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Structure and Stability of Lanthanum−Carbon Cations

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A theoretical study has been carried out to determine the stability of various isomers of the lanthanum−carbon clusters LaC_x^+. Included in this study are linear isomers and several classes of cyclic and graphitic structures. Geometries and energies of the proposed structures are calculated using the B3LYP density functional method. Cyclic isomers are clearly established as more stable than linear isomers over a wide range of cluster sizes. The results reveal that two classes of cyclic isomers, which we denote "open rings" and "closed rings", have a pattern of relative thermodynamic stability that correlates to the pattern of cluster intensities in the ion mobility observations of the LaC_x^+ clustering process. The competitive factors that provide stability to lanthanum−carbon clusters are elucidated, such as ring strain and variations in the lanthanum bonding environment. Graphitic LaC_x^+ with 18 or 20 carbon atoms are shown to be more stable than their cyclic counterparts, and B3LYP is shown to underestimate the stability of graphitic LaC_x^+.

Introduction

The discovery of the fullerenes[1] and the subsequent production of metallofullerenes[2] have prompted a wide range of activity in the area of metal−carbon clusters. Such investigation has been aided by a technique[3] that has been called "ion chromatography" or "ion mobility spectrometry", an experimental method that has been applied to fullerene and metallofullerene generation experiments. This technique measures how rapidly a cluster ion travels through an inert gas under the influence of an electric field, thereby revealing the cluster's cross section, which is then reported as a quantity known as the ion "mobility". Ion mobility results reveal structural information about the clusters which are produced along with the fullerenes[4−6] (or metallofullerenes[7−9]). It has been argued that some of these additional clusters are intermediates in fullerene formation.

In particular, ion mobility experiments[7] have recently been conducted on the process of generating lanthanum metallofullerenes LaC_x^+. Those experiments revealed several classes of lanthanum−carbon clusters along with the lanthanum metallofullerenes, and among these clusters are two families which have been postulated to be roughly "monocyclic", meaning that they consist primarily of a single large ring, with the lanthanum atom either as a member of the ring or bonded to the ring. One family (denoted ring Ia in ref 7) was observed at all cluster sizes, whereas the other (ring Ib) was observed only for clusters with at least nine carbon atoms. Both families appear for cluster sizes up to more than 35 carbon atoms. It was also observed that the intensities of the ion mobility peaks for these two families had an even−odd variation as a function of the number of carbon atoms. Several different structures were shown to be consistent with the ion mobility observations, so that the identities of the clusters actually observed in the experiments were not definitively determined.

In the present work, theoretical calculations are carried out on a wide range of LaC_x^+ clusters, with the goal of addressing several issues related to the stability of the various isomeric forms. What is the energetic relationship between linear and cyclic clusters? Among the various possible cyclic isomers, which are most stable? What are the energy requirements for interconversion between isomers? For each of these questions the energetics of the clusters with respect to cluster size is also addressed.

Computational Methods

The calculations in this work have been carried out using the Gaussian 94 program.[10] Energy calculations and geometry optimizations have been performed using the B3LYP density functional method, which employs the Becke[11] three-parameter (B3) exchange functional and the Lee−Yang−Parr[12] (LYP) correlation functional, as implemented in Gaussian 94. Effective core potentials from Hay and Wadt[13] are used for the lanthanum atoms, and the lanthanum basis set is derived from the LANL2DZ basis from Gaussian 94, with the two outermost p-functions replaced by a (41) split of the optimized outer p-function from Couty and Hall.[14] Further splitting gives the [4s4p3d] basis that is used for the lanthanum atom, and the carbon atoms each have a 6-31G* basis set. All calculations in this work were performed with this basis set. All molecules with even x have singlet ground states, and singlets and triplets were considered for molecules with odd x. Relative energies presented in this work reflect the energy of each molecule in its own ground state. Relative stability between various isomers in this work refers to differences in electronic energy, excluding zero-point vibrational corrections.

Results and Discussion

A set of representative clusters from the various classes of structures examined in this work is shown in Figure 1. The B3LYP relative energies of these clusters, over a range of cluster sizes, are tabulated in Table 1. These clusters include linear molecules (**1**), fanlike cyclic molecules (**2**), and several classes of ring structures (**3**−**8**). The B3LYP results elucidate a number of important ideas regarding the relative stability of LaC_x^+ clusters.

Linear vs Cyclic Clusters. In a previous work,[15] we compared the energies of linear (**1**) and cyclic (**2**) isomers of several classes of clusters (including LaC_x^+) for molecules with

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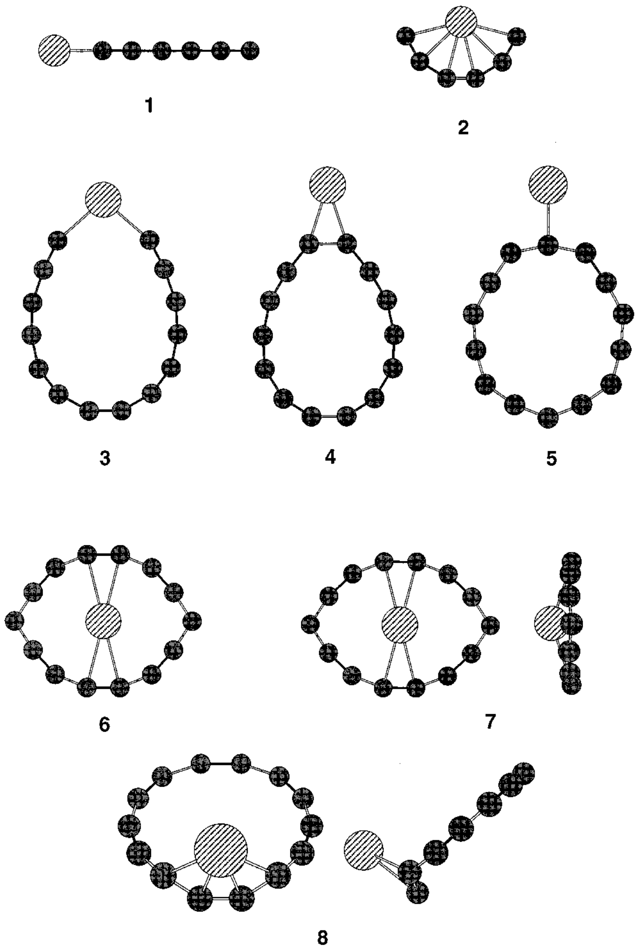

Figure 1. Representative LaC_x^+ in this study: (**1**) linear, (**2**) "fan" ring, (**3**) "open" ring, (**4**) "closed" ring (**5**), "one-carbon" ring, (**6**) "D_{2h} ring" (**7**), "C_{2v} ring", (**8**) "four-bond" ring.

three to six carbon atoms, and the results showed that cyclic isomers were more stable at those small cluster sizes. Previous results have shown similar energetics for neutral LaC_x.[15,16] Here, we incorporate those results for LaC_x^+ into a more exhaustive study involving linear and cyclic (**2** for $x = 3-6$ and **3** for $x > 6$) isomers with up to 14 carbon atoms. The results are shown in Table 1 and demonstrate that as cluster size increases, linear clusters become increasingly unstable with respect to cyclic structures. This is a result of the decrease in ring strain in the cyclic isomer with increasing size, while there exists no such stabilizing influence for the linear chains. The effects of ring strain on cyclic LaC_x^+ will be discussed more fully in the next sections.

"Fan" Rings vs "Open" Rings. In our previous study,[15] the small cyclic structures were "fanlike" (**2**) in that all of the carbon atoms were roughly the same distance from the lanthanum atom. In this way, those cyclic structures may be described as a linear carbon chain curved around a single lanthanum atom. However, there is a limitation to the length of the chain that a lanthanum atom can curve around itself. For sufficiently large clusters, "fanlike" structures give way to "open" (**3**) ring structures in which the lanthanum atom is inserted into a carbon ring by covalently bonding to two carbon atoms. B3LYP calculations indicate that the "fan" (**2**) is more stable (by 0.10 eV) than the open ring (**3**) for six carbon atoms but less stable (by 0.81 eV) than the open ring for eight carbon atoms. For odd-numbered clusters, the crossover occurs at $x = 5$, for which the open ring is very slightly (0.04 eV) more stable than the fan.

"Open" Rings vs Other Planar Rings. An extensive set of B3LYP calculations have been carried out to compare the stability of these open rings (**3**) with the stability of two other planar rings, which we denote "closed" rings (**4**) and "one-carbon" rings (**5**). Examples of open, closed and one-carbon rings are shown in Figure 1. Closed rings consist of a complete all-carbon ring with the lanthanum atom bonded to two consecutive carbons in the ring. One-carbon rings consist of a complete all-carbon ring with the lanthanum atom bonded to only one member of the carbon ring. All three classes of rings are constrained to C_{2v} symmetry for the geometry optimizations. Figure 2 graphically illustrates the relative energies for B3LYP optimized open, closed, and one-carbon rings over the range from 5 to 18 carbon atoms. In each case, the energy of each isomer is the energy of the ground electronic state (for $x = 6$ the "open" ring energy is actually the energy of the "fan" (**2**) isomer).

Several features are evident in the data. The open rings are most stable over this size range, but the energy gap between open rings and the other isomers narrows with increasing cluster size. This is because the increased ring strain in the closed and one-carbon rings becomes less important for larger clusters. Also, there is an alternating pattern in the data. Compared with open rings, closed and one-carbon rings are especially stable for $x = 10$, 14, and 18, while closed rings are even more stable for $x = 9$ and 13. Although closed ring energies approach open ring energies ($\Delta E = 0$ in Figure 2), the one-carbon rings remain around 0.9 eV above open rings even for large numbers of carbon atoms.

The relative energies of closed rings in Figure 2 correlate well with the degree of bond alternation in the open rings and closed rings. Using the B3LYP optimized geometries, the degree of bond alternation in each ring can be computed as an average of the differences between consecutive carbon−carbon bonds around the ring. (The bond between the two carbons bonded to lanthanum is omitted because this bond does not exist in the open ring.) On taking $x = 8$, 10, 12, and 14 as examples, the average bond alternation is 0.09−0.10 Å for all of the open rings. However, the average bond alternations for the closed rings are 0.18 and 0.14 angstroms for $x = 8$ and 12, respectively, and 0.07 Å for $x = 10$ and 14. Apparently, closed rings with higher degrees of bond alternation are more unstable compared to open rings than those with less bond alternation.

B3LYP second derivative analysis of the LaC_{10}^+ "one-carbon" ring indicates that the one-carbon ring is a transition state for what may be called a "ring-walking" process on closed rings. A closed ring with the lanthanum atom bonded to carbon atoms 1 and 2 would be separated from another closed ring with lanthanum bonded to carbons 2 and 3 by a "one-carbon" ring in which lanthanum is bonded solely to carbon 2. Therefore, the energy difference between closed rings and one-carbon rings for a given cluster size is, in fact, the barrier for this "ring-walking" by the lanthanum atom.

B3LYP transition state optimizations have also been carried out to compute the barriers for interconversion between open rings and closed rings, a process that involves the forming or breaking of one carbon−carbon bond. Table 1 lists the B3LYP energetics for this interconversion for $x = 10$, 12, 14, 16, and 18. For the clusters in this size range for which $x = 4n + 2$, the interconversion barriers are consistently 0.8−0.9 eV for the open-to-closed transformation. For the $x = 4n$ clusters in this size range, the barriers are higher, partly because the closed rings themselves are less stable compared to the open rings. Moreover, for $x = 10$, 14, and 18, orbital symmetry analysis

TABLE 1: B3LYP Relative Energies for the LaC_x^+ Clusters Shown in Figure 1 (Energies in eV)

x	linear **1**	open **2**, **3**[a]	**3** ← ts → **4**	closed **4**	one-carbon **5**	D_{2h} ring **6**	C_{2v} ring **7**	four-bond **8**
3	0.79	0.00						
4	1.37	0.00						
5	0.59	0.00		1.64	4.49			
6	0.77	0.00		1.38	2.05			
7	0.79	0.00		1.85	2.58			
8	1.16	0.00		2.30	3.34			
9	0.95	0.00		0.14	2.12			
10	1.42	0.00	0.82	0.44	0.99	12.08	1.17	1.23
11		0.00		0.77	1.80			
12		0.00	2.66	1.07	2.39	2.81	1.66	1.54
13	1.61	0.00		−0.04	1.27			
14	2.04	0.00	0.80	0.19	0.89	0.43	0.33	0.64
15		0.00		0.53	1.43			
16		0.00	2.29	0.64	1.96	0.64	0.62	0.85
17		0.00						
18		0.00	0.89	0.13	0.91	1.03	0.63	0.35
19		0.00						
20		0.00				2.39	1.95	0.48

[a] For $x = 3$, 4, 6, the open ring is structure **2**; for $x = 5$ and $x > 6$, the open ring is structure **3**.

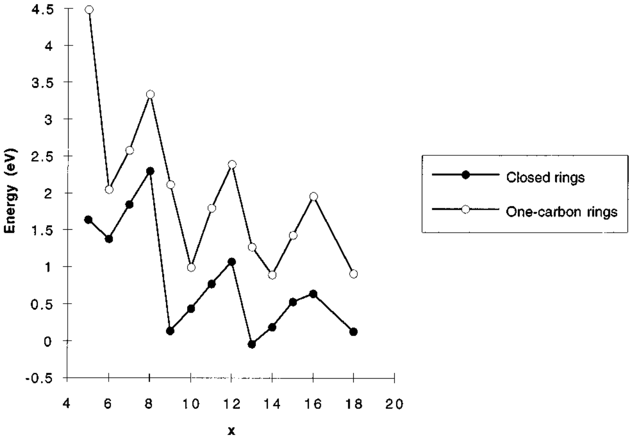

Figure 2. Graphical plot of the B3LYP relative energies for closed and one-carbon LaC_x^+ rings relative to the corresponding open rings (i.e., the energy of the open ring is 0 eV at each cluster size in this figure).

indicates that the open and closed rings have occupied orbitals with the same irreducible representations in the C_{2v} point group. Hence, there are no symmetry-forbidden crossings in the transformation between these open and closed rings. However, for $x = 12$ and 16, the open−closed transformation requires at least one symmetry-forbidden crossing, which explains the much larger interconversion barriers at these cluster sizes.

“High-Coordination” LaC_x^+ Clusters. Planar and nonplanar isomers have been considered with the lanthanum atom coordinated to more than two carbon atoms. Planar (**6**) isomers consist of a ring of carbon atoms with the lanthanum atom at the center. B3LYP optimizations have been carried out in D_{2h} symmetry on planar ring isomers with an even number of carbon atoms. Examples of such isomers are shown in Figure 1, and their energies relative to open rings are presented in Table 1. Second-derivative analysis of these planar D_{2h} rings indicates a single imaginary frequency corresponding to movement of the lanthanum atom along an axis perpendicular to the plane of the cluster, thereby leading to a minimum with C_{2v} symmetry. Optimizations of these C_{2v} rings (**7**) were also carried out, and their relative energies are shown in Table 1 alongside their D_{2h} counterparts. The energies indicate that, for $x = 14$−18, these structures are energetically competitive with open rings. However, for smaller x, the carbon ring is too small to enclose the lanthanum atom, and for larger x, the carbon ring becomes too sharply curved to effectively coordinate to the lanthanum atom without significant ring strain. Therefore, with only a few exceptions, the D_{2h} clusters and their C_{2v} derivatives are high in energy compared to open rings.

Another class of nonplanar (**8**) isomers is explored in which the lanthanum atom is coordinated to four consecutive carbon atoms in “fanlike” fashion. These molecules have only C_s symmetry, and an example of these “four-bond” (**8**) isomers is shown in Figure 1. The energies of “four-bond” isomers are shown in Table 1 and indicate a general trend of increasing stability with increasing size. In contrast to the D_{2h} and C_{2v} rings, whose relative energies increase for sufficiently large clusters, the four-bond rings become progressively more competitive with open rings all the way up to clusters with twenty carbon atoms.

Graphitic Sheets. In considering lanthanum−carbon clusters with up to 20 carbon atoms, it is reasonable to consider graphitic pieces of carbon with lanthanum atoms bonded to the sheets. Such isomers have not been experimentally observed[7] for 20 carbon atoms or less, but theoretical calculations on pure carbon structures indicate that a graphitic C_{20} is more stable than a 20-atom carbon ring.[17] Therefore, graphitic LaC_x^+ are worth considering in terms of their energetics relative to lanthanum−carbon rings. B3LYP optimization has been carried out on graphitic LaC_x^+ for $x = 14$, 16, 18, and 20. The isomers selected for study are pictured in Figure 3, and their B3LYP energies are shown in Table 2. All graphitic sheets in Figure 3 except (A) and (H) have been constrained to be planar.

For $x = 14$, the results indicate that it is energetically favorable to bond the lanthanum atom to the edge of the sheet rather than to the interior of the sheet. This is consistent with the observation that it is the edge of a pure carbon sheet that is most destabilizing, so it is reasonable to suppose that the metal atom can stabilize the edge. Also, coordinating the metal atom to the interior of an otherwise planar graphitic sheet causes the sheet to become curved, which is disruptive to the carbon π-system.

The energies show that for $x = 18$ and 20, B3LYP predicts that these graphitic pieces are actually more stable than the corresponding open rings, a result generally consistent with previous theoretical results for all-carbon clusters.[17] In fact, since previous gradient-corrected density functional (BLYP) calculations[18] have been shown[17] to underestimate the stability of an all-carbon graphitic sheet, it is possible that the same effect is seen in our lanthanum−carbon results. As a test of this

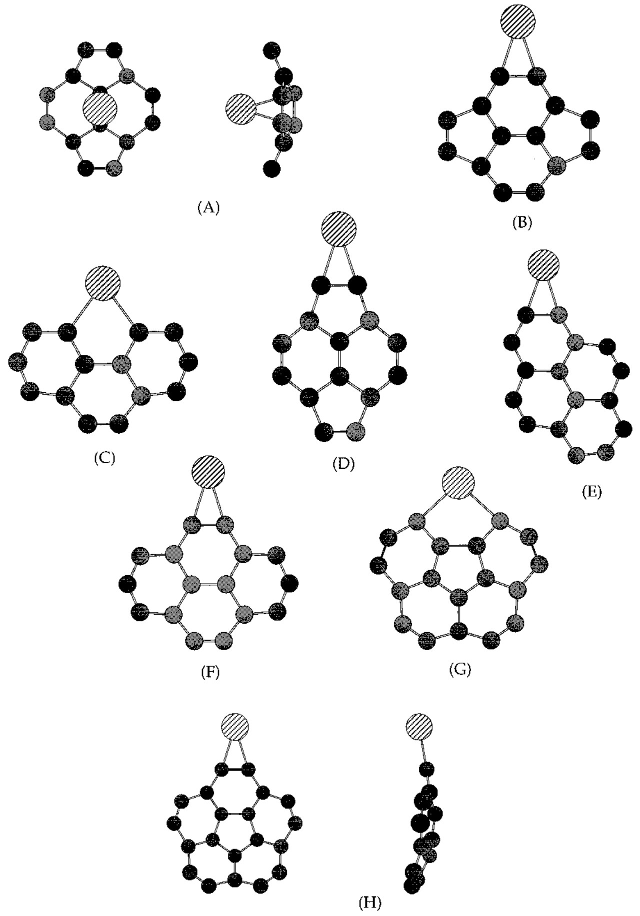

Figure 3. Graphitic LaC_x^+ in this study: (A) two views of LaC_{14}^+, (B, C, D) planar LaC_{14}^+, (E, F) planar LaC_{16}^+, (G) planar LaC_{18}^+, (H) two views of LaC_{20}^+.

TABLE 2: B3LYP Energies of Graphitic LaC_x^+ Relative to the Corresponding Open Rings (Energies in eV)

isomer	x	energy (eV)
A	14	4.59
B	14	3.84
C	14	2.85
D	14	2.50
E	16	1.93
F	16	1.81
G	18	−0.06
H	20	−0.62

TABLE 3: Comparison of B3LYP, BLYP, and MP2//B3LYP for Energies of Graphitic Sheets Relative to Open Rings (Energies in eV)

sheet	x	open ring	B3LYP	BLYP	MP2//B3LYP
D	14	0.0	2.5	3.1	1.3
H	20	0.0	−0.6		−2.9

possibility, MP2 calculations have been carried out at the B3LYP geometries for graphitic sheets (D) and (H) from Figure 3. MP2 calculations are a suitable benchmark because they closely mirror the highly accurate coupled-cluster method for the C_{20} graphitic sheet.[17] BLYP optimizations of (D) have also been carried out so that BLYP and B3LYP can be compared. The results, shown in Table 3, indicate that B3LYP performs better than the BLYP method used in the previous study[18] but that both density functional methods underestimate the stability of graphitic LaC_x^+. This would imply that these $x = 18$ and $x = 20$ sheets are even more stable than B3LYP indicates, and it also raises the possibility that the $x = 16$ sheets are, in reality, energetically competitive with open rings.

Ion Mobility Interpretations. The ion mobility results for the lanthanum metallofullerene generation experiments indicate the presence of two classes of clusters which are referred to as "monocyclic rings" because it was shown that LaC_x^+ isomers which consist primarily of one large ring of atoms have mobilities that are consistent with the experimental observations. One of the two classes (ring Ia) is observed at all cluster sizes, whereas the other (ring Ib) only appears for clusters with at least nine carbon atoms, with both families of rings being observed for cluster sizes up to over 35 carbon atoms. Our results show that the open and closed LaC_x^+ rings are consistent with these experimental observations, with open rings as ring Ia and closed rings as ring Ib. Closed rings first become energetically competitive with open rings for $x = 9$, and it is reasonable that the smaller unstable closed rings would not be observed. One-carbon rings have also been shown to be consistent experimentally,[7] but our findings demonstrate that one-carbon rings are high in energy and that they are transition states between one closed ring and another, and thus one-carbon rings are likely not being observed experimentally because of relaxation to the more stable closed rings.

Lanthanum−carbon clusters with lanthanum bonded to more than two carbon atoms have also been shown to have ion mobilities consistent with experimental observations. Although the nonplanar "four-bond" isomers were not among those candidates tested by previous ion mobility calculations,[7,19] their stability at large size and their approximate structural similarity to other rings make the "four-bond" isomers potentially good candidates for experimentally observed clusters for large numbers of carbon atoms. It seems clear from our B3LYP results that planar rings with the lanthanum atom inside the ring are too unstable to be plausible structures observed in the ion mobility experiments.

Further evidence for open rings as ring Ia and closed rings as ring Ib derives from the relative abundances of the two rings classes in the ion mobility experiments, as shown in Figure 3 of ref 7. For example, ring Ia is dominant over ring Ib in the mobility distribution for $x = 12$, but ring Ib is dominant for $x = 13$ and 14. Our B3LYP calculations indicate that the open ring is much more stable than the closed ring for $x = 12$ and should have a higher abundance in the distribution. For $x = 13$ and 14, the closed ring is energetically competitive with the open ring, and ring Ib is the major isomer. Ring Ia returns to dominance for $x = 16$, and our B3LYP calculations show that $x = 16$ is a local maximum in the relative stability of the open ring over the closed ring. Therefore, open and closed rings effectively model the experimental variations in the abundances of the ion mobility peaks.

Recently, it was proposed[20] that ring Ib was a planar structure similar to **6** from Figure 1, consisting of a carbon ring with a lanthanum atom at the center. BLYP calculations were performed to show that **6** is most stable for $x = 13$. We performed B3LYP calculations that confirmed that result, and in fact, this structure is 0.83 eV more stable than the corresponding open ring for $x = 13$. However, it has been noted previously[7,20] that the 13-membered carbon ring is a fortuitously good geometric fit for the lanthanum atom. The 13 carbon atoms can all coordinate to the electron-deficient lanthanum atom without significant ring strain. If the ring is smaller than $x = 13$, the lanthanum atom does not fit inside, and if the ring is larger than $x = 13$, the coordination of the ring to the lanthanum imposes too much ring strain, as per the previous discussion of isomer **6**. As an example of a larger odd-numbered ring, we performed B3LYP calculations on **6** for $x = 15$, and the energy of that isomer is 1.20 eV above the $x = 15$ open ring. Planar isomers with the lanthanum atom inside the ring are not stable enough over a range of cluster sizes to be good candidates for ring Ib. The open and closed rings are a better model of the experimental observations over a wider range of cluster sizes.

Conclusions

Several general conclusions may be drawn from the results of this study: (1) Lanthanum prefers bonding environments in which it is coordinated to more than one carbon atom. This is seen in the instability of linear isomers relative to cyclic isomers and the instability of "one-carbon" rings relative to other rings, (2) there appears to be a limit of about six on the number of consecutive carbons a lanthanum atom can coordinate, but within that limitation there exists a variety of bonding environments that lead to low-energy structures, even for large rings, and (3) graphitic LaC_x^+ are competitive with rings for clusters at least as small as LaC_{18}^+.

Also, in regard to the ion mobility observations, these calculations have shown that the open rings and closed rings are the best model for the experimental observations concerning the appearance of monocyclic rings in the lanthanum−carbon clustering process. In general, open and closed rings are the two most energetically stable classes of monocyclic rings, and the trends in relative energies between open and closed rings match the experimental abundances of ring Ia and ring Ib. The theoretical data provide a clear illustration of the power of theoretical methods to complement the structural information of ion mobility experiments with energetic information that can refine the process of assigning geometries to ion mobility observations.

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