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Topological Analysis and Quantum Mechanical Structure of C_4 and C_5 Pure Carbon Clusters

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ABSTRACT

Two bonding models i.e cumullenic and acetylenic models have been proposed to account for the bonding patterns in linear carbon clusters while the bonding patterns in cyclic and 3D geometries of these clusters have remained ambiguous.

This work presents the bonding pattems in various C_4 and C_5 pure clusters at MP2/aug-cc-pVTZ level of theory. This subject is studied in the light of modern bonding theory known as Quantum Theory of Atoms in Molecules, QTAIM.

In linear clusters the ethylene like chemical bonds are reported, while in cyclic and 3D geometries the single and triple C-C bonds are found.

Keywords: Caron clusters; C_4, C_5; QTAIM; Chemical bond

INTRODUCTION

The Chemistry of Carbon and its compounds is one of the main domains of researches since 19th century. It is safe to say that the classical concepts of chemistry like 3D molecules, chemical bond, double bond, have been proposed from this branch. It is interesting to note that less attention has been paid to the nonclassical chemical behavior of Carbon in large amounts of pure carbon compounds known as Carbon clusters which is the main subject of research in chemistry of nanotubes.

The first pioneering work on the molecular orbital calculations of carbon clusters has been reported by Pitzer and Clementi [1]. They suggest the cumullenic C-C bonds for all linear carbon clusters with the almost equally C-C bond distances. It should be mentioned that the acetylenic bond model for linear carbon clusters was also supported by subsequent modern ab-initio calculations. These calculations also provided the information on the existence of cyclic and 3D carbon clusters.

In the process of synthesizing the thin layer of diamond and silicium carbide, these are the carbon clusters that act as the intermediate species. These clusters are synthesized from .the hot carbon plasma, for example, C_{60} was the first molecules which it was synthesized in that condition.

These findings encouraged the researcher to start looking at the small carbon clusters both theoretically and experimentally. The complete review of all studies in this field up to 1989 has been reported by Weltner, et al [2]. By the advent of infrared laser spectroscopy in 1989 the experimental studies on small carbon clusters such as C_4, C_7, C_9 and C_{13} were made possible [3-6]. From 1995 the experimental studies of the anionic and cationic carbon clusters, larger than C_3, started [7]. In this regard many carbon cluster species such as C_3-C_{10} were studied theoretically, by powerful methods such as couple cluster [8-10]. Large size carbon clusters such as C_{28} has

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also been studied theoretically by density functional method (DFT) [11-17].

C_4 in the Rhombic [18,19] and linear [20] forms have been detected experimentally however the third form i.e. tetrahedral geometry has been found theoretically. Two recent theoretical works by Martin and Watt [21,22] characterized the rhombic and linear forms on the potential energy surface (PES) of C_4 at MP2 and QCISD level. However they have not provided clear bonding schemes for these clusters.

Only linear geometry has been detected for the C_5 cluster at triplet electronic state [23]. Cyclic and linear forms have been reported theoretically at singlet electronic state as well [24]. The largest quantum chemical calculations done on the PES of C_5 cluster is CCSD(T) level [25]. These calculations supported the cumullene like bonding model for linear C5 with equal C-C bond distances along the chain. No bonding scheme has been proposed for the cyclic C_5.

In this work we examined the potential energy surfaces of C_4 and C_5 clusters at singlet electronic state and provided a uniform and clear bonding scheme for calculated geometries. This bonding scheme originates from the molecular electron density analysis.

COMPUTATIONAL DETAILS

In order to account for the electron correlation, second order møller pelleset method has been chosen in this study. We find the calculation at this level accessible with our computational resources.

MP2/aug-cc-pVTZ ab-initio model chemistry was used in this work. The optimized geometries of C_4 and C_5 clusters have been characterized by frequency computations. Starting from various initial geometries, two local minima (D_{2h} and $D_{\infty h}$) and two local minima (C_{2v} and D_{3h}) have been characterized on the C_4 and C_5 PES respectively.

The geometries of C_2H_6, C_2H_4 and C_2H_2 molecules have also been calculated at the MP2/aug-cc-pVTZ. These molecules were used as the scale for rationalizing the bonds in carbon clusters. The related wave function files for each geometry were produced at the same theoretical level. All MP2 computations were performed using PC GAMESS7.1 firefly [26]. The electron density analysis was done using the AIM2000 software [27].

RESULTS AND DISCUSSION

The geometries and relative energies of C_4 and C_5 isomers are shown in Fig. 1 and Table 1. While the linear geometry of C_4 is characterized as local minimum on the MP2 potential energy surface, the linear geometry of C_5 is characterized as a second order saddle point at this level (with two imaginary frequencies: -750 and -914 cm^{-1}). The comparison between the total energies of the local minimum geometries shows that the cyclic C_4 (rhombic form) is 63 kcal/mol higher in energy than linear form that mainly due to the large steric effect in this small ring cluster. However in C_5 isomers the C_{2v} form is higher in energy by 7.7 kcal/mol than the D_{3h} form.

Table 1. The relative energies for C_4 and C_5 isomers at MP2/aug-cc-pVTZ

Species	Symmetry	E (a.u.)	E_{rel} (kcal.mol^{-1})
C_4			
	D_{2h}	-151.75364	+63.0
	$D_{\infty h}$	-151.85407	0
C_5			
	C_{2v}	-189.66547	+7.7
	D_{3h}	-189.67770	0

The comparison between C-C distances in the linear and cyclic forms of C_4 and C_5 isomers show that these distances in C_5 is longer than C_4 in average (Fig.1). The C1-C2 distance of 1.589Å in C_5 (C_{2v}) implies the weak interactions between two atoms. It is not distinguishable that at this distance the chemical bond between C1-C2 exists or not. To explore the bonding pattern of the carbon clusters we started looking at the electron density of these species.

Since this paper is based on QTAIM methodology, some relevant important points of this theory seem worth-mentioning although, a detailed discussion may be found elsewhere. By applying the Schwinger's principle of stationary action in quantum mechanics, Bader and coworkers have demonstrated that total electron density of molecule (Rho(r)) is divided to 3D parts with well-defined borders [28]. All these parts or fragments, obey the laws of quantum mechanics and the sum of their properties (the expectation values of hermitian operators) produce the corresponding molecular values [28]. In brief, the theory of open quantum systems allows the division of molecule (as a system) to its fragments (as subsystems) uniquely. Therefore, this partitioning scheme does not depend on how the Schrödinger equation is solved (it is "method" independent) [28]. In comparison to known experimental facts, Bader proposed these fragments as the "chemical atoms" and the theory was called "Quantum Theory of Atoms in Molecules" [28].

Topological analysis of all complexes was first started by searching the critical points (CP) on Rho(r). The Poincare-Hopf rule [28-29] was satisfied in all cases:

$$\mathbf{N}\text{-}\mathbf{b}+\mathbf{r}\text{-}\mathbf{c} = 1 \qquad (1)$$

Where **N** is the number of nuclei, **b** is the number of bond critical points (BCPs), **r** is the number of ring critical points (RCPs) and **c** is the number of cage critical points (CCPs). The mathematical properties of critical points of each carbon cluster are listed in Table 2, the corresponding molecular geometries and molecular graphs are depicted in Fig. 1 and 2. The molecular graph provides the structure of the carbon cluster based on network of bond paths.

Table 2. The mathematical characteristics (ρ_b and $\nabla^2\rho_b$) at bond critical points (BCPs) for C_4 and C_5 isomers at MP2/aug-cc-pVTZ

Species	Connected atoms	Inter nuclear distances (Å)	ρ_b a.u	$\frac{1}{4}\nabla^2\rho_b$ a.u.
C_4 (D_{2h})	C1-C3	1.453	0.275	-0.152
	C2-C3	1.453	0.275	-0.152
	C1-C4	1.453	0.275	-0.152
	C2-C4	1.453	0.275	-0.152
	C3-C4	1.531	0.219	-0.007
C_4 ($D_{\infty h}$)	C1-C3	1.252	0.416	-0.388
	C3-C4	1.267	0.401	-0.379
	C4-C2	1.252	0.416	-0.388
C_5 (C_{2v})	C1-C5	1.394	0.293	-0.196
	C2-C5	1.394	0.293	-0.196
	C1-C3	1.325	0.362	-0.349
	C2-C4	1.325	0.362	-0.349
C_5 (C_{3h})	C1-C4	1.498	0.222	-0.083
	C2-C4	1.498	0.222	-0.084
	C1-C3	1.498	0.222	-0.084
	C2-C3	1.498	0.222	-0.084
	C1-C5	1.498	0.222	-0.085
	C2-C5	1.498	0.222	-0.084
C_5 ($C_{\infty h}$)	C1-C3	1.296	0.379	-0.371
	C3-C5	1.288	0.368	-0.310
	C4-C5	1.288	0.368	-0.310
	C2-C4	1.296	0.379	-0.371

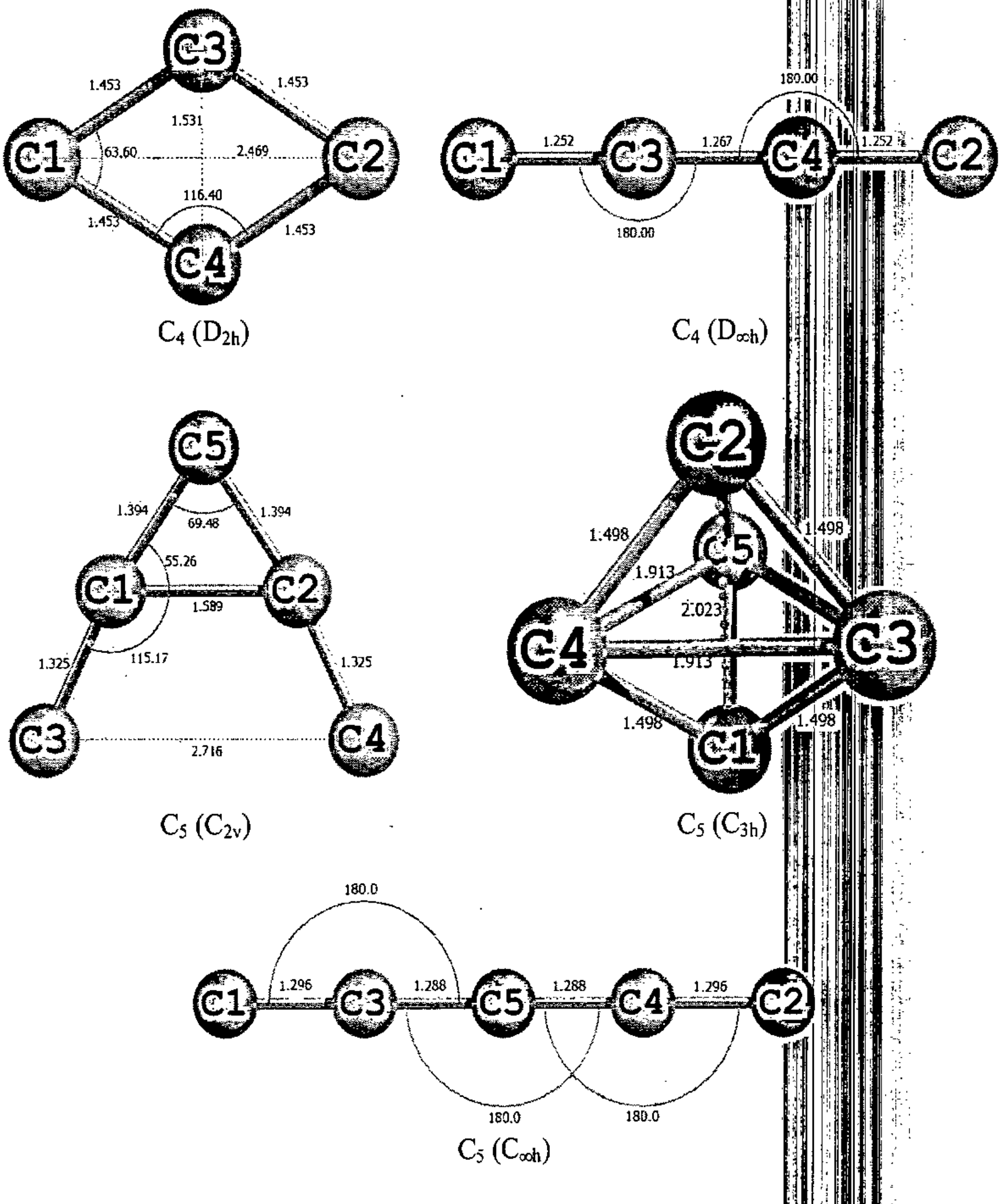
Usually the C-C bonds in C_2H_6, C_2H_4 and C_2H_2 molecules are used as the scale of bonding patterns for carbon clusters. The mathematical properties of the C-C bond critical points are summarized in Table 3.

Table 3. The mathematical caracteristics (ρ_b and $\nabla^2\rho_b$) at bond critical points (BCPs) for C_2H_6, C_2H_4 and C_2H_2 at MP2/aug-cc-pVTZ

Species	C-C distances (Å)	ρ_b a.u	$\frac{1}{4}\nabla^2\rho_b$ a.u.
C_2H_6	1.523	0.247	-0.158
C_2H_4	1.333	0.355	-0.316
C_2H_2	1.212	0.412	-0.319

The molecular graph of C_4 in the cyclic form shows the bond path between C3 and C4 which makes this cluster as bicyclic cluster. However the very close proximity of two RCPs and one BCP gives the topological instability to this cluster, which means that the bond path between C3-C4 is easily broken upon the molecular vibrations. So the cluster will change to topologically stable monocyclic structure. This is an interesting result since the 1.531Å distance between C3 and C4 centers is close to the normal single bond carbon-carbon distance which is not easily broken upon the molecular vibration at room temperature. The comparison between the mathematical characteristics of BCPs in the linear C_4 isomer and that of standard C-C bonds show that the carbon-carbon bonds in this isomer are -essentially acetylene like in nature. These isomers are good examples of the verity non classical bonds which can be found in chemistry of Carbon.

QTAIM analysis of the electron density of the C_{2V} form of the C_5 molecule also provided interesting results. As can be seen in its molecular graph, there is no bond path between C1 and C2 atoms in spite of their 1.589Å distance. Comparison between the properties of electron density at the BCP points in this isomer with that of standard ones listed in Table 3, show that the C1-C5 and C2-C5 bonds are single bonds while two other bonds i.e. C1-C3 and C2-C4 are triple bonds. By using the **single, double and triple (acethylene like) bond** concepts we are trying to show the similarities of bond properties in pure carbon clusters to that of standard scale of classical bonds. In a similar way our analysis shows that C-C bonds in C_{3h} form of the C_5 are similar to that of C-C bond in ethane i.e. classical single bond. Here we found the slight reduction of electron density between C-C which implies a weaker interaction than normal carbon-carbon single bond. The last isomer which we studied its bonding pattern is the linear form of the C_5. As shown in Table 2, all C-C bonds in this isomer resemble that of double bonds in ethylene. Therefore this isomer composed of cumullenic bonds.

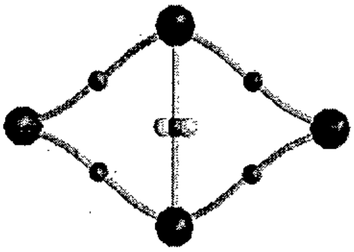


C_4 (D_{2h}) C_4 ($D_{\infty h}$)

C_5 (C_{2v}) C_5 (C_{3h})

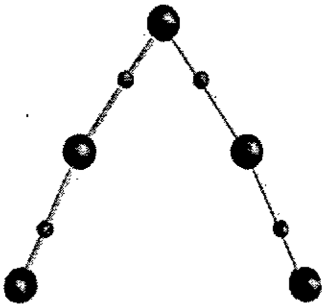
C_5 ($C_{\infty h}$)

Fig. 1. The optimized geometries for C_4 and C_5 isomers at MP2/aug-cc-pVTZ.

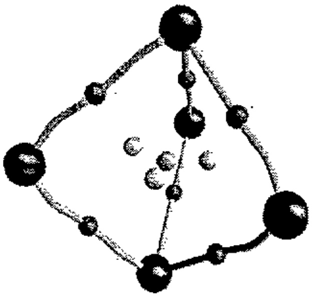


C_4 (D_{2h})

C_4 ($D_{\infty h}$)



C_5 (C_{2v})



C_5 (C_{3h})

C_5 ($C_{\infty h}$)

Fig. 2. The molecular graphs for C_4 and C_5 isomers at MP2/aug-cc-pVTZ.

CONCLUSION

The MP2/aug-cc-pVTZ potential energy surfaces of C_4 and C_5 pure carbon clusters were explored at singlet electronic state. Two local minima with the D_{2h} and $D_{\infty h}$ symmetry point groups have been characterized for C_4 and two local minima with C_{2v} and D_{3h} point groups have been found for C_5 molecule.

Structures of all local minima were assigned based on molecular graphs. These are composed of the bond paths, (the line of maximum electron density), and critical points.

The cyclic form of C_4 is reported as the monocyclic as its stable topological bonding pattern. The bonding between the C-Cs' are all resemble the C-C bonds in acetylene molecule. C_5 in its C_{2v} is reported as the bent chain with single and double bonds topological properties, without any cyclic part. C_5 in its C_{3h} is reported as the hallow cage with the single C-C bonds, however based on the topological properties of its BCPs it is suggested that the C-C bonds are weaker than what is seen in ethane.

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