Structural and electronic properties of $C_{59}X$ (X=B,N): The extended Su-Schrieffer-Heeger model

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The molecules $C_{59}X$ (X=B,N) are investigated by the extended Su-Schrieffer-Heeger model. The obtained results for the energy levels and molecular structures are compared with those from a self-consistent-field molecular-orbital (SCF-MO) method. We have found that by choosing suitable empirical parameters, most of the features included in the results of the SCF-MO method can be well reproduced. Other structural and electronic properties such as the excess electron density and the amplitude of the midgap states have also been studied.

Recently, the doped C_{60} has stimulated a great interest of researchers in physics and chemistry to investigate its structural,[1] electronic,[2] optical,[3,4] and other properties.[5–7] This is because it not only exhibits rather strong nonlinear optical properties,[3] but also because alkali ion doped C_{60} crystals become superconducting at a critical temperature T_c= 18 K for K_3C_{60} (Ref. 8) and 28 K for $R_{b3}C_{60}$,[9] which leads to a great effort to dope different kinds of atoms into the C_{60}, in efforts to find C_{60} samples with higher T_c superconductors. Experimental observations indicate that the lattice and electronic structures of C_{60} change with doping.[10] Besides the alkali metal doping, there is also another type of doping, i.e., substituting one or more carbon atoms of the C_{60} molecule by other atoms.[11] For example, boron and nitrogen atoms have been successfully used to replace carbon atoms of the C_{60} molecule, which led to synthesis of many kinds of modified C_{60} molecules: $C_{60-m-n}X_mY_n$, where X, Y represent the B, N, or other possible substitute atoms and n,m range from zero to a possible maximum value (≤ 3).[12] Although this new type of substituted fullerenes may not be a kind of superconductor with higher T_c, since their band gaps and electronic polarizations can vary much with different substitute doping, they might attain a potential application as semiconductor components and possible building materials for nanometer electronics. Therefore, it is interesting and useful to investigate experimentally and theoretically their structural and electronic properties from the viewpoint of practical applications.

Theoretically, quantum molecular dynamics has been used to study stable structure of $C_{59}B$ and $C_{59}N$,[13] and also the molecular cluster calculations has been made[14] for $C_{58}B_2$ and $C_{58}N_2$. More recently, Kurita *et al.*[12,15] used the molecular-orbital method with Harris-functional and spin-restricted approximations to calculate molecular structures and electronic properties of $C_{59}X$ (X=B, N, and S),[15] as well as $C_{58}B_2$ and $C_{58}N_2$.[12] Their results show that the substitute dopings of the C_{60} with B and N change significantly their energy levels near the Fermi level and the corresponding band gaps between the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO), although their structure and binding energies are almost unchanged. On the other hand, it is well known that the Su-Schrieffer-Heeger (SSH) model proposed originally for the polyacetylene was applied successfully in the study of conducting polymer in the past decade[16] and has also been extended to describe the pure and nonsubstitute doped C_{60} systems satisfactorily.[17,18] Thus, it is natural to ask if the extended SSH model can be employed to study the substituted fullerenes $C_{60-n}X_n$ and to get a reasonable result which is consistent with, or at least compatible with, those obtained by the self-consistent-field molecular-orbital (SCF-MO) method. If it is the case, the advantage is obvious because the extended SSH model is simple and contains only three adjustable empirical parameters, which will significantly reduce complexity and computing time needed in the numerical calculation. In this paper we will perform a numerical calculation on the single substituted molecules $C_{59}X$ by using the extended SSH model and justify such simple model is indeed suitable for that.

The extended SSH model for C_{60} molecule can be written as[17,18]

$$H = \sum_{\langle ij\rangle,s} [-t_0 - \alpha_0 y_{ij}](c_{is}^\dagger c_{js} + \text{H.c.}) + \frac{K_0}{2} \sum_{\langle ij\rangle} y_{ij}^2, \quad (1)$$

where $c_{is}^\dagger$ and c_{is} are, respectively, the usual creation and annihilation operators of a π electron at the ith carbon atom with spin s; t_0 is the hopping integral of the undimerized system, α_0 is the coupling constant between electron and phonon, and y_{ij} is the change of the bond length between the ith and jth atoms.[19] The sum over $\langle ij\rangle$ is taken over nearest-neighbor pair sites $\langle ij\rangle$. The last term is the elastic energy of the phonon system with the K_0 as the spring constant. Notice that Eq. (1) is applied only to the pure C_{60} system. In fact, it should be modified to include the effect of the dopant ions in the

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TABLE I. The energy gaps between LUMO and HOMO and the maximum atomic distortions from the C_{60} calculated with SCF-MO method and SSH model.

	SCF-MO		SSH	
	$C_{59}B$	$C_{59}N$	$C_{59}B$	$C_{59}N$
HOMO-LUMO gaps (eV)	1.06	0.30	1.06	0.302
The maximum atomic distortion from the C_{60} (Å)	0.07	0.06	0.06	0.04

substituted fullerenes $C_{59}X$. So, we rewrite Eq. (1) as $H = H_0 + H_1$ with

$$H_n = \sum_{\langle ij\rangle,s}^{(n)} \left[(-t_n - \alpha_n y_{ij})(c^\dagger_{is}c_{js} + \text{H.c.}) + \frac{K_n}{4} y_{ij}^2\right], \tag{2}$$

where the sum with superscript (0) in H_0 [(1) in H_1] is taken over the nearest-neighbor pairs for the C-C bonds (X-C bonds). The new parameters t_1 represent the hopping integral between the impurity atom and its nearest-neighbor carbon atom for the undimerized system, α_1 is the electron-phonon coupling constant relating to the X-C bond, and K_1 is the spring constant corresponding also to the X-C bonds. Since the number of the substitute impurity atoms is low,[20] H_1 plays a perturbational role. As an approximation, we suppose that the three original empirical parameters in H_0 should not be changed due to the substitute doping. Therefore, in this numerical calculation, all of them are taken to be the same as those in pure C_{60} system: $t_0 = 2.5$ eV, $\alpha_0 = 6.31$ eV/Å, and $K_0 = 49.7$ eV/Å^2.

Equation (2) can be solved by the standard adiabatic approximation method, which leads to the Schrödinger equation for the π electron,

$$\varepsilon_k Z_{ks}(i) = \sum_{n=0,1}\sum_{\langle ij\rangle}^{(n)} (-t_n - \alpha_n y_{ij}) Z_{ks}(j), \tag{3}$$

where ε_k is the eigenvalue of the kth eigenstate and the Z_{ks} is the electronic wave function. The total energy of the molecule $C_{59}X$ is a functional of the set of y_{ij},

$$E_T(\{y_{ij}\}) = \sum_k{}' \varepsilon_k + \sum_{n=0,1}\sum_{\langle i,j\rangle}^{(n)} (K_n/2) y_{ij}^2, \tag{4}$$

where the first sum with a prime runs over only the occupied states. Minimizing the total energy E_T over y_{ij} and using the constraint condition $\sum_{n=0,1}\sum_{\langle ij\rangle}^{(n)} y_{ij} = 0$, we are able to obtain the self-consistency equations for y_{ij}

$$y_{ij}^{(n)} = \frac{2\alpha_n}{K_n} \sum_{k,s}{}' Z_{ks}(i) Z_{ks}(j) - \Delta y, \tag{5}$$

with $n = 0$ for C-C bonds and $n = 1$ for X-C bonds, where

$$\Delta y = \frac{1}{N} \sum_{n=0,1}\sum_{\langle ij\rangle}^{(n)} \left(\frac{2\alpha_n}{K_n}\right) \sum_{k,s}{}' Z_{ks}(i) Z_{ks}(j). \tag{6}$$

Here $N(= 90)$ is the number of π bonds. The coupled equations (3) and (5) can be solved iteratively, and final result should be independent of choosing the different initial values of the set y_{ij}.

In the numerical calculation, we take $t_1 = 1.025$ eV, $\alpha_1 = 5.8$ eV/Å, and $K_1 = 49$ eV/Å^2 for $C_{59}B$ and $t_1 = 0.95$ eV, $\alpha_1 = 6.0$ eV/Å, and $K_1 = 48$ eV/Å^2 for $C_{59}N$. The numerical results for the band gaps between LUMO and HOMO, and the maximum atomic distortions from the C_{60} structure are presented in Table I and compared with those obtained by the SCF-MO method.[12,15] We can see from Table I that the extended SSH model with appropriately chosen parameters for the substitute impurity atoms is able to accurately reproduce the results calculated with the SCF-MO method.[12,15] The total energies of the molecules and the excess electron densities at and around the positions of substitute impurity atoms (B or N) are listed in Table II. It is found that both $C_{59}B$ and $C_{59}N$ have nearly the same total energy, which means that they are equally stable. The excess electron density of the B atom is -0.564 but that of N is 0.27, which implies that electron deficiency is produced at the doped B atom site and the B atom gives up its electronic charge to its neighbors and exists as a donor. Obviously, electronic charge accumulates on the doped N site and the N atom exists as an acceptor. The signs of excess electron density for the B and N atoms are different, which makes $C_{59}B$ and $C_{59}N$ have opposite electronic polarization. This conclusion is well consistent with the SCF-MO calculation[12,15] as well as the experimental observation.[11]

The energy levels near the Fermi level for $C_{59}B$ and $C_{59}N$ are shown in Fig. 1. They are quite different as expected because in $C_{59}B$ one hole is doped in the HOMO of C_{60}, while in $C_{59}N$ one electron is doped into the LUMO of C_{60}. Obviously, these substitute dopings destroy the special icosahedral symmetry of the C_{60} molecule and make the energy degeneracy much reduced. For example, the highest occupied level in $C_{59}B$ splits

TABLE II. The total energies for $C_{59}X$ (X= B, N) and the excess electron densities at and around the impurity atoms. The numbers in square brackets represent the site numbers in the C_{60} molecule, e.g., number 1—the impurity atom site and 5, 9—its two nearest-neighbor sites.

	$C_{59}B$	$C_{59}N$
Total energy (eV)	−228.68	−228.94
Excess electron densities	−0.564[1]	0.2699[1]
	−0.047[5]	−0.026[5]
	−0.072[9]	0.141[9]

from other HOMO of C_{60} and becomes nondegenerate. Its energy shifts upward about 0.9 eV. Similarly, in $C_{59}N$ the original threefold degenerate LUMO of C_{60} splits into one singlet and a twofold degenerate levels with the singlet being half-occupied and shifting downward from the twofold degenerate levels about 0.30 eV. Therefore, the band gaps between the half-filled levels and the LUMO levels of $C_{59}X$ will be able to vary greatly with different substituted impurity atoms (here, the gaps for X=B,N are equal to 1.06 eV and 0.30 eV, respectively). Thus, there exists a possibility to produce the semiconductor components using the $C_{60-n}X_n$ (X=B, N, or others) with various band gaps. We should emphasize here that by adjusting two parameters t_1 and α_1 (among them the effect of t_1 is stronger) the calculated band gaps in the framework of the extended SSH model are well consistent with the results of the SCF-MO method.[12,15] However, there are some differences. For example, in our calculation, the energy difference between the half-filled level and the other four degenerate HOMO levels for $C_{59}B$ is about 0.9 eV, in contrast with the value $\sim$ 0.4 eV calculated by the SCF-MO method.[12,15] Of course, we are

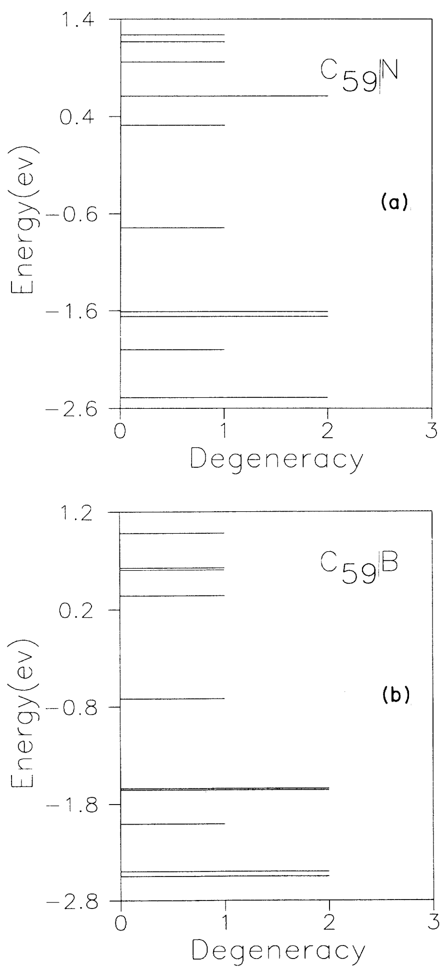

FIG. 1. Energy level structures of the molecules (a) $C_{59}N$ and (b) $C_{59}B$. The energy levels with differences between each other being less than 0.02 eV are regarded as degenerated.

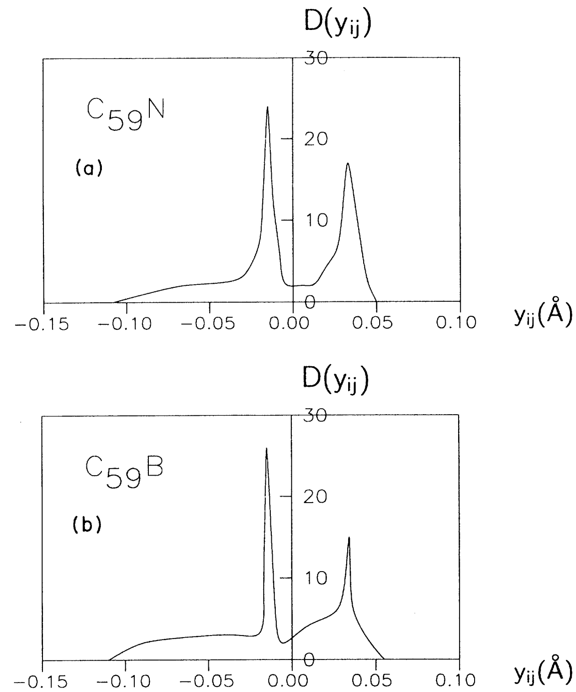

FIG. 2. The distribution function $D(y_{ij})$ of the bond variables for (a) $C_{59}N$ and (b) $C_{59}B$.

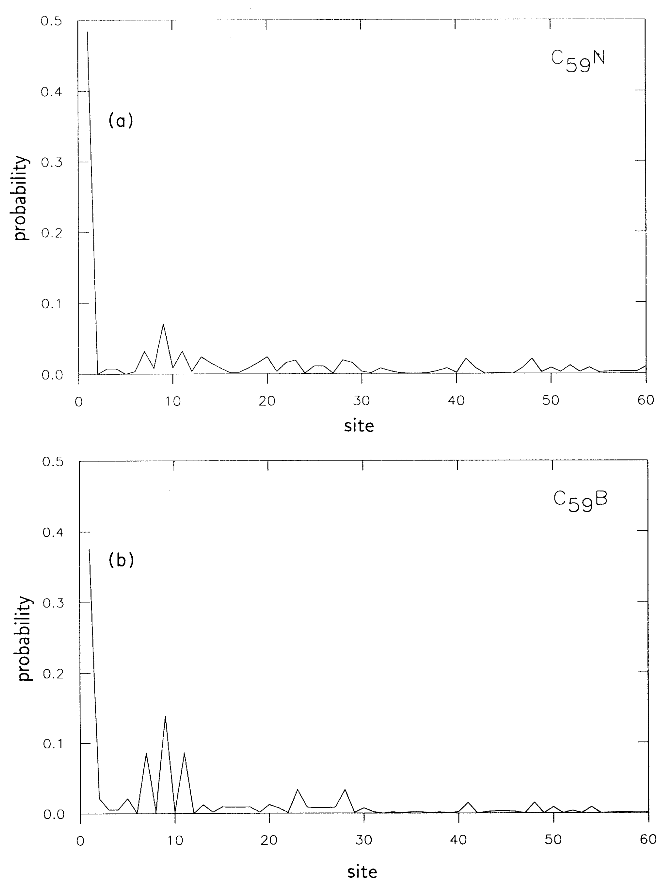

FIG. 3. The site-occupying probability of the HOMO state for molecules (a) $C_{59}N$ and (b) $C_{59}B$.

able to make the value become smaller and closer to that obtained by the SCF-MO method, but in the meantime the difference between the band gaps obtained respectively by the two methods will become bigger. Therefore, which one is better could not be determined up to this step, and the question is left to be answered by future experiments, e.g., spectroscopy observations.

In $C_{59}X$, the difference between the lengths of short and long bonds becomes the smallest along an equatorial line of C_{60}, which is the same as that in the usual doped C_{60} system (e.g., C_{60}^-). The lattice structure of $C_{59}X$ is different from that of pure C_{60} due to effects of the dopant ion, but the deformations of the substituted fullerene cage for the $C_{59}X$ are mainly limited in the vicinity of the dopant ions. The distribution functions $D(y_{ij})$ of the bond variables are shown in Fig. 2, in which a two-peak structure indicates the presence of the dimerization. The narrow peaks in the negative y_{ij} region correspond to the distortion part around the impurity ions. The area of the extended portion for $C_{59}B$ is greater than that for $C_{59}N$, which indicates that the doped B atom will produce stronger distortions around it than that in the N atom. Moreover, the site-occupying probabilities of the HOMO states for $C_{59}X$ are plotted in Fig. 3. There are two large peaks at point 1 (position of the impurity atom in C_{60} molecule) and point 9 for both $C_{59}B$ and $C_{59}N$. The fact that the peak at point 1 in $C_{59}N$ is higher than that in $C_{59}B$ represents that the localization effect coming from the N impurity atom is stronger than that from the B atom. The bond connecting points 1 and 9 is the shortest X-C bond among three X-C bonds and is represented by a thick line in Fig. 4. These structures in Fig. 3 mean that the HOMO states are strongly localized on the X-C double bond. Such electronic behavior looks more like that produced by the deep impurities in the usual semiconductors.

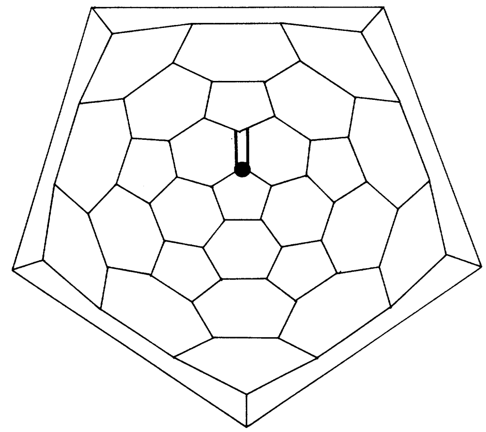

FIG. 4. The plane projective figure of the C_{60} molecule. The black ball corresponds to the substituted impurity atom (B or N). The double line represents the shortest X-C bond.

In conclusion, the calculated results based upon the extended SSH model for the substituted fullerene $C_{59}X$ are well consistent with those from the SCF-MO method.[12,15] It has been found that the lattice structures change due to doping, in particular significantly in the vicinity of the dopant ions. The HOMO-LUMO energy gaps for the molecules $C_{59}B$ and $C_{59}N$ are shown to be smaller than that for C_{60}. The HOMO states are mainly localized on the X-C double bonds and the excess electron densities are concentrated on the impurity sites. From our results, it seems that the general substituted fullerene $C_{60-m-n}X_mY_n$ can also well be described by the extended SSH model.

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[19] When y_{ij} is positive, the hopping integral is larger than t_0, and so the sign before α is negative.
[20] Usually it is less than or equal to 6, but it is set to be 1 in this paper.