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LETTERS

Photorearrangement in a Semiquinone to Yield an Unusual 1,3-Carbon/Carbon Interaction and Spin Delocalization

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Solutions of 1,4-bis(dihydroquininyl)-anthraquinone {$(DHQ)_2AQN$} in either hexamethylphosphoramide (HMPA) or liquid ammonia undergo a photoinduced electron transfer from the solvent to the $(DHQ)_2AQN$. The resulting anion radical {$(DHQ)_2AQN^{\bullet-}$} yields coupling to the six (3 sets of 2 equivalent) protons on the anthraquinone moiety upon EPR analysis. The same anion radical can be generated via alkali metal reduction in tetrahydrofuran. Further exposure of the HMPA solution to visible light causes the anion radical to undergo a conformational change. The photorearranged product allows delocalization of spin into the γ proton on the sp^3 hybridized alkoxy carbon. In $NH_{3(liq)}$ and THF, hydrogen bonding and ion association prevents this photorearrangement, respectively.

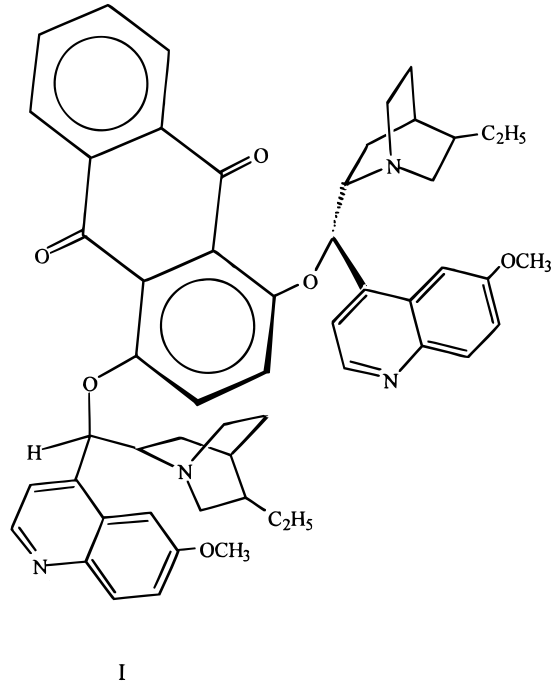
Introduction

Due to the importance of amino acid cation radicals in a number of biological processes including DNA and protein damage and enzymatic reactions,[1] Walden and Wheeler[2] used HF/DFT calculations to provide evidence of through space spin delocalization from the π system of the tryptophan cation radical to the alanyl group. This anchimeric spin delocalization is very conformationally dependent, as proper orbital overlap is essential.[2] It occurred to us that analogous anchimeric spin delocalization might occur in quinone anion radicals, which are also of considerable biological interest. Semiquinones play vital roles in biological redox and electron-transfer processes, some of which involve noncovalent interactions with enzymatic substances.[3]

The transfer of an electron to a π-system of a conjugated molecule is always associated with some alteration in molecular structure.[4] In most cases, the structural perturbation due to electron attachment is rather subtle, as is the case for the benzoquinone system.[5] Gating due to interconversion between two conformational geometries can, however, control the electron transfer.[4] In this type of system, changes in conformation are predicted (by Hoffman and Ratner)[4] to alter both the rate and mechanism of electron transfer. Here we report an example of such gated electron transfer in an anion radical.

Experimental Section

Sharpless and Becker[6] recently synthesized 1,4-bis(dihydroquininyl)-anthraquinone {$(DHQ)_2AQN$, see Structure I}, which



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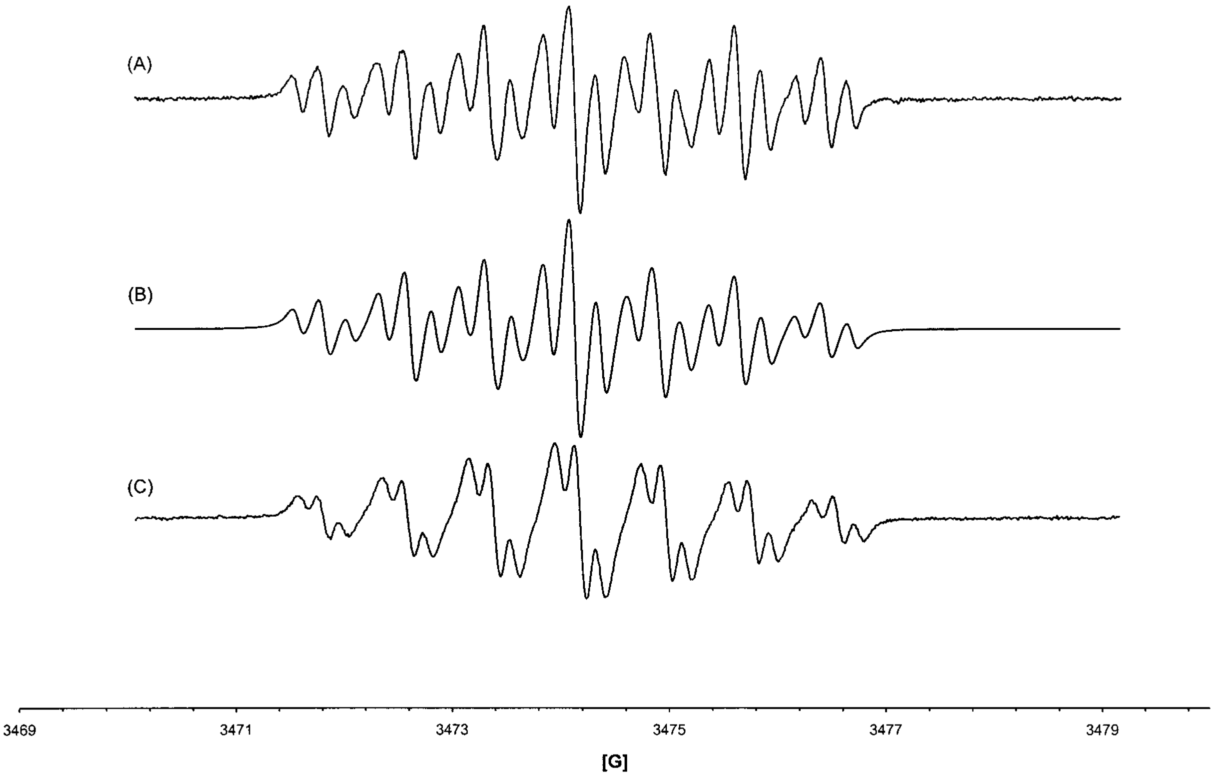


Figure 1. (A) EPR spectrum of a liquid ammonia solution of $(DHQ)_2AQN$ that has been exposed to room light. Immediately below this spectrum (B) is a computer-generated simulation based upon the splitting pattern from three sets of two equivalent protons with hyperfine couplings of 1.521, 0.791, and 0.239 G and a peak-to-peak line width of 0.12 G. The bottom spectrum (C) was obtained by exposing a THF solution containing $(DHQ)_2AQN$ and 18-crown-6 to potassium metal. This spectrum is best simulated using coupling constants of 1.596, 0.780, and 0.186 G and a peak-to-peak line width of 0.15 G. All spectra were recorded at 25 °C.

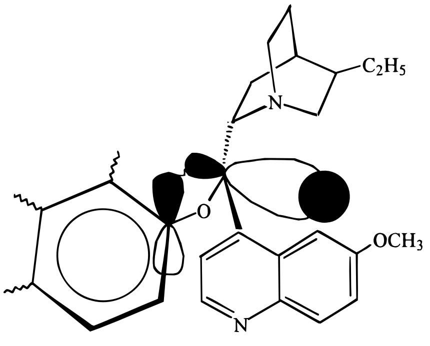
can be used to obtain enantioselectivity in the asymmetric dihydroxylation of olefins. The {$(DHQ)_2AQN$ was purchased from Aldrich Chemicals and was placed in a Pyrex apparatus containing a 3 mm sidearm for EPR analysis. The apparatus was evacuated, and the solvent was distilled from a flask containing potassium metal directly into the evacuated apparatus. A sample of the resulting solution was then poured into the sidearm, which was subsequently sealed from the apparatus. Exposure of the resulting sample to room light effected the electron transfer. All EPR spectra were recorded on a Bruker EMX 6/1 x-band EPR spectrometer with the following settings: modulation amplitude = 0.05 G, power = 0.20 mW, and a 20 G sweep width.

Results and Discussion

Dissolution of $(DHQ)_2AQN$ in liquid ammonia or in hexamethylphosphoramide (HMPA) followed by exposure to room light results in a photoinduced electron transfer from the solvent to the $(DHQ)_2AQN$. The EPR of $(DHQ)_2AQN^{\bullet -}$ is, as expected, represented by three triplets ($a_H = 1.52$ G from 2 Hs, $a_H = 0.79$ G from 2 Hs, and $a_H = 0.24$ G from two Hs). Further exposure of the $NH_{3(liq)}$ solution does not alter the EPR spectrum, Figure 1. However, further exposure of the HMPA solution dramatically perturbs the conformational geometry of the anion radical (Figure 2).

The new photo rearranged anion radical exhibits a splitting from a fourth pair of protons, Figure 2. This new splitting of 0.46 G arises from the two equivalent γ protons on the sp^3 hybridized alkoxy carbons. Upon the initial photo electron transfer, the orientation of the dihydroquininyl side chain does not allow for orbital overlap to yield leakage of spin density to the γ protons. Further exposure to light causes a conformational rearrangement leading to a 1,3-homohyperconjugative carbon/carbon interaction between the alkoxy carbon and the anthraquinone ring, Structure II. This type of 1,3-homohyperconjugative interaction appears to be an example of the anchimeric spin delocalization predicted and described by Walden and Wheeler,[2] and the resulting redistribution of spin density is consistent with their predictions.

It might be expected that the conjugative interaction depicted in Structure II would render the γ protons slightly protic. This proved to be the case, as the 0.464 G splitting collapses to a 0.071 G coupling from 2 equivalent deuteriums upon the addition of D_2O. This leaves little doubt that twisting of the side chains in the anion radical occurs upon further irradiation.[7] The addition of D_2O to the anion radical of methoxybenzoquinone in HMPA does dramatically alter the hyperfine pattern. Methoxybenzosemiquinone does not exhibit a γ proton splitting in HMPA (our experiment) nor in other solvent systems.[8]



II

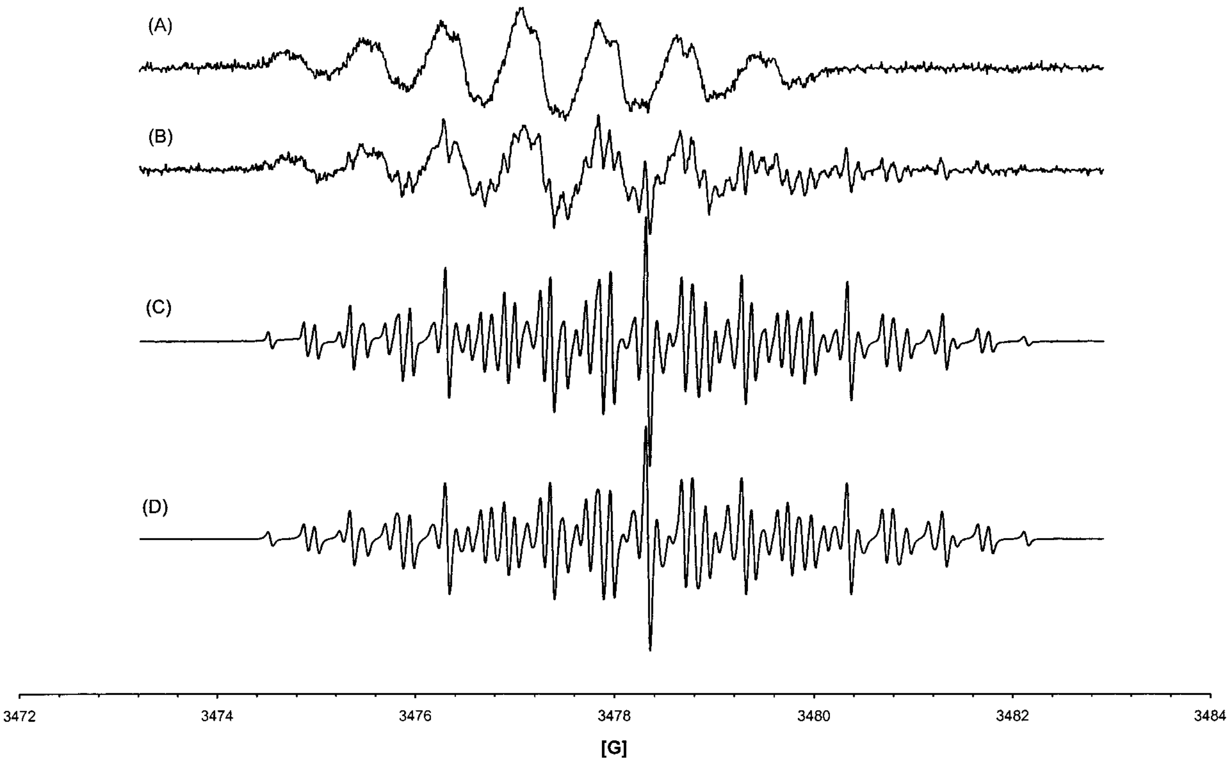


Figure 2. (A) EPR spectrum of an HMPA solution of $(DHQ)_2AQN$ that had been exposed to room light for a few seconds. (B) EPR spectrum of the sample after exposure to room light for 17 min. (C) EPR spectrum of the same sample after exposure to room light for 40 min. The bottom spectrum (D) was computer generated using coupling constants of 2.016, 0.962, 0.359, and 0.464 G and a peak-to-peak line width of 0.03 G. Each splitting is due to two equivalent protons, and the spectra were recorded at room temperature. Since the coupling constants are larger than those in Figure 1, there is less spin density in the carbonyl moiety. This is known to perturb the *g*-value (see, Stevenson, C. D.; Alegria, A. E.; Block A. M. *J. Am. Chem. Soc.* **1975**, *97*, 4859). Such a *g*-value shift associated with the transformation is observed here.

This 1,3-homohyperconjugative carbon/carbon interaction delocalizes spin into the γ protons and simultaneously aligns the faces of the semiquinone and the azanaphthalene moieties so that they are in proper position for efficient spin transfer. This type of 1,3-C/C interaction was first described by Bauld and Cessac,[9] wherein they pointed out how it can perturb spin densities as measured by EPR hyperfine couplings of the benzocyclobutadiene anion radical.

The photorearrangement observed in HMPA leading to II is not observed when $NH_{3(liq)}$ serves as the solvent. Liquid NH_3 is known to form strong hydrogen bonds to anion radcials,[10] and it seems reasonable that the close proximity of the ammonia molecules to the face of the semiquinone would sterically inhibit the approach of the azanaphthalene face. The anion radical of $(DHQ)_2AQN$ is not formed upon exposure of tetrahydrofuran (THF) solutions to white visible light. However, exposure of these solutions to an alkali metal mirror (Na or K) does result in $(DHQ)_2AQN^{\bullet-},M^+$. In THF ion association prevails,[11] and the metal cation would be expected to also prevent the photorearrangement.

The EPR signal for the photorearranged anion radical persists at ambient temperatures for several days. The signal is ultimately lost, presumably, due to cleavage of an ether linkage. Ether linkages are known to undergo spontaneous cleavage in anion radicals.[12] Further irradiation of the photorearranged anion radical with shorter wavelength light (UV) causes immediate loss of the EPR signal.

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