Electron Correlation in C_{4N+2} Carbon Rings: Aromatic versus Dimerized Structures

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The electronic structure of C_{4N+2} carbon rings exhibits competing many-body effects of Hückel aromaticity, second-order Jahn-Teller (SOJT), and Peierls instability at large sizes. This leads to possible ground state structures with aromatic, bond angle, or bond length alternated geometry. Highly accurate quantum Monte Carlo results indicate the existence of a crossover between C_{10} and C_{14} from bond angle to bond length alternation. The aromatic isomer is always a transition state. The gap opening mechanism is the SOJT effect, which coalesces with the Peierls regime as $N \to \infty$.

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The discovery of carbon fullerenes and nanotubes has opened a new materials research area with a vast potential for practical applications. Unfortunately, our understanding of the rich variety of structural and electronic properties of carbon nanostructures is far from satisfactory. For example, experiments [1] indicate that quasi-one-dimensional structures such as chains and rings are among the primary precursors in the formation process of fullerenes and nanotubes. However, our insights into their properties and behavior are incomplete due to the complicated many-body effects involved. In particular, recent studies [2,3] have demonstrated a profound impact of the electron correlation on stability and other properties of such all-carbon structures. An important example of these nanostructures is the system of planar monocyclic carbon rings C_n with $n = 4N + 2$, where N is a natural number. These closed-shell molecules manifest an intriguing competition between conjugated aromaticity, second-order Jahn-Teller, and, at large sizes, Peierls instability effects. Consequently, this leads to different stabilization mechanisms that tend to favor one of the following structures: a cumulenic ring (A), with full D_{nh} symmetry, with all bond angles and bond lengths equal; or either of two distorted ring structures, of lower $D_{(n/2)h}$ symmetry, with alternating bond angles (B) or bond lengths (C). Further structural details are given in Fig. 1. Accurate studies for the smallest sizes (C_6 and C_{10}) find isomer B to be the most stable. However, for larger sizes the results from commonly used methods are contradictory and available experiments [4] are unable to clearly specify the lowest energy structures.

In order to identify the most stable isomers and to elucidate the impact of many-body effects, we carried out an extensive study of electronic structure and geometries of C_{4N+2} rings of intermediate sizes up to 22 atoms (with some methods up to 90 atoms). We employed a number of electronic structure methods including the highly accurate quantum Monte Carlo (QMC) method which has been proven very effective in investigations of C_{20} [2] and larger carbon clusters [3], as confirmed also in an independent study by Murphy and Friesner [5]. Our QMC results reveal that the C_{4N+2} ground state structures have *alternated geometries at all sizes* while cumulenic isomer A is a structural transition state. The results also provide valuable insights into the shortcomings of the density functional approaches such as inaccurate balance between exchange and correlation in commonly used functionals. In addition, this Letter presents a first evaluation of interatomic forces in large systems within the QMC framework.

According to the Hückel rule, the $4N + 2$ stoichiometry implies the existence of a double conjugated π-electron system (in- and out-of-plane). Combined with the ring planarity, this suggests a strong aromatic stabilization in favor of isomer A. Although the highest occupied and the lowest unoccupied molecular orbitals (HOMOs and LUMOs) are separated by a gap of several eV, their symmetry enables configurations with HOMOs → LUMOs excitations to mix into the ground state wave function, thus allowing the possibility of a second-order Jahn-Teller distortion [6,7]. Such distortion halves the symmetry, resulting in either cumulenic B or acetylenic C structures, with an overall energy gain. In fact, the same mechanism can be found in cyclic polyenes $C_{4N+2}H_{4N+2}$, as presented by Salem [8]. The only distinction is the polyene's single π-electron system (out-of-plane only), as opposed to the double π system in the pure carbon rings. As $N \to \infty$, the occurrence of the distortion can also be explained in terms of a Peierls instability [9], since the system becomes a semimetallic

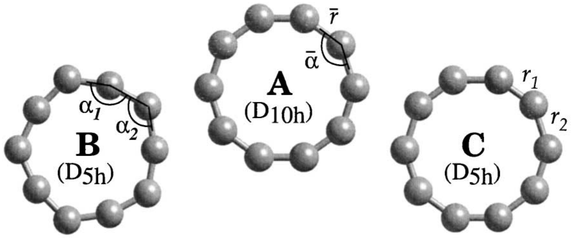

FIG. 1. The most stable isomers of C_{4N+2} rings (shown for C_{10}). The parameters needed to specify the geometries are as follows. Average bond length and bond angle: $\bar{r} = (r_1 + r_2)/2$, $\bar{\alpha} = (\alpha_1 + \alpha_2)/2$; relative bond length and bond angle alternation: $\mathcal{A}_r = (r_1 - r_2)/\bar{r}$, $\mathcal{A}_\alpha = (\alpha_1 - \alpha_2)/\bar{\alpha}$.

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polymer with two half-filled π bands. The symmetry breaking enables the formation of a gap, in analogy to the elusive case of *trans*-polyacetylene [10].

It is very instructive to see how the commonly used computational methods deal with such many-body effects. Density functional theory (DFT) methods tend to favor a "homogenized" electronic structure with delocalized electrons. In fact, for sizes larger than C_{10}, there is no indication of any stable alternation up to the largest sizes we have investigated (C_{90}). Calculations performed within the local density approximation (LDA) and generalized gradient approximations (GGA, with BPW91 functional) consistently converge to the aromatic structure A, in agreement with other studies [11]. Only by extrapolation to the infinite-chain limit, Bylaska, Weare, and Kawai [12] claim to observe a very small, yet stable, bond alternation within LDA. A very different picture arises from the Hartree-Fock (HF) method, which shows a pronounced dimerization for C_{10} and larger. This agrees with the HF tendency to render structures less homogeneous in order to increase the impact of exchange effects. We also verified that using GGA functionals with an admixture of the exact HF exchange (B3PW91) recovers qualitatively the HF results for large sizes ($>C_{46}$), as already observed by others [7,13].

Obviously, this problem calls for much more accurate treatments. High-level post-HF methods, such as multiconfiguration self-consistent field (MCSCF) and coupled cluster (CC), indeed, provide answers for the smallest ring sizes (C_6 [14] and C_{10} [15,16]). In particular, Martin and Taylor [16] have carried out a detailed CC study demonstrating that both C_6 and C_{10} have angle alternated ground state structures, although for C_{10} the energy of the aromatic isomer A is found to be extremely close (1 kcal/mol). In addition, we have performed limited CCSD (CC with single and double excitations) calculations of C_{14} and have found the dimerized isomer to be stable by $\simeq$6 kcal/mol. Unfortunately, these methods are impractical for larger cases or more extensive basis sets [13].

The QMC method was used to overcome these limitations. This method possesses the unique ability to describe the electron correlation explicitly and its favorable scaling in the number of particles enables us to apply it to larger systems [17]. In the variational Monte Carlo (VMC) method we construct an optimized correlated many-body trial wave function Ψ_T, given by the product of a linear combination of Slater determinants and a correlation factor

$$\Psi_T = \sum_n d_n D_n^{\uparrow}\{\varphi_\alpha\} D_n^{\downarrow}\{\varphi_\beta\} \exp \sum_{I,i<j} u(r_{iI}, r_{jI}, r_{ij}), \quad (1)$$

where φ are one-particle orbitals, i, j denote the electrons, I denote the ions, and r_{iI}, r_{jI}, r_{ij} are the corresponding distances. The correlation part, u, includes two-body (electron-electron) and three-body (electron-electron-ion) correlation terms and its expansion coefficients are optimized variationally. Most of the variational bias is subsequently removed by the diffusion Monte Carlo (DMC) method, based on the action of the projection operator $\exp(-\tau H)$; in the limit of $\tau \longrightarrow \infty$, this projector recovers the lowest eigenstate from an arbitrary trial function of the same symmetry and nonzero overlap. The fermion antisymmetry (or sign) problem is circumvented by the fixed-node approximation. More details about the method are given elsewhere [17].

DFT, HF, and MCSCF calculations have been carried out using standard quantum chemistry packages [18]. All calculations employed an accurate basis set, consisting of $10s11p2d$ Gaussians contracted to $3s3p2d$, and smooth effective core potentials [19] to replace the chemically inert core electrons.

The geometries of smaller rings with 6 and 10 atoms have already been established from previous calculations [14–16]. We have verified that the most reliable published structural parameters agree very well (within $\simeq 0.002$ Å and 1°) with our own GGA values. However, since the dimerized isomer C is unstable within DFT, we followed a different strategy. We began from HF geometries, which show that the degree of bond length alternation saturates at $\mathcal{A}_r \approx 14\%$ (Fig. 2). In order to correct for the HF bias favoring acetylenic structures, we performed limited MCSCF calculations (see below) for C_{10}, C_{14}, and C_{18}. The electron correlation has a profound effect on the geometry, to the extent of causing the dimerized isomer to be unstable for C_{10}, while for C_{14} it decreases the dimerization to $\mathcal{A}_r \approx 10\%$. Clearly the limited MCSCF for C_{14} and C_{18} provides rather poor geometry improvement although one expects a larger correction as more correlation energy is recovered. In order to verify this and to estimate the correct degree of dimerization for C_{14}, we

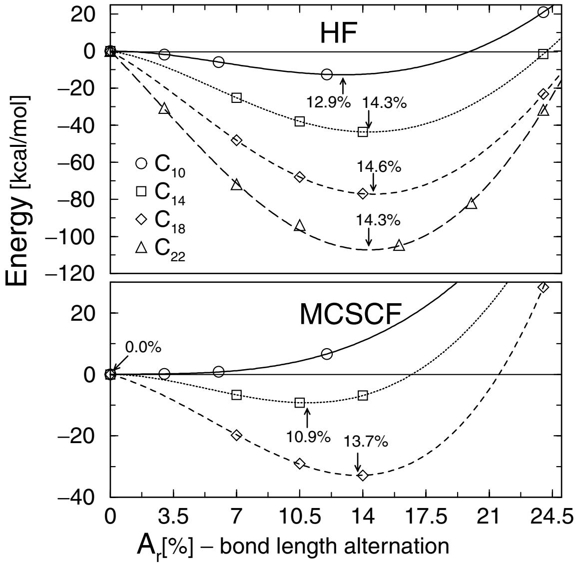

FIG. 2. HF and MCSCF energy as a function of the degree of dimerization $\mathcal{A}_r$. Least-squares estimates of the positions of the minima are indicated by arrows.

carried out the evaluation of the Born-Oppenheimer forces by a finite-difference scheme using correlated sampling, in the VMC method [20]. The computation of interatomic forces is a new development in QMC methodology and, to our knowledge, this is the first application in this range of system sizes. We probed the tangential C-C stretching/shortening which leads to a change in the degree of dimerization, $\mathcal{A}_r$. For $\mathcal{A}_r = 7\%$, our force estimate is $F = -dE/d\theta = 0.010(2)$ a.u. [and a second derivative of $H = 0.30(1)$ a.u.], suggesting proximity to the minimum. Moreover, at $\mathcal{A}_r = 10.5\%$ we find a force of opposite sign: $F = -0.013(3)$ a.u. [$H = 0.33(1)$ a.u.]. For C_{18}, we have instead performed two QMC single point calculations at $\mathcal{A}_r = 7\%$ and 14% and found the first energy to be lower by $\Delta E \simeq -12$ kcal/mol. Finally, we assumed $\mathcal{A}_r = 7\%$ and $\bar{r} = 1.286$ Å (Table I) as our best estimate for calculations of the acetylenic isomer with $n > 10$.

The crucial ingredient for very accurate QMC calculations is a trial function with a small fixed-node error. The quality of the one-particle orbitals is of prime importance for decreasing such error. While HF or DFT orbitals are commonly used for construction of Slater determinants, our recent projects [21] have demonstrated that natural orbitals from limited correlated calculations (e.g., MCSCF) lead to more consistent results. Inclusion of the electron correlation into the method used to generate the orbitals is indeed very relevant for obtaining improved fermion nodes, especially for such systems which exhibit strong nondynamical correlation effects [13,16]. Extensive tests confirmed that orbitals from MCSCF (with an active space consisting of four occupied and four virtual orbitals) yield the lowest energies and so they were used in all of our calculations. In addition, the inclusion of the most important excited configurations into Ψ_T (about 20–30 determinants) provided further significant improvement of the total energies. In particular, the weights of *single* excitations were surprisingly large for the alternated geometries and comparable to the largest weights of configurations with double excitations. A more detailed analysis on the multireference nature of the wave function in these systems will be given elsewhere.

Equipped with such high quality trial functions we have carried out QMC calculations from C_6 to C_{18}. A plot of the energy differences, with comparison to other methods, is shown in Fig. 3. For the very compact C_6 ring, where the overlap between π in-plane orbitals is large, as observed by Raghavachari *et al.* [22], the angle alternated isomer B is the most stable. The aromatic structure A is instead a transition state leading to angle alternation (B_{1u} mode), while the dimerized isomer C is unstable in all methods.

C_{10} is the case which was studied extensively in the past. Our DMC results agree with calculations of Martin and Taylor [16]. We conclude that the angle alternated isomer is still the lowest energy structure, albeit extremely close to the cumulenic A geometry, with an energy difference of $\simeq 1$ kcal/mol. Indeed, the stabilization by aromaticity is almost as strong as the effect of second-order Jahn-Teller distortion which is responsible for the alternation pattern. The aromatic isomer remains a transition state, as it is for C_6, although in this case the energy surface is extremely flat. The C_{10} acetylenic isomer appears unstable in DMC, which implies that our older calculations [21] and also a more recent all-electron study [23], based on a single determinant Ψ_T with HF orbitals, were not accurate enough.

Our perhaps most interesting results come from the C_{14} and C_{18} isomers. The angle alternated structures become unstable since the in-plane orbital overlap is smaller due to the increased ring radius. The trends from HF, MCSCF, and QMC (Fig. 3) are clearly in favor of dimerized geometries, although there is an indication that the HF bias for the Jahn-Teller distortion is much reduced as we recover more of the correlation energy. Nevertheless, since the fixed-node DMC method typically obtains ≈95% of the correlation energy, we argue that margins for possible errors are very small. This is in sharp contrast with the density functional results, which indicate only the aromatic isomer A to be stable. It seems that DFT methods "overshoot" the

TABLE I. Structural parameters used in the calculations.

n	Isom	$\bar{r}$ (Å)	$\bar{\alpha}$ (°)	$\mathcal{A}_\alpha/\mathcal{A}_r$ (%)
C_6	B	1.331	120.0	48.4/0.0
C_{10}	B	1.298	144.0	22.7/0.0
C_{10}	C	1.293	144.0	0.0/6.0
C_{14}	C	1.288	154.3	0.0/7.0
C_{18}	C	1.285	160.0	0.0/7.0

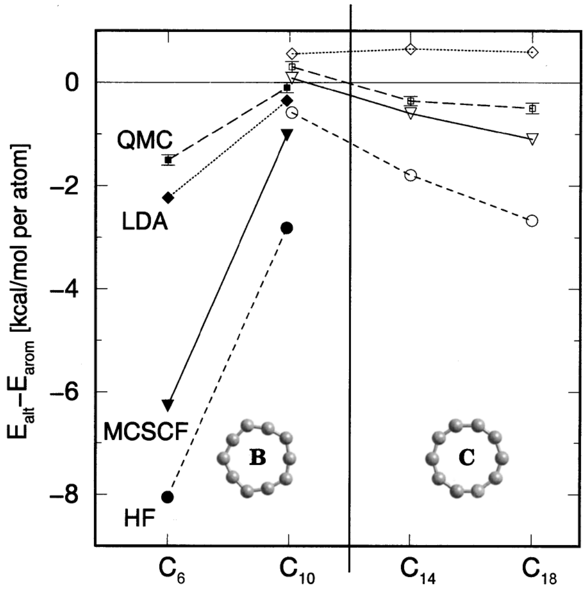

FIG. 3. Relative energies of the angle alternated B (filled symbols) and bond alternated C (empty symbols) structures with reference to the aromatic isomer A (see Fig. 1).

effect of correlation at the expense of exchange, resulting in a qualitative disagreement with QMC results.

The data from HF and QMC calculations enable us to analyze the HF and correlation energy components separately as a function of ring size. For $n \geq 10$, the HF energy difference between aromatic (A) and dimerized (C, $\mathcal{A}_r = 7\%$) isomers can be approximated by

$$E^A_{\mathrm{HF}} - E^C_{\mathrm{HF}} \simeq 5.14n - 45.4 \text{ [kcal/mol]}. \qquad (2)$$

For the correlation energy such an extrapolation is less certain, as we lack data for very large sizes. The following formula reproduced our C_{10}-C_{22} data within the error bars obtained (the value for C_{22} was based on an adjusted single determinant DMC calculation)

$$E^A_{\mathrm{corr}} - E^C_{\mathrm{corr}} \simeq -3.57n + 27.4 \text{ [kcal/mol]}, \qquad (3)$$

while for larger sizes it is probably somewhat less accurate. Nevertheless, the significant difference between the coefficients enables us to recognize the dominance of the Coulomb and exchange contributions for large n. This means that the competition between the stabilization mechanisms, which determine the geometry, gap, and key electronic structure features, is effectively decided *at intermediate ring sizes*. On the basis of these results we suggest that the ground state isomers are alternated at all sizes.

In conclusion, we present a study of C_{4N+2} carbon rings, for which highly accurate fixed-node diffusion Monte Carlo results show that distorted isomers are always preferred with a stability crossover from bond angle to bond length alternation between C_{10} and C_{14}. The fully symmetric aromatic isomer is instead a structural transition state connecting equivalent alternated geometries shifted by one site along the ring, although for C_{10} the angle alternated isomer is below the aromatic one by only $\simeq 1$ kcal/mol. The intermediate size rings (above C_{10}) show a clear trend of dimerization despite a sizable HOMO-LUMO gap, suggesting that the driving stabilization mechanism is the second-order Jahn-Teller effect. The gap persists to large sizes and the effect coalesces with the Peierls regime as $N \to \infty$ [8]. The competition of complicated many-body effects, from aromatic conjugation to symmetry breaking, provides an extremely sensitive probe of the treatment of electron correlation in different theoretical approaches. Our results demonstrate the potential of quantum Monte Carlo not only for evaluation of accurate energy differences, but also for other properties, such as equilibrium structures, which can be obtained by new developments in the QMC methodology.

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