

Development of bond-length alternation in very large carbon rings: LDA pseudopotential results

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Carbon rings C_n and infinite chains C_∞ are investigated by molecular-orbital and band-structure calculations within the local-density approximation. Carbon rings C_{4N} ($N \leq 8$) exhibit a substantial first-order Jahn-Teller distortion that leads to long/short (single/triple) bond alternation decreasing with increasing N . Rings C_{4N+2} show no alternation (i.e., aromatic behavior is retained) until very large sizes ($N \geq 20$). For the infinite carbon chain uniform Brillouin-zone sampling with an even number of points N_s gives bond alternation. An odd number of sampling points gives no bond alternation for less than $N_s = 41$. In the large N_s limit even and odd sampling lead to an upper and lower bound of $0.070a_0$ and $0.065a_0$ for bond alternation and 0.021 – 0.090 millihartrees/atom for condensation energy. [S0163-1829(98)51836-X]

Cyclo[n]carbons, or C_n , of size $10 \leq n \leq 30$ are the dominant precursors to the formation of larger fullerene systems.^{1,2} Recently, new methods of synthesis of large monocyclic ring structures ($n \leq 30$) (Ref. 3) and of experimentally isolating specific size clusters through the mass selection of their anionic species⁴ have been developed. From these techniques new and relatively precise spectral information has been obtained for neutral carbon rings as a function of size.⁵ These results suggest that aromatic behavior (no bond alternation for $n = 4N + 2$ rings, where N is a natural number) is retained for molecules larger than previously predicted by Hartree-Fock^{6,7} (HF) and accepted in structural chemistry.^{8,9}

For moderately large cyclo[n]carbons, $n \geq 6$, there are two nearly degenerate perpendicular half-filled π electron bands. Simple tight-binding (TB) models^{10,11} predict that C_{4N} will display strong first-order Jahn-Teller distortion leading to bond-length alternation (antiaromatic behavior). On the other hand, C_{4N+2} are found to have equal bond lengths (aromatic or cumulenic molecules). In the infinite limit, TB models predict bond alternation via a Peierls mechanism in which the energy of a half-filled band is decreased by doubling the unit cell to form a band gap at the Fermi level. The size at which aromatic and antiaromatic behaviors merge is a topic of considerable interest to the chemistry and physics of one-dimensional systems.

The onset of the loss of aromatic character is difficult to explore with first-principles theoretical methods since fully converged high level calculations are very expensive for $n > 10$, discouraging structural optimization.^{12,13} Martin *et al.*⁶ have reported local-density approximation (LDA) with gradient corrections and HF results for a system up to $n = 18$ using a local basis set approach. We report HF results for systems up to $n = 22$ elsewhere.⁷ The HF and LDA results agree well with experimental data and with high level calculations for $n \leq 10$. However, for $n > 10$ there is a qualitative difference between the results of HF and LDA. The

HF results predict a Peierls-like transition and substantial bond-length alternation ($\delta = 0.34a_0$, $a_0 =$ Bohr radius) for $n \geq 14$. On the other hand, LDA methods, as discussed below, predict that aromatic/antiaromatic behavior persists to much higher n . For the infinite ring system, HF calculations predict a structure consistent in magnitude with the Peierls-like transition of the smaller ring size.¹⁴ The only LDA calculations for infinite ring, which were done using a linear muffin-tin orbital scheme,^{15,16} were roughly in agreement with the HF calculations for bond-length alternation and condensation energy (the energy obtained in forming the altered structure from an optimized equal bond-length ring). However, the LDA results presented here disagree strongly with these results.

Many calculations have been reported for the similar polyacetylene system $[(CH)_n]$, with a single half-filled π structure, whose electronic structure is similar to that of cyclo[n]carbon. Smaller systems, e.g., benzene, show aromatic/antiaromatic behavior. Surprisingly, the predictions of infinite polyacetylene from first principles are still unclear. Because the π band is half filled, a Peierls-type distortion would be expected and is found in the TB model. It is also found in the HF calculations. However, for usually more accurate LDA calculations conflicting results have been reported; some predicted weak bond alternation^{17,18} and others reported results in close agreement with experiment ($\delta = 0.19a_0$).¹⁹ The well converged linearized augmented plane-wave (LAPW) LDA calculations of Ashkenazi *et al.* predicted no alternation at all.²⁰ This work has been criticized by Mintmire and White who found an alternation of $0.06a_0$ and condensation energy of 0.065 millihartrees/atom.^{17,21} The most recent LDA calculation of Suhai²² agree with these results.

The LDA calculations presented here for pure carbon rings were done using the parametrized form of the exchange-correlation energy obtained by Vosko *et al.*²³ The electron-ion interaction was approximated via a generalized

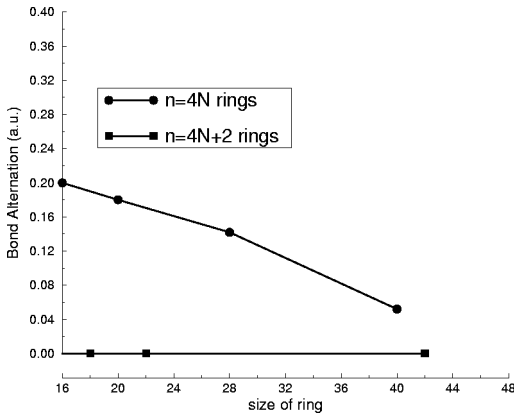


FIG. 1. Bond alternation for the large carbon rings. Bond-length alternation is defined as the difference in lengths between the long and short bonds.

norm-conserving pseudopotential modified to a separable form. To improve convergence the core radii were increased ($r_{cs}=0.80a_0$, $r_{cp}=0.85a_0$, and $r_{cd}=0.85a_0$). Extensive tests have been reported²⁴ that confirmed the accuracy of the calculations reported here ($E_{cut}=42$ hartrees). The supercells were chosen to be large enough to prevent interactions. The larger rings C_{28} , C_{40} , and C_{42} required the use of a supercell of a flat square box, while for the smaller rings a face-centered-cubic supercell with a lattice constant of $a=38a_0$ was used. In order to insure that the structures reported are at least locally stable both steepest descent local optimization and global optimization by *ab initio* molecular dynamic annealing were carried out. There were no symmetry constraints in these calculations.

Bond alternation for the larger rings predicted from our LDA calculations is reported in Fig. 1. For the C_{4N} , there is bond alternation as expected from the degeneracy of the highest filled states and Jahn-Teller considerations. However, no bond alternation was observed for C_{4N+2} even at $N=10$. Rather than increasing the alternation in the C_{4N+2} , as would be expected from the TB models, the alternation in the C_{4N} approaches a near zero value as in the C_{4N+2} .

The calculations for finite sizes beyond C_{42} become very expensive. Therefore, we chose to calculate in the infinite chain limit. This calculation when considered with the ring calculations shown in Fig. 1 provides an accurate view of the size dependence of bond alternation.

To calculate the infinite chain C_∞ , restricted-spin pseudopotential plane-wave local-density approximation band-structure calculations (LDA-band) were carried out. The Kohn-Sham orbitals are expanded in a plane-wave basis using periodic boundary conditions times a phase factor $e^{i\mathbf{k}\cdot\mathbf{r}}$:

$$\psi_{j,\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{g}} c_{\mathbf{g}}^{j,\mathbf{k}} e^{i\mathbf{g}\cdot\mathbf{r}}, \quad (1)$$

$$\mathbf{g} = \left\langle \frac{2\pi}{L_x} n_x, \frac{2\pi}{L_y} n_y, \frac{2\pi}{L_z} n_z \right\rangle. \quad (2)$$

By convention, \mathbf{k} lies within the first Brillouin zone of the reciprocal lattice. The dimensions of the unit cell are L_x , L_y , and L_z , and n_x , n_y , and n_z are integers such that $\frac{1}{2}(\mathbf{g}+\mathbf{k})\cdot(\mathbf{g}+\mathbf{k}) \leq E_{cut} < 42$ hartrees.

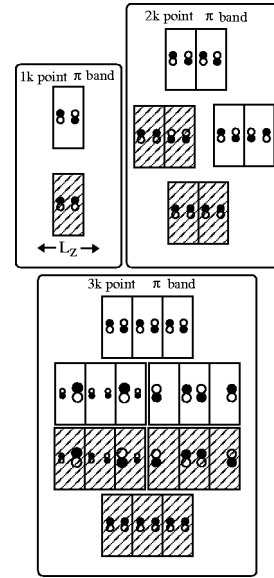


FIG. 2. Γ point molecular orbitals corresponding to a Brillouin-zone sampling scheme with $N_s=1, 2$, and 3 points.

Total-energy calculations were carried out by placing two carbon atoms along the z direction in a rectangular unit cell with lattice constants of $L_z=4.80a_0$, $L_x=L_y=22.0a_0$. The average bond distance is thus set to $2.40a_0$. (Large supercell calculations on cyclo[n]carbons predicted the average bond distance for $n \geq 14$ to be $2.40a_0$.)

A nontrivial numerical error in the total-energy calculations comes from the sampling required in the sum over wave vectors \mathbf{k} (Brillouin-zone integration). The integration in the nearly one-dimensional Brillouin zone was approximated using N_s evenly spaced points

$$\mathbf{k} = \left\langle 0, 0, \frac{2\pi}{L_z} \frac{m}{N_s} \right\rangle$$

$$m = 0, \dots, N_s - 1$$

$$N_s = 10, 11, 20, 21, 30, 31, 40, 41, 50, 51, 60, 61, 70, 71. \quad (3)$$

Mintmire and White²⁵ report, using TB calculations, that approximating the Brillouin-zone integration by an even number of equally spaced points [i.e., chosen via Eq. (3)] leads to an enhancement of bond-length alternation, while approximating the Brillouin-zone integration by an odd number of equally spaced points [i.e., chosen via Eq. (3)] leads to underestimation. In order to understand the consequences of these particular samplings it is useful to consider analogous calculations using only Γ point sampling. In uniform zone sampling choosing a specific set of points corresponds to using a Γ point sampling on a larger unit cell. In Fig. 2 we illustrate this property for one of π bands with the first few selections of sampling points. In the bond altered structure the π band that would be continuous in the equal bond system splits into two bands. Since the band is half filled, only the lowest of these two bands is occupied. The filled bands are illustrated in Fig. 2 by the shaded boxes. We next note that in the $N_s=1$ sampling case the corresponding Γ point calculation would include only one unit cell with the filled wave function being totally symmetric. In the $N_s=2$

sampling case the corresponding Γ point calculation would include two unit cells with filled wave functions consisting of a totally symmetric wave function and a wave function that has a node between the two unit cells. Again these are the shaded boxes in Fig. 2. In this case there is another wave function that would be degenerate in the equal bond-length system but is unfilled in the bond altered system. For the $N_s = 3$ sampling the corresponding Γ point calculation would include three unit cells with three filled wave functions consisting of a totally symmetric wave functions and two wave functions with a single node.

Next consider what happens when the atoms within the cell are moved to form bond alternation. In the odd $N_s = 1$ sampling the orbital energy of the system is not significantly stabilized because the single filled wave function is nodeless at the unit cell boundary. For $N_s = 2$, the orbital energy may be decreased because moving atoms together stabilized the wave function with a node between the two unit cells, decreasing the total energy. For $N_s = 3$, there are again nodes in each upper state. Moving the atoms within the unit cell will not significantly stabilize the orbital energy because the stabilization of one of the orbitals is counterbalanced by the other. Generally, even number samplings are favorable to bond alternation, whereas odd number samplings are not.

From the energy point of view this may be restated by saying that for even N_s there is an advantage to bond alternation whereas for odd N_s sampling there is none or at least not to a first order. When we further make the connection that a Γ -point calculation corresponds to a hypothetical finite linear ring (all angles = 180°) we see that this is just a restatement of the TB $4N + 2$ aromaticity rule. That is, an even number of points, $N_s = n/2 = 2N$, corresponds to the antiaromatic $n = 4N$ rings (without curvature), while an odd number of points, $N_s = n/2 = 2N + 1$, corresponds to the aromatic $n = 4N + 2$ rings (without curvature).

Using the above ideas it is clear that to sample the Brillouin zone stably it is necessary to separate the even sampling from the odd sampling. These two different sampling schemes will lead to upper and lower bounds to bond alternation. Figures 3 and 4 show the calculated energy for various Brillouin-zone sampling sizes from 10 to 71 points. The results for small even sampling in Fig. 3 illustrate that very misleading results will be obtained from too small a zone sample. Note the substantial condensation energy and bond alternation in $N_s = 10$ and the lack of any bond alternation for $N_s = 11$. A closer look at the energy variation with alternation in Fig. 4 shows that a very small stabilization with bond alternation first appears at $N_s = 41$. For $N_s = 70, 71$ we extrapolate our data to give the lower and upper bounds of $0.065a_0$ and $0.070a_0$ for bond alternation and 0.021 millihartrees/atom and 0.090 millihartrees/atom for condensation energy, respectively. This supports the existence of a Peierls mechanism in LDA. However, the bond alternation is considerably smaller than those measured for small linear chains by Lagow *et al.*²⁶ They are consistent with the calculated values reported by Mintmire and White for polyacetylene.¹⁷ This figure also explains our discrepancy with the earlier infinite polyene results in the literature.^{15,16} In these calculations only six points were used in the Brillouin-zone sampling. As the figure shows, this is far too small a number and produces $n = 4N$ -like alternation. This

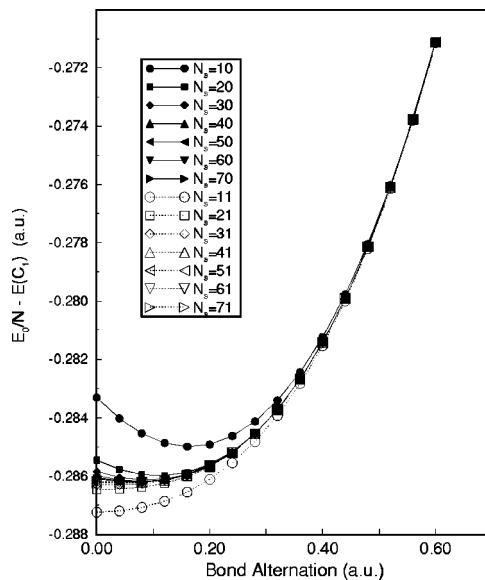


FIG. 3. Atomization energy per atom as a function of bond-length alternation, for a series of band-structure calculations using $N_s = 10$ –71 sampling points. Bond-length alternation is defined as the difference in lengths between the long and short bonds.

produces erroneously strong bond alternation and large condensation energies. We also point out that with odd number sampling it is easy to produce results erroneously implying that the LDA produces no alternation as was reported by Ashkenazi *et al.*²⁰ We have done calculations to check the effects of unit cell size and basis set size on the bond alternation predicted for the very large carbon ring systems. Since we chose a unit cell with very large transverse lengths ($22.0a_0$), changing the box size in these directions has a negligible effect. In the infinite chain calculation the unit cell length along the bond direction was fixed at $4.80a_0$. This could cause a problem because this choice does affect bond alternation. However, we did not optimize the unit cell size

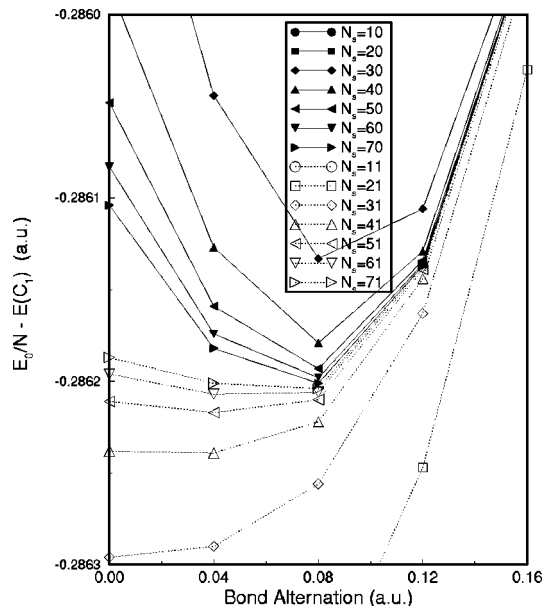


FIG. 4. Same as Fig. 3 except that it is expanded in the area where the different Brillouin-zone samplings differ.

for each case. We have checked that the choice of $2.40a_0$ for average bond length is nearly optimal.

Apart from the result that the LDA calculation does predict weak alternation in the carbon ring system, there are two additional conclusions that we would like to draw. First, we note that the first bond alternation appeared at odd $N_s=41$ sampling and recall that in our calculation of the $n=4N+2=42$ member ring we saw no bond alternation. The direct relation between the molecular and the Γ point calculation suggests that in order to get alternation in a cyclo[n]carbon within LDA we would have to go to ring sizes of $n=82$ or more. Recent experiments suggest that aromatic behavior extends to $n\geq 18$, higher than predicted by HF ($n\leq 14$), but we believe that $n=82$ is a high estimate of the onset of Peierls-like behavior and is related to the tendency of LDA to stabilize delocalized structures.

Finally, again exploiting the relationship between the Γ

point calculation and rings of molecular size $2N_s$, we can estimate the energy required to bend the bonds to form a closed ring. The difference between the energy per atom for the $n=42$ ring calculated with bending and the energy for the $N_s=21$ with no bending is just the energy required to bend the bonds to form a closed rings (create angles in the planar π system). Comparing these two energies we obtain a Hook's law constant of

$$K=0.022 \text{ kcal/mol degree per atom.} \quad (4)$$

This leads to a value of 4.4 kcal/mol for 160° . This is in excellent agreement with a value of 4 kcal/mol for an angle distortion of 160° reported by Diederich and Rubin.⁸

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