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# Second-order Jahn-Teller effect on carbon $4N+2$ member ring clusters

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Occurrence of bond-length alternation of monocyclic carbon $4N+2$ member rings is examined based on the hybrid density-functional calculations. In the case that $N\leqslant 4$, the bond-length nonalternant cumulenic structure $[D_{(2N+1)h}]$ is found to be the most stable and this structure becomes unstable when $N\geqslant 5$. Then the bond-length alternant structure $[C_{(2N+1)h}]$ becomes the most stable among the ring-shape clusters. We observe that the bond-length alternation mode of the stable cumulenic structures is considerably lowered as the size becomes large. This softening is analogous to the Kohn anomaly in crystal systems and is the origin of the Peierls-like (bond-length alternation) distortion of large clusters. These features are discussed in terms of the second-order Jahn-Teller effect. [S0163-1829(99)08035-2]

Occurrence of bond alternation of a variety of carbon bond networks is a fundamental issue in chemistry and is also important in solid-state physics. Cyclobutadien ($C_4H_4$) of a $4N$ member ring with $sp^2$ bonds is a bond-alternant hydrocarbon in contrast with *aromatic* benzene ($C_6H_6$) of a $4N+2$ system without the bond alternation. Meanwhile, polyacetylene, which is an infinite periodic system, is a bond-alternant material because of the Peierls distortion.[1] Therefore, Peierls-like distortion of bond alternation occurs in $4N+2$ member ring annulenes ($C_{4N+2}H_{4N+2}$) when $N$ is large.[2,3] A similar situation is expected for $sp$ bond systems. The infinite polyyne chain is a bond-alternant system while monocyclic carbon $4N(4N+2)$ member rings of small $N$ have bond (non)alternating geometries.[4,5] Understanding of these pure carbon ring clusters is important toward clarification of formation mechanism of fullerenes[6,7] and then a variety of first-principles calculations have been applied.[8] Moreover, examination of bond-length alternation of $4N+2$ member rings is significant to understand how electronic structures of finite systems approach those of infinite periodic systems. Recent local-density-approximation (LDA) calculations[4] on the $4N+2$ member rings indicated that the bond-length alternation is prevented up to $N=10$, while the Hartree-Fock (HF) calculation[5] suggested that the bond-length alternation occurs when $N\geqslant 3$. A hybrid density-functional theory (DFT) calculation[5] concluded that the bond alternation is prevented up to $N=4$.

To carefully examine the occurrence of the bond-length alternation of carbon $4N+2$ member rings, in this paper we adopted the hybrid DFT that suitably includes the electron many-body effects compared with the HF method and the conventional DFT [LDA and generalized gradient approximation (GGA)]: The hybrid DFT gives results comparable with those of accurate electron-correlation calculations.[5,9] It was concluded that when $N\leqslant 4$, the bond-angle alternant cumulenic structure without the bond-length alternation is the most stable, while the bond-length alternation occurs when $N\geqslant 5$. The occurrence of this bond-length alternation was argued in terms of the second-order Jahn-Teller effect (SOJTE).[2,10]

We employed the hybrid DFT method, following Becke's recipe of three parameters (B3LYP):[11] The exchange energy is a mixture of those of the HF and DFT (LDA and the GGA of Beck's type[12]) and the correlation energy consists of those of the LDA (Ref. 13) and of the GGA of the Lee-Yang-Parr[14] type. We used the basis set of Dunning's correlation-consistent polarized valence double zeta (cc-pVDZ) type[15] that well reproduces vibrational frequencies,[5] otherwise stated. In order to reduce the computational time, in some cases we employed the standard double-zeta polarization (SDZP) basis set conventionally labeled by $6-31G(d')$.[16] The six $d$ orbitals ($xx$, $yy$, $zz$, $xy$, $yz$, and $zx$) in the SDZP basis set are legitimately reduced to five orbitals in the cc-pVDZ calculation. All the calculations were performed using the GAUSSIAN 94 program.[17]

We started with geometry optimization with restriction of the high-symmetry $D_{(4N+2)h}$ without alternation of bond length and bond angle and then calculated vibrational frequencies of the optimized geometries to examine the stability ($3\leqslant N\leqslant 6$). It was found that the bond-angle alternating mode of $B_{2u}$ (Fig. 1) was found to have an *imaginary* frequency, indicating that the high-symmetry geometries are *unstable*. In contrast, the bond-stretching mode of $B_{1u}$ that corresponds to the bond-length alternation (Fig. 1) has the real frequency up to $N=4$. The frequency is, however, found to decrease as $N$ becomes large and to be imaginary when $N\geqslant 5$, suggesting that the bond-length alternation occurs in large rings.

Understanding of the imaginary frequencies of the above two modes is important to clarify how the high symmetry ($D_{(4N+2)h}$) of the unstable geometry is lowered in the stable geometry. The softening of the modes is here qualitatively discussed based on the SOJTE. The second derivative of the total energy over a normal mode ($Q_i$) is estimated as

$$k_i=\langle\Phi_0|\partial^2H/\partial^2Q_i|\Phi_0\rangle -2\Sigma_{n\neq 0}|\langle\Phi_n|\partial H/\partial Q_i|\Phi_0\rangle|^2/(E_n-E_0), \qquad (1)$$

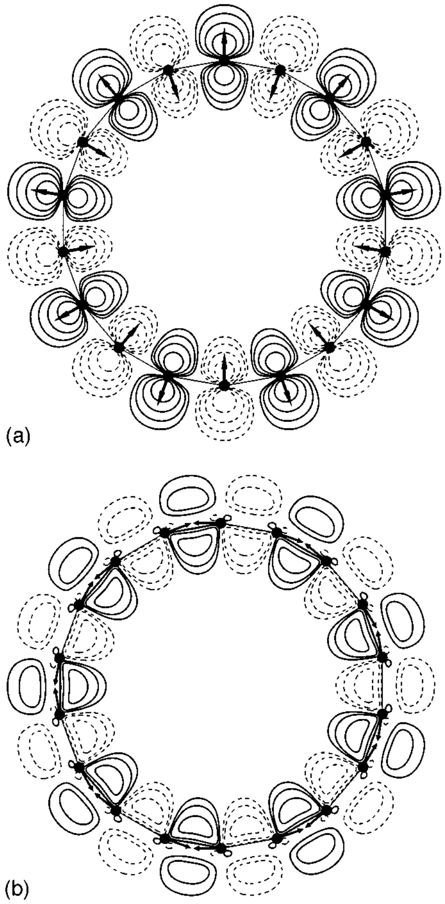

FIG. 1. Transition densities of $B_{2u}$ (a) and $B_{1u}$ (b) for the $C_{18}$ ring with the $D_{18h}$ symmetry. The solid (dashed) contour lines represent positive (negative) values and the absolute values are $0.16\times 2^{-n}e/(\text{Å}^3)$, where $n=0-3$ in (a) and $n=1-3$ in (b). The arrows indicate the corresponding normal mode of bond-angle (a) and bond-length (b) alternations (see text). The calculations are performed by use of the SDZP.

where $\Phi_n$ $(H)$ are the total electronic wave functions (Hamiltonian) and $n=0$ $(n\neq 0)$ corresponds to the ground (excited) state. $E_n$ is the corresponding total energy. The basis set of $\{\Phi_n\}$ is assumed to be complete in the above expression. While the first term is positive, the second term is negative and thus induces softening of the normal mode. Since low-lying excited states give dominant effects on the second term because of the energy denominator in Eq. (1),[2] we focus on excited states of single-electron excitation from an occupied level $(l)$ having a high energy to an unoccupied level $(m)$ having a low energy. Using the single-particle wave functions $(\phi)$ within the mean-field theory, we write the numerator of the second term as $|\int d\mathbf{r}\rho_{l,m}\partial V/\partial Q_i|^2$, where $V$ is the electron-nuclear attractive potential and $\rho_{l,m}$ is the transition density defined as $\rho_{l,m}=\phi_l^*\phi_m$. In the above expression, we neglect the correction of the incompleteness of the present basis set of the localized orbitals. Analysis of the transition density gives information as to which modes are softened. The above-mentioned effect on softening due to low-lying excited states is called the SOJTE.[2]

In the present system, the electron configuration is $\ldots[\pi(E_{N\beta})]^4[\sigma(E_{N\alpha})]^4[\sigma^*(E_{(N+1)\beta})]^0[\pi^*(E_{(N+1)\alpha})]^0\ldots,$ where $\alpha$ denotes $u(g)$ for the odd (even) numbers of $N$ and $\beta$ is vice versa. The $\sigma$ $(\sigma^*)$ mainly consist of $p$ in the radial direction and have energies close to those of $\pi$ $(\pi^*)$ including $p$ perpendicular to the ring plane. We then consider the electron excitations from $\sigma$ to $\sigma^*$, and from $\pi$ to $\pi^*$. Both give the irreducible representations of $B_{1u}$, $B_{2u}$, and $E_{1u}$ of the transition densities. This is the reason why the bond-angle alternation $(B_{2u})$ and bond-length alternation $(B_{1u})$ modes are softened. In Fig. 1, we plotted the transition densities of $\sigma$-$\sigma^*$ excitation for example. The transition density of $B_{2u}$ is large around each atomic position and the phases are opposite between the neighboring atomic sites. Therefore, this transition density corresponds to the softening of the bond-angle alternation mode [the second term in Eq. (1) is large for this mode]. In contrast, the transition density of $B_{1u}$ is large around the bond centers and the signs of the neighboring bond-center sites are opposite to each other. This density thus induces softening of the bond-length alternation mode. As the cluster size becomes large, the electron excitation energies decrease and thus the second term in Eq. (1) becomes significant because of the energy denominator. As a result, the two modes are softened as $N$ increases: The calculated frequencies of the $B_{1u}$ mode are 755 $\text{cm}^{-1}$ and $237i$ $\text{cm}^{-1}$ for $N=4$ and 5, respectively, and the corresponding values of the $B_{2u}$ mode are $988i$ $\text{cm}^{-1}$ and $1278i$ $\text{cm}^{-1}$, respectively. We confirmed that all the $E_{1u}$ modes, which are expected to be softened by the SOJTE as mentioned above, have real frequencies and thus the geometries are stable against the $E_{1u}$ distortion. The $\sigma$-$\pi^*$ and $\pi$-$\sigma^*$ excitations also have low energies and are likely to induce softening of some out-of-plane modes belonging to $B_{1g}$, $B_{2g}$, and $E_{1g}$. It was, however, found that these out-of-plane modes have real frequencies. We thus focus on the distortion of bond-angle and bond-length alternations hereafter.

We then optimized the geometry allowing the bond-angle alternating distortion: The symmetry is accordingly lowered from $D_{(4N+2)h}$ to $D_{(2N+1)h}$. In order to discuss the stability of the optimized geometry, we calculated vibrational frequencies and classified the modes as follows. Since the cyclic group $C_{(2N+1)}$ is a subgroup of $D_{(2N+1)h}$, the normal mode of the bond-stretching mode has the form

$$Q_j=\sum_{m=0}^{2N}\exp[2\pi mj/(2N+1)](\mathbf{C}_{2N+1})^m(c\mathbf{q}_1-c'\mathbf{q}_2), \tag{2}$$

where $\mathbf{q}_1$ and $\mathbf{q}_2$ are the coordinates in the circumference directions of the neighboring atoms labeled by 1 and 2 and $c$ and $c'$ are the corresponding coefficients. $\mathbf{C}_{2N+1}$ is the rotational operator of the angle of $2\pi/(2N+1)$. $j$ ranges from $-N$ to $N$ and the zero (nonzero) value of $j$ corresponds to the $A_2'$ $(E_{|j|}')$ representation. In the infinite limit, $j/(2N+1)$ corresponds to the pseudomomentum in crystal systems. A simple spring model then leads to the conclusion that the frequency of the *optical-phonon*-type bond-stretching modes (the phases of the first and second atoms are opposite to each other) increases as $|j|$ becomes small and the point of $j=0$ corresponding to $\Gamma$ in the crystal Brillouin zone has the maximum value. Yet our hybrid DFT calculation indicates that the $j=0$ mode, which has the bond-length alternation

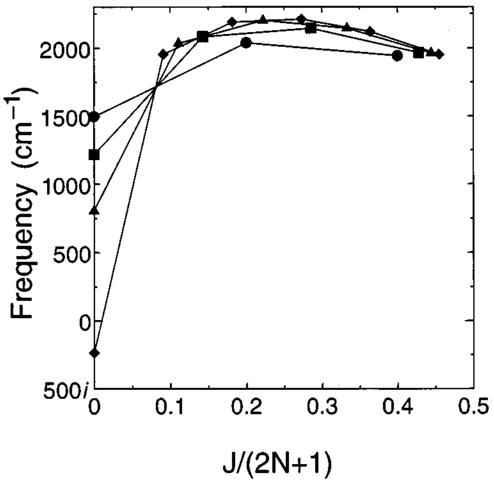

FIG. 2. The vibrational frequencies of the bond-stretching mode for the cumulenic structure. The circles, rectangles, triangles, and diamonds indicate that $N=2$, 3, 4, and 5, respectively. The calculated frequencies for $N=2$, 3, and 4 are the same as those in Ref. 5.

character, is anomalously softened (Fig. 2). As was found in the case of the high-symmetry geometry of $D_{(4N+2)h}$, the softening in $D_{(2N+1)h}$ is enhanced as $N$ becomes large and the frequency becomes imaginary when $N\geqslant 5$. We thus concluded that the cumulenic $D_{(2N+1)h}$ structure is stable when $N\leqslant 4$ and that the geometry is unstable for $N\geqslant 5$ due to the bond-length alternation (we confirmed that there is no imaginary frequency up to $N=4$). The softening of the bond-length alternation mode in the $D_{(2N+1)h}$ symmetry is explained based on the SOJTE as was done in the high-symmetry ($D_{(4N+2)h}$) case. In the low-symmetry case, the transition densities for the $\sigma$-$\sigma^*$ and $\pi$-$\pi^*$ excitations include those of the $A_2'$ representation. We confirmed that these densities resemble those of $B_{1u}$ in the case of $D_{(4N+2)h}$ (Fig. 1) and thus correspond to softening of the bond-length alternation mode of $A_2'$ $(j=0)$. Finally a photoelectron spectroscopy implied[18] that the neutral $C_{18}$ has a cumulenic structure consistent with the present theoretical conclusion.

As was discussed above, the cumulenic structure is unstable when $N\geqslant 5$. We then confirmed that the $C_{(2N+1)h}$ geometry with both bond-angle and bond-length alternations is stable for $N=5$ and 6: It was found that the bond-length alternant mode $(j=0)$, which is totally symmetric $(A')$ in this low symmetry, has a real frequency (Fig. 3). Further using the SDZP basis set, we confirmed that the $C_{(2N+1)h}$ geometry is stable for $N=5$, 6, and 7. The SDZP calculation in the case of $N=6$ somewhat overestimates the frequency of the $j=0$ bond-stretching mode compared with the cc-pVDZ calculation (Fig. 3).[19] Yet the results for $N=6$ and 7 (Fig. 3) suggest that the frequency of the mode increases as the size becomes large in contrast with the decrease of the frequency in the cumulenic $D_{(2N+1)h}$ geometries (Fig. 2). Therefore, the increase of the frequency of this mode is the sign of the bond-length alternation. It should be emphasized that the Raman spectroscopy gives important information on this mode: The totally symmetric $(A_1)$ mode in $C_{(2N+1)h}$ is detectable by Raman spectroscopy, while the corresponding mode $(A_2')$ in the cumulenic structure ($D_{(2N+1)h}$), which is not totally symmetric, is Raman inactive. It is noted that the totally symmetric modes are also expected to be detected by means of photoelectron spectroscopy.[18]

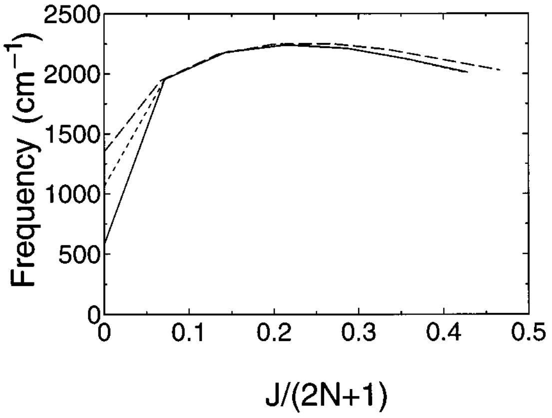

FIG. 3. The vibrational frequencies of the bond-stretching mode of the $C_{(2N+1)h}$ symmetry. The solid line indicates the cc-pVDZ calculation on $C_{26}$. The dotted (dashed) line means the SDZP calculation on $C_{26}$ ($C_{30}$).

We summarized the optimized geometries of stable atomic structures based on the cc-pVDZ and SDZP basis sets (Fig. 4). In the bond-length alternating systems $(N\geqslant 5)$, the difference in the two bond lengths becomes large as the size increases. In contrast, the degree of the bond-angle alternation decreases as the size becomes large $(3\leqslant N\leqslant 7)$. This decrease is expected to be due to the fact that the $sp$ hybridization $\sigma$ frame becomes rigid as the bond angle is close to 180° since the $sp$ hybridization favors that angle. Indeed, the infinite chain (polyyne) is considered to form a linear shape.[20] It is thus likely that the bond-angle alternation is

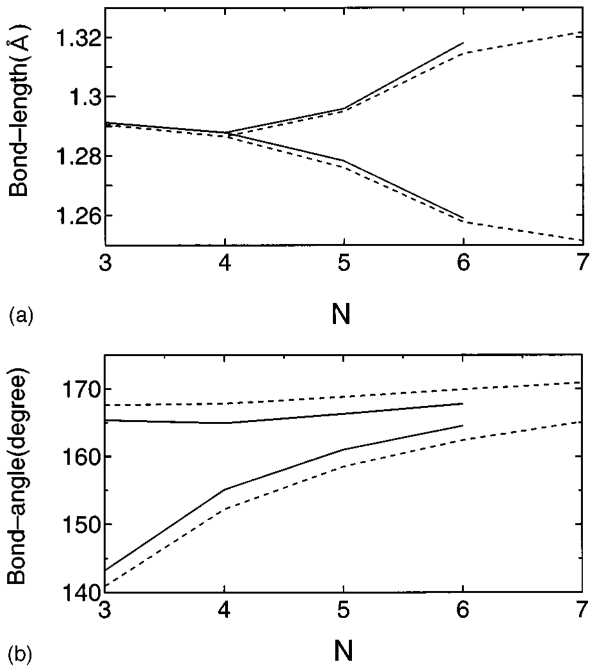

FIG. 4. Bond lengths and bond angles in the optimized structures with the $D_{(2N+1)h}$ symmetry for $N=3$ and 4, and with the $C_{(2N+1)h}$ symmetry for $N=5$, 6, and 7. The solid (dotted) lines indicate the cc-pVDZ (SDZP) calculation.

prevented in very large rings, while the bond-length alternation is preserved. Based on the SDZP calculations, we compare here the $4N+2$ member rings with the linear chains whose ends are terminated by hydrogen atoms. The calculated lengths of the long and short bonds in the central part of $C_{20}H_2$ are 1.334 Å and 1.240 Å, respectively. The degree of this bond-length alternation is expected to be larger than that in the infinite chain since we found that the bond-length alternation is suppressed as the size of the chain becomes large. The degree is actually slightly larger than that in the $C_{30}$ ring, in which the difference between the two bond lengths is expected to be smaller than that in the infinite chain as was discussed above (the two bond lengths calculated based on the same basis set are 1.322 Å and 1.251 Å).

Previous studies[1] reported that the HF (LDA and GGA) method tends to overestimate (underestimate) the degree of bond-length alternation in polyacetylene, while the hybrid DFT as well as the Mǿller-Plesset second-order perturbation theory well reproduces the experimental degree. We expect a similar situation for the present ring systems. Indeed, the critical number ($N$) of the occurrence of the bond-length alternation is 3 in the case of a HF calculation,[5] which is smaller than the present value of 5 based on the hybrid DFT. These results are due to the fact that the HF method overestimates the degree of the bond-length alternation compared with the hybrid DFT. On the other hand, a LDA calculation[4] leads to the conclusion that the critical number is very large (the value is larger than 10), indicating that the LDA underestimates the degree of the alternation.

As Fig. 2 shows, the bond-length alternant mode at the $j=0$ point is anomalously softened among the bond-stretching modes having a variety of $j$. A previous DFT study suggested that a similar situation appears in the clean diamond (111) surface:[21] The $sp^2$-bond zigzag chains of the surface are non-bond-length alternant and as a result the bond-length alternant mode at the $\Gamma$ point is considerably softened due to Kohn anomaly. The softening found in the present finite systems is thus analogous to that of this infinite system. It is interesting that the cluster size ($N$) controls the degree of softening (Fig. 2) and occurrence of the bond-length alternation.

In summary, we have performed hybrid DFT calculations on carbon $4N+2$ member rings. It has been found that the cumulenic structure is stable for small clusters $(N \leqslant 4)$. We have concluded that the bond-stretching mode of $A_2'$ in the cumulenic $D_{2N+1h}$ geometries is anomalously softened and that this softening leads to the bond-length alternation in large clusters $(N \geqslant 5)$.

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