOMO energy levels, and Mulliken's charges for C_{60}, $C_{58}B_2$, and $C_{58}N_2$ isomers. In the $C_{58}X_2$(I) and $C_{58}X_2$(II) cages, the two X's are in the nearest and farthest sites, respectively.

	C_{60}	$C_{58}B_2$(I)	$C_{58}B_2$(II)	$C_{58}N_2$(I)	$C_{58}N_2$(II)
Bond lengths (Å) X-X		1.65		1.55	
X-C		1.49–1.52	1.52–1.58	1.48–1.52	1.48–1.54
C-C	1.43,1.49	1.44–1.56	1.44–1.55	1.44–1.54	1.44–1.52
Bond orders X-X		0.43		0.26	
X-C		0.46	0.45	0.40	0.40
Binding energy (eV/atom)	6.05	6.01	6.03	5.90	5.92
HOMO-LUMO gap (eV)	1.50	0.49	0.54	0.23	0.28
HOMO energy level (eV)	−9.5	−7.8	−7.9	−7.1	−7.0
Mulliken's charges					
X		4.7	4.5	7.1	7.2
Nearest C atoms	6.0	6.2	6.2	5.9	5.9
Other C atoms	6.0	5.95–6.03	5.94–6.02	5.97–6.04	5.98–6.03

method is not formally a method for computing excitation energies, but trends for the HOMO-LUMO energy gap should be qualitatively described by the approximation.

For the multiply substituted fullerenes $C_{58}B_2$ and $C_{58}N_2$, their stable structures slightly depend on the relative positions of each substituted atom. The maximum atomic distortions from the C_{60} structure are 0.13 [$C_{58}B_2$(I)], 0.11 [$C_{58}B_2$(II)], 0.10 [$C_{58}N_2$(I)], and 0.09 Å [$C_{58}N_2$(II)]. These values are larger than those of $C_{58}B$ (0.07 Å) and $C_{59}N$ (0.06 Å).[4] In the $C_{58}X_2$(II) cage, the distortion is not localized in the neighborhood of each substituted atom, but extends throughout the whole cage. On the other hand, in the $C_{58}X_2$(I) cage, there is much distortion around the X_2 pair. As shown in Table I, due to an effect from the C_{58} cage, the distance (1.65 Å) between the B atoms becomes 0.1 Å shorter than that of diatomic B_2 (1.75 Å),[15] while the distance (1.55 Å) between N atoms becomes 0.08 Å longer than that of N_2 (1.47 Å for a single bond).[15]

To study their bonding properties in detail, we estimated the bond orders between two X's and between X and its nearest-neighbor C atoms from the coefficients of the occupied molecular orbitals in Eq. (10). The bond order corresponds to the number of electrons contributing to the bonding, and its magnitude indicates the strength of bonding. As shown in Table I, bond order between B atoms is much larger than that between N atoms in the $C_{58}X_2$(I) cage, and those between B and its nearest-neighbor C atoms are larger than those of N. These results are expected to come from the above-mentioned cage distortions, and to show that the two N atoms in the $C_{58}N_2$(I) cage are weakly bonded to each other. This difference in bond order affects the size of the binding energy, which is the difference in the total energies of the whole system and the fragment. Table I shows that the binding energies of $C_{58}N_2$ isomers are about 0.14 eV/atom smaller than that of C_{60}, while those of $C_{58}B_2$ isomers are about 0.03 eV/atom smaller. The value of $C_{58}B_2$ isomers is comparable to that (0.03 eV/atom) between C_{60} and C_{70} calculated by almost the same method,[13] so that $C_{58}B_2$ is expected to be as stable as C_{70}, at least from the viewpoint of static stability whereas $C_{58}N_2$ is less stable. These results for $C_{58}X_2$ are very different from those of $C_{59}X$;[4] there was only a 0.03 eV/atom difference in binding energy between $C_{59}B$ (6.03 eV/atom) and $C_{59}N$ (6.00 eV/atom). In other words, the difference in substituted atoms notably affects the size of the binding energy for double-substituted fullerenes $C_{58}X_2$, although this effect was small for $C_{59}X$.

The calculated results for $C_{58}X_2$ can explain why nitrogen-doped fullerenes were hardly detected in experiments,[1] from the viewpoint of static stability. As for $C_{59}N$, however, the size of its binding energy cannot explain the experimental result. In our previous paper,[4] we noted that $C_{59}N$ may be energetically stable, but most of the free N atoms might produce stable N_2 molecules and not react with carbon atoms in the formation process of cage molecules.

To verify our calculated results, we also calculated the stable structures of $C_{58}B_2$(I) and $C_{58}N_2$(I), starting with the calculated stable structure of C_{60} (a truncated icosahedral with two types of bond lengths, 1.43 and 1.49 Å), and eliminated the possibility that the obtained structures may be local energy-minimum structures. The results show that the bond lengths and binding energies are almost the same as those obtained by starting with the $C_{59}X$ structures; the differences in bond length are at most 0.03 Å ($C_{58}B_2$) and 0.02 Å ($C_{58}N_2$), and the difference in binding energy is 0.005 eV/atom for $C_{58}B_2$ and $C_{58}N_2$. Consequently, we conclude from the size of the binding energy that $C_{59}B$, $C_{58}B_2$, and $C_{59}N$ are as energetically stable as C_{60} and C_{70}, but $C_{58}N_2$ is not.

As for static stabilities among isomers, there is a 0.02 eV/atom difference in binding energy between the $C_{58}X_2$(I) and $C_{58}X_2$(II) isomers for both X=B and N cases; the $C_{58}X_2$(II) isomer is 0.02 eV/atom more stable. Although this value is smaller than the difference in binding energy between C_{60} and C_{70}, it is comparable to that (0.02 eV/atom) between the two most stable isomers of C_{60}, calculated by a molecular-dynamics tight-binding method.[10] Therefore, we expect that the two substituted atoms prefer to be separated rather than close together in these $C_{58}X_2$ cages. This corresponds to the experimental results[1] indicating that the two B atoms are well separated from each other in the $C_{58}B_2$ cage.

As shown in Table I and Fig. 1, the electronic properties of $C_{58}B_2$ and $C_{58}N_2$ differ from each other, because of the difference in valency of the substituted atoms and their positions. Since the icosahedral symmetry of C_{60} is lost by substitutions and the only remaining symmetry element is a mirror plane, all energy levels of $C_{58}X_2$ split. In Fig. 1, however, the molecular orbitals whose energies agree with each other to within a difference of 0.05 eV are regarded as degenerated, and the length of the horizontal bar shows the orbital degeneracy. Since the structures of $C_{58}X_2$ (X = B and N) are almost the same as that of C_{60}, there are many approximately degenerated orbitals. In the case of the $C_{58}B_2$ isomers, replacing two C atoms by B atoms provides two holes in the fivefold-degenerate HOMO (h_u symmetry) of C_{60}, and the new LUMO of $C_{58}B_2$ shifts to about a 0.5-eV higher-energy region than the other four levels originating from the HOMO of C_{60}, so that the energy gaps between HOMO and LUMO are reduced to 0.49 [$C_{58}B_2$(I)] and 0.54 eV [$C_{58}B_2$(II)] from that for C_{60} (1.50 eV). On the other hand, by doping N atoms, two electrons are doped in the threefold-degenerate LUMO (t_{1u} symmetry) of C_{60}, and it splits into three nondegenerated levels. One of these levels is occupied by two electrons and shifts to about a 0.3-eV lower-energy region, so that the energy gaps between this level (HOMO) and the LUMO of $C_{58}N_2$ are 0.23 [$C_{58}N_2$(I)] and 0.28 eV [$C_{58}N_2$(II)]. These values differ from the energy gaps between the LUMO and half-occupied MO of $C_{59}B$ (1.06 eV) and $C_{59}N$ (0.30 eV).[4] In particular, the energy gaps of the $C_{58}B_2$ isomers are remarkably changed from that of $C_{59}B$, because the half-occupied MO of $C_{59}B$ is transferred to the LUMO of $C_{58}B_2$. These results for the energy levels near the Fermi level predict the possibility that $C_{60-2n}B_{2n}$ and $C_{60-2n}N_{2n}$ might be components of various band-gap semiconductors, if these molecules could be obtained.

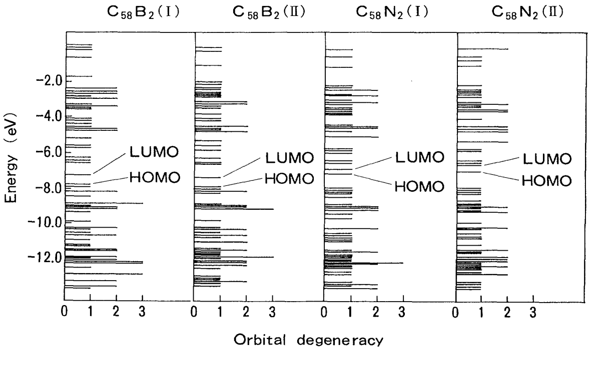

FIG. 1. Energy levels near the Fermi level for $C_{58}X_2$ (X = B and N) isomers. In the $C_{58}X_2$(I) and $C_{58}X_2$(II) cages, the two X's are in the nearest and farthest sites, respectively. The molecular orbitals whose energies agree with each other to within a difference of 0.05 eV are regarded as degenerated, and the length of the horizontal bar shows the orbital degeneracy.

The energy levels with the $2p$ character of the substituted atoms largely depend on their relative positions. For the $C_{58}X_2$(I) isomer, since the two substituted atoms exist in the nearest-neighbor sites, levels with the atomic character of the substituted atoms are split in bonding and antibonding levels. Then, for $C_{58}B_2$(I), the former are in about a 0.0–2.0-eV ($2p_\pi$) higher-energy region than that of LUMO and about a 1.5–4.5-eV ($2p_\sigma$) lower-energy region than that of HOMO, and the latter are in about a 5.4–6.6-eV ($2p_\pi$) and over 18-eV ($2p_\sigma$) higher-energy region than that of LUMO. For $C_{58}N_2$(I), the bonding levels are in about a 6.0–6.2-eV ($2p_\pi$) and a 8.3–11-eV ($2p_\sigma$) lower-energy region than that of HOMO, and the antibonding levels are in about a 0.0–3.8-eV ($2p_\pi$) lower-energy region than that of HOMO and 2.0–7.0-eV ($2p_\sigma$) higher-energy region than that of LUMO. The atomic charges estimated from Mulliken's analysis of B and N are 4.7 and 7.1, respectively. On the other hand, for the $C_{58}X_2$(II) isomer, since the two substituted atoms are separated from each other, the energy levels are similar to those of $C_{59}X$;[4] for $C_{59}B$ the energy levels with the $2p$ character of B are in the 3.5–5.0-eV lower- ($2p_\sigma$) and 0.0–3.5-eV higher- ($2p_\pi$) energy regions than the half-occupied MO level, while they are in the 9.0–11-eV lower- ($2p_\sigma$) energy region and in the region from 6.0-eV lower to 1.5-eV higher ($2p_\pi$) than the half-occupied MO level for $C_{59}N$. For $C_{58}B_2$(II), the energy levels with the $2p_\sigma$ character of B are in about a 2.8–3.8-eV lower region than HOMO, and those with $2p_\pi$ character are in the region from 0.3-eV lower than HOMO to 1.0-eV higher than LUMO; for $C_{58}N_2$(II), those with $2p_\sigma$ character are in about a 7.7–12-eV lower region than HOMO, and those with $2p_\pi$ character are in about a 1.7–5.8-eV lower region than HOMO and a 0.3–1.3-eV higher region than LUMO. Mulliken's charges of B and N are 4.5 and 7.2, respectively, which are the same as those of $C_{59}B$ and $C_{59}N$. The calculated Mulliken's charges show that the B atoms donate electronic charge to their neighbor carbons and exist as donors, while the N atoms accept electronic charge and exist as acceptors in $C_{58}X_2$ as well as $C_{59}X$. The result for $C_{58}B_2$ is consistent with the experimental results[1] that an electron-deficient site was produced at the B position on the cage. When doping into silicon (the IV family in the Periodic Table), doped boron (the III family) exists as an acceptor, while doped phosphorous (the V family) is a donor. Thus, the present results for $C_{58}B_2$ and $C_{58}N_2$ differ very much from that for silicon. This difference is expected to be related to the uniqueness of C_{60} (i.e., its molecular structure, its electronic properties, etc.) and/or the atomic properties of C, B, and N.

As shown in Table I and Fig. 1, the HOMO energy levels of $C_{58}B_2$ and $C_{58}N_2$ are about −7.9 and −7.1 eV, respectively, which are somewhat higher than that of C_{60} (−9.5 eV). Thus, the electronic affinities of $C_{58}B_2$ and $C_{58}N_2$ are smaller than that of C_{60}, so that their solids are expected to be more easily hole doped than the C_{60} solid.

IV. CONCLUSIONS

To investigate the bonding and electronic properties of substituted fullerenes $C_{58}B_2$ and $C_{58}N_2$ and clarify their changes by multiple substitutions, we obtained their stable structures by using a molecular-orbital method with Harris-functional and spin-restricted approximations and calculated their binding energies and electronic properties self-consistently. The binding energies of $C_{58}B_2$ isomers were almost the same as that of C_{60}, while those of the $C_{58}N_2$ isomers were much smaller. These results differed significantly from those of $C_{59}X$ ($X=$B and N) (Ref. 4) and could be related to the experimental finding[1] that it was more difficult to obtain $C_{60-n}N_n$ than $C_{60-n}B_n$. The calculated results for the relative stability between the two isomers could also be related to the experimental finding[1] indicating that the two B atoms are well separated from each other in the $C_{58}B_2$ cage. Therefore, we conclude that $C_{58}B_2$ is expected to be as stable as C_{60} and C_{70}, but $C_{58}N_2$ is not, with respect to static stability.

The electronic properties of $C_{58}X_2$ largely depend on the relative positions of substituted atoms. These properties of the $C_{58}X_2$(I) isomer, in which the two substituted atoms are in the nearest-neighbor sites of the C_{60} cage, differed from those of $C_{59}X$; the HOMO-LUMO energy gaps were 0.49 ($C_{58}B_2$) and 0.23 eV ($C_{58}N_2$) and the atomic charges estimated from Mulliken's analysis of the B and N atoms were 4.7 and 7.1, respectively. On the other hand, for the $C_{58}X_2$(II) isomer, in which the two substituted atoms are on opposite sides of the C_{60} cage, the HOMO-LUMO energy gaps were 0.54 ($C_{58}B_2$) and 0.28 eV ($C_{58}N_2$) and the atomic charges of the B and N atoms were 4.5 and 7.2, which are almost the same as those of $C_{59}X$. The values of the atomic charges show that the N atoms act as acceptors, while the B atoms are donors in the $C_{58}X_2$ cages. The result for $C_{58}B_2$ is consistent with the experimental result,[1] although the charge transfer from the substituted atoms to the host carbon atoms of the cage is in the opposite direction of B or P atom doping into a silicon crystal.

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