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Vicinal tricarbonyls as redox-controlled molecular rotors[†]

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Abstract

Using electrochemistry, spectroelectrochemistry and density functional computational methods, we have demonstrated that tricarbonyl amide $\mathbf{1}_{\mathbf{ox}}$ undergoes reversible conformational switching upon reduction to the corresponding radical anion $\mathbf{1}_{\mathbf{rad-}}$. © 2000 Elsevier Science Ltd. All rights reserved.

Molecular devices provide the ultimate goal in the miniaturization of mechanical systems. In recent investigations, chemical and photochemical stimuli have been used to control the operation of a wide variety of these molecular machines, including shuttles,[1] rotors,[2] and switches.[3] Application of these systems to pragmatic electromechanical devices, however, is complicated by the requirement for electronic input from the computer interface to be converted to either chemical or photonic stimuli for device actuation.

One way to greatly simplify the fabrication and application of multi-scale systems based on molecular devices is through the use of electrochemically-activated devices.[4] With these devices, electronic input is used directly, allowing direct interfacing to computer systems.[5] This simplicity of operation makes redox control of molecular structure an obvious goal in device fabrication; a target complicated by the relative lack of well-behaved acyclic redox systems. To expand the diversity of structural motifs available for electronically-controlled devices, we have explored the redox chemistry of vicinal tricarbonyls. These systems can be synthesized with a wide variety of structures, making them potentially versatile components for device fabrication.[6,7] We report here the use of electrochemical, spectroelectrochemical and density functional (DFT) computational methods to demonstrate redox-controlled conformational switching of aryl-substituted tricarbonyl $\mathbf{1}_{\mathbf{ox}}$ (Scheme 1).

For our investigations, we used aryl tricarbonyl $\mathbf{1}_{\mathbf{ox}}$. In this system, the aryl substituent was selected to provide potential electron delocalization and stabilization, and the amide functionality to inhibit hydration.[8] Tricarbonyl $\mathbf{1}_{\mathbf{ox}}$ was synthesized starting from the commercially available β-keto ester as shown in Scheme 2.[9]

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[†] Dedicated to Professor Harry H. Wasserman: a mentor, scholar, and colleague.

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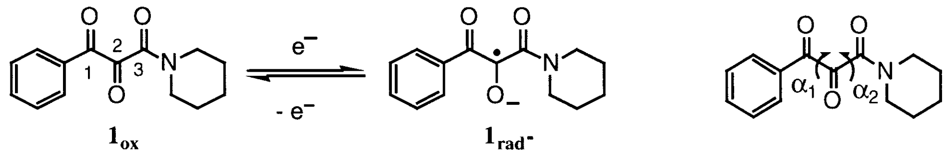
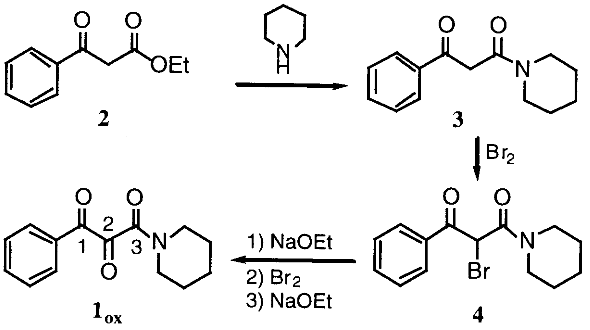


Scheme 1. Redox chemistry and numbering of tricarbonyl **1**. α represents the dihedral angle between neighboring carbonyls



Scheme 2. Synthesis of tricarbonyl $\mathbf{1}_{ox}$

As expected, tricarbonyl $\mathbf{1}_{ox}$ is a well-behaved redox unit. Simultaneous electrochemistry and EPR (SEEPR) demonstrated the clean conversion of $\mathbf{1}_{ox}$ to $\mathbf{1}_{rad^-}$ (Fig. 1a). In contrast to cyclic tricarbonyl analogs, however, the reduction of $\mathbf{1}_{ox}$ to $\mathbf{1}_{rad^-}$ possesses a very large peak potential difference ($\Delta E_p = \sim 400$ mV, compared to ferrocene, $\Delta E_p = \sim 90$ mV[10]) (Fig. 1b).[11] This large ΔE_p is diagnostic of dramatic structural reorganization upon reduction, a required feature for redox-activated devices.[12]

To establish the nature of the structural reorganization that occurs upon reduction of $\mathbf{1}_{ox}$, we performed B3LYP-DFT calculations for $\mathbf{1}_{ox}$ and $\mathbf{1}_{rad^-}$. In recent studies, we have demonstrated the ability of these calculations to accurately predict not only the energetics of radical anion systems,[13] but also fundamental electronic properties such as hyperfine splittings (Fig. 1a).[14] Geometry optimization studies of $\mathbf{1}_{ox}$ showed that the carbonyl groups are arranged in a helical conformation resulting from electrostatic repulsions between the oxygen atoms ($\alpha_1 = 89°$; $\alpha_2 = 83°$). Calculations on $\mathbf{1}_{rad^-}$, however, indicated that major conformational restructuring takes place after reduction of $\mathbf{1}_{ox}$. After electron transfer, the central (O(2)) carbonyl unit rearranges into an antiperiplanar position (*trans* relative to O(1)), and coplanar with the aromatic moiety ($\alpha_1 = 179°$; $\alpha_2 = -77°$). Calculations show that this conformation of $\mathbf{1}_{rad^-}$ is stabilized by ~20 kcal mol^{-1} relative to the helical conformation adopted by $\mathbf{1}_{ox}$. This stabilization clearly arises from an increased energetic benefit from electron delocalization: the electrostatic potential maps reveal that the one-electron reduction greatly increases the negative potential of both the oxygen atoms and phenyl ring. This enhanced delocalization is also supported by the SEEPR spectrum, where extensive electron spin density in the phenyl ring of $\mathbf{1}_{rad^-}$ is demonstrated by large hyperfine couplings arising from the aromatic protons (Fig. 2).

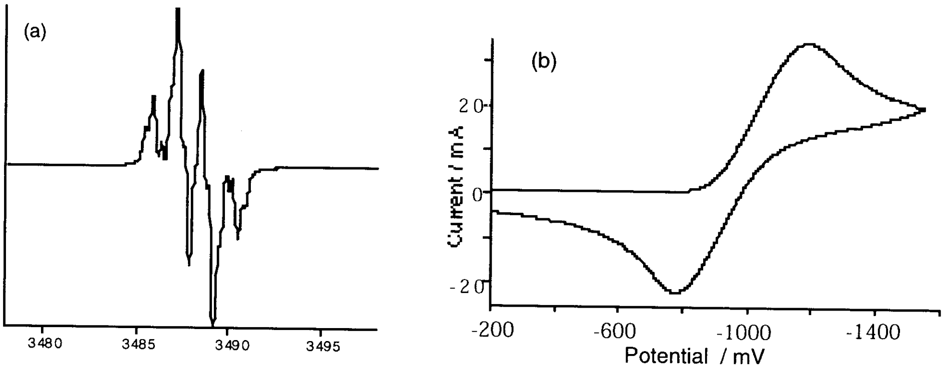


Figure 1. (a) SEEPR of $\mathbf{1}_{\mathrm{rad}-}$ in CH_2Cl_2. 0.1 M TBAP electrolyte. $[\mathbf{1}_{\mathrm{ox}}]=1\times10^{-3}$ M. (b) Cyclic voltammogram of $\mathbf{1}_{\mathrm{ox}}$ in CH_2Cl_2. 0.1 M TBAP electrolyte, 296 K, 275 mV/s scan rate. $[\mathbf{1}_{\mathrm{ox}}]=1\times10^{-3}$ M. $E_{1/2}=1000$ mV; relative to ferrocene

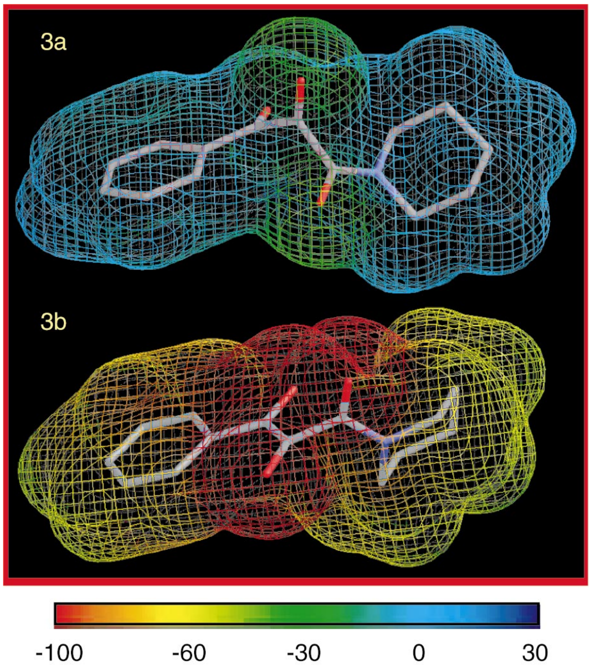


Figure 2. Electrostatic potential maps derived from B3LYP/6-31G*//UHF/3-21G* calculations for tricarbonyl $\mathbf{1}_{\mathrm{ox}}$ in (a) the oxidized ($\mathbf{1}_{\mathrm{ox}}$) and (b) the radical anion ($\mathbf{1}_{\mathrm{rad}-}$) forms. Clearly noticeable is the conformational rearrangement that occurs after reduction

In summary, we have used electrochemical techniques to demonstrate redox-controlled conformational switching of tricarbonyl $\mathbf{1}_{\mathrm{ox}}$. Through computational methods, we established that this switching arises from changes in the conformational preferences of the carbonyl groups upon reduction of $\mathbf{1}_{\mathrm{ox}}$ to $\mathbf{1}_{\mathrm{rad}-}$. The application of this switching process to the creation of effective molecular devices is currently underway, and will be reported in due course.

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