

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

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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 cycloadducts 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, inflexible shaped clusters, graphitic fragments, and fullerenes [5,6]. The linear chains with

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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 polycyclic 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 continuous 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 theoretically, 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 compositions 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 clusters, the density functional calculations at B3LYP/6-311G* level were adopted in this work [24,25]. For geometrical optimizations, the calculations should supply initial orbital 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

strain caused by acute inflexions. Using stabilization energy as well as average energy per atom, the structural stabilities with strains can be reliably quantified. All of calculations for geometries, thermodynamic properties, and IR frequencies were performed with Gaussian 03 program [26].

3 Results and discussion

3.1 Change trend of stabilities of carbon chains

Ultraviolet photoelectron spectra of linear carbon clusters led to the conclusion that the small isomers of $C_3 \sim C_9$ take the form of linear chains and the large isomers of $C_{10} \sim C_{29}$ take the form of monocyclic rings [27]. Recently, carbon chains were observed by transmission electron microscope as electron beam being shot onto the graphene sheet row by row [28]. The vibration spectra of carbon chains indicated that the chains are bending rather than linear as two terminals link with radicals, respectively. This conclusion was supported by calculations simultaneously [29]. For an isolated carbon chain, the optimized geometries show that all bond angles of linear chains are 180° without any bending. The calculations for short carbon chains concluded that the triplet electronic states ($^3\Sigma_g$) of even-numbered clusters have higher stabilities, and contrariwise the singlet electronic states ($^1\Sigma_g$) of odd-numbered clusters contradictorily [27]. The result is consistent with early UPS conclusion that the odd-numbered chains have the singlet state, whilst the even-numbered chains, on the contrary, have the triplet state. This work proved that the foregoing result is also available for long chains. The bond lengths of geometrical optimization exhibit the average tendency, where the conjugate structures are formed. The values distributing from 126.5 to 130.0 pm indicate that the bond strength are between double and triple bonds, which present a the group of active vibration frequencies around 2100cm^{-1} . All linear chains are thermodynamically stable without imaginary frequency. The average energies per atom decrease sharply before C_{14} and smoothly after C_{15} . See Fig. 1. However, carbon linear chains are chemical active molecules since the energy levels of LUMO are very low, especially for even-numbered series, and they possess many triple bonds. See Table 1. They tend to react with other carbon clusters as electrons acceptor.

The linear chains are hard to connect continuously into the long chains. On the one hand, a short chain has high velocity and a relatively long chain occupies wide space so that both of them have high probability of collisions with varieties of clusters. On the other hand, both of them with high reactivity are easy to transform into other kinds of clusters. The calculating results indicated that the collisions between two chains are effective to form monocyclic clusters so long as they approach as paralleling as possible. The $\pi - \pi$ conjugate interactions between two chains are advantageous to form this paralleling attitude, and simultaneously keep certain distance to avoid the connection at the middle of chains. Two terminals have high reactivity as they possess dangling bonds, where they are easy to link with other clusters. Varieties of attachments between chains

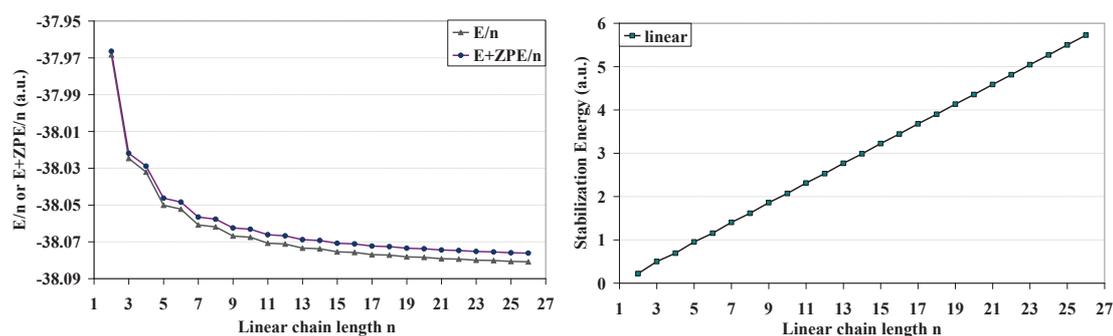


Figure 1: Trend lines of average energy per atom versus n (left) and of stabilization energy versus n (right) of linear chains.

Table 1: Relative stabilized energies and frontier orbital energies of linear chains.

cluster	Sym.	State	E_T (a.u.)	E_T+ZPE (a.u.)	E_{ST} (a.u.)	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	$E_{LUMO}-E_{HOMO}$	Lowest Freq.(cm ⁻¹)
lc-C ₄	D _{∞h}	³ Σ _g	-152.128365	-152.115408	0.691456	-0.3211(Π _g)	-0.2164(Π _g)	0.1047	170.0(Π _u)
lc-C ₆	D _{∞h}	³ Σ _g	-228.313503	-228.290339	1.154411	-0.2961(Π _u)	-0.2127(Π _u)	0.0834	102.6(Π _u)
lc-C ₈	D _{∞h}	³ Σ _g	-304.494974	-304.461589	1.613685	-0.2805(Π _g)	-0.2099(Π _g)	0.0706	63.6(Π _u)
lc-C ₁₀	D _{∞h}	³ Σ _g	-380.675031	-380.631469	2.071589	-0.2696(Π _u)	-0.2079(Π _u)	0.0617	42.1(Π _u)
lc-C ₁₂	D _{∞h}	³ Σ _g	-456.854280	-456.800951	2.529095	-0.2616(Π _g)	-0.2063(Π _g)	0.0553	29.6(Π _u)
lc-C ₁₄	D _{∞h}	³ Σ _g	-533.033090	-532.969589	2.985757	-0.2555(Π _u)	-0.2050(Π _u)	0.0505	21.9(Π _u)
lc-C ₁₆	D _{∞h}	³ Σ _g	-609.211561	-609.138468	3.442660	-0.2505(Π _g)	-0.2040(Π _g)	0.0465	16.8(Π _u)
lc-C ₁₈	D _{∞h}	³ Σ _g	-685.389816	-685.307103	3.899319	-0.2465(Π _u)	-0.2031(Π _u)	0.0434	13.3(Π _u)
lc-C ₂₀	D _{∞h}	³ Σ _g	-761.567950	-761.475222	4.355462	-0.2432(σ _g)	-0.2024(σ _g)	0.0408	10.8(Π _u)
lc-C ₂₂	D _{∞h}	³ Σ _g	-837.745944	-837.643675	4.811939	-0.2403(Π _u)	-0.2017(Π _u)	0.0386	8.9(Π _u)
lc-C ₂₄	D _{∞h}	³ Σ _g	-913.923867	-913.811602	5.267890	-0.2379(Π _g)	-0.2012(Π _g)	0.0367	7.5(Π _u)
lc-C ₂₆	D _{∞h}	³ Σ _g	-990.101698	-989.979962	5.724274	-0.2357(Π _u)	-0.2007(Π _u)	0.0350	6.4(Π _u)
lc-C ₃	D _{∞h}	¹ Σ _g	-114.073963	-114.065760	0.497796	-0.3388(Σ _u)	-0.1698(Π _g)	0.1690	107.9(Π _u)
lc-C ₅	D _{∞h}	¹ Σ _g	-190.250595	-190.231422	0.951482	-0.3335(Π _g)	-0.1818(Π _u)	0.1517	118.7(Π _u)
lc-C ₇	D _{∞h}	¹ Σ _g	-266.425705	-266.395703	1.403787	-0.3068(Π _u)	-0.1874(Π _g)	0.1194	76.6(Π _u)
lc-C ₉	D _{∞h}	¹ Σ _g	-342.601512	-342.561911	1.858019	-0.2895(Π _g)	-0.1904(Π _u)	0.0991	48.4(Π _u)
lc-C ₁₁	D _{∞h}	¹ Σ _g	-418.777849	-418.727695	2.311827	-0.2772(Π _u)	-0.1923(Π _g)	0.0849	33.6(Π _u)
lc-C ₁₃	D _{∞h}	¹ Σ _g	-494.954457	-494.894846	2.767002	-0.2680(Π _g)	-0.1935(Π _u)	0.0745	24.4(Π _u)
lc-C ₁₅	D _{∞h}	¹ Σ _g	-571.131256	-571.062005	3.222185	-0.2609(Π _u)	-0.1943(Π _g)	0.0666	18.5(Π _u)
lc-C ₁₇	D _{∞h}	¹ Σ _g	-647.308219	-647.228779	3.676983	-0.2551(Π _g)	-0.1949(Π _u)	0.0602	14.6(Π _u)
lc-C ₁₉	D _{∞h}	¹ Σ _g	-723.485242	-723.396269	4.132497	-0.2504(Π _u)	-0.1953(Π _g)	0.0551	11.7(Π _u)
lc-C ₂₁	D _{∞h}	¹ Σ _g	-799.662361	-799.563229	4.587481	-0.2464(Π _g)	-0.1956(Π _u)	0.0508	9.6(Π _u)
lc-C ₂₃	D _{∞h}	¹ Σ _g	-875.839502	-875.730900	5.043176	-0.2430(Π _u)	-0.1959(Π _g)	0.0471	8.1(Π _u)
lc-C ₂₅	D _{∞h}	¹ Σ _g	-952.016679	-951.898560	5.498860	-0.2401(Π _g)	-0.1961(Π _u)	0.0440	6.8(Π _u)

Note: $E_{ST} = E_n - (E_T + ZPE)$, $E_n = nE_C$, $E_C = -37.855988$ a.u..

form different cyclic clusters. Once the monocyclic cluster forms, the collisions between linear and monocyclic clusters occur, and so do the collisions between two monocyclic clusters.

3.2 Change trend of stabilities of monocyclic carbon rings

The monocyclic rings are a kind of planar cyclic polynes with large π conjugate bonds which all of p_z orbitals vertical to ring overlap. Analogous to the organic aromatics, the

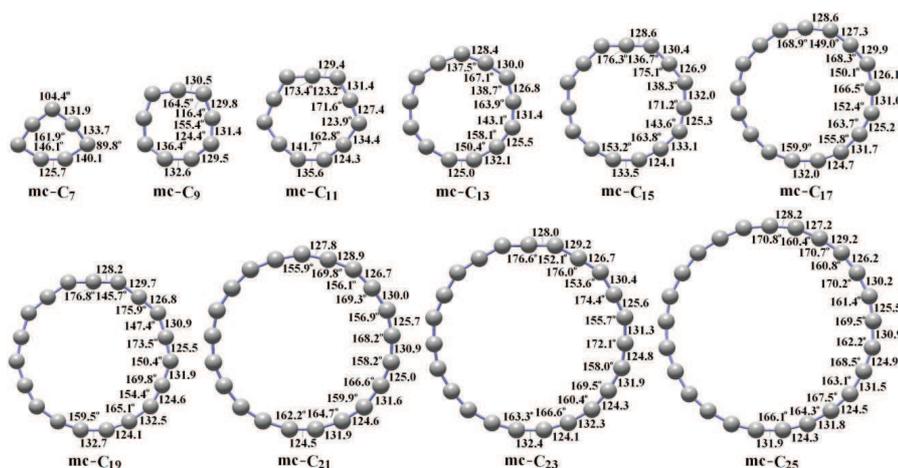


Figure 2: Optimized structures of odd-numbered monocyclic clusters at B3LYP/6-311G* level (bond length in pm).

monocyclic clusters are divided into three series, odd-numbered series with C_{2v} symmetry, $4m$ -numbered series with C_{2mh} symmetry, and $(4m+2)$ -numbered series with $D_{(2m+1)h}$ symmetry [22,30]. Their geometries revealed that both odd-numbered and $4m$ -numbered series have alternative double and triple bonds, respectively. See Fig. 2 and Fig. 3. However, the bond lengths are identical for $(4m+2)$ -numbered monocyclic rings with carbon atoms fewer than 20, and are different for those with carbon atoms more than 20. The reason of causing this geometrical difference may be that the increases of ring size are advantageous to orbital overlaps between adjacent atoms which align the center of rings.

The $(4m+2)$ -numbered series show the Hückel aromaticities, because not only the number of electrons satisfy $(4m+2)$ rule, but also the average energies per atom decrease to relatively minimum points in E-n curve in comparison with the values of adjacent monocyclic rings. See Fig. 4. The conjugate effects for small $(4m+2)$ -numbered monocyclic rings with atoms fewer than 20 are most evident and show the periodic structures which repeat according to the unit of two adjacent bonds with larger bond angle. The periodic structures keep the same repeating unit as ring size enlarges over C_{22} , but the bond lengths of these structural units show the different characteristics of alternative double and triple bonds. See Fig. 3. This result is consistent with that obtained by Saito and his co-workers that the smaller $(4m+2)$ -numbered monocyclic rings are more stable than the larger rings [30]. However, calculations in this work proved that the structures of larger monocyclic rings are thermodynamically stable structures without imaginary frequency. The conjugate effects are more evident than $4m$ -numbered monocyclic rings by comparing the bond lengths of two series of clusters.

The odd-numbered series have relatively high energies in comparison with adja-

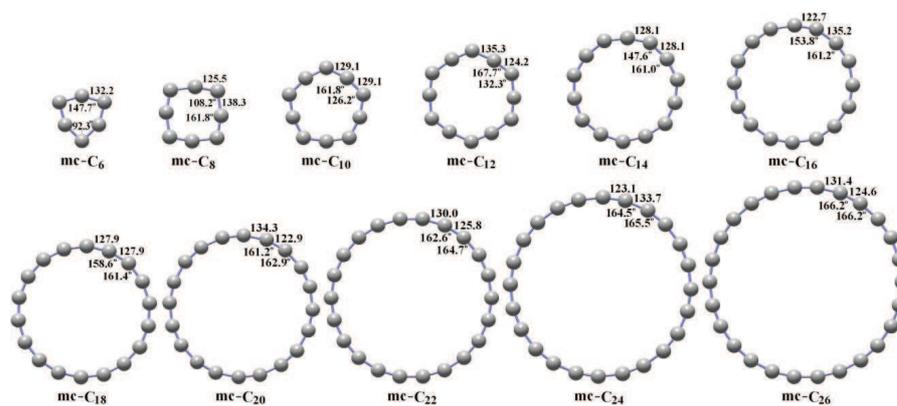


Figure 3: Optimized structures of even-numbered monocyclic clusters at B3LYP/6-311G* level (bond length in pm).

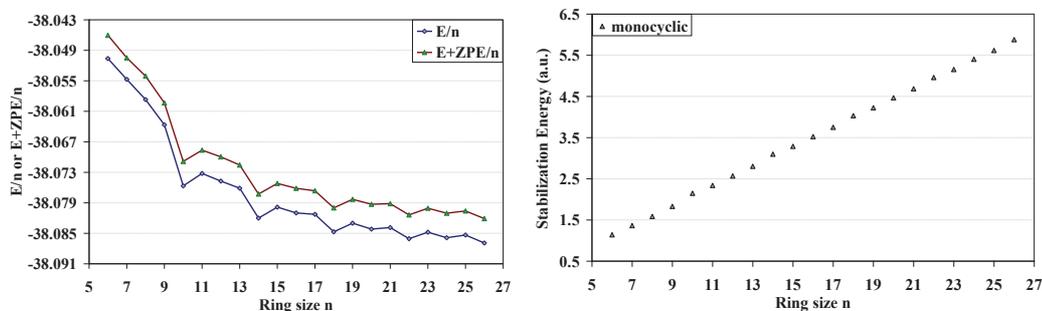


Figure 4: Trend lines of average energy per atom versus n (left) and stabilization energy versus n (right) of monocyclic rings.

cent even-numbered series. The change trend of average energy per carbon atom indicates that the stabilities of $4m$ -numbered series are between $(4m+2)$ -numbered and odd-numbered series. See Fig. 4. The C_9 ring is an exception. Unlike other odd-numbered monocyclic rings, it is a non-planar molecule without any conjugate triple bond. The maximum frequency of 1841.5cm^{-1} is much lower than those of about 2050cm^{-1} of conjugate triple bonds.

The change trends that the average energies per atom decrease with the enlargement of cluster sizes are available not only for linear chains but also for monocyclic rings. See Fig. 1 and Fig. 4. Moreover, the magnitude of decreasing becomes smaller and smaller after C_{18} . This can be explained by the changes of structures that the increases of bond angles lead to the increases of overlap between p_z orbitals aligning to the center of rings. Using the stabilization energy instead of average energy per atom, the change trends turn into the increases with the enlargement of cluster sizes, as shown in right diagram of Fig. 4. Calculations proved that the proposed resonance structures of larger monocyclic rings are most stable as the change trend of average energy per atom shows.

Comparing with two trend lines of the average energy per atom versus cluster size, the intersection point was determined at C_{10} . See Fig. 4. It should be observed that the decreases of monocyclic rings are larger than those of linear chains after C_{10} . This result elucidated the experimental conclusion that monocyclic rings are more stable than linear chains as the numbers of carbon atoms are more than 10 [9]. In contrast to foregoing result, the linear chains become more stable than monocyclic rings as the numbers of carbon atoms are fewer than 10.

There are some stable and metastable resonance structures for every monocyclic cluster. These resonance structures are quite different with different average energies and stabilities. The monocyclic $mc-C_{12}$ has two stable resonance structures of $mc-C_{12}(a)$ and $mc-C_{12}(b)$, and one unstable $mc-C_{12}(c)$ with an imaginary frequency. They have C_{6h} , D_{6h} , and D_{6d} symmetries, respectively. See Fig. 5. The conversion between two stable isomers was supposed but is irreversible under the common condition.

For the conversion, $C_{12}(b) = C_{12}(a)$ at standard state with 298.15 K, the Gibbs energy change, and the entropy change are $-97.23 \text{ kJ}\cdot\text{mol}^{-1}$, $-102.44 \text{ kJ}\cdot\text{mol}^{-1}$, and $-17.47 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively. At 2000 K, these values increase to $-77.35 \text{ kJ}\cdot\text{mol}^{-1}$, $-94.86 \text{ kJ}\cdot\text{mol}^{-1}$, and $-2.09 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, correspondingly. The conversion is hard to reverse due to still very low Gibbs energy change at 2000 K. The change values of these thermodynamic variables increase with temperature elevation. The conversion is spontaneously exothermic due to the negative value of enthalpy change and may undergo the metastable state of $mc-C_{12}(c)$. However, some of the odd-numbered monocyclic clusters have resonance structures with little energy differences and show almost the same thermodynamic stabilities. Monocyclic $mc-C_{13}$ has two resonance structures of $mc-C_{13}(a)$ and $mc-C_{13}(b)$. The $mc-C_{13}(a)$ is slightly more stable than the $mc-C_{13}(b)$. See Fig. 5. In this case, the conversion between two resonance structures, $C_{13}(a) = C_{13}(b)$, needs little energy. At standard state, the Gibbs energy change, the entropy change, and the enthalpy change of reaction are $2.58 \text{ kJ}\cdot\text{mol}^{-1}$, $-8.66 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, and zero, respectively. The standard equilibrium constant of reaction is 0.353. The entropy and the enthalpy changes are invariable as temperature elevation, but the Gibbs energy change increases with temperature elevation, which satisfy the formulae $\Delta_r G_m = \Delta_r H_m - T\Delta_r S_m$. Other monocyclic rings have the similar resonance structures.

Comparing monocyclic rings with carbon chains, the former has far less reactivity

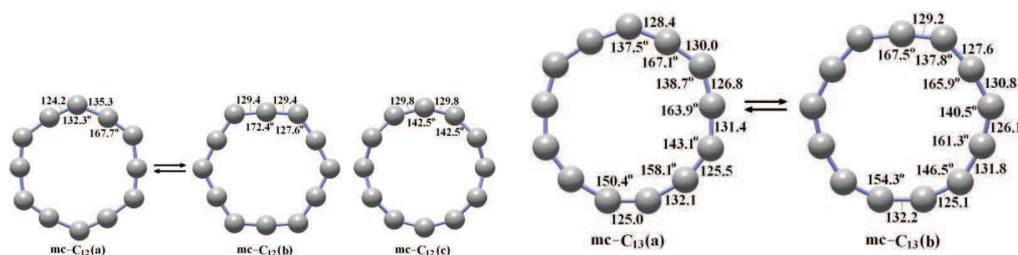


Figure 5: Three resonance structures of $mc-C_{12}$ (left) and two resonance structures of $mc-C_{13}$ (right).

Table 2: Relative stabilized energies and frontier orbital energies of monocyclic clusters.

cluster	Sym.	State	E_T (a.u.)	E_T+ZPE (a.u.)	E_{ST} (a.u.)	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	$E_{LUMO}-E_{HOMO}$	Lowest Freq.(cm ⁻¹)
mc-C ₆	D _{3h}	¹ A ₁ '	-228.303695	-228.276288	1.140360	-0.3097(E')	-0.1652(A' ₁)	0.1445	431.3(A'' ₂)
mc-C ₈	D _{4h}	¹ A _g	-304.469525	-304.432620	1.584716	-0.2345(B _u)	-0.1343(B _u)	0.1002	119.9(B _g)
mc-C ₁₀	D _{5h}	¹ A ₁ '	-380.756681	-380.708689	2.148809	-0.2777(E' ₂)	-0.0814(E'' ₂)	0.1963	187.1(E' ₂₄)
mc-C ₁₂ (a)	D _{6h}	¹ A _g	-456.896701	-456.839527	2.567671	-0.2300(B _g)	-0.1454(B _g)	0.0846	109.2(E _{2g})
mc-C ₁₂ (b)	D _{6h}	¹ A _{1g}	-456.863487	-456.800883	2.529027	-0.2032(B _{1g})	-0.1793(B _{2g})	0.0239	48.1(B _{1g})
mc-C ₁₂ (c)	D _{6d}	¹ A ₁	-456.882465	-456.831787	2.559931	-0.2323(E ₃)	-0.1464(E ₃)	0.0859	434.8i
mc-C ₁₄	D _{7h}	-	-533.148185	-533.081912	3.098080	-0.2531	-0.1109	0.1422	99.7
mc-C ₁₆	C _{8h}	-	-609.295857	-609.218438	3.522630	-0.2260	-0.1439	0.1092	74.2
mc-C ₁₈	D _{9h}	-	-685.524781	-685.439908	4.032124	-0.2416	-0.1277	0.1139	61.3
mc-C ₂₀	C _{10h}	-	-761.683428	-761.585943	4.466183	-0.2247	-0.1489	0.0758	48.6
mc-C ₂₂	D _{11h}	-	-837.893482	-837.790594	4.958858	-0.2362	-0.1379	0.0983	19.8
mc-C ₂₄	C _{12h}	-	-914.060941	-913.945279	5.401567	-0.2241	-0.1525	0.0716	34.1
mc-C ₂₆	D _{13h}	-	-990.259799	-990.135121	5.879433	-0.2343	-0.1424	0.0919	29.5
mc-C ₇	C _{2v}	¹ A ₁	-266.383084	-266.353347	1.361431	-0.2411(A ₁)	-0.1300(B ₁)	0.1111	278.7(B ₁)
mc-C ₉	C ₂	¹ A	-342.572901	-342.534135	1.830243	-0.2464(B)	-0.1703(A)	0.0761	43.3(B)
mc-C ₁₁	C _{2v}	¹ A ₁	-418.805410	-418.755048	2.339180	-0.2162(B ₂)	-0.1473(A ₂)	0.0689	25.0(B ₂)
mc-C ₁₃ (a)	C _{2v}	¹ A ₁	-494.989675	-494.930518	2.802674	-0.2274(A ₂)	-0.1770(B ₂)	0.0504	5.1(B ₂)
mc-C ₁₃ (b)	C _{2v}	¹ A ₁	-494.989676	-494.930504	2.802660	-0.2274(B ₁)	-0.1770(A ₁)	0.0504	9.3(B ₂)
mc-C ₁₅	C _{2v}	¹ A ₁	-571.197658	-571.127811	3.287991	-0.2091(B ₂)	-0.1572(A ₂)	0.0519	29.0(B ₂)
mc-C ₁₇	C _{2v}	¹ A ₁	-647.381691	-647.302837	3.751041	-0.2205(B ₁)	-0.1802(A ₁)	0.0403	6.0(B ₂)
mc-C ₁₉	C _{2v}	¹ A ₁	-723.577112	-723.488047	4.224275	-0.2050(B ₂)	-0.1638(A ₂)	0.0412	8.8(B ₂)
mc-C ₂₁	C _{2v}	¹ A ₁	-799.761103	-799.662571	4.686823	-0.2157(A ₂)	-0.1819(B ₂)	0.0338	4.4(B ₂)
mc-C ₂₃	C _{2v}	¹ A ₁	-875.950150	-875.841670	5.153946	-0.2029(B ₂)	-0.1686(A ₂)	0.0343	7.6(B ₂)
mc-C ₂₅	C _{2v}	¹ A ₁	-952.133650	-952.015202	5.615502	-0.2122(B ₁)	-0.1827(A ₁)	0.0295	0.7(B ₂)

than the latter. (4m+2)-numbered series show the chemical stabilities that they have higher energy levels of LUMO and wider HOMO-LUMO gaps than 4m-numbered series, and are consistent with the aromatic stabilities. The reactivity of odd-numbered rings gradually increase with the enlargement of ring size since the energy levels of LUMO increase and the HOMO-LUMO gap become narrow. See Table 2.

3.3 Cycloadducts derived from two monocyclic rings

The cycloadducts were demonstrated a sort of thermodynamically stable carbon clusters which were first suggested by Strout and his coworkers [31]. A group of cycloadducts with 24 carbon atoms were designed in this work and their stabilization energies were obtained at the same calculation level in order to find the most stable isomers among all C₂₄ carbon clusters. The third ring is usually formed at joint between two monocyclic rings. It was called [2+4] cycloadduct that two carbon atoms of first ring and four of second ring construct the third ring with 2+4 carbon atoms. Early studies stated that the [2+4] and [4+6] cycloadditions with 4m+2 electrons analogous to organic aromatics are able to produce stable cycloadducts [32]. The [2+2] cycloaddition between two monocyclic rings give a large monocyclic cluster [14]. The consistency result was also obtained in this work and illustrated in Fig. 6.

The optimized geometries of these 3D polycyclic rings exhibit serious deformations. The arched chains are composed of polyne loops with conjugations being interrupted

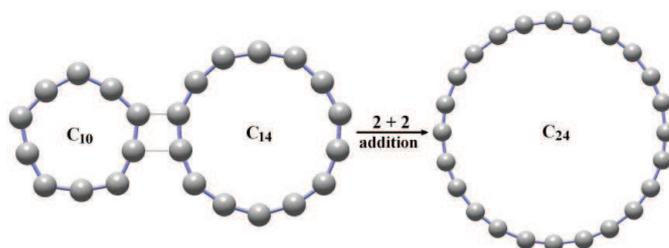


Figure 6: [2+2] cycloaddition between mc-C₁₀ and mc-C₁₄ forming a large monocyclic ring C₂₄.

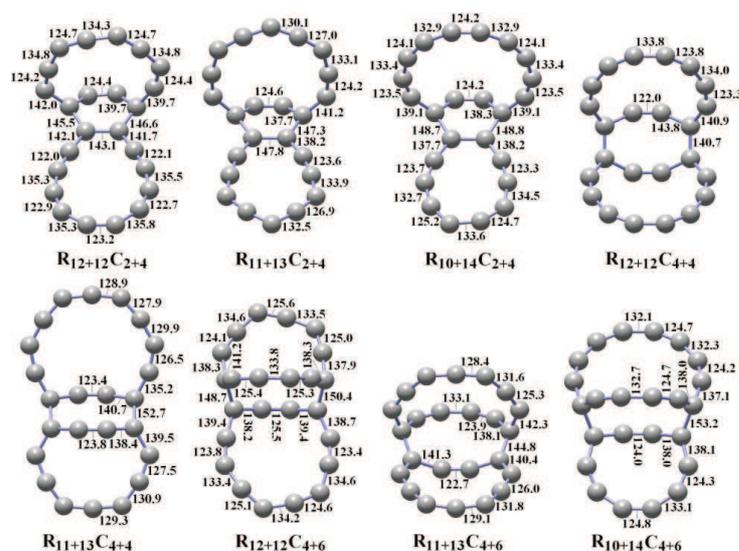


Figure 7: Optimized structures of cycloadducts with 24 carbon atoms at B3LYP/6-311G* level (bond length in pm).

at joints where the single C-C bonds are formed. See Fig. 7. This is one of the reasons why their stabilization energies are less than those of monocyclic isomers and even those of linear isomers. The collision between two rings should be in staggering face-to-face orientation in order to satisfy the maximum overlap of p_z orbitals perpendicular to the rings. The geometries at joints indicate that the hybridization of joint carbon atoms transforms from sp to sp^3 . The ring strains increase so that the parent rings deform to fit these changes. The spatial conformations are similar to those higher cycloadducts obtained by Strout and his coworkers [14]. See Fig. 7. The cycloadducts of [4+4] addition were considered as anti-aromatic resultants which the third rings have eight π electrons. According to the stabilization energy and energy gap, it was reconfirmed that the [4+4] cycloadducts are less stable than the [2+4] and [4+6] cycloadducts. Some cycloadducts derived from smaller monocyclic clusters were not discussed as those with carbon atoms fewer than 10 have low abundances. However, the stabilization energies at B3LYP/6-311G* level indi-

Table 3: Relative stabilized energies and frontier orbital energies of cycloadducts.

Adducts	Sym.	State	E_T (a.u.)	E_T+ZPE (a.u.)	E_{ST} (a.u.)	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	Lowest Freq.(cm ⁻¹)	D.M. (Debye)
R ₁₂₊₁₂ C ₂₊₄	C ₁	¹ A	-913.875302	-913.755602	5.211890	-0.2277(A)	-0.1493(A)	31.0(A)	0.707
R ₁₀₊₁₄ C ₂₊₄	C ₁	¹ A	-913.914852	-913.795578	5.251866	-0.2396(A)	-0.1318(A)	27.7(A)	0.871
R ₁₁₊₁₃ C ₂₊₄	C ₁	¹ A	-913.866701	-913.749090	5.205378	-0.2319(A)	-0.1819(A)	29.7(A)	3.438
R ₁₂₊₁₂ C ₄₊₄	C ₁	¹ A	-913.898918	-913.779620	5.235908	-0.2292(A)	-0.1350(A)	50.4i(A)	0.560
R ₁₁₊₁₃ C ₄₊₄	C _s	¹ A'	-913.854979	-913.736181	5.192469	-0.2298(A')	-0.1604(A')	42.3(A')	2.498
R ₁₂₊₁₂ C ₄₊₆	C ₁	¹ A	-913.860062	-913.740397	5.196685	-0.2316(A)	-0.1559(A)	49.7(A)	0.671
R ₁₀₊₁₄ C ₄₊₆	C ₁	¹ A	-913.895954	-913.776943	5.233231	-0.2402(A)	-0.1335(A)	47.4(A)	0.090
R ₁₁₊₁₃ C ₄₊₆	C ₁	¹ A	-913.869932	-913.751763	5.208051	-0.2325(A)	-0.1785(A)	46.1(A)	2.133

cate that the stabilities of cycloadducts are as a whole less stable than those of graphitic, monocyclic, and fullerene isomers. See Table 3. Cycloadduct structures still have many triple bonds and are very reactivity. They are able to react with linear chains continuously to grow into fullerenes, which have tetragons or heptagons or adjacent pentagons with low symmetries. The most possibility is that a cycloadduct converts into a larger monocyclic ring or tadpole structures.

3.4 3D polycyclic clusters derived from monocyclic rings and linear chains

According to the foregoing results that short linear chains are more abundant than monocyclic isomers in capsule, the possible reactions with monocyclic clusters may happen. This kind of reaction requires certain orientations for linear chains and monocyclic rings. The terminal atoms of chains attaching to the circumferences of monocyclic rings lead to the formation of 3D polycyclic clusters. The structures of resultants show that the triple bonds at the joints are broken and the deformation happens, but the characteristics of polyynes are unchanged. See Fig. 8. These combinations are diversified. The tadpole structures were suggested by Dugourd from high resolution ion chromatography [33]. One of tadpole with 24 atoms, L₂R₂₂, was calculated, which has middle stability. The most possible combinations are that two terminal atoms simultaneously combine with two remote atoms of monocyclic circumference as the lengths of linear chains match the diameters of monocyclic rings. Several possible resultants with 24 carbon atoms derived from short linear chains and monocyclic clusters were first suggested in this work and the optimized structures were illustrated in Fig. 8. The stabilization energies indicate that the L₆R₁₈ is the most stable due to the good geometrical match. See Table 4. When the carbon chains are shorter than the diameters of monocyclic rings, the monocyclic rings deform to the ellipse shape in order to link with chains. See the L₅R₁₉(b). Contrariwise, the combinations between long chains and relatively small rings either lead to the bending of parent chains or cause the curvature of parent ring, which may form polygon at joints. See the L₇R₁₇ and L₈R₁₆. Besides L₆R₁₈, both L₄R₂₀ and L₅R₁₉(a) are very stable too in comparison with the remains and have higher stability than the corresponding cycloadducts and linear isomers.

The maximum overlaps between the non-bonding p_x orbitals of two terminal atoms

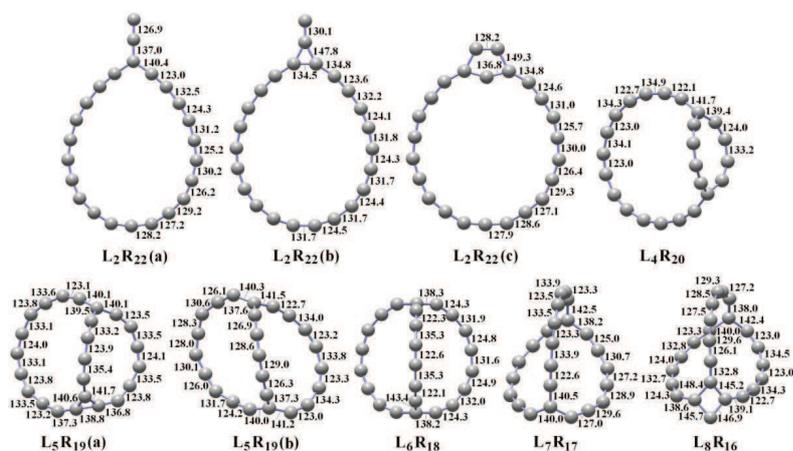


Figure 8: Optimized structures of 2D and 3D polycyclic clusters with 24 carbon atoms at B3LYP/6-311G* level (bond length in pm).

of chains and the p_z orbitals of carbon atom of rings lead parent chains bending to arched shape. Since the hybridization of carbon atoms at joints transforms from sp to sp^2 , the parent planar rings curve to fit this bonding. The structures have the characteristics that the even-numbered arches lose some conjugation with triple and double bonds alternately and the odd-numbered arches gain some conjugation with the average bond lengths. The C-C bonds at joints are longer than isolated double bond. These kinds of clusters with three loops have high reactivity due to many triple bonds. These 3D polycyclic rings are strongly suggested as the precursors of fullerenes, because they have high stabilities and are able to react with abundantly short chains. The reactions lead to the formations of triangles, tetragons, pentagons, and arched chains. These arched chains approach so that they are able to link together. Further linkages in themselves and combinations with short carbon chains eliminate the triple bonds and change the stereoscopic structures of polycyclic clusters.

Fullerenes from these 3D polycyclic clusters have low symmetries in which structures construct some tetragons and other polygons. Since the fullerene with tetragon has already been synthesized recently, the formation mechanism from 3D polycyclic clusters is possible to happen [34]. Other thermodynamically stable resultants are suggested and the optimized structures are illustrated in Fig. 8. One of structures $L_2R_{22}(c)$ with a pentagon is formed as C_2 fragments strike to the rings of $mc-C_{22}$ in the orientation of paralleling. Moreover, the frontier orbital symmetry of C_2 matches that of $mc-C_{22}$. Most of 3D polycyclic isomers are stable than the cycloadducts being derived from two monocyclic rings. The calculation results that structures of $L_5R_{19}(a)$ and L_8R_{16} with trigon and tetragon are stable clusters respectively indicate that the affections of ring strains on the stabilities of polycyclic clusters are not dominant. It is consistent with recent conclusion that three C_{24} fullerenes with tetragons have high stabilities in comparison with other

Table 4: Relative stabilized energies and frontier orbital energies of 3D polycyclic clusters.

Clusters	Sym.	State	E_T (a.u.)	E_T+ZPE (a.u.)	E_{ST} (a.u.)	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	Lowest Freq.(cm ⁻¹)	D.M. (Debye)
L ₂ R ₂₂ (a)	C ₅	¹ A'	-913.953524	-913.839660	5.295948	-0.2271(A')	-0.1907(A')	29.7(A')	11.190
L ₂ R ₂₂ (b)	C ₅	¹ A'	-913.945475	-913.832021	5.288309	-0.2330(A')	-0.1497(A'')	29.8(A')	4.975
L ₂ R ₂₂ (c)	C ₅	¹ A'	-913.890925	-913.778976	5.235264	-0.2162(A'')	-0.1617(A'')	36.4(A'')	0.758
L ₃ R ₂₁	C ₂	¹ A	-913.916296	-913.800697	5.256985	-0.2304(A)	-0.1339(B)	422.1i	0.839
L ₄ R ₂₀	C ₂	¹ A	-913.970882	-913.851978	5.308266	-0.2231(A)	-0.1509(B)	42.6(B)	0.529
L ₅ R ₁₉ (a)	C ₁	¹ A	-913.967793	-913.847947	5.304235	-0.2252(A)	-0.1366(A)	48.4(A)	1.558
L ₅ R ₁₉ (b)	C ₁	¹ A	-913.925270	-913.809739	5.266027	-0.2141(A)	-0.1587(A)	32.0(A)	1.552
L ₆ R ₁₈	C ₅	¹ A'	-913.972335	-913.854044	5.310332	-0.2172(A')	-0.1593(A')	53.7(A'')	0.755
L ₇ R ₁₇	C ₁	¹ A	-913.929611	-913.813511	5.269799	-0.2217(A)	-0.1581(A)	39.5(A)	1.353
L ₈ R ₁₆	C ₁	¹ A	-913.881127	-913.763834	5.220122	-0.2207(A)	-0.1593(A)	53.3(A)	1.855

carbon clusters [35].

3.5 Small fullerenes, graphitic cluster, and 2D polycyclic ring with 24 atoms

Theoretical calculations proved that there are four stable fullerenes for C₂₄ carbon clusters, which were reproduced in this work in order to compare them with linear chains, monocyclic rings, and 3D polycyclic rings at the same B3LYP/6-311G* level. See Fig. 9. The consistency results were obtained that three isomers with tetragon unit are obviously more stable than the usual D_{6d} isomer [35]. The stabilization energy of the most stable fullerene f-C₂₄(a) is 179.2kJ·mol⁻¹ higher than that of monocyclic isomer mc-C₂₄ and is 164.4kJ·mol⁻¹ higher than that of graphitic isomer g-C₂₄. These fullerenes have lowest chemical reactivity in comparison with graphitic and monocyclic and linear isomers. The stability of graphitic cluster catches up with that of most stable monocyclic isomer due to the very small energy difference of 14.8kJ·mol⁻¹.

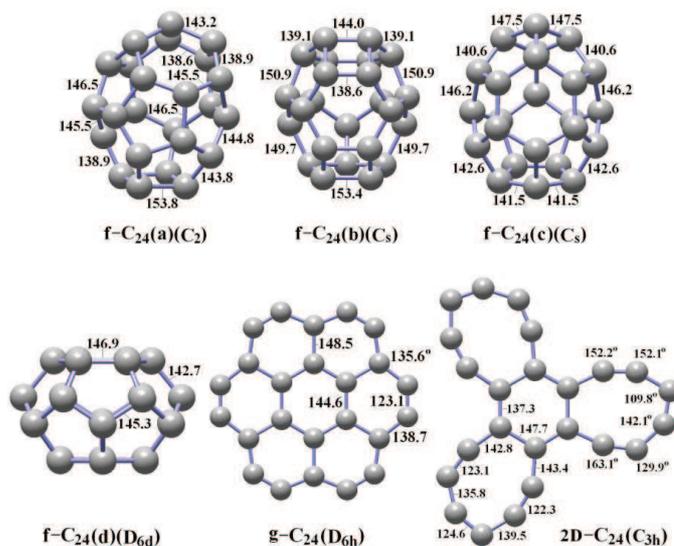
Comparing the stabilities of four fullerenes with those of other carbon clusters, it was obtained that four fullerene isomers are relatively less stable than the monocyclic and planar graphitic isomers, but are evidently more stable than the cycloadducts, 3D polycyclic isomers, 2D tetracyclic ring, and linear chain, as shown in table from 1 to 5. According to the aforementioned discussions for the relative stabilities of C₂₄, it can be concluded that monocyclic, planar graphitic, fullerenes, and some 3D polycyclic clusters are possible carbon clusters contributing to the mass intensity.

3.6 IR spectra

The IR spectra of linear chains have characteristic bands, from 1450 to 1750cm⁻¹ and from 2000 to 2300cm⁻¹, which belong to the stretching vibration of double and triple bonds, respectively. The bands from 1750 to 2000cm⁻¹ appear as the chains lengthen which are attributed to the conjugated bonds. With the mathematical induction, the general formulae of irreducible representations of odd-numbered and even-numbered clusters

Table 5: Comparison of relative stabilities of various carbon clusters C_{24} .

Fullerene	Sym.	State	E_T (a.u.)	E_T+ZPE (a.u.)	E_{ST} (a.u.)	R.E. $\text{kJ}\cdot\text{mol}^{-1}$	E_{HOMO} (a.u.)	E_{LUMO} (a.u.)	Lowest Freq.(cm^{-1})
mc- C_{24}	C_{12h}	–	-914.060941	-913.945279	5.401567	636.70	-0.2241	-0.1525	34.1
g- C_{24}	D_{6h}	$^1A_{1g}$	-914.068495	-913.939650	5.395938	621.93	-0.2512(E_{2u})	-0.1222(A_{2g})	74.8(E_{2u})
f- C_{24} (a)	C_2	1A	-914.015581	-913.877008	5.333296	457.52	-0.2310(B)	-0.1385(B)	310.0(A)
f- C_{24} (b)	C_S	$^1A'$	-914.010043	-913.872061	5.328349	444.54	-0.2215(A')	-0.1414(A'')	305.2(A'')
f- C_{24} (c)	C_S	$^1A'$	-914.007535	-913.870278	5.326566	439.86	-0.2240(A'')	-0.1542(A')	157.0(A'')
f- C_{24} (d)	D_{6d}	3A_1	-913.967277	-913.817455	5.273743	301.22	-0.1986(E_4) α	-0.1596(E_1) α	198.1(E_4)
							-0.2193(E_3) β	-0.1492(E_3) β	
lc- C_{24}	$D_{\infty h}$	$^3\Sigma_g^-$	-913.923867	-913.811602	5.267890	285.86	-0.2379(Π_g)	-0.2012(Π_g)	7.5(Π_u)
2D- C_{24}	C_{3h}	$^1A'$	-913.823397	-913.702683	5.158971	0.0	-0.2437(E')	-0.1269(E'')	56.6(A'')

Figure 9: Thermodynamically stable fullerenes, planar graphitic cluster and 2D tetracyclic ring of C_{24} (bond length/pm).

are respectively expressed as,

$$\Gamma_{odd} = \frac{2}{n-1} \sum_g + \frac{2}{n-1} \sum_u + (n-3) \Pi_g + (n-1) \Pi_u$$

$$\Gamma_{even} = \frac{2}{n} \sum_g + \left(\frac{2}{n} - 1\right) \sum_u + (n-2) \Pi_g + (n-2) \Pi_u$$

where n is number of carbon atoms. The frequencies with \sum_u and Π_u symmetric states are active and those with \sum_g and Π_g symmetric states are inactive.

The IR spectra of monocyclic rings have the similar characteristics as those of linear chains. The general formula of irreducible representation of odd-numbered clusters is written as,

$$\Gamma_{odd} = (n-1)A_1 + \frac{n-3}{2}A_2 + \frac{n-3}{2}B_1 + (n-2)B_2.$$

The frequencies with A_1 , B_1 , and B_2 symmetric states are active and those with A_2 symmetric states are inactive.

Three C_2 symmetrical fullerenes has 66 active IR frequencies with the irreducible representation $\Gamma = 34a + 32b$, and so do two Cs isomers with $\Gamma = 34a' + 32a''$, where the bands from 1900 to 2200 cm^{-1} are absent. The conjugate effects in structures are also low due to the absence of bands from 1500 to 1900 cm^{-1} . The D_{6d} isomer has triplet state with higher stability in comparison with singlet state. This high symmetrical isomer with the irreducible representation $\Gamma = 4a_1 + a_2 + 2b_1 + 3b_2 + 10e_1 + 12e_2 + 12e_3 + 12e_4 + 10e_5$ has only 8 IR active frequencies, including 457.2(e_1), 558.4(e_1), 691.8(b_2), 756.9(b_2), 921.5(e_1), 1069.6(e_1), 1173.0(e_1), and 1202.2(b_2).

4 Conclusions

The theoretical studies for carbon clusters led to several conclusions which are consistent with those of early UPS and ion chromatography. The small linear isomers of $C_3 \sim C_9$ are more stable than the cyclic isomers. Comparing with the stabilities of triplet and singlet states of linear clusters, it was found that the triplet states of even-numbered clusters have higher stabilities, and so do the singlet states of odd-numbered clusters contrarily.

The monocyclic isomers become more stable than the linear isomers as cluster size is larger than C_{10} . $(4m+2)$ -numbered series are aromatic with high chemical stabilities, but $4m$ -numbered series are anti-aromatic with relatively low stabilities. Comparing the total energies of variety of C_{24} carbon clusters, the monocyclic rings, planar graphitic, fullerenes, and some 3D polycyclic clusters were quantitatively confirmed the more stable carbon clusters. This stability comparison for C_{24} carbon clusters concluded that there are at least three kinds of stable carbon clusters contributing to the intensity of mass spectrum. The result is also consistent with that for C_{20} carbon clusters that bowl shaped cluster, monocyclic ring and fullerene are thermodynamically stable isomers [36-38]. The calculations of including more C_{24} isomers give the most correct conclusion than that obtained before [39].

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