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Low-temperature Photoelectron Spectroscopy of Aliphatic Dicarboxylate Monoanions, $HO_2C(CH_2)_nCO_2^-$ ($n = 1-10$): Hydrogen Bond Induced Cyclization and Strain Energies

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Photoelectron spectra of singly charged dicarboxylate anions $HO_2C(CH_2)_nCO_2^-$ ($n = 1-10$) are obtained at two different temperatures (300 and 70 K) at 193 nm. The electron binding energies of these species are observed to be much higher than the singly charged monocarboxylate anions, suggesting that the singly charged dicarboxylate anions are cyclic due to strong intramolecular hydrogen bonding between the terminal $-CO_2H$ and $-CO_2^-$ groups. The measured electron binding energies are observed to depend on the chain length, reflecting the different $-CO_2H\cdots{}^-O_2C-$ hydrogen bonding strength as a result of strain in the cyclic conformation. A minimum binding energy is found at $n = 5$, indicating that its intramolecular hydrogen bond is the weakest. At 70 K, all spectra are blue shifted relative to the room-temperature spectra with the maximum binding energy shift occurring at $n = 5$. These observations suggest that the cyclic conformation of $HO_2C(CH_2)_5CO_2^-$ (a ten-membered ring) is the most strained among the 10 anions. The present study shows that the $-CO_2H\cdots{}^-O_2C-$ hydrogen bonding strength is different among the 10 anions and it is very sensitive to the strain in the cyclic conformations.

1. Introduction

The study of strain energy in molecules has been a topic of interest in chemistry.[1−5] Strained molecules can have significantly different chemical properties and lead to unpredicted chemical reactivity. In ring compounds, the concept of strain energy is known to play an important role in understanding the reactivity trends in chemical reactions. In protonated polyfunctional molecules, cyclic structures are often induced by intramolecular hydrogen bonds. In particular, strong intramolecular hydrogen bonds are often the dominant factor for determining the conformations of molecules,[6−8] and they are identified in many organic molecules, supramolecular systems, and biological molecules. In some enzymatic reactions, it has been suggested that strong hydrogen bonding is involved in the transition states to provide extra stabilization energy.[9−12] Such hydrogen bonds can provide as high as 20 kcal/mol stabilization energy in certain enzymatic systems.[10]

Using a newly constructed low-temperature electrospray ionization photoelectron spectroscopy (ESI-PES) apparatus, we have recently observed the formation of cyclic structures in a series of aliphatic carboxylate molecules, $CH_3(CH_2)_nCO_2^-$ ($n = 0-8$) at low temperatures[13] due to the weak $C-H\cdots O$ hydrogen bonding between the terminal $-CH_3$ and the $-CO_2^-$ group when $n > 4$. Herein, we extend our study to another series of aliphatic dicarboxylate anions, $HO_2C(CH_2)_nCO_2^-$ ($n = 1-10$), where strong hydrogen bonding is expected to form between the terminal $-CO_2H$ and $-CO_2^-$ groups. We observed, even at room temperature, that all of these monoanions exist in cyclic conformations due to the strong hydrogen bonding. At low temperatures, all PES spectra show a blue shift relative to the room-temperature spectra due to the reduction of the entropic effect that strengthens the $-CO_2H\cdots{}^-O_2C$ hydrogen bonding. However, this blue shift is n-dependent in $HO_2C(CH_2)_nCO_2^-$ with a maximum shift occurring at $n = 5$. The n-dependent blue shift reflects the trend of strain energies present in the cyclic conformations, revealing that the cyclic structure of $HO_2C(CH_2)_5CO_2^-$ is the most strained.

2. Experimental and Theoretical Methods

2.1. Low-temperature ESI-PES. The low-temperature ESI-PES apparatus has been described in several recent studies.[13−16] A key feature of the new ESI-PES apparatus is a temperature-controlled ion trap that is used for ion accumulation and cooling. The ion trap is attached to the cold head of a closed-cycle helium refrigerator, which can reach down to a low temperature of 10 K and can be controlled up to 350 K. The anions of interest, $HO_2C(CH_2)_nCO_2^-$ ($n = 1-10$), were produced by electrospray of 1 mM solutions of the corresponding acids in a mixture of methanol/water solvent (3:1 volume ratio). Anions produced were guided by a RF-only octopole into a quadrupole mass filter operated in the RF-only mode. Following the mass filter, ions were directed by a 90° ion bender to the temperature-controlled ion trap, where they were accumulated and cooled via collisions with a background gas. The background gas used was ~0.1 mTorr N_2 for the temperature range between 350 and 70 K. Ions were trapped and cooled for a period of 20 to 80 ms before pulsed into the extraction zone of a time-of-flight mass spectrometer at a repetition rate of 10 Hz.

During the PES experiment, ions were mass selected and decelerated before being intercepted by a probe laser beam in the photodetachment zone of the magnetic-bottle photoelectron analyzer. In the current experiment, a photodetachment photon energy of 193 nm (6.424 eV) from an ArF excimer laser was

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used. The laser was operated at a 20 Hz repetition rate with the ion beam off at alternating laser shots for shot-by-shot background subtraction. Photoelectrons were collected at nearly 100% efficiency by the magnetic bottle and analyzed in a 5.2 m long electron flight tube. Time-of-flight photoelectron spectra were collected and converted to kinetic energy spectra, calibrated by the known spectra of I^- and ClO_2^-.[17] The electron binding energy spectra were obtained by subtracting the kinetic energy spectra from the detachment photon energy used. The energy resolution ($\Delta E/E$) was about 2%, that is, ~20 meV for 1 eV of electrons.

2.2. Theoretical Methods. Density functional theory (DFT) was used to determine the geometry and electronic structure of the dicarboxylate monoanions and their corresponding neutrals. Geometry optimizations and single-point energy calculations were performed using the hybrid B3LYP exchange-correlation functional[18] and the 6-311++G(d,p) basis set. The electronic energies were corrected with zero-point vibrational energy (ZPVE) using the harmonic vibrational frequencies calculated at the same level of theory. To estimate the effect of hydrogen bond induced cyclization, we also performed the same procedures on the linear conformations of $HO_2C(CH_2)_nCO_2^-$. The adiabatic detachment energies (ADEs) of the anions were obtained by taking the energy difference between the anion and the ground state of the neutral in their optimized geometry. All of the DFT calculations were carried out with the Gaussian 03 package of programs.[19]

Effort has been made to locate the global minimum for the individual folded structures of the $HO_2C(CH_2)_nCO_2^-$ ($n = 1-10$) anions. For the lower n members of $HO_2C(CH_2)_nCO_2^-$ ($n = 1-6$), because of the relatively short chain length, the conformation to form the required O−H···O hydrogen bond is constrained. The minimum structures are located such that the dicarboxylic groups are oriented in a trans-orientation relative to the molecular plane. For the higher n members of $HO_2C(CH_2)_nCO_2^-$ ($n = 7-10$), there are a few possible conformations because of the flexibility of the folded chain. In such cases, the minimum structure is located with the least possible steric hindrance between the methylene groups. On the basis of the minimum structures of $HO_2C(CH_2)_nCO_2^-$ anions, we directly carried out the full geometrical optimization to the corresponding neutral. It turns out that the optimized structure of neutral is similar to that of the anion.

3. Results and Discussion

3.1. Photoelectron Spectra. The 193-nm (6.424 eV) photoelectron spectra of $HO_2C(CH_2)_nCO_2^-$ ($n = 1-10$) were measured at both room temperature and 70 K, as shown in Figure 1. Because no photodetachment transition occurs below 4.0 eV, all the spectra were plotted from 3.0 to 6.4 eV binding energy scale for clearer presentation. Spectral features are similar for all species, which have adiabatic detachment energies around 4.5 eV because the aliphatic chain length has very little effect on the binding energies of the carboxylate group. The observed bands are due to photodetachment from the oxygen lone pairs on the $-CO_2^-$ moiety.[16,20,21] Compared with the $CH_3(CH_2)_nCO_2^-$ series, which all have ADEs around 3.4 eV, the ADEs of $HO_2C(CH_2)_nCO_2^-$ are ~1 eV higher. This suggests that the singly charged dicarboxylate anions are much more stable than the monocarboxylates. The stabilizing factor is most likely from the formation of the intramolecular O−H···O hydrogen bond between the terminal $-CO_2H$ and $-CO_2^-$ groups. The higher ADEs suggest that strong hydrogen bonds are already formed even at room temperature, that is, all $HO_2C(CH_2)_nCO_2^-$ are always in a cyclic conformation. A recent ion mobility measurement showed that the singly charged dicarboxylate anions maintain the cyclic conformations even at 500 K.[22]

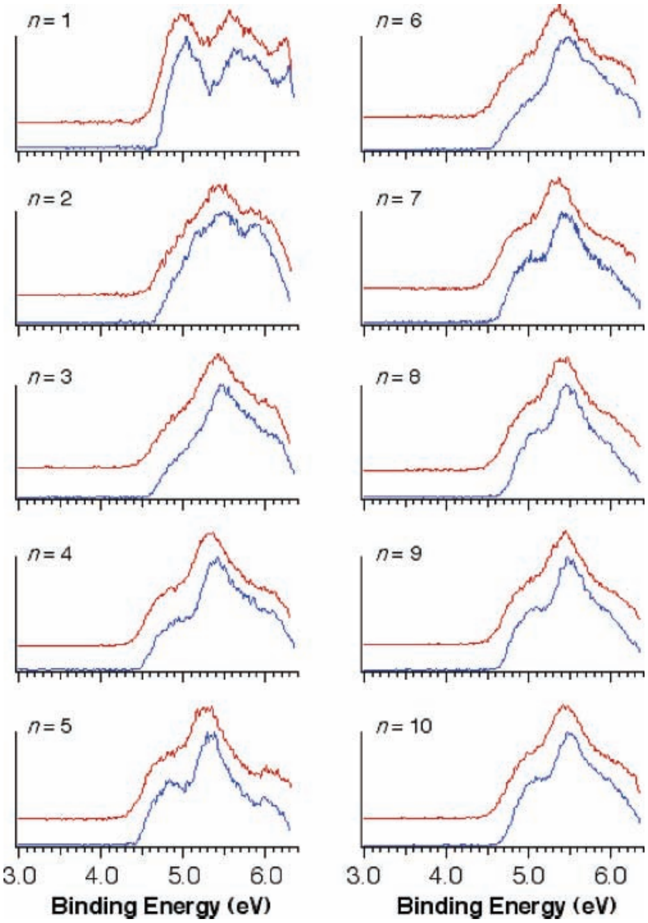

Figure 1. Photoelectron spectra of $HO_2C(CH_2)_nCO_2^-$ ($n = 1-10$) measured at 193 nm (6.424 eV) and at two different ion-trap temperatures. Note that all the 70 K spectra are blue shifted relative to the 300 K: red, 300 K; blue, 70 K.

Surprisingly, the spectra at 70 K were not significantly improved relative to those at room temperature, except a shift to higher binding energies. In our previous study on *trans*-$HO_2CCH{=}CHCO_2^-$ (similar to $n = 2$ in the current case),[15] which exhibits no intramolecular hydrogen bond, we were able to resolve vibrational progressions due to OCO bending modes at low temperatures. However, in the present cases, no vibrational progressions were observed for any species. This was most likely due to the large geometry change between the anions and the corresponding neutrals, induced by their very different hydrogen bonding strength, which would smear out the OCO bending vibrational structures.[13,15]

The long tail observed at the lower binding energy side in all of the 70 K spectra is consistent with a large geometry change between the anion and neutral ground states. Due to the low signal-to-noise ratio and lack of vibrational resolution in the threshold region, we were only able to estimate the ADEs from the onset of appreciable photoelectron signals. The ADEs estimated from the 70 K spectra are given in Table 1. These ADEs should probably be viewed as the upper limits since the Franck−Condon factors for the 0−0 transition may be negligible.

The measured ADEs at 70 K for $HO_2C(CH_2)_nCO_2^-$ are plotted in Figure 2 (solid curve) as a function of the chain length. Interestingly, the ADEs were observed to decrease from 4.65

TABLE 1: Experimental and Theoretical Adiabatic Detachment Energies (ADEs), and Calculated Energy Difference Δ*E*, O−H···O, O···O Distances, and ∠ OH···O Angles of $HO_2C(CH_2)_nCO_2^-$

$HO_2C(CH_2)_nCO_2^-$ *n*	ADE (eV) exp[a,b]	theor[c]	Energy Difference Δ*E* (eV)[c,d]	O−H···O distance (Å)[c]	O···O distance (Å)[c]	∠OHO[c]
1	4.65	4.47	−0.70	1.378	2.430	162.1°
2	4.64	4.46	−0.74	1.349	2.444	176.0°
3	4.59	4.41	−0.75	1.384	2.469	178.0°
4	4.46	4.31	−0.70	1.471	2.510	175.6°
5	4.41	4.26	−0.68	1.546	2.566	172.2°
6	4.54	4.32	−0.74	1.422	2.486	175.5°
7	4.60	4.32	−0.74	1.498	2.518	167.0°
8	4.69	4.42	−0.82	1.534	2.559	171.3°
9	4.64	4.39	−0.83	1.523	2.550	171.4°
10	4.66	4.42	−0.83	1.540	2.556	167.9°

[a] Uncertainties are ±0.05 eV in all cases. [b] Threshold detachment energy (TDE), representing the upper limit for ADE. [c] Computed at the B3LYP/6-311++G(d,p) level plus ZPVE corrections. [d] Calculated energy difference between the cyclic and linear anions.

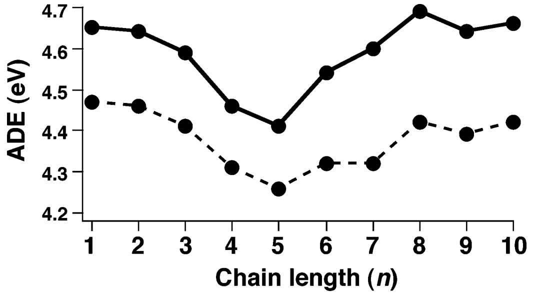

Figure 2. Experimental and theoretical ADEs for $HO_2C(CH_2)_nCO_2^-$ as a function of chain length *n*. Note that, in both cases, the minimum ADE was observed at $n = 5$: solid line, experiment; dashed line, theory.

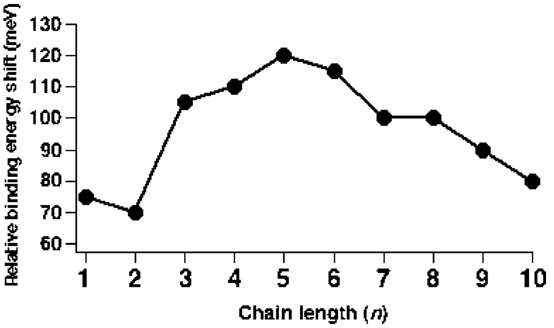

Figure 3. Relative binding energy shift (millielectronvolts) for $HO_2C(CH_2)_nCO_2^-$ as a function of chain length *n*. The maximum shift occurred at $HO_2C(CH_2)_5CO_2^-$.

eV for $n = 1$ to 4.45 eV for $n = 4$, reach a minimum value of 4.40 eV for $n = 5$, and increase for $n > 5$. The chain length dependence of the ADEs suggested that the hydrogen bond strength in the cyclic conformation of $HO_2C(CH_2)_nCO_2^-$ is not the same. While hydrogen bonds between the terminal carboxylate groups are readily formed in the cases of $n = 1$ and 2, the formation of the intramolecular hydrogen bond for $n \geq 3$ would require a properly folded structure of the backbone. The observation of the *n*-dependence of the ADE values implied that the strain energy in the folded backbone plays a major role in determining the hydrogen bond strength in the cyclic $HO_2C(CH_2)_nCO_2^-$ anions.

The increase in the electron binding energies in all of the 70 K spectra relative to the room-temperature spectra suggested that the intramolecular hydrogen bond in $HO_2C(CH_2)_nCO_2^-$ is further stabilized at low temperatures due to the entropic effect. However, the blue shift is *not* systematic and shows a clear maximum at $n = 5$ (Figure 3). Interestingly, $HO_2C(CH_2)_5CO_2^-$ also possesses the lowest ADE among all of the $HO_2C(CH_2)_nCO_2^-$ anions. These observations indicate that the strain energy in $HO_2C(CH_2)_5CO_2^-$ is the highest. Thus, Figure 3 can be viewed also as the trend of the strain energy in $HO_2C(CH_2)_nCO_2^-$. This trend is similar to that predicted in cycloalkanes. By the use of the assumption that cyclohexane is strainless, the strain energy of a series of cycloalkanes were calculated as a function of ring size by Chickos et al.,[23] who obtained a local maximum of strain energy at cyclononane (nine-membered ring), similar to the pattern shown in Figure 3.

3.2. Theoretical Calculations. To obtain further insight into the nature of hydrogen bonding and strain energies in the $HO_2C(CH_2)_nCO_2^-$ anions, we performed theoretical calculations on the linear and folded structures for $n = 1-10$. All linear structures of $HO_2C(CH_2)_nCO_2^-$ ($n = 1-10$) have a straight $-CH_2-$ chain and an intramolecular O−H···O bond at the carboxylic acid end, that is, all the linear anions are calculated in the trans-conformation. All the folded conformations are more stable than the linear structures (Table 1), and the optimized cyclic structures of $HO_2C(CH_2)_nCO_2^-$ ($n = 1-10$) are shown in Figure 4. There is more than one type of hydrogen bonding when $n > 5$: other than the strong O−H···O hydrogen bond, C−H···O type hydrogen bonds may also form between the methylene group and the carboxylate group.[13] Using the geometrical criteria for C−H···O hydrogen bond formation (C−H···O < 3.0 Å and ∠CHO > 120°),[24] we observed one C−H···O hydrogen bond for $n = 6$ and three C−H···O hydrogen bonds for $n = 7-10$, respectively. This type of C−H···O hydrogen bond due to the methylene group is also observed in our previous study of $CH_3(CH_2)_nCO_2^-$, where we estimated that the averaged bond strength is <3 kcal/mol.[13] Compared with the O−H···O type hydrogen bond, which usually has the strength of >15 kcal/mol,[25−27] the C−H···O type is commonly referred as weak hydrogen bonding. As demonstrated in our previous study,[13] the C−H···O hydrogen bond should also play a role in cyclization, albeit a minor one, compared with the strong O−H···O hydrogen bond.

Table 1 shows the experimental and theoretical ADE values and the theoretical energy difference (Δ*E*) between the cyclic and linear conformations. The calculated ADE values are plotted in Figure 2 (dashed line) for easy comparison with the experimental measurements. All the calculated ADEs are lower than the experimental values by ~0.2 eV, but the overall trend in the predicted ADE is in very good agreement with the trend observed in the experiment. More importantly, the ADE of $HO_2C(CH_2)_5CO_2^-$ is calculated to be the lowest among the 10 species studied, consistent with the experimental observation. The minimum Δ*E* was also observed at $HO_2C(CH_2)_5CO_2^-$, with $\Delta E = 0.68$ eV (15.7 kcal/mol), consistent with the fact that $n = 5$ is the most strained. The range of Δ*E* is from 0.68 to 0.83

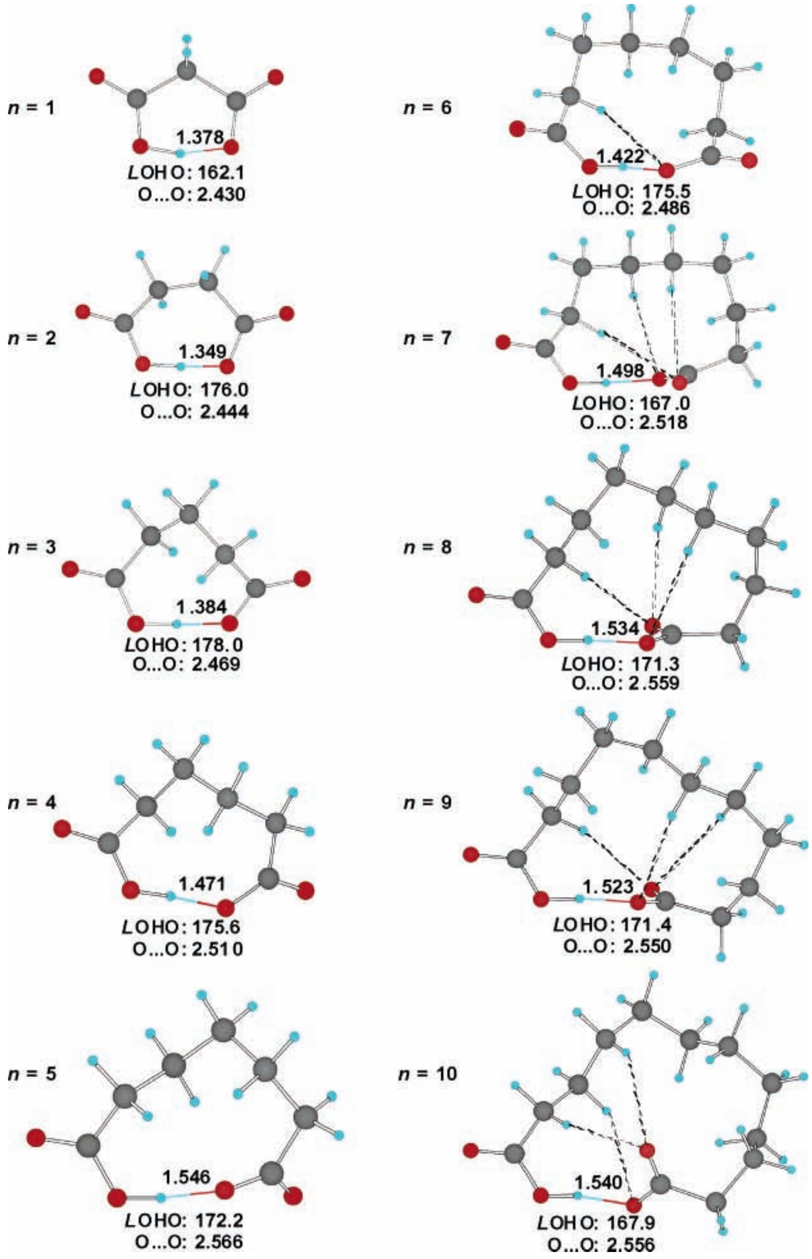

Figure 4. Optimized structures for the cyclic conformations of $HO_2C(CH_2)_nCO_2^-$ ($n = 1-10$) at the B3LYP/6-311++G(d,p) level of theory. Selected O−H···O and O···O bond distances are indicated in angstroms and the OHO angle in degrees. The dashed lines indicate C−H···O hydrogen bonds.

eV, and its variation is also nonlinear. When $n > 7$, ΔE levels off at about ~0.83 eV. We want to emphasize that our calculations only estimate the energy difference between the linear and cyclic structures. In more precise theoretical studies, the strain energy due to the addition of each methylene group in the chain can be estimated.[28−30]

Geometrical criteria have been suggested for hydrogen bond formation, with the O−H···O distance < 3.0 Å and ∠OHO angle > 110°.[24] The O−H···O distance, ∠OHO, and O···O distance for $n = 1-10$ are listed in Table 1. In all cases, the O−H···O distances and ∠OHO angles fall well within these criteria. One point worth noting is that both the O−H···O and O···O are the longest in $n = 5$, which suggest that the hydrogen bond strength is the weakest in $HO_2C(CH_2)_5CO_2^-$ and thus the lowest ADE. Theoretically, the intramolecular hydrogen bond strength can be estimated with a suitable choice of reference structures.[31−33] In the current experiment, since a strong hydrogen bond was already formed at room temperature, we cannot estimate the hydrogen bond strength based on the binding energy shift between the room temperature and 70 K spectra.[13]

4. Conclusions

In summary, photoelectron spectra of $HO_2C(CH_2)_nCO_2^-$ ($n = 1-10$) were measured at 300 and 70 K. Cyclic structures were observed due to the formation of strong intramolecular hydrogen bonds between the terminal $-CO_2H$ and $-CO_2^-$ groups. From the relative binding energy shift between the 300 and 70 K spectra, the pattern of the strain energies in the $HO_2C(CH_2)_nCO_2^-$ cyclic conformation was revealed as a function of ring size. The strain energy was found to be n-dependent, exhibiting a local maximum at $n = 5$.

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