DFT studies on configurations, stabilities, and IR spectra of neutral carbon clusters

Ping Li*

College of Chemistry, Sichuan University, Chengdu 610064, China

Abstract. The linear chains and monocyclic rings with carbon atoms fewer than 26 were studied at B3LYP/6-311G* level. The change trends that the stabilities of linear chains and monocyclic rings increase with the enlargement of cluster sizes were obtained, respectively. The theoretical calculations for carbon clusters lead to the conclusions that the small linear isomers of $C_3 \sim C_9$ are more stable than the cyclic isomers and the monocyclic isomers contrarily become more stable than the linear isomers as cluster size is larger than C_{10}, which are consistent with those of early UPS and ion chromatography. Comparing with the stabilities of triplet and singlet states of linear clusters, it was confirmed that the triplet states of even-numbered clusters have higher stabilities, and so do the singlet states of odd-numbered clusters contradictorily. The average energies per atom of even-numbered monocyclic rings indicate that (4m+2)-numbered series are aromatic and 4m-numbered series are anti-aromatic. The total energy comparisons give the conclusion that the 2D tetracyclic cluster and the cycloadduts with 24 carbon atoms are absolutely less stable than monocyclic isomer and three fullerenes. Several 3D polycyclic clusters and fullerene with D_{6d} symmetry have middle stabilities. In addition, the theoretical IR spectra of linear chains and odd-numbered monocyclic rings were predicted.

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Key words: carbon cluster, linear chain, monocyclic ring, fullerene, 3D polycyclic cluster

1 Introduction

Carbon clusters attracted both theoretical and experimental attentions due to their peculiar mass spectrum which indicated that carbon atoms have diversities of combinations in gaseous state. [1–4].From the theoretical calculations, many stable configurations were found theoretically, including linear chains, monocyclic rings, polycyclic rings, inflective shaped clusters, graphitic fragments, and fullerenes [5,6]. The linear chains with

*Corresponding author. *Email address:* lp660305@scu.edu.cn (P. Li)

few carbon atoms were verified the most stable isomers and vastly consumed to form monocyclic and polycyclic rings. Electronic absorption spectra verified the existences of even-numbered linear chains and monocyclic rings [7,8]. Ion chromatography of carbon clusters showed that monocyclic rings have lower energy as the number of carbon atoms are more than 10 and always have high yields in ion chromatogram [9–12]. The poly-cyclic rings are the naturally colliding products between linear and monocyclic clusters. These early stage resultants were usually regarded as the precursors of other clusters. The reactive power arises from the triple and double bonds in structures, where the con-tinuous reactions occur till all triple bonds are completely eliminated. Fullerenes without any triple bond become more stable as the numbers of carbon atoms increase. Therefore, small carbon clusters are important to their formations which are composed of stepwise eliminations of triple bonds. The stabilities of those carbon clusters should be determined in comparisons with the stabilities of varieties of carbon clusters.

The arrival time distribution figure being obtained by ion chromatography showed that there are principally three sorts of isomers which touch the detector of equipment in the sequences of fullerenes, polycyclic, and monocyclic clusters [9,11,13]. In order to find the stable carbon clusters, various kinds of structures were suggested theoret-ically, including linear chains, monocyclic rings, and interactive resultants from small carbon clusters, cycloadducts between linear and monocyclic [14–17]. Except the even-numbered monocyclic rings were studied recently, the odd-numbered monocyclic rings and neutrally linear chains have not been studied in details up to now [18–23]. Proposed polycyclic carbon clusters before are incomplete. It is significant to find the resonance structures of odd-numbered monocyclic rings and to predict the stabilities through the change regularities and trends of stabilities of monocyclic rings. Moreover, quantifying the stability differences of various carbon isomers seems important to determine the com-positions of carbon clusters and the formation mechanisms of fullerenes. Quantifying the relative stabilities led to the suggestion that the most possible 3D polycyclic rings are the precursors of fullerenes, which are derived from linear chains and monocyclic rings.

2   Methodology

In order to obtain the change trends of stabilities of linear and monocyclic carbon clus-ters, the density functional calculations at B3LYP/6-311G* level were adopted in this work [24,25]. For geometrical optimizations, the calculations should supply initial or-bital functions with good guess to avoid performing interruption. The fine integral grid in the route section was specified to get the accurately lowest frequencies. Besides, the trend lines of average energy per atom (E/n and $(E+ZPE)/n$) and stabilization energy versus cluster size were plotted. The average energy per atom of a cluster is composed of three parts of energies, involving atomic energy of all carbon atoms, chemical bonding energy, and conjugation energy. Two formers enable the total energy to decrease with the enlargement of cluster size, but the latter occasionally becomes small due to the large