Hückel and Anti-Hückel Rings of Pure Carbon Clusters

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Bond-alternation in polyyne-rings with neutral and negative charges is examined based on hybrid-density-functional theory. A prominent difference in the symmetry-lowering distortions between the 4N and 4N+2 member rings was reported. These distortions are discussed in terms of physics (Peierls distortion and the Kohn anomaly) and of chemistry (the first- and second- order Jahn-Teller effects).

Key Words: carbon cluster, Peierls distortion, Jahn-Teller effect, density functional theory

1. INTRODUCTION

The occurrence of bond alternation in various carbon bond networks is a fundamental issue in both chemistry and solid state physics. Among the hydrocarbon sp^2 bond systems, cyclobutadiene (C_4H_4) is a 4N member anti-Hückel ring with bond alternation, while benzene (C_6H_6) is a 4N+2 Hückel system without the bond alternation. The infinite periodic system, polyacetylene , is a bond alternant material because of the Peierls distortion [1]. Likewise, 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].

Here we argue a similar situation exists for sp bond systems. The infinite polyyne chain is a bond-alternant system due to the Peierls distortion while monocyclic carbon 4N (4N+2) member rings of small N have bond-length alternating (non-alternating) geometries [4,5]. Thus, as in the annulenes, the bond-length alternation is expected to occur for 4N+2 member rings for large N. Understanding these pure carbon ring clusters is important toward clarification of the formation mechanism of fullerenes [6,7]. Moreover, examination of bond alternation will help explain how the electronic structures of finite systems approach those of infinite periodic systems.

In this paper, we examine the mechanism of bond alternation in carbon ring systems in terms of physics and chemistry: Through solid-state physics, the bond alternation in periodic systems is considered based on the Peierls distortion and through chemistry for finite systems the alternation is discussed based on the first-order Jahn-Teller effect (FOJTE) and second-order Jahn-Teller effect (SOJTE). We discuss our findings obtained through these two approaches to clarify the relation between infinite (crystal) and finite (cluster) systems. To examine the occurrence of the bond alternation, we used the hybrid density functional theory (DFT) because it more accurately incorporates the electron many body effects than does the Hartree-Fock (HF) method or conventional DFT [local density approximation (LDA) and generalized gradient approximation (GGA)]: The hybrid DFT gave results comparable with those of accurate electron-correlation calculations[8,9].

We used the hybrid DFT method, following Becke's method of three parameters (B3LYP) [10]: The exchange energy was a mixture of those of the HF and DFT (LDA and the GGA of Beck's type [11]) and the correlation energy consisted of those of the LDA [12] and of the Lee-Yang-Parr type GGA [13]. We used the basis set of Dunning's correlation consistent polarized valence double zeta (cc-pVDZ) type [14] which accurately reproduces vibrational frequencies [5]. All the calculations were performed using the Gaussian 94 program [15].

2. RESULTS

We started with 4N member rings and found that the high symmetry atomic structure of D_{4Nh} is unstable for both the neutral and negative charge states and that the stable structure has C_{2Nh} symmetry as a consequence of bond-angle and bond-length alternations (Fig. 1). The difference between the two bond-lengths was found to be larger in the neutral charge state than in the negative charge state, while the difference between the two bond-angles was slightly smaller in the neutral charge state (Fig. 2). As the size became larger, the bond-angle alternation decreased for both charge states.

Next the 4N+2 member rings with the neutral charge states were examined. Up to N=4, the stable structure was found to have D_{2N+1h} symmetry with bond-angle alternation and without bond-length alternation. When N was larger than 4, bond-length alternation occured and thus the symmetry was lowered to C_{2N+1h}. The bond-length alternation

increased as the size became larger, while the bond-angle alternation decreased (Fig. 2). For the negative charge state (N=2-4), the symmetry was lowered drastically to C_{2v}.

3. DISCUSSION

Here we qualitatively discuss the mechanism of the bond alternation revealed through the above first-principles calculations. In the high symmetry geometry (D_{2n}) for 2n member rings, the molecular orbital is given by

$$\Psi_{k,\kappa} = \sum_{i=1}^{2n} \theta_\kappa(i)\exp[2\pi(i-1)k/2n],$$

(1)

where k ranges from -n+1 to n. $\theta_\kappa(i)$ is the localized atomic orbital at the i-th site and the subscript κ differentiates π and σ. The π orbitals mainly consist of out-of plane p and the σ orbitals mainly consist of in-plane p in the direction perpendicular to the bond axis. Our electronic structure calculations indicated that the molecular orbitals for π and σ are nearly degenerated. Hereafter, we assume that these two orbitals have the same energy. We introduce K defined as $|k/2n|$, which, in the periodic linear polyyne, corresponds to the dimensionless crystal wave number. In this periodic system, the Fermi wave number is K_f=0.25 and the $2K_f$ phonon induces the Peierls distortion (bond-length alternation) because this phonon opens the band gap at K_f. In the neutral 4N member rings, the highest occupied molecular orbitals (HOMO) have K= K_f and are half occupied.
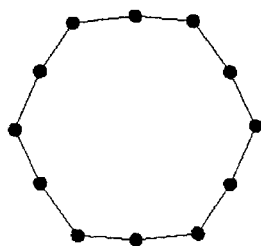

Fig.1 The C_{6h} structure of C_{12}. The neighboring bond-lengths (angles) are different from each other. (The bond-length alternation is small, thus somewhat unclear from the figure).
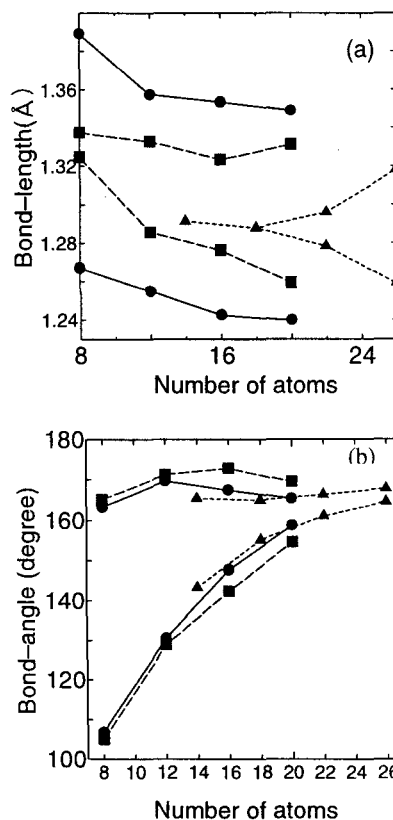

Fig. 2 Geometrical parameters of carbon rings. The circles, rectangles, and triangles indicate neutral 4N, negatively charged 4N, and neutral 4N+2 rings, respectively.

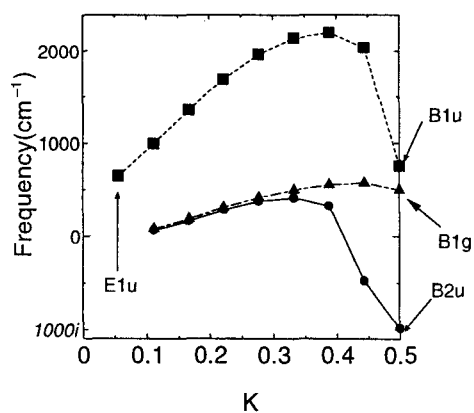Fig. 3 Vibrational frequencies of C_{18} (D_{18h}). The rectangles, circles and triangles indicate the bond-stretching, bond-bending and out-of-plane modes, respectively.

This is why the 4N member rings have bond-length alternation (K= $2K_f$) that opens the gap for the HOMO. In contrast, the neutral 4N+2 member rings have a fully occupied HOMO with K=N/(4N+2) and a lowest unoccupied molecular orbital (LUMO) with K=(N+1)/(4N+2). Because *there is no level at K_f=0.25*, the bond-length alternation is prevented for small N. However, both HOMO and LUMO approach K_f as N becomes large, and the bond-length alternation occurs for large N as was indicated by our calculation. A similar discussion concerning K for the finite and infinite systems was provioded by Bylaska et al.[4]: They argued that a relation exists between the sampling points in the Brillouin zone integration for the periodic system and the discrete levels of ring clusters.

In chemistry, the instability of the high symmetry is explained as shown in the following equation [2]:

$$E(Q) = E_{eq} + FQ + \frac{1}{2}SQ^2,$$

(2)

where the total energy is expanded over a vibrational mode that was not totally symmetric, Q. Here, F and S are given by the following equations:

$$F = < \Phi_0 \, | \frac{\partial H}{\partial Q} | \Phi_0 >,$$

(3)

and

$$S = < \Phi_0 \, | \frac{\partial^2 H}{\partial Q^2} | \Phi_0 >$$
$$- 2 \sum_{n \neq 0} \frac{|< \Phi_n \, | \partial H / \partial Q | \Phi_0 >|^2}{(E_n - E_0)},$$

(4)

where H and Φ_n are the total hamiltonian and the wavefunction of the n -th electronic state (Φ_0 indicates the ground state). In the following discussions, the electron many-body effect is neglected (When the Slater determinant is used for Φ, the analysis based on Eq. (2) should be different from the present one because an exchange effect splits degenerated levels in some cases [2]). When the HOMO is degenerated and is partially filled, F is non-zero and the FOJTE is active. In contrast, when the HOMO is completely filled and the energy difference between the HOMO and the LUMO is small, the second term of S becomes significant because of the energy denominator and thus the potential curvature becomes negative. This case corresponds to the SOJTE.

In the neutral 4N member rings of D_{4Nh}, the half-filled HOMO belongs to E_{Nx} (K=0.25), where x is u or g depending on the characteristics of σ and π. Thus, the FOJTE occurs. $E_{Nx} \times E_{Nx}$ includes the symmetric products, B_{1g} (K=0.5.) and B_{2g} (K=0.5), that correspond to the bond-angle and bond-length alternations, respectively, and these alternations lower the symmetry to C_{2Nh}. The bond-angle (bond-length) distortion has a *transverse* (*longitudinal*) characteristic so bond-angle distortion is prevented in an infinite periodic system whereas the bond-length alternation is preserved. In the negatively charged rings, the HOMO (K=0.25) is also partially occupied, therefore the FOJTE occurs as in the neutral rings.

In the neutral 4N+2 member rings, the HOMO belong to E_{Nx} [K=N/(4N+2)] and is fully occupied. Therefore, the FOJTE is inactive. However, when the HOMO-LUMO gap is small, the second term in Eq. (4) induces softening of modes belonging to the representations of the product of HOMO and LUMO. The LUMO belongs to $E_{N+1x'}$ [K=(N+1)/(4N+2)] so the HOMO-LUMO product includes B_{1u} (K=0.5), B_{2u} (K=0.5), B_{1g} (K=0.5) and E_{1u} [K=1/(4N+2)]. B_{1u} (B_{2u}) corresponds to the bond-length (bond-angle) alternation and the B_{1g} mode is characterized by out-of-plane displacement. In Fig. 3, we show the vibrational frequencies of C_{18} (D_{18h}). The B_{1u} and B_{2u} modes were prominently softened and this softening corresponds to the *Kohn-anomaly* at $2K_f$ in a periodic system [16]. The B_{1g} mode was slightly softened. In contrast to the three high-wave-number modes (K=0.5), substantial softening of the low-wave-number mode, E_{1u}, was not observed. Our calculation indicated that the frequency of B_{2u} is imaginary up to N=6, whereas the B_{1u} mode has a real frequency up to N=4 and an imaginary frequency when N > 4. This imaginary frequency arises because the energy denominator of the second term in Eq. (4) becomes small as N increases. Thus, as mentioned, the symmetry determined by our calculation was D_{2n+1h} when N≤4 and was lowered to C_{2n+1h} for N>4. In both 4N (neutral and negative charge) and 4N+2 (neutral) member rings, the

bond-angle alternation decreased [Fig. 2(b)] since the $2K_f$ distortion with the transverse character does not occur in an infinite periodic system.

As for the negative charge state of 4N+2 member rings, the LUMO of the neutral charge state is occupied by a single electron, and so the FOJTE occurs. $E_{N+1x} \times E_{N+1x}$ includes the symmetric product, E_{2Nx} [K=2N/(4N+2)], leading to drastic symmetry lowering as shown by our calculation.

4. CONCLUSION

We have performed first-principles calculations concerning bond alternation in carbon rings. In 4N member rings, both bond-length and bond-angle alternation were found to occur for neutral and negative charge states. In the neutral 4N+2 member rings, only the bond-angle alternation was found to occur when N was small and both alternations were found to occur when N > 4. For the negative charge state of 4N+2 member rings, we found that the symmetry was lowered drastically to C_{2v}. We explained these symmetry lowering features in terms of the FOJTE and SOJTE and of the Peierls distortion.

The carbon ring geometries that we have found help to explain obsereved photoelectron vibrational fine structures of anions which also provide important information about the carbon-ring geometries: According to the Franck-Condon principle, the fine structures originate from the difference in geometry between the negative and neutral charge states [17,18]. Also, an experiment has indicated that the structure differs significantly between the 4N and 4N+2 member rings [17]. Our theoretical analysis of spectroscopy experiments will be reported elsewhere.

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