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# On the Association and Structure of Radicals Derived from Dipyridil[3,2-*a*:2′3′-*c*]phenazine. Contrast between the Electrochemical, Radiolytic, and Photochemical Reduction Processes

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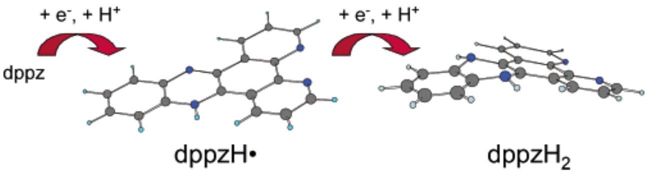
*Received September 22, 2005*



The reduction of dipyridil[3,2-*a*:2′3′-*c*]phenazine, dppz, by pulse radiolytically generated $e^-_{sol}$ or by the reaction of the dppz excited states with electron donors produces the radical dppzH$^{\bullet}$. The dimer radical, (dppz)$_2$H$^{\bullet}$, exists in equilibrium with dppz with an association constant, $K = 10^3$ M$^{-1}$. The rate constant for the reaction of dppzH$^{\bullet}$ with dppz is $k = 4.3 \times 10^6$ M$^{-1}$ s$^{-1}$. DFT calculations on the structures of dppzH$^{\bullet}$ and the doubly reduced and doubly protonated dppzH$_2$ rendered a planar structure for the former species and a bent one for the latter.

Interest in dipyridil[3,2-*a*:2′3′-*c*]phenazine, dppz, has been motivated by the intercalation of dppz, free and complexed to transition metals, in DNA and the differences between the photophysical and photochemical properties when they are free or intercalated.[1−7] In addition to photopysical and photochemical work, some studies have been concerned with the reduction products of dppz.[8,9] Theoretical calculations have shown that the added electron in the radical anion, dppz$^{\bullet-}$, can be localized in different sectors of the molecule.[8,9] These sectors have been identified as an antibonding orbital, b$_1$*(phz)*, placed in the phenazine region and two orbitals, $b_1(\Psi)$ and $a_2(\chi)$, localized in the bipyridinic region of the ligand. The former orbital is generically described as “the redox orbital”, while the latter orbitals are denominated “optical orbitals”. Despite the work done on the radical anion produced by the electrochemical reduction of dppz, the formation of oligomers by reaction of the radical anion with dppz has not been investigated. We communicate here the formation of such an oligomer, (dppz)$_2$H$^{\bullet}$, in ground- and excited-state reactions of dppz.

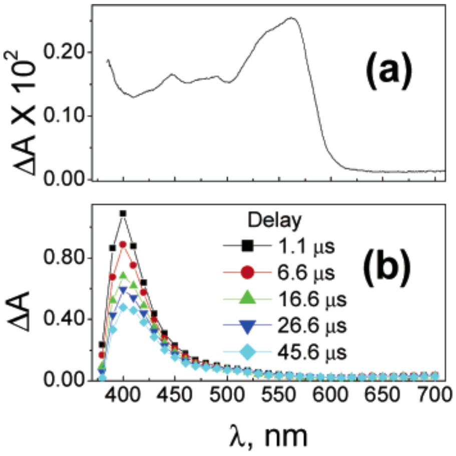
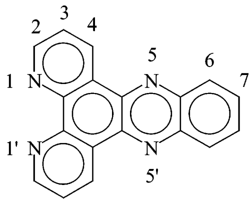


**FIGURE 1.** Spectra of the products formed in the elctrochemical and phtochemical reduction of dppz. The spectrum in (a) corresponds to the product formed when $3.0 \times 10^{-4}$ M dppz in CH$_3$CN is reduced over a Pt working electrode. Transient spectra, (b), recorded with different delays from the 351 nm laser flash irradiation of $2 \times 10^{-5}$ M dppz and 0.93 M TEOA in CH$_3$CN.



dppz with atom labels

Spectroelectrochemical experiments were carried with deaerated $3 \times 10^{-4}$ M solutions of dppz in acetonitrile. The spectrum of the reduced dppz, Figure 1a, was in very good agreement with a literature spectrum assigned to dppz$^{\bullet-}$.[10] However, the dependence of the spectrum on dppz concentra-

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tion, comunicated elsewhere in the text, demonstrates that this is the absorption spectrum of a dimer radical.

The 351 nm flash irradiation of deaerated solutions containing 2 × $10^{-5}$ M dppz and 0.93 M triethanolamine, TEOA, in methanol or acetonitrile produced excited states that readily reacted with TEOA, Figure 1b. This reaction of the dppz excited state, dppz*, with TEOA to produce the dppzH$^\bullet$ radical is shown in eqs 1 and 2.

$$\mathrm{dppz} \xrightarrow{h\nu} \mathrm{dppz}^{*} \xrightarrow{\mathrm{TEOA}} \mathrm{dppz}^{\bullet-} + \mathrm{TEOA}^{\bullet+} \qquad (1)$$

$$\mathrm{dppz}^{\bullet-} + \mathrm{BH} \rightleftarrows \mathrm{dppzH}^{\bullet} + \mathrm{B}^{-} \qquad (2)$$

This spectrum in Figure 1b and the spectrum of related phenazine radicals, e.g., the 1,10-phenanthrolineH$_2^{\bullet+}$ radical, exhibit shared spectroscopic features.[11−13] Because of the strong base character of these anion radicals, the spectrum must be assigned to the dppzH$^\bullet$ radical. The strong base character of anion radicals related to dppz$^{\bullet-}$ has been well established in the literature reports.[11,14,15] In the reaction media used in our experiments, the protonation by any proton donor, i.e., BH = methanol and/or TEOA in eq 2, it is expected to be too fast, and it cannot be kinetically decoupled of the eq 1.

To confirm the nature of the species observed in the already described flash photolysis experiments, 2 × $10^{-5}$ M dppz in $N_2$ saturated methanol was reduced with pulse radiolytically generated $e^-_{sol}$, eq 3.

$$\mathrm{dppz} \xrightarrow{e_{\mathrm{sol}}^{-}} \mathrm{dppz}^{\bullet-} \xrightarrow{\mathrm{CH_3OH}} \mathrm{dppzH}^{\bullet} + \mathrm{CH_3O}^{-} \qquad (3)$$

An absorption band at 400 nm in the spectrum of the product, Figure 2, was identical to the one observed in flash photolysis, Figure 1b. This observation showed that the same radical dppzH$^\bullet$ was formed in the photochemical and radiolytic reductions of dppz. The redox potentials of the couples $CH_2O$, $H^+$/$C^\bullet H_2OH$, $E^0 = -0.92$ V vs NHE, and dppz/dppz$^{\bullet-}$, $E^0 = -1.0$ V vs NHE, show that the reduction of the dppz by $C^\bullet H_2OH$ has a Gibs free energy $\Delta G^0 > 0$. In accordance with the endoergonicity of the reaction, no transient spectrum indicative of a reaction between $C^\bullet H_2OH$ and dppz was observed in pulse radiolysis experiments with $N_2O$-saturated solutions of dppz. An extinction coefficient for dppzH$^\bullet$, $\epsilon_{400} \sim 1.0 \times 10^4$ $M^{-1}$ $cm^{-1}$, was calculated on the basis of the absorbance change at 400 nm and the concentration of dppzH$^\bullet$ estimated on the basis of the dosimetry.

The pronounced differences between the spectra recorded in the reduction of dppz by electrochemical and flash photochemical means could also be attributed to the formation of oligomers, (dppz)$_n$ where $n > 1$. Since changes in the UV−vis spectrum with dppz concentrations equal to or less than 2 × $10^{-4}$ M obey Beer's law, no oligomers were formed in the solutions used for this work. The association of the dppzH$^\bullet$ radical with dppz was investigated in pulse radiolysis experiments with a concentration of dppz between $10^{-3}$ and $10^{-5}$ M. Spectral changes followed after the completion of the eq 3, i.e., $t > 1.0$ $\mu$s, became more evident with dppz concentration. While the spectral changes were insignificant in the $10^{-5}$ M dppz solution, the formation of the reaction product was easily observed with the $10^{-3}$ M solution of dppz, Figure 2. These spectral changes are accounted by the formation of the species with the spectrum recorded in the electrochemical experiments in a proportion that increases with dppz concentration. Moreover, the kinetics of the spectral changes at 400 and 470 nm, Figure 2, are in accordance with a relaxation of the equilibrium in eq 4.

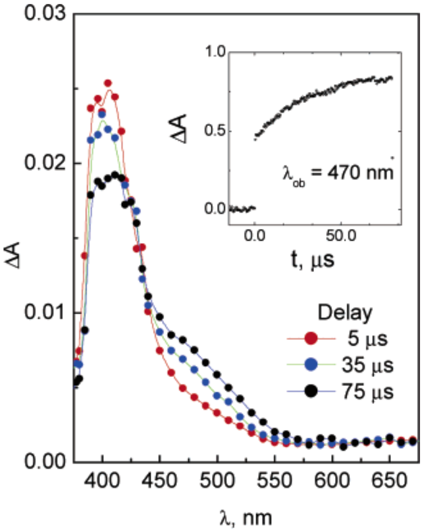

**FIGURE 2.** Transient spectra recorded when a $N_2$-saturated, $10^{-3}$ M dppz solution in methanol was pulse radiolyzed. An oscillographic trace in the inset shows the association of the dppzH$^\bullet$ radical with dppz.

$$\mathrm{dppzH}^{\bullet} + \mathrm{dppz} \underset{k_2}{\overset{k_1}{\rightleftarrows}} (\mathrm{dppz})_2\mathrm{H}^{\bullet} \qquad (4)$$

Based on the kinetics of the spectral change in solutions containing, respectively, $10^{-3}$ and $10^{-4}$ M dppz, i.e., processes related to the association equilibrium in eq 4, the calculated equilibrium constant is $K = k_1/k_2 = (1.1 \pm 0.3) \times 10^3$ $M^{-1}$ and the rate constant of the association is $k_1 = 4.3 \times 10^6$ $M^{-1}$ $s^{-1}$. The same value for the equilibrium constant was calculated from the dependence of the spectral change at 470 nm on the dppz concentration. On the basis of the value of the equilibrium constant, concentrations equal to or larger than 1.0 × $10^{-3}$ M are required to have more than 50% of the (dppz)$_2$H$^\bullet$ radical in equilibrium with dppzH$^\bullet$. The observation of the (dppz)$_2$H$^\bullet$ spectrum in spectroeletrochemical experiments, i.e., in Figure 1a, must also fulfill this condition. The dppz concentration in the vicinity of the electrode must be, threfore, equal to or larger than 1.0 × $10^{-3}$ M. An equilibrium constant, $K = 1 \times 10^3$ $M^{-1}$, accounts for the photoinduced spectral changes in Figure 1b. The value of $K$ also suggests that literature ESR and Raman spectra of the reduced dppz may have been recorded under conditions where the dimer (dppz)$_2$H$^\bullet$ achieved significant concentrations.[10]

In the photochemical experiment, the low concentration of dppz prevents the formation of (dppz)$_2$H$^\bullet$, and the kinetics of the transient spectrum decay is in accordance with a dimerization/disproportionation of the radical, eq 5.

$$2\mathrm{dppzH}^{\bullet} \xrightarrow{-2\mathrm{H}^{+}} (\mathrm{dppz})_2 \text{ and/or } \mathrm{dppz} + \mathrm{dppz}^{2-} \qquad (5)$$

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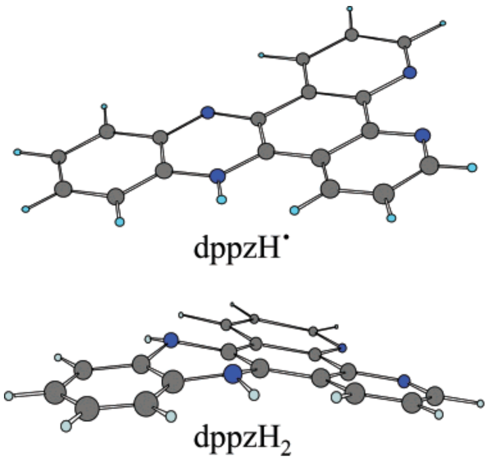


**FIGURE 3.** Calculated structures for the planar dppzH• radical and the bent doubly reduced $dppzH_2$ species.

Indeed, a plot of the reciprocal of the absorbance change, $1/\Delta A$, vs time was linear. A ratio, $2k/\epsilon_{400} = (2.6 \pm 0.2) \times 10^4$ cm $s^{-1}$, of the decay rate constant, $2k$, to the extinction coefficient, $\epsilon_{400}$, at 400 nm was calculated from the slope of the line. To calculate the decay rate constant, $2k \approx 2.8 \times 10^8$ $M^{-1}$ $s^{-1}$, $2k/\epsilon_{400}$ was multiplied by the value of $\epsilon_{400}$ communicated above. The value of the rate constant is close to values communicated in the literature for the decay rate constant of the 1,10-phenanthroline radical, $2.2 \times 10^9 \geq 2k \geq 0.5 \times 10^9$ $M^{-1}$ $s^{-1}$,[11] and may likewise approach the diffusion limit.

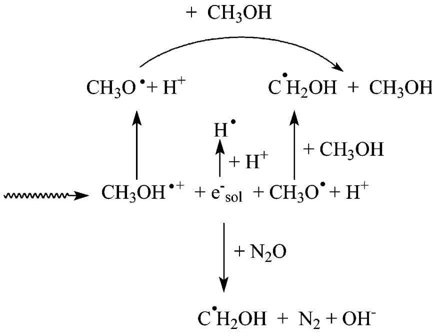
On the basis of the p$K_a$ of related azine radical anions, the protonation of the radical anion, eqs 2 and 3, is highly probable under our experimental conditions.[14,15] Our calculations of the structure and electronic spectroscopy of the one- and two-electron-reduced species in acetonitrile are in accordance with this proposition. They show that protonation of $dppz^{\bullet-}$ on N(5) produces a species ca. 30 kJ/mol more stable than the species protonated on N(1) with the latter being ca. 30 kJ/mol more stable than the radical anion. Our calculations also show that the electronic spectrum of the species protonated on N(5) shows the best agreement with the spectrum of the transients observed in pulse radiolysis and flash photolysis experiments. Different structures were calculated for the dppzH• radical and the twice reduced and protonated $dppzH_2$ species, Figure 3. While the former is planar, the species produced by the addition of an electron and a proton to the dppzH• radical is stabilized in a bent configuration when the protons are on N(5) and N(5′). Isomers of $dppzH_2$ with protons on N(1) and N(5) or N(1) and N(5′) are ca. 63 kJ/mol less stable than the isomer with protons on N(5) and N(5′).

## Experimental Section

**Flash Photochemical Procedures.** Absorbance changes, $\Delta A$, occurring in a time scale longer than 10 ns were investigated at room temperature with a flash photolysis apparatus described elsewhere.[16] In these experiments, 10 ns flashes of 351 nm light were generated with an excimer laser.

**Electrochemical Measurements.** Apparatuses used for the dc and ac voltammetries have been described elsewhere.[17−19] Spectroelectrochemical measurements were made by modulating the electrode potential at 11 Hz around the potential of the appropriate CV wave. Reflected light with the spectroscopic information was demodulated with a lock-in amplifier.

**SCHEME 1**



**Pulse-Radiolytic Procedures.** The instrument for the pulse radiolysis experiments and the computerized data collection for time-resolved UV−vis spectroscopy and reaction kinetics have been described elsewhere in the literature.[20−23] The liquids were deaerated with streams of the $O_2$-free gas, $N_2$, or $N_2O$, that was required for the experiment. These studies have shown that pulse radiolysis can be used as a convenient source of $e^-_{sol}$ and $C^\bullet H_2OH$ radicals, Scheme 1.[23−25]

Since $e^-_{sol}$ and $CH_2O$, $H^+/C^\bullet H_2OH$ have, respectively, the reduction potentials −2.8 V vs NHE and −0.92 V vs NHE, they are frequently used for the reduction of organic and inorganic compounds and for the initiation and study of fast electron-transfer reactions. The yield of $e^-_{sol}$ in $CH_3OH$ (G. 1.1)[22] is about one-third of the *G* value in the radiolysis of $H_2O$ (G. 2.8)].[25] In solutions where $e^-_{sol}$ was scavenged with $N_2O$, the $C^\bullet H_2OH$ radical appears to be the predominant product (yield > 90%) of the reaction between $CH_3OH$ and $O^{\bullet-}$.

**Computational Details.** Density functional theory (DFT) was used to calculate the structure and stability of the dppz radical anion, its protonated form, dppzH•, and the diprotonated form of the doubly reduced anion, $dppzH_2$. Geometries were initially optimized at the Hartree−Fock level using a small split-valence basis, HF/3-21G.[26] Structures were then refined in DFT calculations with the gradient-corrected hybrid B3LYP functional,[26] using first the heavy-atom polarized, split-valence 6-31G* basis,[25] and later with a more flexible basis of triple-$\zeta$ quality augmented with diffuse functions of the heavy atoms, 6-311+G(d,p).[29] The effect of the solvating medium was recovered employing the IEFPCM variant of the polarized continuum approach.[30] At the optimized geometries, vertical excitation energies were calculated with time-dependent DFT and a basis set that included diffuse functions on the heavy

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atoms (6-31+G*). The solvent used was acetonitrile. All calculations were spin-unrestricted and conducted with the Gaussian 03 series of programs.[31]

**Materials.** The dppz and 1,10-phenanthroline-5,6,-dione were prepared by a literature procedure.[32−34] The melting point, the UV−vis spectrum, and the half-wave potential of the dppz/dppz$^{\cdot-}$ couple, $E_{1/2} = -1.19$ V vs Ag/AgCl/KCl$_{sat}$, were all in good agreement with those communicated in the literature reports.[8,9] Furthermore, the $^1$H NMR spectra of the samples used for the photochemical work indicated that they were free of major impurities which could have affected the experimental results. The 250 MHz dppz's $^1$H NMR in CD$_3$CN exhibited the following resonances: H(standard solvent signal) 9.597 (H4, dd), 9.203 (H2, dd), 8.366 (H6, dd), 8.004 (H7, dd) and 7.867 (H3, dd) with the proton numbering given in the Introduction. To verify that the results were not affected by impurities that remained undetected with the previous analyses, samples of the dppz, already purified by recrystallization according to the literature procedure, were sublimated under vacuum, i.e., ∼0.2 g sublimated at ∼ 443 K under a pressure of ∼0.027 Torr. The pale yellow material and the material purified only by recrystallization showed the same UV−vis spectrum and insignificant differences in their photophysical properties.

Other materials were reagent grade and used without further purification.

**Acknowledgment.** We acknowledge support from the Office of Basic Energy Sciences of the U.S. Department of Energy. This is Contribution No. NDRL-4615 from the Notre Dame Radiation Laboratory. We thank Dr. E. Wolcan for his assistance with the electrochemical experiments. G.R. acknowledges support from CONICET.

**Supporting Information Available:** Two pages with computational data: the level of theory, specific programs, basis set, and a list of coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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