

Observation of New Ring Isomers for Carbon Cluster Anions

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High-resolution ion-mobility measurements have resolved a number of isomers for carbon cluster anions in the drift-time region previously assigned to monocyclic rings. Tight-binding calculations have been performed to generate feasible geometries, which were compared to the experimental data by calculating their mobilities. Structures composed of a short chain of carbon atoms attached to a carbon ring are found to be the most plausible geometries for these new isomers. A number of different bicyclic ring isomers have also been resolved for the first time. [S0031-9007(98)06131-6]

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The structure of carbon clusters is of basic interest in a variety of fields including astrophysics, materials synthesis, and combustion [1]. Fullerenes [2], which can be prepared in macroscopic quantities [3], and small linear carbon chains [1] are well characterized species. Much less is known about medium-sized clusters. A variety of structures have been proposed [4–8] but unambiguous experimental verification is often lacking. Chemical reactivity [9] and photoelectron spectroscopy [10] studies have shown that there is a transition from linear chains to rings with increasing cluster size. However, ion-mobility measurements, where structural isomers are separated on the basis of their different mobilities, have provided most of what is known about the larger ring isomers. Previous ion-mobility measurements have resolved a variety of isomers that were assigned to linear chains, monocyclic rings, bicyclic rings, polycyclic rings, graphite sheets, and fullerenes [11,12]. However, the previous ion-mobility measurements were hindered by poor resolution. Here we report high-resolution ion-mobility measurements for carbon cluster anions, where the resolution has been improved by a factor of 10. These measurements reveal the presence of a variety of previously unresolved ring isomers for carbon cluster anions with more than 12 atoms.

The new high-resolution ion-mobility apparatus has been described in detail in a recent publication [13]. The apparatus consists of a source region coupled directly to a 63 cm long drift tube. Carbon cluster anions are produced by pulsed laser vaporization of a graphite rod. For some experiments, a second pulsed laser beam was directed into the source region shortly after the vaporization laser in order to anneal the clusters. Ions pass from the source region into the drift tube through an ion gate. The ion gate has a buffer gas counterflow to prevent neutral clusters from entering the drift tube. The drift tube and source region contain helium buffer gas at a pressure of around 500 Torr, and the voltage across the drift tube is typically 10 000 V. The high drift voltage employed here is primarily responsible for the enhanced resolution. After traveling through the drift tube, some of the ions exit through a small aperture. The ions are then focused into

a quadrupole mass spectrometer, and, after mass analysis, they are detected with an off-axis collision dynode and dual microchannel plates. Drift-time distributions are recorded with a multichannel analyzer.

Figure 1 shows drift-time distributions recorded for (a) C_{13}^- , (b) C_{17}^- , and (c) C_{18}^- . The intense peak with the longest drift time in each of these distributions occurs in the region expected for a linear chain on the basis

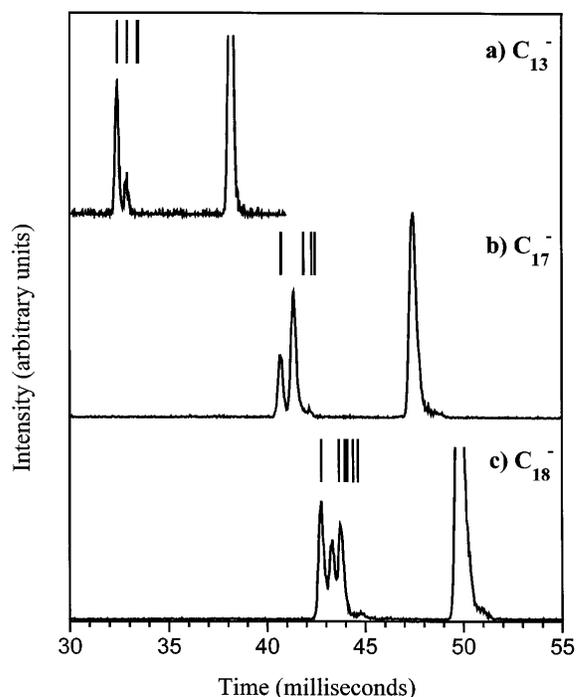


FIG. 1. High-resolution drift-time distributions recorded for (a) C_{13}^- , (b) C_{17}^- , and (c) C_{18}^- . Drift times estimated for calculated monocyclic ring and tadpole structures are shown by the solid vertical lines. The estimated drift times are normalized so that the drift time of the monocyclic ring corresponds to the first peak in the distribution. For C_{13}^- , calculated drift times are shown for tadpoles with 1–3 atom chains. Drift times for tadpoles with 1–5 atom chains are shown for C_{17}^- , and for 1–6 atom chains for C_{18}^- . The values of the calculated relative drift times for each tadpole are given in Table I.

of the previous measurements and assignments [11,12]. The linear chain is known to persist to larger cluster sizes for anions than for cations [11,12]. This has been attributed to the excess electron in the anion localizing at the dangling bonds at the end of the chain. This decreases the energy obtained by making a chemical bond between the two ends of the chain and destabilizes the ring relative to the chain [11,12]. We have observed linear chains up to C_{50}^- . At drift times around 6 ms shorter than the peak attributed to the linear chain, there is a group of two or three closely spaced peaks in each of the distributions in Fig. 1. These peaks occur in the region expected for a monocyclic ring on the basis of the previous measurements and assignments [11,12,14]. In the previous measurements, the peaks attributed to the monocyclic ring were not completely resolved from the peaks attributed to linear chains. This illustrates the dramatic improvement in resolving power achieved in these measurements. For C_{13}^- and C_{17}^- , two relatively intense peaks are clearly resolved in the region assigned to the monocyclic ring, and for C_{18}^- three relatively intense peaks are present. In addition, there are small peaks at slightly longer times for C_{17}^- and C_{18}^- . Two to four isomers are clearly resolved in the region assigned to the monocyclic ring for all clusters with 13 to 26 atoms. For larger clusters, the peaks coalesce into a single broad peak, which persists up to at least 60 atoms. For the well resolved peaks in the smaller size regime, the evolution of the arrival times and intensities is not regular from one cluster size to the next, and so it is difficult to group them into families. The difference in mobility between two successive peaks in this region is on the order of 1.5%. This can be compared with the difference in mobility between linear chains and monocyclic rings, which is on the order of 10%. In an effort to determine which of the resolved isomers is the most stable, some annealing experiments were performed with the output of a second pulsed laser (308 nm) directed into the source region shortly after the vaporization laser. The second pulsed laser results in an increase in the intensity of the peak with the shortest drift time, and a corresponding decrease in the intensity of the peaks at longer drift times. This behavior was observed for most of the clusters examined in the $C_{13}^- - C_{26}^-$ range. However, these results are not unambiguous, as they could be influenced by fragmentation or electron detachment.

In order to determine the structures of the resolved isomers, it is necessary to obtain plausible structures and calculate their mobilities for comparison with the experimental data. C_{13}^- is the first cluster for which multiple isomers are observed at drift times close to that assigned to the monocyclic ring. We have performed an exhaustive search of the possible planar structures for C_{13}^- using a tight-binding model with parameters from Xu *et al.* [15]. This model allows a fast determination of the energy of a given geometry, and, in addition, the

charge can relatively easily be incorporated into these calculations. A large number of configurations were generated using a Metropolis algorithm. Several isomers are found within the first few electron volts in binding energy: linear chains, monocyclic rings, some bicyclic rings, and "tadpole" structures. A tadpole, as recently described by Scuseria and collaborators [16] and Morokov and collaborators [17], is a monocyclic ring with a small linear chain attached to the ring. According to our tight-binding calculations, the linear part is attached to the ring by a single sp^2 carbon. The calculated structures for the monocyclic ring, and tadpoles with 1, 2, and 3 atoms in the chain, are shown in Fig. 2. Monocyclic ring and tadpole geometries have also been optimized for clusters with 17, 18, and 24 atoms using the tight-binding model and assuming C_{2v} symmetry. The relative energies of the different structures are given in Table I. The tadpole geometries are generally less stable than the monocyclic rings. It appears that tadpoles with an even number of atoms in the chain are more stable than those with an odd number, while simple ideas about the chemical bonding in these species suggest that tadpoles with an odd number of atoms in the ring should have the lowest energies since this would permit a polyynic bonding scheme to propagate around the ring.

Mobilities were estimated for the calculated geometries using a trajectory method with a realistic interatomic potential [18]. This method has been shown to be uniformly superior to the projection approximation previously used to analyze the mobilities of carbon clusters [11,12]. It has recently been found that the degree of charge localization, and the location of the charge within the ion, can affect the mobility [19]. In the carbon cluster isomers studied previously, the charge is either uniformly or symmetrically distributed. When the charge distribution is symmetric, it has only a small effect on the mobility. However, for the

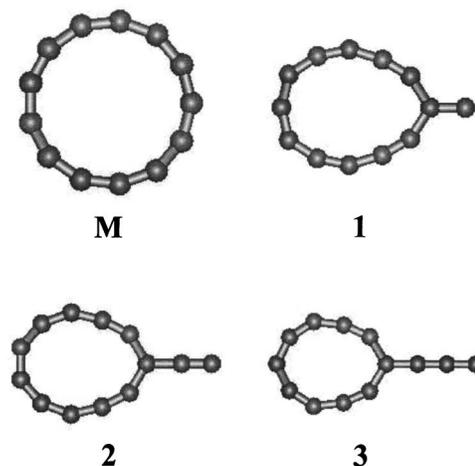


FIG. 2. Calculated monocyclic ring and tadpole structures for C_{13}^- . The number label corresponds to the number of atoms in the chain of the tadpole; *M* corresponds to the monocyclic ring.

TABLE I. The estimated relative drift times $(t - t_{\text{ring}})/t_{\text{ring}}$ and the relative energies $(E - E_{\text{ring}})$ (in brackets) for the calculated tadpole structures relative to the calculated monocyclic ring. The tadpoles are labeled by the number of atoms in the chain. Relative drift times are reported in %; relative energies are reported in eV.

Atoms in chain	C ₁₃ ⁻	C ₁₇ ⁻	C ₁₈ ⁻	C ₂₄ ⁻
1	3.1 (2.51)	2.9 (2.59)	2.1 (2.24)	2.0 (1.66)
2	3.3 (0.61)	4.3 (0.64)	3.1 (1.22)	2.0 (-0.02)
3	1.5 (1.74)	0.1 (1.91)	4.4 (1.77)	1.6 (1.20)
4		2.8 (1.05)	3.8 (0.82)	2.3 (0.74)
5		3.9 (2.23)	2.8 (1.80)	3.4 (0.97)
6			3.0 (1.82)	3.1 (0.29)
7				2.9 (0.99)

tadpole structures the charge is expected to be localized at the end of the carbon chain, and the degree of charge localization has a significant effect on the mobility. We employed the charge distribution given by the tight-binding calculations in the mobility calculations. The tight-binding model tends to overestimate the charge localization, so the effect of the asymmetric charge distribution may be slightly overestimated in the mobility calculations. The estimated drift times of the tadpoles and the monocyclic rings for C₁₃⁻, C₁₇⁻, C₁₈⁻, and C₂₄⁻ are compared in Table I. The monocyclic ring has the shortest estimated drift time. This is consistent with the laser annealing results which suggest that the isomer with the shortest drift time is the most stable. The solid vertical lines in Figs. 1 and 3 show the estimated drift times of the rings and tadpoles. The drift times have been normalized so that the estimated drift time of the monocyclic ring corresponds to the peak with the shortest drift time. The estimated drift times are in qualitative, but not good quantitative, agreement with the experimental results. The estimated drift times of the tadpoles vary with the length of the chain and with the degree to which the charge is localized at the end of the chain. If the charge is distributed equally over all of the atoms in the cluster, the calculated drift times of the tadpoles with short chains are generally slightly *less* than for the monocyclic ring, and the drift times increase gradually as the chain length increases. Drift times calculated with a uniform charge distribution are in poor agreement with the experimental results and cannot account for the separation between the peaks observed for the larger clusters like C₂₄⁻. When the charge is localized on the end of the chain, even the estimated drift times for tadpoles with shorter chains are significantly longer than for the monocyclic ring and in closer agreement with the experimental results. So it appears that the charge localization is primarily responsible for the resolution of these isomers in the mobility measurements. When the charge is localized, the calculated drift times no longer increase smoothly with the length of the chain. For example, the estimated drift time for C₁₇⁻ with a three atom chain is less than for C₁₇⁻ with a one or two atom

chain because, according to the tight-binding calculations, somewhat less charge is localized at the end of the three atom chain than at the end of the one and two atom chains. This presumably explains why the separation between the peaks in the drift-time distributions is not regular. It also seems likely that at least some of the resolved peaks consist of more than one isomer, even with the improved resolving power employed here. This is particularly clear in the results shown for C₂₄⁻ in Fig. 3, where the first peak at around 55.8 ms probably corresponds to the monocyclic ring, while the two peaks at slightly longer drift times appear to be due to tadpoles with one, two, and three atom chains (peak at 56.7 ms) and tadpoles with four, five, and six atom chains (peak at 57.5 ms). This probably explains why the distributions become broad and featureless for slightly larger clusters.

While the agreement between the measured and calculated mobilities is not perfect, the tadpoles are the best candidates for the geometries of the new isomers that have been resolved in our high-resolution ion-mobility measurements. No other plausible, low-energy geometries with mobilities similar to the monocyclic rings were found in our tight-binding calculations. It is apparent from Figs. 1 and 3 that the calculated drift times for the tadpoles are generally at slightly longer times than observed in the experiments. This may be explained by the tight-binding model slightly overestimating the degree of charge localization. It is likely that the agreement between the measured and calculated drift times will be improved if the structures and charge distributions are obtained from more rigorous calculations. However, such calculations are not trivial for anions and are beyond the scope of this work.

While we have focused on the region of the drift-time distributions previously assigned to monocyclic rings, additional isomers have been resolved for larger clusters in other regions of the drift-time distributions. In the drift-time distribution for C₂₄⁻ shown in Fig. 3, the linear chain (*L*) and three peaks assigned to tadpoles and a monocyclic ring are present. In addition, there are three small peaks (*B1*, *B2*, and *B3*) at shorter drift times. These are in the drift-time region previously assigned to bicyclic rings.

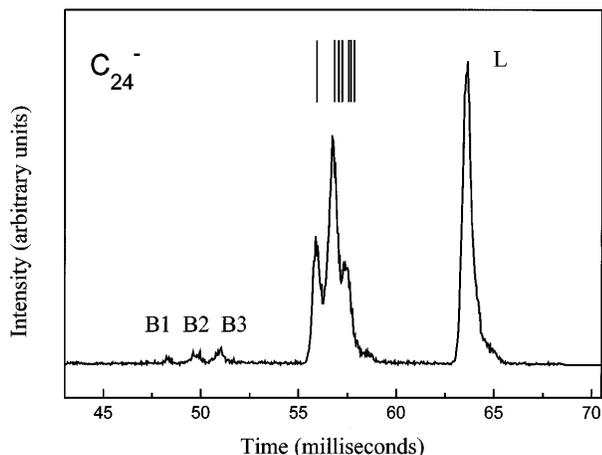


FIG. 3. High-resolution drift-time distribution of C_{24}^- . The linear chain isomer is labeled L , and the bicyclic ring isomers are labeled as $B1$ – $B3$. Drift times estimated for calculated monocyclic ring and tadpole structures are shown by the solid vertical lines. The estimated drift times are normalized so that the drift time of the monocyclic ring corresponds to the first peak in the distribution. The other solid vertical lines represent tadpoles with 1–7 atoms in the chain. The values of the calculated relative drift times for each tadpole are given in Table I.

The existence of a variety of bicyclic ring isomers had been deduced from previous ion-mobility measurements, because the peak assigned to the bicyclic ring for larger clusters was found to be slightly too broad to be accounted for by a single isomer [14]. However, the isomers were not resolved in the previous measurements. The three peaks resolved here are probably due to bicyclic rings where the two rings contain different numbers of atoms such as 12 + 12, 14 + 10, and 16 + 8 [16,20]. Three major bicyclic ring peaks with relative drift times similar to those shown for C_{24}^- are observed for clusters with 24 to 30 atoms. Finally, as the size of the cluster increases further, a variety of polycyclic ring isomers are resolved in the high-resolution ion-mobility measurements, and, for larger clusters, isomers have been resolved in the drift-time regions assigned to the graphite sheets and fullerenes.

In summary, a new family of structural isomers has been resolved for carbon cluster anions using high-resolution ion-mobility measurements. Structures composed of a short carbon chain attached to a carbon ring are the best candidate geometries for the new isomers, both in terms of their stability and their estimated mobilities. Although the estimated mobilities of these structures are not in good quantitative agreement with the measured mobilities over the whole size range, tadpoles are the only structures found with mobilities close to the measured values. It is plausible that tadpole structures will form in an environment rich in carbon chains and rings, as occurs in the early stages of carbon cluster growth. Furthermore, the observation that tadpoles appear to anneal into mono-

cyclic rings when irradiated with a laser, suggests that tadpoles may be intermediates in the growth of larger carbon rings.

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