CCSD calculations on C_{14}, C_{18}, and C_{22} carbon clusters

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The structure and energetics of the ring isomers of C_{4n+2} ($n=3-5$) carbon clusters were studied by using coupled-cluster singles and doubles excitation theory to overcome the vast differences existing in the literature. The results obtained in the present study clearly indicate that C_{14}, C_{18}, and C_{22} carbon rings have bond-length and bond-angle alternated acetylenic minimum energy structures. Contrarily, density functional theory calculations were unable to predict these acetylenic-type structures and they ended up with the cumulenic structures. It is found from the coupled-cluster studies that the lowest-energy ring isomer for the first two members of C_{4n+2} series is a bond-angle alternated cumulenic $D_{(2n+1)h}$ symmetry structure while the same for the remaining members is a bond-length and bond-angle alternated $C_{(2n+1)h}$ symmetry structure. In C_{4n+2} carbon rings, Peierls-type distortion, transformation from bond-angle alternated to bond-length alternated minimum energy structures, occurs at C_{14} carbon ring. © *2008 American Institute of Physics.*
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I. INTRODUCTION

Carbon clusters C_n attract much interest in connection with the formation of fullerenes, nanotubes, conducting polymers, and thin solid diamond films.[1–6] These clusters also play an important role in the interstellar chemistry of carbon-rich evolved stars as stable species or reactive chemical intermediates.[7] Nonetheless, our understanding of structure and electronic properties of carbon clusters, especially of smaller-sized ones, is far from satisfactory.

The nature of the carbon clusters varies from linear chains to rings to closed cages to nanotubes as the cluster size increases. It has long been recognized that the carbon clusters smaller than C_{10} possess low-energy linear structures with triplet nature. When the cluster size increases, the ring stability increases due to the reduction in angle strain and hence clusters larger than C_{10} were thought to exist as monocyclic rings. For the ring structures, further stability comes from an additional C–C bond. It has been found in the recent years that even for the small clusters such as C_4, C_6, and C_8, ring isomers are isoenergetic with or lower in energy than their linear counterparts.[8–12]

In recent years many experimental studies were made to observe C_n rings. While some of these studies identified the C_n rings without doubt, identification made in a few others were tentative. Zajfman *et al.*[13] reported the experimental evidence for a nonlinear C_6 isomer. Wakabayashi *et al.*[14] found the indication of the stability of C_{4n+2} ($n=2-4$) rings. Two research groups[15–18] presented the spectroscopic identification of C_6 and C_8 rings. Diederich *et al.*[19] reported the synthesis of C_{18}. Raman spectra observed for C_{14}, C_{16}, C_{18}, and C_{20} clusters were assigned to linear chains; however, the fluorescence spectra observed for C_{14} and C_{18} clusters in the

same experimental conditions were attributed to cumulene rings.[20,21] The electronic absorption spectra of the even-numbered C_6-C_{14} clusters measured in neon matrices combined with the *ab initio* calculations on C_6 led to the identification of cyclic C_{10}, C_{12}, and C_{14}.[22] Recently, the electronic spectra of C_{18} and C_{22} were detected in the gas phase and the observed spectra have been assigned to several transitions of monocyclic cumulenic isomers with D_{9h} symmetry for C_{18} and D_{11h} for C_{22} rings.[23] So great progress has been made in observing and identifying C_n rings unlike in the past where only linear chains were observed[6] in the vast majority of studies.

Among the C_n clusters, C_{4n+2} carbon rings attracted much attention because they exhibit competing many-body effects of Huckel aromaticity, second-order Jahn–Teller effect, and Peierls instability at large sizes. This leads to possible ground state structures with aromatic, bond-angle, or bond-length alternated geometry. In the C_{4n+2} carbon rings, Huckel's rule for aromaticity is an added stability to the rings in addition to the factors mentioned above. Additionally, some members of the C_{4n+2} series, carbon clusters with 10, 14, 18, and 22 atoms attract special attention. These magic numbers manifest themselves in the mass spectra with ionization of neutral molecules produced by laser ablation of graphite.[24] They also appear to correspond to size of preferential neutral loss by collision-induced dissociation.[25–27]

It has been predicted recently by using high-level calculations that the ground state structure of C_6, the first member of the C_{4n+2} family, has cumulenic D_{3h} symmetry.[10–12] The next member of this series, C_{10}, that has long been recognized as a geometric transition point for small clusters from linear to rings, is showed to have a cumulenic D_{5h} ground state structure.[12,28] For higher members of C_{4n+2} series, however, high-level theoretical results are not available and the existing results are contradictory to each other. For example,

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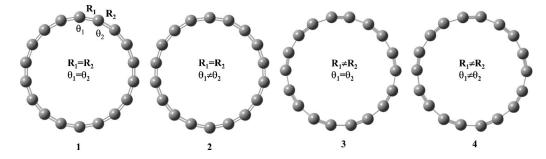
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FIG. 1. CCSD/D95(d) optimized structures of four ring isomers of C_{18}. (1) D_{18h}, (2) D_{9h} (cumulenic), (3) D_{9h} (acetylenic), and (4) C_{9h}.

in the case of C_{18}, Hartree–Fock (HF) calculations supported for a structure with alternating bond lengths (acetylenic D_{9h}), while calculations using Moller–Plesset (MP2) resulted for D_{18h} symmetric structure.[19,29,30] In density functional theory (DFT) calculations, gradient-corrected functionals supported for D_{18h} symmetric ground state structure but the calculations using hybrid functionals resulted for D_{9h} cumulenic ground state structure.[31–33,20,21] It should be noticed here that MP2 has shown to overestimate resonance stabilization and hence leads to artificially high symmetries for C_n clusters,[12,28,33] and the reliability of DFT results on C_n ($n \geq 10$) clusters is not been checked.

Apart from these factors, occurrence of Peierls-like distortion of bond alternation is one of the important topics in $4n+2$ rings. Small rings of $4n+2$ are expected to be aromatic, resulting in equal bond lengths, while $4n$ rings should be antiaromatic, resulting alternation in bond lengths. For large rings a transition, the Peierls transition,[34] from aromatic to nonaromatic behavior, takes place. Above Peierls transition, both $4n$ and $4n+2$ rings show similar properties, and the size at which aromatic and antiaromatic behaviors merge is a topic of interest to the chemistry and physics of extended π-bonded systems. Unfortunately, various studies predicted different sizes at which Peierls transition occurs in C_{4n+2} rings.[35–39]

Forgoing facts reveal the importance of high-level quantum mechanical studies on C_{4n+2} ($n \geq 2$) carbon rings. Hence we have undertaken the present study to find the accurate structure and energetics of a few C_{4n+2} ($n \geq 2$) carbon rings and to solve the existing contradictions.

The main focus of the present study is to obtain the most reliable structure and energetics of the ring isomers of C_{4n+2} ($n=3$, 4, and 5), C_{14}, C_{18}, and C_{22}, carbon clusters by using high-level coupled-cluster singles and doubles excitation (CCSD) theory. Four ring isomers of all the three clusters were considered for this study. These isomers are (i) with $D_{(4n+2)h}$ symmetry (equal both lengths and bond angles) denoted as $D_{(4n+2)h}$, (ii) with $D_{(2n+1)h}$ symmetry (equal bond lengths and different bond angles) denoted as $D_{(2n+1)h}$ (cumulenic), (iii) with $D_{(2n+1)h}$ symmetry (different bond lengths and equal bond angles) denoted as $D_{(2n+1)h}$ (acetylenic), and (iv) with $C_{(2n+1)h}$ symmetry (different bond lengths and bond angles) denoted as $C_{(2n+1)h}$. See Fig. 1, example for C_{18}. Apart from solving the existing contradictories about the structure and energetics of these C_{4n+2} carbon clusters, the

present study could also help to resolve the controversy surrounding the critical size at which the Peierls transition occurs in the C_{4n+2} rings.

II. COMPUTATIONAL DETAILS

All the calculations were performed with GAUSSIAN 03 suite of programs.[40] At first the four ring isomers of all the three selected carbon clusters, C_{14}, C_{18}, and C_{22}, were optimized by using BLYP,[41,42] B3LYP,[43,42] PBE,[44,45] and PBE0 (Refs. 44 and 45) density functionals with Dunning's[46] correlation-consistent polarized valence triple-zeta (cc-pVTZ) basis set. The nature of the optimized structures was analyzed by using frequency calculations. Finally, CCSD theory[47–49] was used to obtain the structures of all four ring isomers of C_{14}, C_{18}, and C_{22} molecules. In the CCSD calculations, core orbitals are excluded from the correlation calculations. Three different basis sets, Pople's 6–31G(d),[50] Dunning's double-zeta [D95(d,p)],[51] and Dunning's correlation-consistent polarized valence double-zeta (cc-pVDZ),[52] were utilized for this purpose. All the energies calculated in this work were without zero-point energy corrections.

III. RESULTS AND DISCUSSIONS

A. C_6 and C_{10}

Before going for the calculations on target carbon clusters, C_{14}, C_{18}, and C_{22}, we studied the structure and energetics of the first two members of the C_{4n+2} series, C_6 and C_{10}, to show the reliability of the CCSD results by comparing the calculated values with the available highly reliable CCSD with perturbative corrections for triples excitations [CCSD(T)] and multireference configuration interaction (MRCI) results.

The first *ab initio* calculations on C_6 were performed by Raghavachari *et al.*[53] by using HF and other theories including MP4 level with 6-31G basis set and it was found that the D_{3h} cumulenic structure ($^1A_1$ state) is the ground state structure. Contrarily, a study using multiconfiguration self-consistent field (MCSCF) and MRCI theories concluded that linear structure ($^3\Sigma_g^-$) is more stable than the D_{3h} ring structure.[54] Later, studies using CCSD(T) and MRCI studies overcome these contradictions and provided conclusive results: The D_{3h} cumulenic structure is the minimum energy structure and it is more stable than the cumulenic linear structure by 10.7 and 7 kcal/mol at CCSD(T) and MRCI

TABLE I. CCSD optimized geometries (R in Å and θ in deg) and relative energies (ΔE in kcal/mol) of ring isomers of C_{10} with different basis sets.

Isomer	CCSD			Past studies		
	6-31G(d)	D95(d,p)	cc-pVDZ	CCSD/ cc-pVDZ[a]	CCSD(T)/ cc-pVDZ[a]	CCSD(T)/ cc-pVDZ[b]
D_{10h}	$R=1.2952$	$R=1.3013$	$R=1.3039$	$R=1.304$	$R=1.312$	$R=1.312$
	$\theta=144.0$	$\theta=144.0$	$\theta=144.0$	$\theta=144.0$	$\theta=144.0$	$\theta=144.0$
	$\Delta E=9.45$	$\Delta E=10.07$	$\Delta E=8.55$	$\Delta E=8.60$		$\Delta E=2.93$
D_{5h} (cummulenic)	$R=1.3020$	$R=1.3090$	$R=1.3125$	$R=1.311$		$R=1.3168$
	$\theta=166.33$	$\theta=166.19$	$\theta=166.64$	$\theta=166.0$		$\theta=164.06$
	$\theta=121.67$	$\theta=121.81$	$\theta=121.36$	$\theta=122.0$		$\theta=123.94$
	$\Delta E=0.00$	$\Delta E=0.00$	$\Delta E=0.00$	$\Delta E=0.00$		$\Delta E=0.00$
D_{5h} (acetylenic)	$R=1.3423$	$R=1.3516$	$R=1.3480$	$R=1.344$		
	$R=1.2580$	$R=1.2621$	$R=1.2683$	$R=1.271$		
	$\theta=144.0$	$\theta=144.0$	$\theta=144.0$	$\theta=144.0$		
	$\Delta E=8.65$	$\Delta E=8.96$	$\Delta E=7.85$	$\Delta E=7.8$		
C_{5h}	$R=1.3021$	$R=1.3089$	$R=1.3127$			
	$R=1.3020$	$R=1.3085$	$R=1.3123$			
	$\theta=166.22$	$\theta=166.06$	$\theta=166.67$			
	$\theta=121.78$	$\theta=121.94$	$\theta=121.33$			
	$\Delta E=0.00$	$\Delta E=0.00$	$\Delta E=0.00$			

[a]Reference 28.
[b]Reference 12.

level of theories, respectively, with ANO basis set.[10,11] Again at the CCSD(T) level of theory with cc-pVDZ and cc-pVTZ basis sets, the D_{3h} isomer is calculated to be lying 7.1 and 11 kcal/mol, respectively, lower than the linear structure.[12]

We studied both the D_{3h} cumulenic ring and linear structures by using CCSD theory with 6−31G(d), D95(d,p), and cc-pVDZ basis sets. With all the three basis sets, the D_{3h} cumulenic structure is found to be the ground state structure for C_6 as predicted by earlier CCSD(T) and MRCI calculations. The D_{3h} cumulenic structure is calculated to be more stable than the linear by 6.66, 6.82, and 2.96 kcal/mol with 6-31G(d), D95(d,p), and cc-pVDZ basis sets, respectively. These results show good agreement with the available CCSD(T) and MRCI results. It should be noticed that the structure obtained for the ground state D_{3h} cumulenic isomer using CCSD theory also agrees very well with that obtained using CCSD(T) theory. To check the influence of the size of the basis set, CCSD calculations were also made using cc-pVTZ basis set. With this basis set, again the D_{3h} cumulenic structure is found to be the minimum energy structure and it is more stable than the linear by 6.11 kcal/mol. These results show that reliable structure and energetics can be derived by using CCSD theory with 6-31G(d), D95(d,p), and cc-pVDZ basis sets.

It is well established now that the linear form of C_{10} is much higher in energy than the cyclic forms and so only cyclic structures are considered for discussions here. Watts and Bartlett[28] reported that C_{10} has D_{5h} cumulenic ground state structure and the structure with D_{10h} symmetry ($^1A_{1g}$ state) is lying 8.6 kcal/mol above the ground state at the CCSD/cc-pVDZ level. At the CCSD(T)/cc-pVDZ//CCSD/cc-pVDZ level, this energy gap reduces to 2.8 kcal/mol and the D_{5h} acetylenic structure

($^1A_1$ state) is found to be lying 5.8 kcal/mol higher in energy than the ground state structure.[28] However, both MP2 and MP4 levels of theories were unable to provide the correct results and according to these theories, the D_{10h} symmetrical structure is the most stable structure.[28] Martin and Taylor[12] finally concluded through their calculations at the CCSD(T)/ cc-pVDZ level of theory that the D_{10h} structure is a transition state lying an estimated 2.9 kcal/mol energy above the D_{5h} minimum. With cc-pVTZ basis set used, this energy gap found to be reduced to 1 kcal/mol.[12]

We studied four ring isomers (previously studied three structures and a new structure with C_{5h} symmetry) of C_{10} cluster and the results were tabulated in Table I along with the available results obtained using high-level theories. The results agree qualitatively well with the available CCSD(T) results. The present CCSD calculations using all the three selected basis sets show that the D_{5h} cumulenic structure is the most stable structure as concluded in the CCSD(T) calculations. Symmetry relaxation to C_{5h} does not lower the energy; the structure with C_{5h} symmetry has identical energy to that with the cumulenic D_{5h} structure. Inspection of Table I indeed reveals that the C_{5h} structure actually has D_{5h} symmetry within the convergence threshold of the geometry optimization which means that this structure collapses to D_{5h} cumulenic structure. This shows that the ground state structure of C_{10} cluster has a D_{5h} (cumulenic) symmetry. The D_{10h} symmetrical structure is higher in energy by 8.55 kcal/mol than the ground state D_{5h} cumulenic structure at the CCSD/ cc-pVDZ level. This energy gap is about 5 kcal/mol more than that obtained at the CCSD(T)/cc-pVDZ level of theory. The table shows that the geometrical parameters obtained for D_{10h} and D_{5h} cumulenic structures using CCSD calculations agree very well with those of CCSD(T) calculations.

The CCSD calculations made for C_6 and C_{10} clusters conclude the following. The results derived using the CCSD level of theory agree well with those obtained using the CCSD(T) level. The CCSD calculations correctly identify the ground state structures of these carbon clusters and the geometries obtained using CCSD calculations are in good agreement with those obtained using the CCSD(T) level of theory. So the present calculations on C_6 and C_{10} support that the CCSD theory with double-zeta plus polarization-type basis sets could be used to obtain qualitative results for C_{4n+2} carbon clusters. By considering the size of the clusters taken for the present study, it is a pleasing result. We used the same level of theory to study the target C_{14}, C_{18}, and C_{22} carbon rings.

B. C_{14}, C_{18}, and C_{22}

As mentioned in the Introduction, the relative stabilities of the ring isomers of these large C_{4n+2} clusters have been a subject of controversy. At HF, the acetylenic form (D_{9h} acetylenic) of C_{18} is the lowest-energy structure.[19] Two cumulenic forms, D_{9h} and D_{18h} isomers are 37.6 and 58.3 kcal/mol less stable. SCF calculations by Parasuk *et al.*[29] also confirmed the earlier conclusion (D_{9h} acetylenic ground state); however, their MP2 calculations resulted for D_{18h} symmetric ground state structure. Similar kinds of results were also obtained by Feyereisen *et al.*[30] A DFT study (BLYP functional with triple zeta basis set) by Hutter *et al.*[32] predicted that the minimum energy structure of C_{14} and C_{18} molecules has D_{14h} and D_{18h} symmetries, respectively; however, only C_{14} was found to be the local minima on the potential energy surface. On the other hand, a study by using B3LYP functional with cc-pVDZ basis set found cumulenic D_{7h} and D_{9h} symmetry ground state structures for C_{14} and C_{18} clusters, respectively.[33] In the same year, Plattner and Houk[38] presented theoretical arguments (by considering the DFT errors in similar cases) from their combined HF and DFT calculations that C_{18} has a flattened circular polyyne structure (C_{9h} symmetry). A few other DFT studies later supported cumulenic isomers: Studies on C_{14} and C_{18} clusters by using B3LYP functional with cc-pVDZ basis set concluded that the minimum energy structure for these clusters has cumulenic D_{7h} and D_{9h} symmetries, respectively.[20,21] A recent study on C_{18} cluster by Boguslavskiy *et al.*[23] at B3LYP/6-31G(d) level also found that the D_{9h} cumulenic is the ground state structure which is 2.54 kcal/mol more stable than the D_{18h} structure. The D_{9h} acetylenic structure is found to be a saddle point and the C_{9h} symmetrical structure effectively converged to D_{9h} cumulenic structure. Interestingly, results derived from a recent quantum Monte Carlo (QMC) study by Torelli and Mitas[37] indicated the existence of a crossover between C_{10} and C_{14} from bond-angle to bond-length alternation. It should be noticed, however, that though such QMC studies provide highly reliable results, two previous such calculations provided incorrect results for C_{10} clusters.[55,56] Hence the existing results are highly contradictory to each other.

We studied all the four ring isomers of C_{14}, C_{18}, and C_{22}

TABLE II. CCSD optimized geometries (R in Å and θ in deg) and relative energies (ΔE in kcal/mol) of C_{14} with different basis sets.

Isomer	CCSD		
	6-31G(d)	D95(d,p)	cc-pVDZ
D_{14h}	$R=1.2905$	$R=1.2961$	$R=1.2987$
	$\theta=154.29$	$\theta=154.29$	$\theta=154.29$
	$\Delta E=15.80$	$\Delta E=18.18$	$\Delta E=14.06$
D_{7h} (cumulenic)	$R=1.2933$	$R=1.2988$	$R=1.3029$
	$\theta=170.75$	$\theta=169.29$	$\theta=170.21$
	$\theta=137.82$	$\theta=139.28$	$\theta=138.36$
	$\Delta E=9.82$	$\Delta E=11.94$	$\Delta E=10.42$
D_{7h} (acetylenic)	$R=1.3710$	$R=1.3789$	$R=1.3783$
	$R=1.2345$	$R=1.2390$	$R=1.2433$
	$\theta=154.29$	$\theta=154.29$	$\theta=154.29$
	$\Delta E=1.72$	$\Delta E=3.08$	$\Delta E=0.82$
C_{7h}	$R=1.3678$	$R=1.3753$	$R=1.3769$
	$R=1.2368$	$R=1.2412$	$R=1.2444$
	$\theta=164.12$	$\theta=161.07$	$\theta=161.06$
	$\theta=144.45$	$\theta=147.50$	$\theta=147.51$
	$\Delta E=0.00$	$\Delta E=0.00$	$\Delta E=0.00$

carbon clusters by using CCSD theory with various basis sets and the results were summarized in Tables II–IV.

The tables reveal some interesting results for large C_{4n+2} carbon rings. The results obtained for C_{14} cluster (Table II) using all the selected basis sets clearly show that the C_{7h} symmetrical isomer is the most stable ring isomer: The C_{7h} structure is more stable than the D_{14h} structure by 15.8, 18.2, and 14.1 kcal/mol with 6-31G(d), D95(d,p), and cc-pVDZ basis sets, respectively. The bond-angle alternated cumulenic structure, D_{7h} cumulenic one, is higher in energy than the C_{7h} minimum energy structure by around 10 kcal/mol in calculations with all the basis sets. The bond-length alternated D_{7h} symmetric structure, however, is lying very close to the most stable ring isomer: the energy difference between these two structures is 1.72 and 0.82 kcal/mol with 6-31G(d) and cc-pVTZ basis sets, respectively. These results clearly support for the acetylenic structures contrary to most of the existing studies where only cumulenic structures are favored. It is seen from the table that the difference in neighboring bond lengths (ΔR) in the most stable C_{7h} structure is around 0.13 Å. It should be noticed, however, again that the C_{10} cluster has a cumulenic ground state structure. The difference in neighboring bond angles ($\Delta \theta$) in the most stable C_{7h} ring structure is 13.6° at the CCSD/cc-pVDZ level of theory.

Table III shows the results derived for the C_{18} cluster. As in the case of C_{14} carbon cluster, all the calculations show that bond-length and bond-angle alternated structure, structure with C_{9h} symmetry, is the most stable isomer among all the other ring structures. The high symmetry D_{18h} structure is lying 32.11 kcal/mol higher in energy than the minimum energy C_{9h} structure at the CCSD/cc-pVDZ level of theory. The results obtained using the other basis sets also show a similar trend. The angle-alternated D_{9h} cumulenic structure is 0.62 kcal/mol more stable than the D_{18h} structure at the CCSD/cc-pVDZ level of theory. Once again, as in C_{14} car-

TABLE III. CCSD optimized geometries (R in Å and θ in deg) and relative energies (ΔE in kcal/mol) of C_{18} with different basis sets.

Isomer	CCSD		
	6-31G(d)	D95(d,p)	cc-pVDZ
D_{18h}	$R=1.2886$	$R=1.2944$	$R=1.2971$
	$\theta=160.0$	$\theta=160.0$	$\theta=160.0$
	$\Delta E=34.77$	$\Delta E=37.16$	$\Delta E=32.11$
D_{9h} (cumulenic)	$R=1.2886$	$R=1.2936$	$R=1.2971$
	$\theta=163.75$	$\theta=162.94$	$\theta=162.85$
	$\theta=156.25$	$\theta=157.06$	$\theta=157.15$
	$\Delta E=33.26$	$\Delta E=32.20$	$\Delta E=31.49$
D_{9h} (acetylenic)	$R=1.3757$	$R=1.3833$	$R=1.3828$
	$R=1.2291$	$R=1.2336$	$R=1.2381$
	$\theta=160.0$	$\theta=160.0$	$\theta=160.0$
	$\Delta E=1.75$	$\Delta E=2.75$	$\Delta E=0.59$
C_{9h}	$R=1.3744$	$R=1.3807$	$R=1.3827$
	$R=1.2295$	$R=1.2347$	$R=1.2379$
	$\theta=165.71$	$\theta=164.79$	$\theta=163.27$
	$\theta=154.29$	$\theta=155.21$	$\theta=156.73$
	$\Delta E=0.00$	$\Delta E=0.00$	$\Delta E=0.00$

TABLE IV. CCSD optimized geometries (R in Å and θ in deg) and relative energies (ΔE in kcal/mol) of C_{22} with different basis sets.

Isomer	CCSD		
	6-31G(d)	D95(d,p)	cc-pVDZ
D_{22h}	$R=1.2876$	$R=1.2934$	$R=1.2963$
	$\theta=163.64$	$\theta=163.64$	$\theta=163.64$
	$\Delta E=54.85$	$\Delta E=56.72$	$\Delta E=51.14$
D_{11h} (cumulenic)	$R=1.2873$	$R=1.2928$	$R=1.2962$
	$\theta=168.31$	$\theta=166.19$	$\theta=166.20$
	$\theta=158.97$	$\theta=161.08$	$\theta=161.08$
	$\Delta E=52.01$	$\Delta E=51.65$	$\Delta E=50.44$
D_{11h} (acetylenic)	$R=1.3763$	$R=1.3837$	$R=1.3835$
	$R=1.2268$	$R=1.2317$	$R=1.2358$
	$\theta=163.64$	$\theta=163.64$	$\theta=163.64$
	$\Delta E=2.12$	$\Delta E=2.35$	$\Delta E=0.48$
C_{11h}	$R=1.3753$	$R=1.3819$	$R=1.3832$
	$R=1.2268$	$R=1.2326$	$R=1.2362$
	$\theta=167.89$	$\theta=167.76$	$\theta=165.92$
	$\theta=159.39$	$\theta=159.52$	$\theta=161.35$
	$\Delta E=0.00$	$\Delta E=0.00$	$\Delta E=0.00$

bon ring, the D_{9h} acetylenic structure is close in energy with the C_{9h} structure: the energy difference of about 0.6 kcal/mol is obtained with the cc-pVDZ basis set. Due to the reduction in the in-plane strain energy because of the increase in the ring size, the $\Delta\theta$ is reduced for the most stable isomer of C_{18} from that for the C_{14} ring cluster. The $\Delta\theta$ value obtained in C_{18} is 6.54° using CCSD theory with the cc-pVDZ basis set. On the other hand, the difference in neighboring bond lengths ΔR is increased from 0.1325 Å in C_{14} to 0.1448 Å in C_{18} (at the CCSD/cc-pVDZ level).

The calculated results for C_{22} rings were tabulated in Table IV. These results clearly indicate that, as in the case of C_{14} and C_{18} carbon rings, isomer with the lowest symmetry is found to be the most stable structure. At the CCSD/cc-pVDZ level of theory, the high symmetry D_{22h} structure is less stable than the C_{11h} structure by 51.14 kcal/mol. Again, the bond-length alternated D_{11h} acetylenic structure is lying close in energy with the most stable C_{11h} ring structure while the bond-angle alternated D_{11h} cumulenic isomer is close in energy with the D_{22h} structure. Bond lengths calculated for the most stable structure reveal that neighboring bonds have alternative single and triple bonds. At the same time, the $\Delta\theta$ value of this C_{22} ring structure is decreased from that of the C_{18} ring structure to around 4°.

All these results obtained for these C_{14}, C_{18}, and C_{22} carbon rings show undoubtedly that the most stable structure of these C_{4n+2} rings has bond-length and bond-angle alternated geometries. Differing completely from the earlier DFT and MP2 conclusions, the present study reveals that bond alternated acetylenic structures, not the cumulenic structures, are energetically favorable for these three carbon ring clusters. In these C_{14}, C_{18}, and C_{22} clusters, the second-order Jahn–Teller distortion possibly plays an important role and it overcomes the stabilization of aromaticity and hence results for the bond alternated structures.

C. Peierls transition

Peierls distortion, transformation from bond-angle alternation to bond-length alternation, is an important phenomenon in the C_n rings. HF calculations predicted that the transition to nonaromatic behavior occurs by ring sizes C_{14}.[33,36] Hybrid B3LYP density functional calculations by Martin et al.[33] concluded that the bond alternation is prevented at least up to C_{18}. Later it was shown by Sato and Okamoto[39] using the same hybrid functional that Peierls transition occurs at C_{22}. Bylaska et al.[35,36] concluded, however, from their molecular-orbital and band-structure calculations within the local-density approximation (LDA) that the C_{4n+2} rings show no alternation (i.e., aromatic behavior is retained) until very large sizes (C_{82}). In the same year, a study using LDA and GGA (BPW91) calculations by Torelli and Mitas[37] also showed no indication of bond alternation up to C_{90}. However, B3PW91 hybrid functional showed to recover qualitatively the HF results for large sizes ($>C_{46}$).[37] Interestingly, quantum Monte Carlo results in the same study[37] indicated the existence of a crossover between C_{10} and C_{14} from bond-angle to bond-length alternation. So there is no unanimity among the existing results regarding the size at which the Peierls distortion from bond-angle to bond-length alternated ground state structures occurs in the C_{4n+2} carbon rings.

High-level coupled-cluster studies could make the necessary reliable and decisive conclusion about this matter. It is now well known that in the case of C_6 and C_{10} carbon rings, the bond-angle alternated structures are more stable than the bond-length alternated structures. The results obtained from the present study (Tables II–IV) reveal that the most stable structures of C_{14}, C_{18}, and C_{22} rings have bond-length alternated structures. This clearly reveals that the transformation from bond-angle to bond-length alternated minimum energy structures occurs at C_{14} in the C_{4n+2} carbon ring series. Decrease in difference in neighboring bond angles and increase
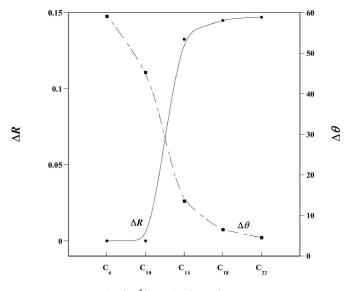
FIG. 2. Variation of ΔR (in Å) and $\Delta \theta$ (in deg) with the increase in C_{4n+2} ring size at the CCSD/cc-pVDZ level of theory.

in difference in neighboring bond lengths are clearly noticed when the size of the C_{4n+2} carbon ring increases (Fig. 2). The figure undoubtedly show the existence of a crossover between C_{10} and C_{14} from bond-angle to bond-length alternation as predicted by a QMC study.[37]

D. Density functional theory results

As it is mentioned in previous sections, there is no unanimity among the earlier DFT results. One point worth to be noticed here is that in most of those earlier calculations, relatively smaller basis sets were used. Hence to thoroughly check the ability of DFT calculations in finding the correct structure and energetics of the carbon rings, we studied all the four ring isomers of C_{4n+2} ($n=2-5$) clusters using four

different density functionals with Dunnings' cc-pVTZ basis set. The results obtained in these calculations were tabulated in Tables V–VIII.

Calculations show some interesting results. As predicted by CCSD(T) calculations,[12,28] the D_{5h} cumulenic is found to be the ground state structure for C_{10} (Table V) in calculations with all the four density functionals. The energy difference between the most stable D_{5h} cumulenic structure and the full symmetric D_{10h} structure obtained in the DFT calculations is close to the value obtained using CCSD(T) theory. At the same time the structure, especially bond angles, is somehow functional dependent. The nature of the D_{10h} structure was a subject of interest in the previous studies.[12,28] The present calculations with all the functionals show that the D_{10h} isomer is a transition state as concluded by the CCSD(T) study.[12] We studied this isomer also at the B3LYP/cc-pVQZ level of theory to know the nature of this structure and found that it has an imaginary frequency ($377i$) corresponding to the deformation to D_{5h} structure. Thus for the case of C_{10} ring, all DFT calculations provide results similar to those of CCSD(T) calculations.

For C_{14}, calculations show some interesting differences: while pure functionals (BLYP and PBE) indicate that the full symmetric D_{14h} structure is the most stable ring structure for C_{14}, the calculations with hybrid functionals show that this D_{14h} structure is a transition state. We found that even with the large cc-pVQZ basis set, this isomer is found to be a transition state ($69i$) in B3LYP functional calculations. Both the hybrid functionals seem to support for a bond-angle alternated D_{7h} cumulenic structure for C_{14} ring (Table VI). Nevertheless, it should be noticed here that all the density functional calculations indicate that all the four ring isomers are very close in energies, lying within 0.2 kcal/mol difference. All these results differ from those obtained using CCSD theory.

TABLE V. Optimized geometries (R in Å and θ in deg) and relative energies (ΔE in kcal/mol) of ring isomers of C_{10} with various density functionals using cc-pVTZ basis set.

Isomer	BLYP	B3LYP	PBE	PBE0
D_{10h}	$R=1.2916$	$R=1.2822$	$R=1.291$	$R=1.2809$
	$\theta=144.0$	$\theta=144.0$	$\theta=144.0$	$\theta=144.0$
	$\Delta E=1.36$	$\Delta E=3.68$	$\Delta E=1.56$	$\Delta E=4.94$
	(saddle point)	(saddle point)	(saddle point)	(saddle point)
D_{5h} (cumulenic)	$R=1.2957$	$R=1.2884$	$R=1.2955$	$R=1.2882$
	$\theta=158.48$	$\theta=161.89$	$\theta=159.47$	$\theta=163.52$
	$\theta=129.52$	$\theta=126.11$	$\theta=128.53$	$\theta=124.48$
	$\Delta E=0.00$	$\Delta E=0.00$	$\Delta E=0.00$	$\Delta E=0.00$
D_{5h} (acetylenic)	$R=1.2916$	$R=1.2823$	$R=1.291$	$R=1.2809$
	$R=1.2916$	$R=1.2822$	$R=1.2907$	$R=1.2809$
	$\theta=144.0$	$\theta=144.0$	$\theta=144.0$	$\theta=144.0$
	$\Delta E=1.36$	$\Delta E=3.68$	$\Delta E=1.56$	$\Delta E=4.94$
	(saddle point)	(saddle point)	(saddle point)	(saddle point)
C_{5h}	$R=1.2957$	$R=1.2885$	$R=1.2955$	$R=1.2883$
	$R=1.2957$	$R=1.2884$	$R=1.2955$	$R=1.2882$
	$\theta=158.48$	$\theta=161.89$	$\theta=159.47$	$\theta=163.52$
	$\theta=129.52$	$\theta=126.11$	$\theta=128.53$	$\theta=124.48$
	$\Delta E=0.00$	$\Delta E=0.00$	$\Delta E=0.00$	$\Delta E=0.00$

TABLE VI. Optimized geometries (R in Å and θ in deg) and relative energies (ΔE in kcal/mol) of ring isomers of C_{14} with various density functionals using cc-pVTZ basis set.

Isomer	BLYP	B3LYP	PBE	PBE0
D_{14h}	$R=1.2869$	$R=1.2780$	$R=1.2869$	$R=1.2774$
	$\theta=154.29$	$\theta=154.29$	$\theta=154.29$	$\theta=154.29$
	$\Delta E=0.00$	$\Delta E=0.02$	$\Delta E=0.00$	$\Delta E=0.11$
		(Saddle point)		(Saddle point)
D_{7h} (cumulenic)	$R=1.2867$	$R=1.2785$	$R=1.2866$	$R=1.278$
	$\theta=154.40$	$\theta=158.58$	$\theta=154.31$	$\theta=160.92$
	$\theta=154.17$	$\theta=149.99$	$\theta=154.26$	$\theta=147.65$
	$\Delta E=0.07$	$\Delta E=0.00$	$\Delta E=0.05$	$\Delta E=0.01$
D_{7h} (acetylenic)	$R=1.2869$	$R=1.2778$	$R=1.2866$	$R=1.2769$
	$R=1.2868$	$R=1.2777$	$R=1.2866$	$R=1.2768$
	$\theta=154.29$	$\theta=154.29$	$\theta=154.29$	$\theta=154.29$
	$\Delta E=0.12$	$\Delta E=0.07$	$\Delta E=0.08$	$\Delta E=0.13$
		(Saddle point)		(Saddle point)
C_{7h}	$R=1.2869$	$R=1.2784$	$R=1.2866$	$R=1.2785$
	$R=1.2868$	$R=1.2783$	$R=1.2864$	$R=1.2774$
	$\theta=154.45$	$\theta=158.55$	$\theta=154.30$	$\theta=160.89$
	$\theta=154.13$	$\theta=150.02$	$\theta=154.27$	$\theta=147.69$
	$\Delta E=0.06$	$\Delta E=0.02$	$\Delta E=0.05$	$\Delta E=0.00$

In the case of C_{18}, results obtained (Table VII) using all the four density functionals show that all the four ring isomers lay within 0.02 kcal/mol energy difference and none of the isomers has any imaginary frequency showing that all are minimum energy structures. The table also reveals that the calculated geometries of all the four isomers are very much the same indicating that the remaining small differences in the geometrical parameters among the isomers are simply due to the symmetries imposed on the calculations. Hence it is clear that the DFT calculations conclude for a symmetric D_{18h} structure for the C_{18} ring.

Again as in the case of C_{14}, the results obtained for C_{22} using DFT calculations show some differences: pure functionals conclude that the lowest-energy ring isomer is a full symmetric D_{22h} cumulenic ring structure but interestingly the bond-length alternated acetylenic structures are favored by the hybrid functionals (Table VIII). Both the hybrid functionals found that the D_{22h} and D_{11h} cumulenic structures are transition states. Nevertheless, the energy difference obtained between the cumulenic and acetylenic structures is very small: 0.18 and 0.89 kcal/mol with B3LYP and PBE0 functionals, respectively.

All these DFT results, derived for C_{4n+2} rings, differ much from those obtained using coupled-cluster theories, the

TABLE VII. Optimized geometries (R in Å and θ in deg) and relative energies (ΔE in kcal/mol) of ring isomers of C_{18} with various density functionals using cc-pVTZ basis set.

Isomer	BLYP	B3LYP	PBE	PBE0
D_{18h}	$R=1.2853$	$R=1.2766$	$R=1.2849$	$R=1.2757$
	$\theta=160.0$	$\theta=160.0$	$\theta=160.0$	$\theta=160.0$
	$\Delta E=0.02$	$\Delta E=0.01$	$\Delta E=0.00$	$\Delta E=0.00$
D_{9h} (cumulenic)	$R=1.2852$	$R=1.2765$	$R=1.2849$	$R=1.2756$
	$\theta=160.01$	$\theta=160.02$	$\theta=160.02$	$\theta=160.02$
	$\theta=159.99$	$\theta=159.98$	$\theta=159.98$	$\theta=159.98$
	$\Delta E=0.02$	$\Delta E=0.01$	$\Delta E=0.00$	$\Delta E=0.00$
D_{9h} (acetylenic)	$R=1.2851$	$R=1.2768$	$R=1.2849$	$R=1.2757$
	$R=1.2850$	$R=1.2765$	$R=1.2849$	$R=1.2757$
	$\theta=160.0$	$\theta=160.0$	$\theta=160.0$	$\theta=160.0$
	$\Delta E=0.01$	$\Delta E=0.00$	$\Delta E=0.00$	$\Delta E=0.00$
C_{9h}	$R=1.2851$	$R=1.2769$	$R=1.2848$	$R=1.2758$
	$R=1.2851$	$R=1.2759$	$R=1.2846$	$R=1.2756$
	$\theta=160.04$	$\theta=160.03$	$\theta=160.01$	$\theta=160.03$
	$\theta=159.96$	$\theta=159.97$	$\theta=159.99$	$\theta=159.97$
	$\Delta E=0.00$	$\Delta E=0.01$	$\Delta E=0.00$	$\Delta E=0.00$

TABLE VIII. Optimized geometries (R in Å and θ in deg) and relative energies (ΔE in kcal/mol) of ring isomers of C_{22} with various density functionals using cc-pVTZ basis set.

Isomer	BLYP	B3LYP	PBE	PBE0
D_{22h}	$R=1.2842$	$R=1.2756$	$R=1.2844$	$R=1.2752$
	$\theta=163.64$	$\theta=163.64$	$\theta=163.64$	$\theta=163.64$
	$\Delta E=0.00$	$\Delta E=0.18$	$\Delta E=0.00$	$\Delta E=0.89$
		(saddle point)		(saddle point)
D_{11h} (cumulenic)	$R=1.2842$	$R=1.2756$	$R=1.2842$	$R=1.275$
	$\theta=163.65$	$\theta=163.65$	$\theta=163.64$	$\theta=163.65$
	$\theta=163.62$	$\theta=163.62$	$\theta=163.64$	$\theta=163.63$
	$\Delta E=0.00$	$\Delta E=0.18$	$\Delta E=0.00$	$\Delta E=0.89$
		(saddle point)		(saddle point)
D_{11h} (acetylenic)	$R=1.2841$	$R=1.2988$	$R=1.2841$	$R=1.3091$
	$R=1.2841$	$R=1.2546$	$R=1.2841$	$R=1.2452$
	$\theta=163.64$	$\theta=163.64$	$\theta=163.64$	$\theta=163.64$
	$\Delta E=0.01$	$\Delta E=0.01$	$\Delta E=0.01$	$\Delta E=0.01$
C_{11h}	$R=1.2844$	$R=1.2988$	$R=1.2845$	$R=1.3085$
	$R=1.2844$	$R=1.2546$	$R=1.2841$	$R=1.2457$
	$\theta=163.64$	$\theta=163.65$	$\theta=163.65$	$\theta=163.66$
	$\theta=163.63$	$\theta=163.63$	$\theta=163.63$	$\theta=163.61$
	$\Delta E=0.00$	$\Delta E=0.00$	$\Delta E=0.00$	$\Delta E=0.00$

only exception is C_{10}. [Our calculations on the C_6 cluster at the B3LYP/cc-pVTZ level predict that the linear triplet is more stable (6.01 kcal/mol) than the D_{3h} cumulenic ring structure which is contradictory from the conclusion made in the coupled-cluster calculations.] These results reveal that DFT cannot provide reliable results for C_{4n+2} rings.

IV. CONCLUDING REMARKS

The structure and energetics of four monocyclic ring isomers of C_{14}, C_{18}, and C_{22} molecules were studied using high-level *ab initio* CCSD theory with various basis sets including Dunnings' correlation-consistent double-zeta basis set. Results show clearly that all these three carbon ring clusters have bond-length and bond-angle alternated minimum energy structures contrary to the conclusions made in many of the earlier studies. The bond alternated acetylenic structures, not the cumulenic ones predicted by earlier calculations, are the minimum energy structures of C_{4n+2} ($n=3-5$) carbon rings. Now it is certain that while the lowest-energy ring isomer of the C_{4n+2} ($n=1,2$) rings has a bond-angle alternated $D_{(2n+1)h}$ symmetric structure, the C_{4n+2} rings with $n=3-5$ have bond-length and bond-angle alternated $C_{(2n+1)h}$ symmetry structures as their most stable ring structures. The results reveal that Peierls-type distortion, transformation from bond-angle to bond-length alternated structures, occurs at C_{14} in the C_{4n+2} carbon rings. The present study also shows that the density functional calculations cannot provide reliable results for these interesting C_{4n+2} carbon rings.

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