

CCSD calculations on  $C_{18}$  and  $C_{22}$  carbon clusters

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Carbon clusters  $C_n$  attract interest in connection with the formation of fullerenes, nanotubes, and conducting polymers. These carbon chains play an important role in the interstellar chemistry of carbon-rich evolved stars as stable species or chemical intermediates. However, our understanding of the structural and electronic properties of carbon clusters, especially smaller-sized ones, is far from satisfactory.

Among the  $C_n$  clusters,  $C_{4n+2}$  carbon rings attracted both experimentalists and theoreticians because they exhibit competing many-body effects of Huckel aromaticity, second-order Jahn-Teller, and Peierls instability at large sizes. This leads to possible ground state structures with aromatic, bond angle, or bond length alternated geometry. Because of the involvement of these many-body effects, high-level calculations are very much important to obtain reliable structure and electronic properties of these clusters. Many studies were made in the past to know the structure of these clusters; however, the results obtained even for the first two members of the  $C_{4n+2}$  family,  $C_6$  and  $C_{10}$ , are not consistent. Recently it has been concluded that the structure of  $C_6$  is cumulenic  $D_{3h}$  ring and the ground state structure of cyclic  $C_{10}$  clearly has  $D_{5h}$  symmetry. However, the inconsistency regarding the structures of the other members of  $C_{4n+2}$  clusters remains. We carried out the present study to make the concrete conclusion regarding the ground state structures of  $C_{14}$ ,  $C_{18}$ , and  $C_{22}$  rings.

At first, structures were optimized by using different density functionals including the popular B3LYP functional with different basis sets. The nature of the optimized structures was analyzed by using frequency calculations. Finally we used CCSD theory for the optimization of the ground state structures. Four different isomers (example, Fig. 1 for  $C_{18}$ ) of  $C_{14}$ ,  $C_{18}$ , and  $C_{22}$  rings were considered for the present study.

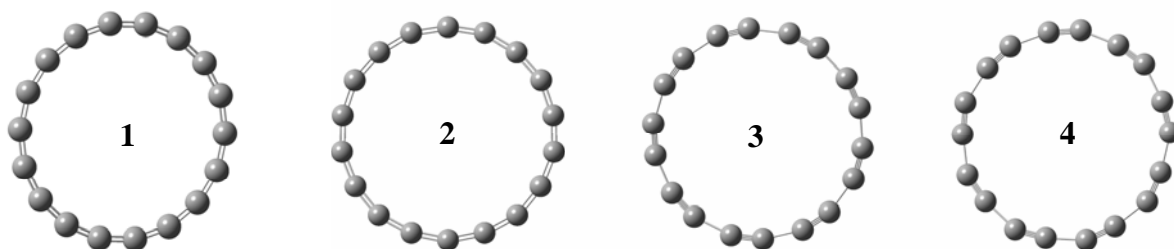


Fig. 1. CCSD/D95 optimized structures of four ring isomers of  $C_{18}$ . (1)  $D_{18h}$  cumulenic, (2)  $D_{9h}$  cumulenic (3)  $D_{9h}$  acetylenic, and (4)  $C_{9h}$  acetylenic.

The results derived for  $C_{18}$  using different density functionals with cc-pVTZ basis set were presented in Table 1. Basically all the four ring structures have the same geometrical parameters and the energies obtained for all the structures are almost same. Hence, the density functional results clearly support that the ground state structure of  $C_{18}$  has  $D_{18h}$  symmetry (**1**).

Table 1.  $C_{18}$  structures using cc-pVTZ basis set with different density functionals.

Isomer	B3LYP	PBEPBE	PBE1PBE
$D_{18h}$ ( <b>1</b> )	$R = 1.2766 \text{ \AA}$ $\theta = 160.0^\circ$	$R = 1.2849 \text{ \AA}$ $\theta = 160.0^\circ$	$R = 1.2757 \text{ \AA}$ $\theta = 160.0^\circ$
$D_{9h}$ Cumulenic ( <b>2</b> )	$R = 1.2765 \text{ \AA}$ $\theta_1 = 159.98^\circ$ $\theta_2 = 160.02^\circ$	$R = 1.2849 \text{ \AA}$ $\theta_1 = 159.98^\circ$ $\theta_2 = 160.02^\circ$	$R = 1.2756 \text{ \AA}$ $\theta_1 = 159.98^\circ$ $\theta_2 = 160.02^\circ$
$D_{9h}$ Acetylenic ( <b>3</b> )	$R_1 = 1.2765 \text{ \AA}$ $R_2 = 1.2768 \text{ \AA}$ $\theta = 160.0^\circ$	$R_1 = 1.2849 \text{ \AA}$ $R_2 = 1.2849 \text{ \AA}$ $\theta = 160.0^\circ$	$R_1 = 1.2757 \text{ \AA}$ $R_2 = 1.2757 \text{ \AA}$ $\theta = 160.0^\circ$
$C_{9h}$ ( <b>4</b> )	$R_1 = 1.2769 \text{ \AA}$ $R_2 = 1.2759 \text{ \AA}$ $\theta_1 = 159.97^\circ$ $\theta_2 = 160.03^\circ$	$R_1 = 1.2846 \text{ \AA}$ $R_2 = 1.2848 \text{ \AA}$ $\theta_1 = 159.99^\circ$ $\theta_2 = 160.01^\circ$	$R_1 = 1.2756 \text{ \AA}$ $R_2 = 1.2758 \text{ \AA}$ $\theta_1 = 159.97^\circ$ $\theta_2 = 160.03^\circ$

CCSD optimized structures of four ring isomers of  $C_{18}$  were given in Fig. 1 and their geometrical parameters were given in Table 2. Table shows some interesting results.

Table 2.  $C_{18}$  structures and relative energies ( $\Delta E$  in kcal/mol) using CCSD theory.

Isomer	D95	D95(d)
$D_{18h}$ ( <b>1</b> )	$R = 1.3087 \text{ \AA}$ $\theta = 160.0^\circ$ $\Delta E = 40.56$	$R = 1.2944 \text{ \AA}$ $\theta = 160.0^\circ$ $\Delta E = 37.16$
$D_{9h}$ Cumulenic ( <b>2</b> )	$R = 1.3080 \text{ \AA}$ $\theta_1 = 157.52^\circ$ $\theta_2 = 162.48^\circ$ $\Delta E = 36.47$	
$D_{9h}$ Acetylenic ( <b>3</b> )	$R_1 = 1.2477 \text{ \AA}$ $R_2 = 1.3976 \text{ \AA}$ $\theta = 160.0^\circ$ $\Delta E = 1.72$	$R_1 = 1.2336 \text{ \AA}$ $R_2 = 1.3833 \text{ \AA}$ $\theta = 160.0^\circ$ $\Delta E = 2.75$
$C_{9h}$ ( <b>4</b> )	$R_1 = 1.2486 \text{ \AA}$ $R_2 = 1.3956 \text{ \AA}$ $\theta_1 = 156.80^\circ$ $\theta_2 = 163.20^\circ$ $\Delta E = 0.00$	$R_1 = 1.2347 \text{ \AA}$ $R_2 = 1.3807 \text{ \AA}$ $\theta_1 = 155.21^\circ$ $\theta_2 = 164.79^\circ$ $\Delta E = 0.00$

Contrary to the results obtained using density functionals in the present study and to those obtained using MP2 calculations available in the literature, the CCSD calculations conclude that the ground state structure of  $C_{18}$  is clearly  $C_{9h}$  acetylenic (**4**). Relative energies calculated at CCSD theory show that the  $C_{9h}$  structure (**4**) of  $C_{18}$  is around 40 kcal/mol more stable than the DFT/MP2-predicted  $D_{18h}$  cumulenic structure (**1**). The present study overcomes the earlier contradictory conclusions and provides the much-needed reliable structure for  $C_{18}$ . All these results and the results obtained for the  $C_{10}$ ,  $C_{14}$ , and  $C_{22}$  carbon clusters will be presented and discussed in the present talk.