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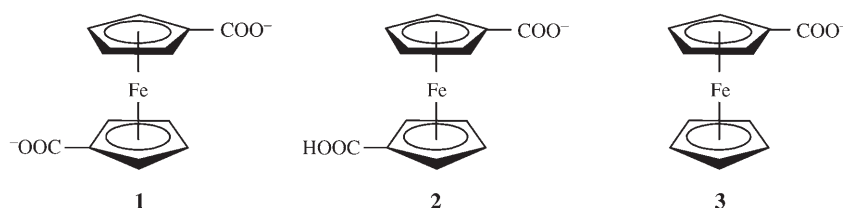
## Intramolecular Rotation through Proton Transfer: $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CO}_2^-)_2]$ versus $[(\eta^5\text{-C}_5\text{H}_4\text{CO}_2^-)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{H})]$ \*\*

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Intramolecular rotation is important in molecular dynamics; it is a fundamental molecular property and can be used to understand the concept of molecular motors. Inspired by elegant biological and macroscopic analogues,<sup>[1–3]</sup> the fabrication of molecular machines has been very actively pursued recently,<sup>[4]</sup> resulting in a variety of molecular devices, such as rotors,<sup>[5–8]</sup> shuttles,<sup>[9–11]</sup> and ratchets.<sup>[12]</sup> The central theme of molecular devices is to control molecular motions and bindings upon external stimuli. The smallest molecular machine can downscale to a single molecule, and such a single molecular rotor has been observed.<sup>[13]</sup> Herein, we report the observation of intramolecular rotations of a single ferrocene derivative through proton transfer.

Ferrocene is a prototypical sandwich complex with an iron atom symmetrically situated between two  $\text{C}_5\text{H}_5$  (cyclopentadienyl, Cp) rings and has been the subject of many experimental and theoretical studies since its discovery.<sup>[14–19]</sup> It has many applications in both fundamental research and materials science. In the solid phase the two Cp rings are in a staggered confirmation ( $D_{5d}$ ),<sup>[14]</sup> whereas in the gas phase they are eclipsed ( $D_{5h}$ ).<sup>[20]</sup> The rotational barrier of the two rings along the  $C_5$  axis is very small in the gas phase ( $E \approx 1.1 \text{ kcal mol}^{-1}$ ).<sup>[20]</sup> Therefore, ferrocene would be an ideal candidate

for a molecular rotor if the rotational freedom can be controlled. Proton transfer, that is, acid–base chemical reaction, is one of the most commonly used external stimuli along with photoinduced processes and electrochemical reactions in realizing molecular devices.<sup>[4,21]</sup> Proton transfer is also ubiquitous and plays a vital role in biological motors.<sup>[22]</sup> It changes the charge state of a molecule to result in alternation of electrostatic interactions. Such effects may influence molecular binding, particularly in the gas phase or hydrophobic environments. Here, we study the energetics and conformations of two ferrocene derivatives, the doubly charged  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CO}_2^-)_2]$  ( $[\text{FeCp}'_2]$ , **1**) and the singly charged  $[(\eta^5\text{-C}_5\text{H}_4\text{CO}_2^-)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CO}_2\text{H})]$  (**2**; see Scheme 1), and demonstrate that they can be viewed to form a model molecular rotor system controlled by proton transfer.

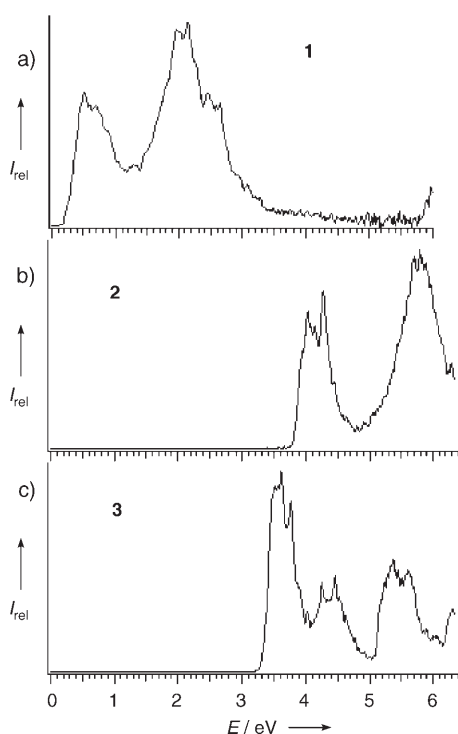


Scheme 1. Structures of the ferrocene derivatives 1–3.

Complexes **1** and **2** were produced using electrospray ionization, and their geometric and electronic structures were probed by photoelectron spectroscopy (PES) and theoretical calculations. The experiments were carried out on a newly developed low-temperature PES apparatus coupled with an electrospray source.<sup>[23]</sup> We detected abundant **1** and **2** by electrospray of a 1 mM solution of 1,1'-ferrocenedicarboxylic acid in a water/methanol mixed solvent system. The 193-nm (6.424 eV) PES spectrum of **1** (Figure 1 a) reveals two broad spectral bands, which likely contain many overlapping detachment transitions. No transitions were observed beyond binding energies of 3 eV owing to the cut-off by the repulsive coulomb barrier, unique to photodetachment of multiply charged anions.<sup>[24–26]</sup> We also measured the photoelectron spectrum of **1** at 266 nm (4.661 eV) with slightly better resolution. Molecular orbital analysis based on the optimized structure (see below) indicates that the lower-binding-energy features (0.2–1 eV) are due to detachments from primarily lone-pair electrons of the carboxylate groups, whereas the higher-binding-energy features (1.5–2.5 eV) are due to detachments from the ferrocene framework, which contains closely spaced molecular orbitals from both the Fe 3d orbitals and the Cp' rings. The surprising observation is the extremely low electron-binding energy for **1**. We measured an adiabatic detachment energy (ADE) of  $0.25 \pm 0.05 \text{ eV}$  for **1** (Figure 1 a). This low electron-binding energy is a result of the strong intramolecular coulomb repulsion due to the two negative charges in **1**. To assess the influence of the coulomb repulsion, we performed a control experiment on a monocarboxylated ferrocene anion,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CO}_2^-)]$  (**3**, Scheme 1), as shown in Figure 1 c. Three spectral bands were observed, all with very high electron-binding energies, in

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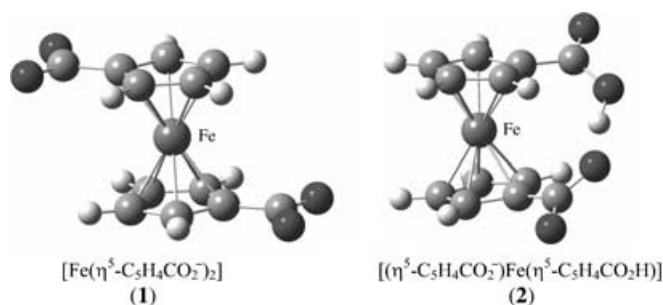


**Figure 1.** Photoelectron spectra at 193 nm (6.426 eV) of a) the  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CO}_2^-)_2]$  dianion (**1**), b) its protonated singly charged anion **2**, and c) the monocarboxylated ferrocene anion,  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CO}_2^-)]$  (**3**).

contrast to **1**. The ADE of **3** was measured to be  $3.31 \pm 0.03$  eV, which is almost identical to that of acetate and other long-chain aliphatic carboxylate groups.<sup>[27]</sup> Thus, the extremely low ADE of **1** is purely due to the intramolecular coulomb repulsion, which can be approximately estimated as the difference in ADE between **3** and **1**; a very large value of approximately 3 eV is obtained.

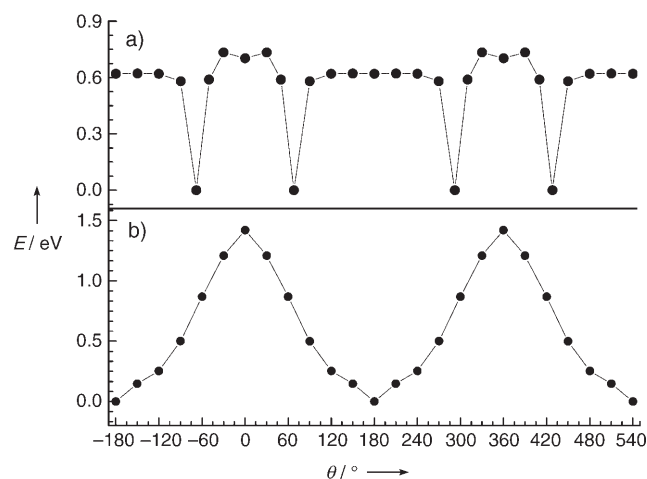
Figure 1b displays the 193-nm spectrum of **2**, which reveals spectral patterns that are similar to those for **1** but at much higher binding energies. We expected that **2** would have binding energies similar to **3** because the first electron detachment in both systems should be from the  $\text{CO}_2^-$  group. However, the ADE of **2** was measured to be  $3.80 \pm 0.03$  eV, about 0.5 eV higher than that of **3**. This observation suggests that the  $\text{CO}_2^-$  group in **2** is stabilized relative to that in **3**. The only mechanism for this stabilization is through an intramolecular hydrogen-bonding interaction between the  $\text{CO}_2^-$  group and the  $\text{COOH}$  group on the second  $\text{Cp}'$  ligand. This is possible if the two  $\text{Cp}'$  ligands in **2** would adopt a staggered conformation, that is, if the two  $\text{Cp}'$  ligands would be rotated  $180^\circ$  relative to each other, as shown in Scheme 1.

To obtain more definitive information about the structures and energetics, we performed theoretical calculations on the three species.<sup>[28]</sup> The optimized structure of **1** indeed shows  $C_{2h}$  symmetry (Figure 2), in which the two  $\text{CO}_2^-$  groups are opposite each other in a *trans* conformation. For **2**, an intramolecular hydrogen bond is observed between the  $-\text{COOH}$  and  $-\text{COO}^-$  groups, as expected, that lock the two  $\text{Cp}'$  ligands in a *cis* conformation. The two  $\text{Cp}'$  ligands are not



**Figure 2.** Optimized structures of the  $[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{CO}_2^-)_2]$  dianion (**1**) and its protonated singly charged anion **2** (O dark gray, C pale gray, H white). Note that the two  $\text{Cp}'$  ligands in **2** are staggered by  $68^\circ$ .

precisely staggered. Instead, there is a  $68^\circ$  angle between them to optimize the intramolecular hydrogen-bond formation. The *trans* conformation of **2** lies 0.62 eV higher in energy relative to the *cis* form (also see Figure 3a). The calculated



**Figure 3.** Calculated energies as a function of rotational angle defined by the two carboxylate groups for a) **2** and b) **1**. The two minima located at  $68^\circ$  and  $-68^\circ$  for **2** are identical. At these angles, the intramolecular hydrogen bond is optimized. Deviation from these angles disrupts the hydrogen bond to result in a non-hydrogen-bonded form of **2**. The sharp minima in (a) reflect the narrow angles for the hydrogen bonding, outside which the rotational potential is relatively flat. The potential for **1** is primarily coulombic and is simpler: the minimum at  $180^\circ$  corresponds to the *trans* structure, whereas the maxima at  $0^\circ$  and  $360^\circ$  correspond to the *cis* form.

ADEs for **1**, **2**, and **3** are compared with the experimental values in Table 1. Although the theoretical values are consistently lower than the experimental values by approximately 0.2 eV, they reproduce the experimental trend very well. In particular, a significantly smaller ADE is predicted for the *trans* confirmation of **2**. In fact, the predicted ADE for the *trans* form of **2** is in remarkable agreement with the ADE of **3**, and confirms unequivocally that the hydrogen-bonded *cis* form is more stable and is the structure that was observed experimentally.

Therefore, we see that the different electrostatic interactions lock **1** and **2** in two different conformations. The

**Table 1:** Experimental adiabatic detachment energies (ADEs [eV]) of **1**, **2**, and **3**, compared to calculated values.

Species	Experimental	Calculated
<b>1</b>	0.25 ± 0.05	−0.03
<b>2</b> ( <i>cis</i> )	3.80 ± 0.03	3.64
<b>2</b> ( <i>trans</i> )		3.32
<b>3</b>	3.31 ± 0.03	3.18

intramolecular coulomb repulsion dictates that the two negative charges in **1** lie as far apart as possible, locking it in the *trans* conformation, whereas intramolecular hydrogen bonding locks **2** in the *cis* conformation. Deviation from the optimal angle of 68° disrupts the hydrogen bond and results in non-hydrogen-bonded forms of **2**. The rotational barriers for **1** and **2** are 1.4 and 0.6 eV, respectively (see Figure 3), in the gas phase, which are much higher than thermal energies at ambient temperatures. As shown in the Figure 2, structures **1** and **2** are controlled by a proton-transfer process. Protonation of **1** induces a 112° rotation that leads to **2**, while deprotonation of **2** results in **1** by also involving a 112° intramolecular rotation.

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 [23] The experiments were carried out on a new homebuilt instrument, which couples electrospray ionization with a magnetic-bottle time-of-flight photoelectron spectrometer and the capability of controlling ion temperatures. The electrospray source and the magnetic-bottle photoelectron spectrometer are similar to that described previously (L. S. Wang, C. F. Ding, X. B. Wang, S. E. Barlow, *Rev. Sci. Instrum.* **1999**, 70, 1957). Briefly, the anions of interest were produced from a solution of the corresponding acids under slightly basic conditions in a mixed solvent system of methanol/water (3:1 v/v). After their desolvation from the electrospray source, anions were guided by a RF-only (RF = radiofrequency) octopole device and transported through a quadrupole mass filter (operated at RF-only mode), before they entered a 3D Paul trap. The trap was attached to a cryostat, which consists of a closed-cycle helium refrigerator and a feedback heater. Temperatures of the trap can be controlled from 18–400 K. Ions were trapped for a period of 20–100 ms and collisionally cooled by using a 10<sup>−4</sup> Torr He background gas containing about 10% H<sub>2</sub>. The cold anions were then unloaded from the trap and were analyzed using a time-of-flight mass spectrometer. The ions of interest were selected and decelerated before they were intercepted with a laser beam in the interaction zone: 266 nm from a Nd:YAG laser and 193 nm from an ArF excimer laser. The lasers were operated at 20 Hz repetition rate, with the ion beam off at alternate laser shots for background subtraction. The photodetached electrons were collected with nearly 100% efficiency by a magnetic bottle and analyzed in a 5-m long electron-flight tube. The electron-energy resolution of the apparatus is  $\Delta E/E \approx 2\%$ , that is, 20 meV for 1 eV electrons. Photoelectron time-of-flight spectra were collected and then converted to kinetic-energy spectra, calibrated by the known spectra of ClO<sub>2</sub><sup>−</sup> and I<sup>−</sup>. The electron-binding-energy spectra presented were obtained by subtracting the kinetic-energy spectra from the detachment photon energies.  
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