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Electronic Structure and Near-Infrared Spectra of Diquinone Anion Radicals

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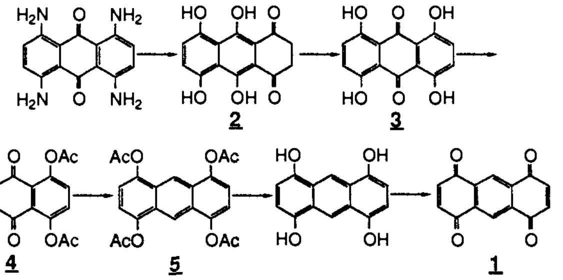
Abstract: The preparation of several substituted anthracene diquinones (1,4,5,8-anthracenetetrones), 1,4,6,11-naphthacenetetrone, and 5,7,12,14-pentacenetetrone is reported. These compounds, which have two quinones separated by one aromatic ring, were reduced electrochemically in aprotic solvents containing $Bu_4N{\cdot}BF_4$ to produce the anion radicals (semiquinones) and dianions. $E°$ values were estimated by cyclic voltammetry. The semiquinones were characterized by ESR and were stable in the absence of air. The semiquinones have intense, sharp bands in the near-infrared (1–1.5 μm). These bands are not found for monoquinone anion radicals. Solvent, counterion, and substituent effects are described. Ab initio theoretical calculations were performed on neutral diquinones, semiquinones, and semiquinone excited states to reveal the origin of the spectra as $\pi^*-\pi^*$ excitations from delocalized anions. Infrared spectra are reported for 1,4,5,8-anthracenetetraone and its anion radical which demonstrate that the semiquinone does not have a localized charge on the IR time scale. Dianions were diamagnetic and gave electronic excitation bands near 880 nm.

As part of a study directed toward molecular electronics, we had occasion to prepare several polyacenequinones.[1] These compounds are linearly annulated with up to 11 rings in a row. The properties of these unusual molecules seemed of interest since they provided rigid rods with long delocalization lengths. Our initial investigations, indeed, showed that these compounds could exhibit unusual physical properties. They form oriented monolayers,[2] provide "molecular rulers" for electron microscopy measurements,[3] and conducting salts.[4] We have described the unusual near-infrared (near-IR) absorption spectra from anion radicals of several di- and triquinones,[5] and in this paper we explore that subject by using several simple diquinone anion radicals as models. The UV-vis-near-IR-IR spectra of organic anion radicals and dianions have received scant attention. Vis spectra of anion radicals from aromatic hydrocarbons, nitro, and carbonyl compounds have been reported and analyzed to some extent.[6-8] Vis[9] and IR[10] spectra of several simple semiquinones have also been reported.

The primary emphasis here is on anthradiquinone derivatives where the quinones are the outside rings, i.e. substituted or benzo-annelated 1,4,5,8-anthracenetetrones. The desired materials were not known, and suitable syntheses of the neutral compounds were developed. Also reported are IR, ESR, and electrochemical data which characterize the anion radicals and dianions. Ab initio molecular orbital calculations provide the basis for the detailed interpretations.

Results and Discussion

Synthesis. 1,4,5,8-Anthracenetetrone (**1**) is the unelaborated example of central interest here. This diquinone was previously prepared from 1,4,5,8-anthracenetetrol.[11] Using the sequence of reactions shown[12,13] we were unable to get satisfactory yields of pure material.



Previous work in this laboratory has tested the utility of Diels–Alder reactions in the construction of linear di- and triquinones.[1] Among other Diels–Alder approaches, we have generated dimethoxy-*o*-xylylene as a reactive diene that adds to quinones. After aromatization and oxidative demethylation, this provides diquinones, and it seemed an appropriate approach to **1** and derivatives of **1**. Of the several precursors for such xylylenes, we chose dimethoxybenzocyclobutenol (**10**). Thermolysis of this compound has been reported to give good yields of Diels–Alder products under mild conditions for dienophiles other than quinones,[15] and other benzocyclobutenols have been reacted with quinones to provide aromatic products after dehydration.[16] The hydroxyl substituent is important both to speed up the ring opening and to provide a convenient way to aromatize the product.

The synthesis of **10** was undertaken as shown below. 2,5-Dihydroxybenzoic acid was obtained commercially and methylated

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[1] Thomas, A. D.; Miller, L. L. *J. Org. Chem.* **1986**, *51*, 4160. Christopfel, W. C.; Miller, L. L. *J. Org. Chem.* **1986**, *51*, 4169. Christopfel, W. C.; Miller, L. L. *Tetrahedron* **1987**, *43*, 3681.

[2] Kenny, P. W.; Miller, L. L.; Rak, S. F.; Jozefiak, T. R.; Christopfel, W. C.; Kim, J. H.; Uphaus, R. A. *J. Am. Chem. Soc.* **1988**, *110*, 4445.

[3] Furuya, F.; Miller, L. L.; Kenny, P. W.; Christopfel, W. C.; Hainfeld, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 641.

[4] Miller, L. L.; Jozefiak, T. H. *Synth. Metals* **1988**, *27*, B431.

[5] (a) Jozefiak, T. H.; Miller, L. L. *J. Am. Chem. Soc.* **1987**, *109*, 6560. (b) Jozefiak, T. H. Ph.D. Thesis University of Minnesota, 1988. (c) Almlöf, J.; Jozefiak, T. H.; Feyereisen, M. W.; Miller, L. L. *J. Am. Chem. Soc.*, in press.

[6] Kaiser, E. T.; Kevan, L. *Radical Ions*; J. Wiley and Sons, Inc.: New York, 1968. (See especially Chapter 9.)

[7] Buschow, K. H. J.; Hoijtink, G. J. *J. Chem. Phys.* **1964**, *40*, 2501. Balk, P.; DeBruijn, S.; Hoijtink, G. J. *Recl. Trav. Chim. Pays-Bas* **1947**, *76*, 813.

[8] Shida, T.; Iwata, S. *J. Phys. Chem.* **1971**, *75*, 2591. Shida, T.; Iwata, S. *J. Am. Chem. Soc.* **1973**, *95*, 3473. Shida, T.; Iwata, S.; Imamura, M. *J. Phys. Chem.* **1974**, *78*, 741.

[9] 1,4-Benzosemiquinone and derivatives: Iida, Y. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1777. Phenanthrasemiquinone and acenaphthenesemiquinone: Staples, T. L.; Szwarc, M. *J. Am. Chem. Soc.* **1970**, *92*, 5022. Anthrasemiquinone: Mitzner, R.; Dorst, H.; Frosch, D. *Z. Chem.* **1975**, *15*, 400. Carlso, S. A.; Hercules, D. M. *Photochem. Photobiol.* **1973**, *17*, 123. Other semiquinones: Mikhailov, G.; Trfonov, A. *Izv. Otd. Khim. Nauki* (*Bulg. Akad. Nauk*) **1971**, *4*, 533.

[10] Clark, B. R.; Evans, D. H. *J. Electroanal. Chem.* **1976**, *69*, 181. Eargle, D. H., Jr. *J. Org. Chem.* **1974**, *39*, 1295.

[11] Boldt, P.; Vardakis, F. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1078.

[12] Dimroth, O.; Hilcken, V. *Chem. Ber.* **1921**, *54*, 3050.

[13] A literature route to **3** (Ashnagar, A.; Bruce, J. M.; Dutton, P. L.; Prince, R. C. *Biochim. Biophys. Acta* **1984**, *801*, 351. Kumar, A. M.S. Thesis, University of Manchester, 1982 failed at the stage of nitration of 1,5,8-trihydroxyanthraquinone.

[14] Brockmann, H.; Budde, G. *Chem. Ber.* **1953**, *86*, 432.

[15] Azadi-Ardakani, M.; Wallace, T. W. *Tetrahedron Lett.* **1983**, *24*, 1829.

[16] Curry, M. J.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1391. Kametani, T.; Chihiro, M.; Takeshita, M.; Takahashi, K.; Fukumoto, K.; Takano, S. *Chem. Pharm. Bull.* **1978**, *26*, 556 and 3820.

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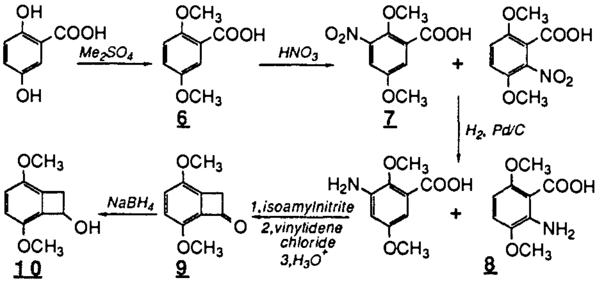
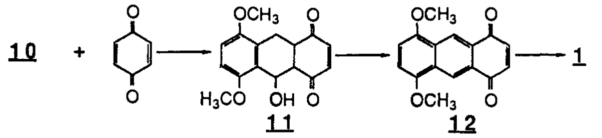
by using a conventional procedure. The original authors[15] report a good yield of nitro acid **7** from nitration of **6**. In these laboratories, this nitration provided two isomers in moderate yield. After hydrogenation, these isomers were easily separated by chromatography or recrystallization. The benzyne precursor **8** was easily diazotized and reacted with vinylidene chloride to provide dichlorobenzocyclobutene. Hydrolysis with aqueous acid gave **9**, and borohydride reduction resulted in **10**, which was purified by chromatography over silica gel.

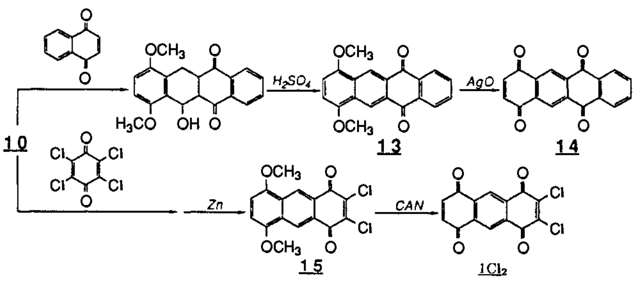


With **10** in hand, the synthesis of anthracene diquinone **1** was attempted. When refluxed with 1 equiv of benzoquinone in toluene, **10** was completely consumed after 4 days. A 77% yield of cycloadduct **11** was obtained. Unfortunately, the dehydrative aromatization does not occur under these conditions, and the dehydration using H_2SO_4, tosic acid, or trimethylsilyl triflate was not successful.

Fortunately, it was discovered that when the original cycloaddition of **10** with benzoquinone was run with an excess (three times) of benzoquinone, the desired quinone **12** was obtained directly and in >90% yield. The oxidation of **12** to anthracene diquinone **1** was performed with silver(II), cerium(IV), or nitric acid, to give in each case high yields of diquinone as a pale yellow solid, which tends to darken on storage.

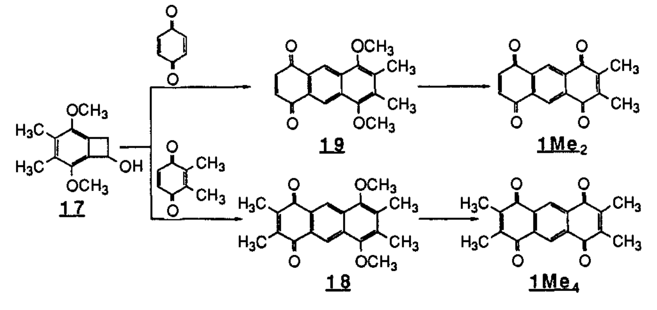


Benzocyclobutenol **10** was also employed to prepare compounds **1Cl₂** and **14**. The adduct of **10** with naphthoquinone formed as expected, but did not dehydrate to **13** until reacted with concentrated H_2SO_4. Oxidation of **13** gave **14**. Reaction of chloranil with **10** gave a tetrachloro adduct, which with zinc dust gave **15**. Oxidation with $Ce(NH_4)_2(NO_3)_6$(CAN) produced **1Cl₂**. An attempt was also made to prepare pentacenetriquinone **16**. However, a quite insoluble adduct was obtained from **10** and 0.5 equiv of benzoquinone, and its oxidized product **16** was too insoluble to study.

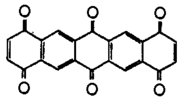


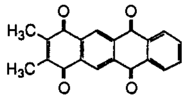
The successful use of **10** led us to prepare and use dimethyldimethoxybenzocyclobutenol **17** for the synthesis of methyl substituted di- and triquinones. These were used to investigate the origin of the near-IR absorption. The route to **17** involved bromomethylation of 1,4-dimethoxy-2,3-dimethylbenzene followed by oxidation to the aldehyde and then to 2,5-dimethoxy-3,4-dimethylbenzoic acid. Further transformations were carried out as they were in the case of **10** with only minor modifications.

Reactions of **17** with quinone dienophiles are shown below. Condensation with benzoquinone and 2,3-dimethylbenzoquinone were carried out in refluxing toluene in the same fashion as the reactions of **10**. It was found that in the case of **17**, considerable amounts of benzocyclobutenol remained unchanged after 4 days at reflux. 3,6-Dimethoxybenzocyclobuten-1-ol (**10**) undergoes electrocyclic ring opening more slowly than benzocyclobuten-1-ol due to steric interference of the peri substituents on the conrotatory outward motion of the hydroxyl group, and, apparently, the steric demands of the methoxy substituents are intensified in **17** due to constraints on methoxy group rotation imposed by methyl substitution. Despite the low conversion, the desired polyacenequinone products were obtained. Interestingly, the Diels–Alder cycloadducts were dehydrated under the reaction conditions to provide **18** and **19** directly. Polyacenequinones **18** and **19** were purified by chromatography on silica and then oxidized by Ag_2O or CAN to diquinones **1Me₄** and **1Me₂**.



In order to prepare a bromo derivative, **1** was treated with bromine in acetic acid. The product gave an elemental analysis and spectra proper for tribromo derivative **1Br₃**, but the sample may not have been pure. Compound **21** was available,[17] and two other diquinones of interest, **22** and **23**, were prepared for comparison by using literature methods.[29]


16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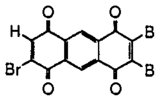
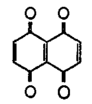

1Br₃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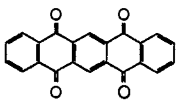
23

Calculations. To gain some understanding of the experimental observations reported below, ab initio calculations were performed at the Hartree–Fock SCF level of approximation for several molecules and their anion radicals. The basis sets used were the 7s3p and 3s sets of van Duijneveldt[18a] with a general split valence contraction. All calculations were carried out on the Cray-2 and the ETA-10 computers at the Minnesota Supercomputer Center, using the Direct SCF code DISCO.[18b]

The molecules were assumed planar;[19] the bond lengths and angles for benzoquinone, naphthoquinone, and **22** were taken from single-crystal X-ray diffraction structures.[20,21] For other molecules, **22** was used as a model. Anion radical structures were calculated with the geometry of the neutral. All molecules except naphthoquinone were run in D_{2h} symmetry, with the C═O bonds in the *X*–*Z* plane parallel to the *X* axis. For a given molecule, the closed-shell electronic structure and lowest excited state structures for various symmetries were calculated. Spin-restricted Hartree–Fock theory was used for the open-shell systems. For the ion of central interest, $\mathbf{1}^{\bullet-}$ the odd electron is held in a π^*

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[17] Prepared by J. Nerenberg in this laboratory.

[18] (a) Almlöf, J.; Faegri, K.; Korsell, K. *J. Comput. Chem.* **1983**, *3*, 3003. (b) Van Duijneveldt, F. B. IBM Res. Rep. RJ 945, 1971.

[19] Erikson, J.; Jorgensen, K. A.; Linderberg, J.; Lund, H. *J. Am. Chem. Soc.* **1984**, *106*, 5083.

[20] Trotter, J. *Acta Crystallogr.* **1960**, *13*, 86. Gautier, P. J.; Hauw, C. *Acta Crystallogr.* **1965**, *18*, 179. Herbstein, F. H.; Kapon, M. *Acta Crystallogr.* **1982**, *B38*, 3123.

[21] Since completion of this work, we have obtained a single-crystal structure of $\mathbf{23}^{\bullet-}$, Me_4N^+. The semiquinone is planar and symmetrical. The C–O bond lengths are 1.23 Å. Unpublished work of Matt Forkner.

Table I. Relative Energies (in eV) of the Anion States (I.e. Negative Electron Affinities) and Virtual Orbital Energies for Some Different Quinones[a]

benzoquinone	naphthoquinone	anthraquinone	**1**	**22**	**23**
		Anion Radical State Energies			
−0.70 (B_{1g})	−0.53 (A_2)	−0.03 (B_{1g})	−1.01 (A_u)	−1.76 (B_{1g})	−1.20 (A_u)
2.88 (A_u)	1.82 (B_2)	1.78 (B_{2u})	0.28 (B_{1g})	0.30 (A_u)	0.30 (B_{1g}
4.10 (B_{2u}					
		π^*-Orbital Energies of Neutral Quinones			
−0.11 (b_{1g})	0.39 (a_2)	0.59 (b_{1g})	−0.60 (a_u)	−1.18 (b_{1g})	−0.67 (a_u)
3.55 (a_u)	2.39 (b_2)	2.10 (b_{2u})	0.58 (b_{1g})	0.63 (a_u)	0.61 (b_{1g})
4.75 (b_{2u})	3.36 (a_2)	3.21 (a_u)	1.24 (b_{2u})	3.04 (b_{1g})	0.70 (b_{2u})
		3.72 (b_{3g})	2.89 (a_u)	3.53 (b_{3g})	2.22 (b_{3g})

[a] The orbitals are all of π-type.

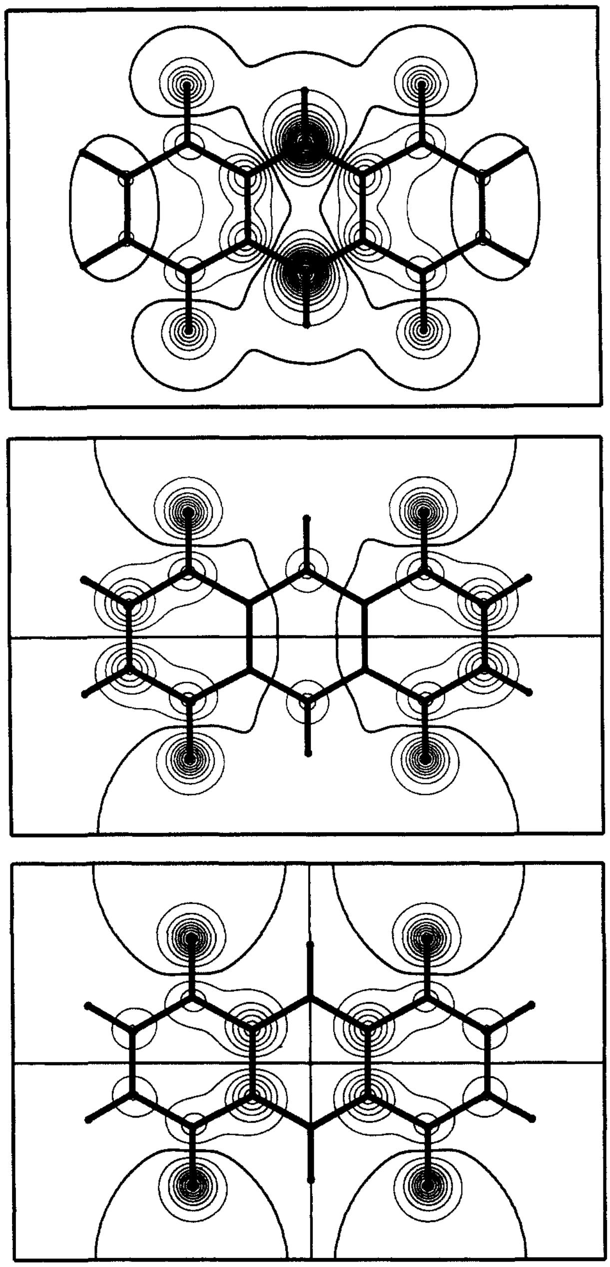

Figure 1. π^* orbitals of $1^{\bullet -}$: top b_{2u}; middle b_{1g}; bottom a_u.

orbital; the ground state is A_u. The lowest lying π^*-orbitals are shown in Figure 1.

The low-lying virtual orbitals, as well as the low-lying electronic states of the negative ion, are largely of C–O antibonding character. It might at first seem surprising to find an A_u ground state, since orbitals are generally ordered in energy according to the number of nodal planes. If the orbitals were pure π(C–O)*, one would indeed expect b_{2u} to be the lowest virtual orbital. However, the a_u and b_{1g} orbitals are stabilized by a significant antibonding contribution from the end C=C bonds (see Figure 1), which is not possible for b_{2u} or b_{3g}. From the central ring, the e_{2u} and b_{2g} are low-lying virtual orbitals available for mixing (D_{6h} notation, correspond to $a_u + b_{2u}$ and b_{2g}, respectively, in D_{2h}). It is much more favorable to mix in the e_{2u} than the b_{2g} orbital since it is less antibonding, and this is consistent with the A_u state being the lowest.

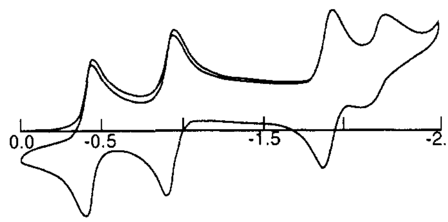

Figure 2. Cyclic voltammogram of **23**: DMF, 0.1 M $Bu_4N{\cdot}BF_4$, 100 mV s^{-1}.

The ordering of the low-lying states of the other negative ions in the series is consistent with this general model. This is illustrated by the energies of the lowest anion radical states which are shown in Table I along with the orbital energies from the neutral molecules. A similar ordering of anthraquinone anion radical orbitals has been reported.[19]

Electrochemistry. Although quinones are perhaps the most well known organic electrophores, electrochemical studies[22] have focused almost exclusively on simple monoquinones. The anion radicals and dianions of conjugated diquinones had not been reported prior to this study. The potentials characteristic of anion radical and dianion formation were obtained by cyclic voltammetry. Although some variations in solvent and electrolyte were explored, the common data were obtained with degassed DMF, 0.1 M Bu_4NBF_4, and a polished glassy carbon electrode. Ferrocene was usually added as an internal standard to check the saturated calomel electrode (SCE) reference electrode. All potentials are reported vs SCE.

Conjugated diquinones might provide voltammograms with four reversible redox waves which interconvert the five stable oxidations states; Q, Q^-, Q^{-2}, Q^{-3}, and Q^{-4}. As seen in Figure 2, the voltammograms always indicated two reversible couples (60-mV peak separation and nearly equal anodic and cathodic peak currents) and a more complex process at more cathodic potentials. The anodic peak current of this third process is usually less than that of its cathodic peak, and the cathodic–anodic peak potentials are frequently separated by more than 100 mV, rather than the 60- or 30-mV separation expected for a one- or two-electron reversible reduction. Relative to the first two reversible couples, this quasi-reversible couple has larger cathodic peak currents and is most likely a two-electron wave. Indeed for 5,7,12,14-pentacenetetrone (**23**), voltammetry shows that this third wave is resolved into two closely spaced couples (Figure 2).

Table II contains a compilation of reduction potentials for mono- and diquinones. The $E°$ values were taken from cyclic voltam-

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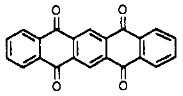
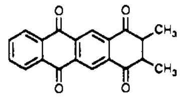
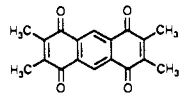
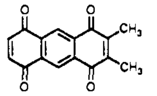
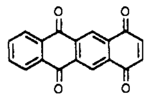
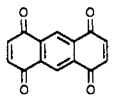
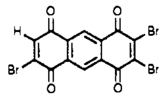
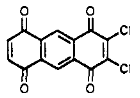
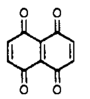
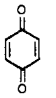
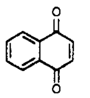
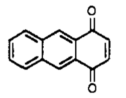
[22] Chambers, J. Q. In *The Chemistry of the Quinonoid Compounds*; Patai, S., Ed.; J. Wiley and Sons: New York, 1974; p 737.

Table II. Spectroscopic and Electrochemical Data[a]

no.	structure	λ_{max} (nm) (log ϵ)[b] anion	dianion	$E°$ (V, SCE)	
23		1335 (4.50)	880 (4.54)	−0.42	−0.92
21		1400 (4.19)		−0.41	−0.93
1Me$_4$		1480 (4.50)	886 (4.46)	−0.41	−0.89
1Me$_2$		1500 (4.11)	876 (4.27)	−0.31	−0.83
14		1200–1650 (4.00)		−0.30	−0.85
1		1560 (4.21)	866 (4.15)	−0.25	−0.74
1Br$_3$		1615 (4.16)	900 (4.26)	−0.05	−0.55
1Cl$_2$		1200–1700 (4.00)	890 (4.14)	−0.08	−0.57
22		900 (3.65)	640 (3.74)	+0.14	−0.59
		450		−0.43	−1.34
		480 (3.71)		−0.61	−1.41
		510 (3.76)		−0.69	−1.41

[a] Measured in DMF, 0.1 M $Bu_4N{\cdot}BF_4$. [b] Maximum of the longest wavelength band in nanometers.

metry peak potentials as $(E_a + E_c)/2$.

A comparison of the monoquinones shows that benzo substitution shifts both the first and second $E°$ to more negative values. This shift in the first $E°$ is well known[22] and can be ascribed to a greater benzo stabilization of the neutrals than the anion radicals. In this regard it is not surprising that naphthalenediquinone (**22**) is the most easily reduced compound in Table I, that diquinones reduce more easily than monoquinones with an equal number of rings, and that benzo substitution on **1** (compare **1**, **14**, and **23**) gives a shift to more negative $E°$ values. These data demonstrate that the anthradiquinone unit can be considered one electrophore, which is modified by substituents on either or both ends. A striking confirmation of this concept is that there is a constant 0.5 V separation between the first and second $E°$ values for each of the eight diquinones in this series.

Electron affinities were calculated for several compounds by the ab initio MO method. Although these could be estimated from the virtual-orbital energies of neutral quinones or from the singly occupied orbital energies of the anion radicals, the most reliable approach was taken to be the total energy difference between the neutral and the anion radical. A comparison of the theoretical results with experimental $E°$ values is shown in Table III. Because the reduction potentials are measured in solution against a SCE reference while the calculated EA are for isolated molecules, there is no reason to have the values agree. With the exception of **23**, there is a satisfactory ordering; indeed, a linear relationship between EA and $E°$ exists. The $E°$ for **23** is firm, and it is unclear why the calculated EA for **23** does not correspond with expectations.

Table III. Electron Affinities and $E°$ Values

compd	EA (eV) calc	exp[a]	$-E°$ (V, SCE)
22	1.76		−0.14
23	1.20		0.42
1	1.02		0.26
benzoquinone	0.70	1.91	0.43
naphthoquinone	0.53	1.81	0.61
anthraquinone	0.03	1.59	0.84

[a] Henis, T.; et al. *J. Am. Chem. Soc.* **1988**, *110*, 400.

Table IV. EPR a_H

anion	a_H, G (no. of H)	a_H(calc)
$\mathbf{22}^{\bullet-}$	0.40 (4)	0.45
$\mathbf{1}^{\bullet-}$	0.90 (4), 0.58 (2)	0.64,[a] 0.0[b]
$\mathbf{1Me_4}^{\bullet-}$	0.53 (12), 0.11 (2)	
$\mathbf{23}^{\bullet-}$	0.32 (8), 0.20 (2)	0.18[c], 0.15[d], 0.0[e]

[a] "Outside" hydrogens. [b] "Inside" (9,10) hydrogens. [c] 1,4,8,11 hydrogens. [d] 2,3,9,10 hydrogens. [e] "Inside" (6,13) hydrogens.

With use of a divided cell and carbon sponge cathode, constant potential electrolysis at a potential just cathodic of a one-electron couple resulted in the passage of 1 equiv of negative charge, as verified by coulometry. Cyclic voltammetry of the reduced solutions showed that the voltammogram had not changed as a result of reduction except for the expected shift on the current axis. Further reduction just cathodic of the second peak gave stable solutions of the dianions. In both cases reoxidation gave back the original neutral (CV and reisolation).

The electrochemical preparation of the semiquinones was verified in most cases by analysis of reduced quinone solutions by electron paramagnetic resonance (EPR) spectroscopy.[23] In each of these cases samples of the dianions were also prepared and did not give an EPR signal. Spectra from unsymmetrical anion radicals were complex and too poorly resolved to interpret.

Spectra of symmetrical diquinone anion radicals ($\sim 10^{-4}$ M in DMF 0.1 M $Bu_4N{\cdot}BF_4$) show that the two ends of the molecule are equivalent on this time scale, and, therefore, the spectra can be interpreted on a first-order basis (Table IV). $\mathbf{1}^{\bullet-}$ shows hyperfine splitting from the four equivalent "outside" hydrogens (a_H = 0.90 G) and the two "inside" 9,10 hydrogens (a_H = 0.58 G). **1Me$_4$** shows coupling to the 12 methyl hydrogens (a_H = 0.53 G); the two inside hydrogens show a_H = 0.11 G. $\mathbf{23}^{\bullet-}$ (dibenzo-**1**) showed nine lines, each split into a triplet. The triplet arises from the two inside hydrogens (a_H = 0.2 G) and the nonet is assigned to the accidentally equivalent splitting from the eight benzo hydrogens.

With use of the calculated π-electron densities of the anion radical HOMO and the McConnell equation with Q = 23 G, the a_H values were estimated. Satisfactory agreement was found for benzoquinone (calc 2.74, exp 2.45) and naphthoquinone (calc 3.50, 0.31, 0.59; exp 3.33, 0.28, 0.65). For the diquinones (Table IV), the calculations expressed several aspects of the hyperfine coupling of $\mathbf{1}^{\bullet-}$, $\mathbf{22}^{\bullet-}$, and $\mathbf{23}^{\bullet-}$. Thus the calculated a_H for $\mathbf{22}^{\bullet-}$ was quite close to experiment, and the relative magnitudes for the "outside" hydrogens on $\mathbf{1}^{\bullet-}$, $\mathbf{22}^{\bullet-}$, and $\mathbf{23}^{\bullet-}$ are in the right order and of approximately the experimental magnitude. There is, however, a significant discrepancy for $\mathbf{1}^{\bullet-}$ where the "inside" (9,10) hydrogens show a_H = 0.58, while the calculated value is exactly zero for symmetry reasons. A similar problem is encountered for $\mathbf{23}^{\bullet-}$.

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(23) EPR spectra are shown in the Ph.D. Thesis of T. H. Jozefiak, University of Minnesota, 1988.

Given that an unrestricted Hartree–Fock calculation would give a nonzero value, the 0.58 G value for **1**$^{\bullet-}$ is not unexpected. An explanation that the ground state is actually B_{1g} would put more spin density on the "inside" hydrogens, but not enough; and the outside a_H would be much too large. Our calculations show that **1**$^{\bullet-}$ and **23**$^{\bullet-}$ are quite polarizable,[24] and this might have an effect on the accuracy of the calculation.

Although we have not done a theoretical calculation, the methyl coupling constant for **1Me$_4$**$^{\bullet-}$ is of the approximate magnitude expected by comparison with model compounds. Thus, **1Me$_4$**$^{\bullet-}$ has $a_H(CH_3)$ which is slightly smaller than a_H(H-outside) for **1**. This is similar to $a_H(CH_3)$ for duroquinone compared to a_H for benzoquinone, which are 1.9 and 2.45 G, respectively.

In total the EPR results demonstrate that paramagnetic anions of expected structure and diamagnetic dianions are formed by cathodic reduction. We do note, however, that the anion **23**$^{\bullet-}$, Li^+ forms a diamagnetic solid. This solid is conductive and has different vis–near-IR–IR from **23**$^{\bullet-}$ in solution.[4]

Vis–Near-IR Spectra. Of primary interest here are the electronic spectra of diquinone anions and dianions. It will be of interest, however, to consider first the spectra of several neutral quinones and diquinones to provide a context for the discussion. The π–π^* absorptions for monoquinones with more and more rings, e.g. naphthoquinone, the anthraquinones, etc., have been documented and analyzed, especially by Nepras and Titz.[25] As with reduction potentials, the observations contrast with those for linear acenes, e.g. anthracene, naphthacene, etc., where there is a trend to longer wavelengths as the number of rings increases. For monoquinones the longest π-system on one side of the quinone determines the position of the long-wavelength π–π^* transition. This can be attributed to the "cross-conjugated" quinone moiety "interrupting" the delocalization. Compare 9,10-anthraquinone(λ_{max} 323 nm) with 1,4-naphthoquinone (327 nm); or 6,13-pentacenequinone (403 nm) with 1,4-anthraquinone (405 nm).

Anthradiquinone **1** shows λ_{max} at 352 nm for its longest wavelength intense band. Pentacenediquinone **23** (dibenzo-**1**) shows 335 nm. These bands are assigned π–π^*, not n–π^*, on the basis of their intensity. Thus, the longest wavelength π–π^* transitions of these diquinones are in the same region as naphthoquinone and 9,10-anthraquinone transitions. They are at shorter wavelength than 1,4-anthraquinone. Therefore, these neutral diquinones can be understood to behave like monoquinones. The longest π-system on one side of the quinone determines the position of the long-wavelength band.

In Table II are shown data for a few monoquinone anion radicals. All these ions show strong bands ($\epsilon = (5\text{–}10) \times 10^3$ M^{-1} cm^{-1}) in the 400–600-nm region. Comparison of the spectra shows that more rings give modest shifts to longer wavelength.[26]

The electronic spectra of anthracene diquinone anions, i.e. **1**$^{\bullet-}$ and derivatives, are quite different. Instead of a band near 500–600 nm, semiquinone **1**$^{\bullet-}$ exhibits an intense, sharp band at 1560 nm in the near-IR (Figure 3). This band is at much longer wavelength than either, 1,4-anthraquinone anion radical (510 nm) or anthracene anion radical (714 nm). Naphthalene diquinone anion (**22**$^{\bullet-}$) also shows an unexpectedly long wavelength transition at 900 nm.

For **1**$^{\bullet-}$ and **23**$^{\bullet-}$, the spectra were measured at various concentrations and found to obey Beer's law. A variation of the counterion from lithium to tetrabutylammonium resulted in no change whatsoever in the observed spectra measured in DMF or DMSO, indicating that in these solvents, the anions are free-solvated and the nature of the counterion is of no consequence. Also it was found that, in keeping the counterion large and noncoordinating (Bu_4N^+), the same spectrum (±5 nm) was obtained in a variety of less polar solvents including dimethoxyethane, tetrahydrofuran, and methylene chloride. This shows that the anions are free-solvated in relatively nonpolar solvents as well, when the counterion is Bu_4N^+. More importantly, this result indicates that the spectrum of the free-solvated ion is not solvent dependent. Thus the strong, low-energy band cannot be associated with an inter- or intramolecular charge transfer.

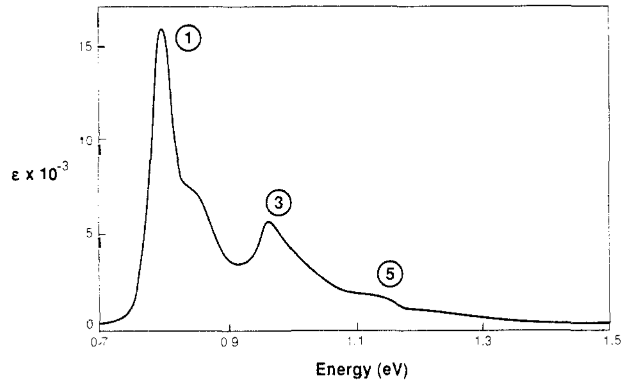

Figure 3. Vis–near-IR spectrum of **1**$^{\bullet-}$ in DMF.

These observations led us to investigate a set of diquinones related to **1**, and the electronic spectra of eight anions and six dianions were measured. The spectra of the anions were similar, each featuring a prominent band near 1500 nm (Table II). As the data in Table II shows, the wavelength of the near-IR band for **1**$^{\bullet-}$ derivatives varies from 1335 nm to 1615 nm. This is a span of 3.7 kcal/mol in energy. Electron-donating substituents such as benzo and methyl shift the transition to higher energy. Electron-withdrawing substituents move the band further into the IR region, as in **1Br$_3$** and **1Cl$_2$**. This trend is consistent throughout the series and is correlated to the reduction potentials (Table II). It is concluded that electron-withdrawing groups on the "outside" positions stabilize the ground-state anion, but stabilize the electronically excited anion even more.

The shape of the spectrum is also of interest. As shown in Figure 3, **1**$^{\bullet-}$ shows several smaller peaks at higher energy which we assign to vibrational splitting. This same pattern (both frequency and intensity) is seen for the other symmetrical anions, **1Me$_4$**$^{\bullet-}$ and **23**$^{\bullet-}$. In each case the bands correspond to two vibrational frequencies of about 350 and 1350 cm^{-1}. The larger splitting is assigned to peaks 1, 3, and 5 in Figure 3. Expectedly, the resolution under these conditions does not permit any consideration of the origin of the vibrational structure. We do note that aromatic hydrocarbons (neutral) typically show a 1400-cm^{-1} splitting. Anthracene and substituted anthracenes show intense lines in their low-temperature-fluorescence spectra corresponding to 1400- and 400-cm^{-1} splitting.[27]

Analysis of the vibrational splitting of the near-IR band of the asymmetrically substituted derivatives, **14**$^{\bullet-}$, **1Me$_2$**$^{\bullet-}$, **21**$^{\bullet-}$, is hampered by progressive broadening of the band. Thus, **21**$^{\bullet-}$ (dimethylbenzo-**1**) gives relatively sharp bands with the expected vibrational pattern; **1Me$_2$**$^{\bullet-}$ and **14**$^{\bullet-}$ (benzo-**1**) give merged peaks, and **1Cl$_2$**$^{\bullet-}$ gives a single broad band. Clearly the greater the asymmetry in terms of the electron-donating/-releasing character, the less definition to the band shape.

Due to the different shape of the near-IR band for **1Cl$_2$**$^{\bullet-}$, and its electronically unbalanced substitution, the optical spectrum of this anion was also recorded in dimethoxyethane in the presence of $Bu_4N \cdot BF_4$ to determine if a solvent effect on the low-energy band could be found for this most asymmetric case. Interestingly,

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(24) Feyereisen, M. Unpublished work.

(25) Nepras, M.; Fabian, J.; Titz, M. *Collect. Czech. Chem. Commun.* **1981**, *46*, 20. Titz, M.; Nepras, M. *Int. J. Quantum Chem.* **1979**, *16*, 543 and references therein including: Titz, M.; Nepras, M. *Collect. Czech. Chem. Commun.* **1972**, *37*, 2674.

(26) Two examples of radical anions of monoquinones with longer wavelength absorptions are discussed in ref 5b.

(27) Berks, J. B. *Photophysics of Aromatic Molecules*; J. Wiley and Sons: New York, 1970; p 44. Carter, T. P.; Gillespie, G. D. *J. Phys. Chem.* **1982**, *86*, 2691.

(28) Syper, L.; Mlochowski, J.; Kloc, K. *Tetrahedron* **1983**, *39*, 781.

(29) Smith, L. I.; Austin, F. L. *J. Am. Chem. Soc.* **1942**, *64*, 528. This method was used except that the oxidation of aminophenol was performed by the action of $FeCl_3$ in acidic aqueous solution, by stirring with the substrate in ether overnight.

Table V. Calculated and Experimental Lowest Transition Energies

compd	transition	$\Delta\epsilon^a$	ΔE^b	exp^c
benzoquinone anion radical	$B_{1g} \rightarrow A_u$	8.52	3.57	2.77
naphthoquinone anion radical	$A_2 \rightarrow B_2$	2.01	2.07	2.00
$1^{\bullet-}$	$A_u \rightarrow B_{1g}$	1.17	1.29	0.80
$22^{\bullet-}$	$B_{1g} \rightarrow A_u$	1.82	2.06	1.38
$23^{\bullet-}$	$A_u \rightarrow B_{1g}$	1.25	1.50	0.93

^{a} From virtual orbital energies. ^{b} Difference between total energy of the states. ^{c} Determined in DMF, 0.1 M $Bu_4N{\cdot}BF_4$.

the optical spectrum measured in dimethoxyethane was found to be virtually superimposable on the spectrum measured in DMF. This result underscores the lack of solvent effect described for $\mathbf{1}^{\bullet-}$ and $\mathbf{23}^{\bullet-}$.

We assign these long-wavelength near-IR bands to π^*–π^* transitions from delocalized anion radicals. The sharpness of the bands, the vibrational structure, and the lack of solvent dependence rule out charge-transfer bands, and it is necessary to delocalize the odd electron over both quinones to get such long wavelengths.

It is of interest that although the spectra of diquinone neutrals are not unusual in comparison to monoquinones, the diquinone anions are quite different from monoquinone anions. This difference can be understood in detail from the quantum mechanics calculations, but it can also be rationalized by using a perturbation picture. Consider a union of two enedione fragments with a benzenoid fragment. Of interest are the lowest energy π^* orbitals of the two enediones, which will mix with each other through one of the benzenoid lowest π^* orbitals. This generates two low-lying π^* orbitals, one of which (π_1^*) holds the odd electron of $\mathbf{1}^{\bullet-}$. Because the splitting is small, the wavelength for the allowed excitation from π_1^* to π_2^* is long. In comparison, naphthalene diquinone is formed by the union of two enedione fragments with an ethylenoid fragment. The mixing is more effective through the smaller central unit, the splitting between the two lower π^* orbitals is larger, and the absorption wavelength for $\mathbf{22}^{\bullet-}$ is shorter than that for $\mathbf{1}^{\bullet-}$. This model also provides a simple picture of the relative reduction potentials of **1** and **22** because the larger perturbation gives **22** a lower energy π^* orbital than **1**.

The electronic excitation energies for anion radicals computed as energy differences between different electronic states are shown in Table V. The $\Delta\epsilon$ energies were determined by using a frozen-orbital approximation, as differences between orbital energies for the neutral molecule. With the exception of benzoquinone anion radical, the results agreed with experiment, theory being about 0.4 eV too large for diquinone anion radicals. Alternatively each state of the anion radical was separately calculated, and the transition energies were taken as differences between individually optimized states. In this case the agreement with experiment was similar, being about 0.6 eV too high.

Pilot calculations were carried out for benzoquinone and its anion with larger basis sets and with correlation effects included. These calculations showed small effects on lower excitation energies, whereas they can be significant on higher excitations. Transition dipole moments were unchanged within a factor of two, and spin densities were within 20% with the split-valence basis sets used here.

Of particular interest for $\mathbf{1}^{\bullet-}$ is the assignment $A_u \rightarrow B_{1g}$, which corresponds to a movement of electron density from the central ring to the outside carbons of the anion radical (Figure 1). This explains the substituent effect (Table II) observed for the series of $\mathbf{1}^{\bullet-}$ derivatives and gives confidence to our proposal that the long-wavelength bands are $\pi^* \rightarrow \pi^*$ transitions from a delocalized A_u ground state.

The spectra of the dianions of the anthracene diquinones were also recorded. The spectra are self-consistent in that there is always one intense band ($\epsilon \sim 20000$) in the range 860–900 nm (Table II). Of these dianions, $\mathbf{1}^{2-}$ has the longest wavelength band and there is no correlation with electron-withdrawing/-donating substituents as there is for the monoanions. The observation that dianions absorb at shorter wavelengths has previously been found for aromatic hydrocarbon ions,[6] where diamagnetic dianions absorb at shorter wavelength than the paramagnetic anion radicals.

Figure 4. Carbonyl region of the IR spectra of **1** and **23** neutral (top), anion and dianion in DMSO, $LiClO_4$.

The spectra of $\mathbf{1}^{\bullet-}$ and its derivatives are unusual for organic compounds in that the narrow, intense band is observed at such long wavelengths. The literature reveals several similar spectra at $\lambda > 1$ μm, and in each case the compound is an anion radical of a conjugated dielectrophore. The examples we have found are dinitrostilbene anion radical (1220 nm), dinitrobiphenyl anion radical (1160 nm), 1,1-diphenylethylene anion radical (1180 nm),[8] and a homoconjugated bis-indanone anion radical (1590 nm).[30] The latter is assigned to an intervalence transfer band. Recently, we have measured similarly shaped spectra (at shorter wavelengths) for pyromellitic imide anion radicals derivatives[31] and a tetracyanopentacenequinone anion radical.[32]

IR Spectra of Semiquinones. It is expected that reduction of a quinone to its semiquinone will result in a reduced carbonyl bond strength, and it has been found[10] that the carbonyl stretch of the quinone, which is typically near 1675 cm^{-1}, is lost upon reduction and replaced by new, lower frequency bands due to the semiquinone. The shift is typically 150 cm^{-1}. Upon further reduction to the dianion, new bands again replace those of the semiquinone, and in certain cases one broad, strong band can be identified near 1400 cm^{-1}. The trend is consistent with the assumption that the added electrons primarily occupy orbitals which are C–O antibonding. This is illustrated in Figure 1 for the low-lying states of $\mathbf{1}^{\bullet-}$.

The IR spectra of the anions of diquinones are expected to show a diminished carbon–oxygen bond order as well. However, for conjugated diquinones, the added electron is delocalized over four carbonyls rather than two; therefore the magnitude of the shift in the carbonyl-stretching frequency should be less than that seen for monoquinones. The two diquinones **1** and **23** were reduced electrochemically in DMSO containing $LiClO_4$, and IR spectra were measured for the neutral, the anion radical, and the dianion, by syringing the reduced solution into a nitrogen purged IR cell with calcium fluoride windows (0.1 mm). Only two regions of the spectrum (1450–1400 and 1310–1320 cm^{-1}) were rendered unusable due to strong DMSO absorptions, and the region of interest for the carbonyl bands of quinones and semiquinones (1680–1460 cm^{-1}) was clear. Figure 4 shows the carbonyl-

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[30] Schroeder, A. H.; Mazur, S. *J. Am. Chem. Soc.* **1978**, *100*, 7339. Mazur, S.; Sreekumar, C.; Schroeder, A. H. *J. Am. Chem. Soc.* **1976**, *98*, 6713.

[31] Rak, S. Unpublished work.

[32] Kenny, P. W.; Jozefiak, T. H.; Miller, L. L. *J. Org. Chem.* **1988**, *53*, 5007.

stretching region for both diquinones at each stage of reduction. For $1^{\bullet-}$ the carbonyl stretch of the neutral at 1672 cm^{-1} was replaced in the anion radical by bands at 1581, 1540, and 1520 cm^{-1}, reflecting a 91-cm^{-1} shift to lower energy for the most intense band. 1^{2-} gave a strong band at 1525 cm^{-1}, reflecting an additional shift of 56 cm^{-1}. For **23** a similar progression was found; 1673 to 1572 to 1529 cm^{-1}, representing shifts of 101 and 43 cm^{-1} in reducing to the anion radical and dianion, respectively.

This result again indicates that these diquinone anions are delocalized. Due to the extremely rapid time scale of the IR experiment (10^{-13} s), it can be expected that the anion radical would exhibit carbon–oxygen stretching bands for both the semiquinone (~1520 cm^{-1}) and quinone (~1675 cm^{-1}) moieties if the unpaired electron was trapped on one quinone.

Experimental Section

General. ^{1}H NMR spectra were measured with IBM-NR-300-AR (300 MHz) or IBM-NR-200-AR (200 MHz) FT-NMR spectrometers. Chemical shifts are in ppm downfield of tetramethylsilane. For ^{1}H NMR spectra measured in CDCl$_3$, chemical shift values are reported with the CDCl$_3$ protonic impurity peak at 7.25 ppm downfield of tetramethylsilane. Infrared spectra were measured with a Perkin-Elmer 7100 Fourier transform instrument. Electron-impact and chemical-ionization mass spectra were measured with AEI MS-30 and Finnigan 4000 mass spectrometers.

1,4,5,8-Anthracenetetrone (1).[11] **Method 1: From Disperse Blue 1 via 1,4,5,8-Tetraacetoxyanthracene.** From commercial Disperse Blue 1 (500 mg), compounds **2** (76% yield),[13] **3** (69%),[13] **4** (40%),[13] and **5** (62%)[14] were prepared[5b] according to the literature. 1,4,5,8-Tetraacetoxyanthracene (100 mg, 0.23 mmol) (**5**) was placed in a nitrogen-purged reaction vessel, along with a stir bar. A nitrogen-purged 1% NaOH solution (5 mL) was added to the reaction vessel via syringe. A dark red solution resulted and was stirred for 5 min. A nitrogen-purged 6 N HCl solution was then added by syringe and the reaction mixture became bright yellow. The yellow solution was placed under an aspirator vacuum and gently heated to dryness to provide a brown/yellow residue. Ethanol (25 mL) was introduced to the reaction flask, and the solid was triturated. The ethanol was then filtered and evaporated to reveal a yellow solid. This solid was dried in vacuo. Dry dioxane (10 mL) was added along with anhydrous CaSO$_4$ (100 mg). Freshly precipitated Ag$_2$O (167 mg, 0.72 mmol) ws introduced, and the dioxane solution was stirred magnetically for 30 min, after which it was filtered, and the dioxane was evaporated. A brown residue remained from which 1,4,5,8-anthracenetetrone (12 mg, 0.05 mmol, 22% yield) was obtained after chromatography over silica with chloroform as the eluant. ^{1}H NMR (CDCl$_3$): δ 7.14 (s, 2 H), 8.82 (s, 4 H). IR (KBr, cm^{-1}): 1667, 1599, 1270, 1125, 849. High-resolution mass spectrum (EI, 70 eV) calcd for C$_{14}$H$_6$O$_4$: $M^{+\bullet}$ = 238.0270. Found: 238.0262.

1,4,5,8-Anthracenetetrone (1). Method 2: From 5,8-Dimethoxy-1,4-anthraquinone. 5,8-Dimethoxy-1,4-anthraquinone (152 mg, 0.57 mmol) was placed in a 50 mL round-bottom flask with a small stir bar. Dioxane (15 mL) was added along with AgO (285 mg, 2.3 mmol). The mixture was sonocated briefly resulting in a fine suspension. Aqueous 6 N HNO$_3$ (0.57 mL) was then introduced with good stirring. After 5 min, the reaction mixture was poured into chloroform/water and extracted. The chloroform extracts were dried over Na$_2$SO$_4$, and the solvent was removed. The yellow/brown residue was recrystallized from dioxane/cyclohexane to provide anthracenediquinone (104 mg, 0.44 mol, 72% yield). This material may be chromatographed over silica with chloroform eluant. The spectral data were identical with that from **1** prepared by method 1.

3,6-Dimethoxybenzocyclobuten-1-ol (10).[15] In a sequence of reactions starting from 2,5-dihydroxybenzoic acid (10 g), compounds **6** (77%), **8** (63%), and **9** (75%) were prepared according to the literature.[15] 3,6-Dimethoxybenzocyclobutenone (36 mmol) was placed in a 250-mL Erlenmeyer flask containing ethanol (50 mL). Sodium borohydride (5.45 g, 144 mmol) was added in portions with magnetic stirring. After the addition was complete, the solution was stirred for 2.5 h and then poured into ice/HCl. The aqueous solution was extracted with chloroform; the extracts were combined and dried with anhydrous Na$_2$SO$_4$. The solvent was then evaporated to leave a dark solid. This solid was dissolved in ethyl acetate, treated with activated charcoal, and filtered over diatomaceous earth. 3,6-Dimethoxybenzocyclobuten-1-ol (6.36 g, 35 mmol, 97% yield) may be purified by chromatography over silica with ethyl acetate/petroleum ether eluant. ^{1}H NMR (CDCl$_3$): δ 2.5 (br, hydroxyl, 1 H), 3.07 (ddd, J = 14.11, 1.80, 0.60 Hz, 1 H), 3.68 (dd, J = 13.96, 4.65 Hz, 1 H), 5.78 (s, 3 H), 5.89 (s, 3 H), 5.29 (br, 1 H), 6.67 (AB quartet, J = 9.00 Hz, $\Delta\nu$ = 19.064, 2 H). IR (KBr, cm^{-1}): 3434, 2948, 1485, 1431, 1260, 1139, 1107, 1050, 1027, 996, 823. High-resolution mass spectrum (EI, 70 eV) calcd for C$_{10}$H$_{12}$O$_3$: 180.0786. Found: 180.0794. Anal. Calcd: C, 66.65; H, 6.71. Found: C, 66.80; H, 6.75.

5,8-Dimethoxy-1,4-anthraquinone (12). 3,6-Dimethoxybenzocyclobuten-1-ol (1.0 g, 5.5 mmol) was placed in a 50-mL round-bottom flask containing toluene (30 mL) and a stir bar. Benzoquinone (2.9 g, 27 mmol) was added. The solution was bubbled with nitrogen, and then a reflux condenser connected to a nitrogen bubbler was fitted to the flask. The mixture was heated to reflux for 4 days, becoming red and heterogeneous during this time. The solution was cooled and filtered. A dark red solid (1.2 g) was collected and freed from solvent and benzoquinone under high vacuum. The filtrate was evaporated, and the residue was chromatographed over silica with chloroform eluant to afford an additional amount (0.24 mg) of product. 5,8-Dimethoxy-1,4-anthraquinone (1.45 g, 5.4 mmol, 98% yield) may be purified further by chromatography over silica with chloroform eluant. ^{1}H NMR (CDCl$_3$): δ 4.00 (s, 6 H), 6.90 (s, 2 H), 7.06 (s, 2 H), 9.00 (s, 2 H). IR (KBr, cm^{-1}): 1665, 1615, 1473, 1388, 1302, 1273, 1216, 1117, 822. High-resolution mass spectrum (EI, 70 eV) calcd for C$_{16}$H$_{12}$O$_4$: 268.0732. Found: 268.0733. UV–vis (CH$_2$Cl$_2$): 491 nm (ϵ = 3500), 325 nm (ϵ = 2100), 256 nm (ϵ = 40 000).

7,10-Dimethoxy-5,12-naphthacenequinone (13). 3,6-Dimethoxybenzocyclobuten-1-ol (0.2 g, 1.1 mmol) was placed in a 100-mL round-bottom flask containing toluene (30 mL) and 1,4-naphthoquinone (0.174 g, 1.1 mmol). The solution was bubbled with nitrogen, and a reflux condenser connected to a nitrogen bubbler was fitted to the flask. The mixture was heated for 4 days and became dark yellow during this time. The toluene was then removed to reveal an orange solid. This solid was recrystallized from ethanol to provide a cycloadduct (197 mg, 0.59 mmol, 54% yield). ^{1}H NMR (CDCl$_3$): δ 2.22 (m, 1 H), 2.60 (dd, J = 18.61, 7.50 Hz, 1 H), 3.41 (m, 1 H), 3.61 (m, 1 H), 3.73 (s, 3 H), 3.84 (s, 3 H), 5.39 (br m, 1 H), 6.71 (AB quartet, J = 8.7 Hz, $\Delta\nu$ = 28.71, 2 H), 7.67 (m, 2 H), 7.98 (m, 1 H), 8.13 (m, 1 H).

The cycloadduct (116 mg, 0.34 mmol) was placed in a 50-mL round-bottom flask, and concentrated H$_2$SO$_4$ (3 mL) was introduced. The mixture was stirred for 1 h, after which distilled water (30 mL) was introduced, and a red precipitate was observed. The red solid was filtered and dried in vacuo to provide the product quinone (0.1 g, 0.31 mmol, 91% yield). 7,10-Dimethoxy-5,12-naphthacenequinone may be purified by chromatography over silica with chloroform eluant. ^{1}H NMR (CDCl$_3$): δ 4.02 (s, 6 H), 6.89 (s, 2 H), 7.80 (m, 2 H), 8.39 (m, 2 H), 9.22 (s, 2 H). IR (KBr, cm^{-1}): 1675, 1617, 1472, 1389, 1346, 1326, 1287, 1264, 712. High-resolution mass spectrum (EI, 70 eV) calcd for C$_{20}$H$_{14}$O$_4$: 318.0892. Found: 318.0867. Vis (CH$_2$Cl$_2$): 460 nm, (ϵ = 6100).

1,4,6,11-Naphthacenetetrone (14). 7,10-Dimethoxy-5,12-naphthacenequinone (19 mg, 0.06 mmol) was placed in a 25-mL round-bottom flask with a small stir bar. Dioxane (8 mL) was added along with AgO (30 mg, 0.24 mmol). The mixture was sonocated briefly, resulting in a fine suspension. Aqueous 6 N HNO$_3$ (0.06 mL) was then introduced with good stirring. After 5 min, the reaction mixture was poured into chloroform/water and extracted. The chloroform extracts were dried over Na$_2$SO$_4$, and the solvent was removed. The yellow/brown residue was recrystallized from dioxane/cyclohexane to provide diquinone **14** (14 mg, 0.05 mmol, 82% yield). ^{1}H NMR (CDCl$_3$): δ 7.15 (s, 2 H), 7.87 (m, 2 H), 8.37 (m, 2 H), 9.02 (s, 2 H). IR (KBr, cm^{-1}): 1667, 1595, 1327, 1285, 1131, 951, 710. High-resolution mass spectrum (EI, 70 eV) calcd for C$_{18}$H$_8$O$_4$: 288.0422. Found: 288.0413.

2,3-Dichloro-5,8-dimethoxy-1,4-anthraquinone (15). 3,6-Dimethoxybenzocyclobuten-1-ol (0.32 g, 1.8 mmol) was placed in a 50-mL round-bottom flask containing toluene (25 mL) and chloranil (0.44 g, 1.8 mmol). The solution was bubbled with nitrogen. A reflux condenser connected to a nitrogen bubbler was fitted to the flask, and the solution was heated to reflux for 3 days. The dark solution was then cooled, and the toluene was removed to reveal a dark solid. After removal of the volatiles under vacuum, the dark solid was taken up in acetic acid (50 mL), and zinc dust (500 mg) was added with good stirring. Upon the addition of the zinc, the dark solution immediately became warm and light yellow in color. After the mixture was stirred for an additional 30 min, water (150 mL) was then introduced, and the mixture was extracted with chloroform (3 × 100 mL). The extracts were washed with aqueous 3% NaHCO$_3$ (3 × 150 mL) and then with water (1 × 150 mL). During this extraction procedure, the yellow chloroform layer turned a dark red/purple. The solution was dried with Na$_2$SO$_4$ and decanted, and the solvent was evaporated to reveal the anthraquinone derivative **15** (0.54 g, 1.6 mmol, 90% yield) as a blue solid. Purification may be achieved by chromatography over silica with chloroform eluant. ^{1}H NMR (CDCl$_3$): δ 4.00 (s, 6 H), 6.91 (s, 2 H), 8.98 (s, 2 H). IR (KBr, cm^{-1}): 1681, 1673, 1619, 1570, 1470, 1273, 1218, 845, 727. High-resolution mass spectrum (EI, 70 eV) calcd for C$_{16}$H$_{10}$O$_4$Cl$_2$: 335.9954. Found: 335.9936. Anal. Calcd: C, 57.00; H, 2.99; Cl, 21.03. Found: C, 56.87; H, 3.13; Cl, 20.87. Vis (CH$_2$Cl$_2$): 522 nm (ϵ = 5100).

2,3-Dichloro-1,4,5,8-anthracenetetrone ($1Cl_2$). 2,3-Dichloro-5,8-dimethoxy-1,4-anthraquinone (50 mg, 0.15 mmol) was placed in a 25-mL round-bottom flask with acetonitrile (15 mL) and a small stir bar. Ceric ammonium nitrate (247 mg, 0.45 mmol) dissolved in water (1 mL) was added via pipet, and the reaction mixture was stirred for 30 min. The solution was then poured into chloroform/water and extracted. The chloroform extracts were dried over Na_2SO_4, and the solvent was removed. The yellow/brown residue was chromatographed over silica with $CHCl_3$ eluant to provide the desired diquinone $1Cl_2$ (31 mg, 0.10 mmol, 69% yield). ^1H NMR ($CDCl_3$): δ 7.17 (s, 2 H), 8.91 (s, 2 H). IR (KBr, cm^{-1}): 1671, 1274, 1254, 1122, 841, 724. High-resolution mass spectrum (EI, 70 eV) calcd for $C_{14}H_4O_4Cl_2$: 305.9487. Found: 305.9493.

2,5-Dimethoxy-3,4-dimethylbenzoic Acid. 2,5-Dimethoxy-3,4-dimethylbenzaldehyde was prepared from 2,3-dimethyl-1,4-hydroquinone via 2,3-dimethyl-1,4-hydroquinone dimethyl ether (96%), 1,4-dimethoxy-2,3-dimethyl-5-bromomethylbenzene (80%), and then the aldehyde (96%) according to the literature.[28] The crude aldehyde prepared above (3.75 g, 19 mmol) was placed in a 250-mL round-bottom flask, with 1 M aqueous NaOH (150 mL). Silver oxide (4.4 g, 41 mmol) was then added. The solution was refluxed for 0.5 h and stirred overnight at room temperature. After filtration, the solution was acidified with concentrated HCl. The resultant white suspension was collected by filtration and washed with water. 2,5-Dimethoxy-3,4-dimethylbenzoic acid (2.54 g, 12 mmol, 64% yield) was dried in vacuo. ^1H NMR ($CDCl_3$): δ 2.20 (s, 3 H), 2.25 (s, 3 H), 3.84 (s, 3 H), 3.85 (s, 3 H), 7.42 (s, 1 H). IR (KBr, cm^{-1}): 2965, 1467, 1328, 1292, 1232, 1118.

2-Nitro-3,6-dimethoxy-4,5-dimethylbenzoic Acid. With good stirring, 3,6-dimethoxy-4,5-dimethylbenzoic acid (2.54 g, 12 mmol) was added in small portions to a 150-mL beaker containing nitric acid (10 mL) at 0 °C. The bright yellow slurry was stirred for 2 h at 0 °C after the addition was complete. Water was then added, and the mixture was filtered over a medium frit. The yellow solid was washed with water and dried in vacuo. The filtrate was then extracted with chloroform. The chloroform extracts were dried over Na_2SO_4 and decanted, and the solvent was removed. The resultant pale yellow solid was dissolved in 1 M NaOH (150 mL), extracted with ether (3 × 50 mL), and then cooled in ice and acidified with concentrated HCl. An additional amount of crude product then precipitated. This material was collected by filtration, washed, dried in vacuo, and combined with the material collected earlier. The desired 2-nitro-3,6-dimethoxy-4,5-dimethylbenzoic acid (0.95 g, 3.7 mmol, 31% yield) was recrystallized from ethyl acetate/hexane. ^1H NMR ($CDCl_3$): δ 2.29 (s, 3 H), 2.30 (s, 3 H), 3.83 (s, 3 H), 3.86 (s, 3 H). IR (KBr, cm^{-1}): 1702, 1535, 1443, 1391, 1367, 1228, 1091, 1017.

2-Amino-3,6-dimethoxy-4,5-dimethylbenzoic Acid. The nitro arene (0.86 g, 3.4 mmol), prepared as described above, was placed in a 250-mL round-bottom flask containing absolute ethanol (80 mL). Palladium on activated carbon (140 mg, 10% Pd) was added, and the solution was stirred magnetically under a positive pressure of hydrogen for 2 days. The reaction mixture was then filtered over diatomaceous earth, and the solvent was removed, revealing 2-amino-3,6-dimethoxy-4,5-dimethylbenzoic acid (0.68 g, 3.0 mmol, 88% yield) as a pale brown solid. ^1H NMR ($CDCl_3$): δ 2.09 (s, 3 H), 2.19 (s, 3 H), 3.67 (s, 3 H), 3.79 (s, 3 H). IR (KBr, cm^{-1}): 3460, 3342, 1699, 1619, 1460, 1405, 1248, 1083. High-resolution mass spectrum (EI, 70 eV) calcd for $C_{11}H_{15}NO_4$: 225.1001. Found: 225.1001.

3,6-Dimethoxy-4,5-dimethylbenzocyclobutenone. 2-Amino-3,6-dimethoxy-4,5-dimethylbenzoic acid (1.37 g, 6.1 mmol) was placed in a reaction tube with absolute ethanol (10 mL) and concentrated HCl (0.5 mL) and was chilled to 0 °C in an ice bath. Isoamyl nitrite (1.5 mL) was introduced. The reaction tube was stirred in an ice bath for 15 min, and then the volatiles were removed under aspirator vacuum. The resultant brown residue was washed into a 250-mL round-bottom flask with 1,2-dichloroethane (50 mL), propene oxide (5 mL), and freshly distilled vinylidene chloride (5 mL). A Friedrichs condenser was fitted to the flask, and the mixture was refluxed for 10 h. The reaction mixture was then cooled, and the solvent was evaporated. Aqueous 3% H_2SO_4 was added to the dark residue, and the mixture was refluxed overnight. The next day, the solution was cooled and extracted with chloroform. The extracts were dried over Na_2SO_4, decanted, and evaporated, revealing 3,6-dimethoxybenzocyclobutenone (0.41 g, 2.05 mmol, 34% yield) as an off-white solid after chromatography over silica with chloroform eluant. ^1H NMR ($CDCl_3$): δ 2.10 (s, 3 H), 2.17 (s, 3 H), 3.88 (s, 3 H), 4.07 (s, 2 H), 4.11 (s, 3 H). IR (KBr, cm^{-1}): 1752, 1477, 1408, 1259, 1112, 1059.

3,6-Dimethoxy-4,5-dimethylbenzocyclobuten-1-ol (17). The benzocyclobutenone prepared above (0.75 g, 3.6 mmol) was placed in a 250-mL round-bottom flask with methanol (100 mL). Sodium borohydride (0.54 g, 14.4 mmol) was added in small portions with good stirring. The solution was stirred magnetically for 2.5 h and then poured into ice/HCl. The 3,6-dimethoxy-4,5-dimethylbenzocyclobuten-1-ol (0.61 g, 2.9 mmol, 80% yield) then precipitated. It was collected, washed, and dried in vacuo. This material may be purified by chromatography over silica with chloroform eluant. ^1H NMR ($CDCl_3$): δ 2.09 (s, 6 H), 2.38 (d, J = 10.6 Hz, 1 H hydroxyl), 3.13 (d J = 13 Hz, 1 H), 3.79 (dd, J = 13, 4.6 Hz, 1 H), 3.82 (s, 3 H), 3.99 (s, 3 H), 5.30 (br, 1 H). IR (KBr, cm^{-1}): 1598, 1473, 1405, 1267, 1150, 1114, 1014. High-resolution mass spectrum (EI, 70 eV) calcd for $C_{12}H_{16}O_3$: 208.1100. Found: 208.1098.

2,3,6,7-Tetramethyl-5,8-dimethoxy-1,4-anthraquinone (18). 3,6-Dimethoxy-4,5-dimethylbenzocyclobuten-1-ol (17) (20 mg, 0.096 mmol) was placed in a 25-mL round-bottom flask containing 2,3-dimethylbenzoquinone (26 mg, 0.192 mmol) and toluene (15 mL). The solution was bubbled with nitrogen, and a condenser connected to a nitrogen bubbler was fitted to the flask. The solution was then heated to reflux for 4 days. Once cooled, the toluene was removed to reveal an orange brown solid. The solid was chromatographed over silica with chloroform eluant. The product, **18** (10 mg, 0.031 mmol, 32% yield) eluted as a orange band. ^1H NMR ($CDCl_3$): δ 2.23 (s, 6 H), 2.40 (s, 6 H), 3.91 (s, 6 H), 8.81 (s, 2 H). IR (KBr, cm^{-1}): 1660, 1605, 1457, 1427, 1327, 1293, 1091, 1007. High-resolution mass spectrum (EI, 70 eV) calcd for $C_{20}H_{20}O_4$: 324.1362. Found: 324.1378.

6,7-Dimethyl-5,8-dimethoxy-1,4-anthraquinone (19). 3,6-Dimethoxy-4,5-dimethylcyclobuten-1-ol (34 mg, 0.16 mmol) was placed in a 25-mL round-bottom flask containing benzoquinone (8.6 mg, 0.08 mmol) and toluene (15 mL). The solution was bubbled with nitrogen, and a condenser connected to a nitrogen bubbler was fitted to the flask. After reflux was maintained for 4 days, the solution was cooled overnight in a refrigerator. The next day, a bright yellow solid was filtered, collected, and dried in vacuo. The filtrate was collected, and the solvent was removed to reveal an orange/brown residue. This residue was chromatographed over silica with chloroform eluant. The 1,4-anthraquinone derivative **19** eluted as an orange band (7 mg, 0.024 mmol, 15% yield). ^1H NMR ($CDCl_3$): δ 2.42 (s, 6 H), 3.91 (s, 6 H), 7.06 (s, 2 H), 8.82 (s, 2 H). IR (KBr, cm^{-1}): 1667, 1604, 1457, 1321, 1296, 1144, 1090, 997, 844. High-resolution mass spectrum (EI, 70 eV) calcd for $C_{18}H_{16}O_4$: 296.1049. Found: 296.1022. Vis (CH_2Cl_2): 450 nm (ϵ = 4500).

2,3,6,7-Tetramethyl-1,4,5,8-anthracenetetrone ($1Me_4$). 2,3,6,7-Tetramethyl-5,8-dimethoxy-1,4-anthraquinone (**18**) (16.3 mg, 0.05 mmol) was placed in a 25-mL round-bottom flask with acetonitrile (10 mL) and a small stir bar. Ceric ammonium nitrate (83 mg, 0.15 mmol) dissolved in water (1 mL) was added via pipet, and the solution was stirred for 30 min. The solution was then poured into chloroform/water and extracted. The chloroform extracts were dried over Na_2SO_4, and the solvent was removed. The yellow/brown residue was chromatographed over silica with $CHCl_3$ eluant to provide the desired $1Me_4$ diquinone (12 mg, 0.04 mmol, 88% yield). ^1H NMR ($CDCl_3$): δ 2.23 (s, 12 H), 8.79 (s, 2 H). IR (KBr, cm^{-1}): 1655, 1614, 1381, 1305, 1295, 1022, 703. High-resolution mass spectrum (EI, 70 eV) calcd for $C_{18}H_{14}O_4$: 294.0892. Found: 294.0872. Anal. Calcd: C, 73.46; H, 4.79. Found: C, 73.40; H, 4.90.

2,3-Dimethyl-1,4,5,8-anthracenetetrone ($1Me_2$). 6,7-Dimethyl-5,8-dimethoxy-1,4-anthraquinone (**19**) (17.5 mg, 0.06 mmol) was placed in a 25-mL round-bottom flask with a small stir bar. Dioxane (5 mL) was added along with AgO (30 mg, 0.24 mmol). The mixture was sonocated briefly, resulting in a fine suspension. Aqueous 6 N HNO_3 (0.06 mL) was then introduced with good stirring. After 5 min, the reaction mixture was poured into chloroform/water and extracted. The chloroform extracts were dried over Na_2SO_4, and the solvent was removed. The yellow/brown residue was chromatographed over silica with $CHCl_3$ eluant to provide the $1Me_2$ diquinone (10.6 mg, 0.04 mmol, 71% yield). ^1H NMR ($CDCl_3$): δ 2.24 (s, 6 H), 7.12 (s, 2 H), 8.80 (s, 2 H). High-resolution mass spectrum (EI, 70 eV) calcd for $C_{16}H_{10}O_4$: 266.0579. Found: 266.0571.

Solvents and Salts. Anhydrous DMF was obtained from the Aldrich Chemical Co., used fresh, and stored under nitrogen. DMSO and d_6-DMSO was distilled under vacuum from calcium hydride and sodium amide prior to use and stored under nitrogen over 4-Å molecular sieves. HPLC grade acetonitrile was distilled from calcium hydride under nitrogen prior to use. Tetrabutylammonium tetrafluoroborate (electrometric grade) was purchased from Southwestern Analytical Chemicals Inc. (Austin, TX), recrystallized from water/methanol 3:1, and dried in vacuo. Lithium perchlorate was recrystallized from water/methanol 1:1 and dried in vacuo at 150 °C.

Voltammetry. Voltammetric experiments were performed with a BAS-100 electrochemical analyzer. All potential measurements were referred to a saturated calomel electrode (SCE). In order to isolate the SCE from the nonaqueous voltammetry solution, a nonaqueous salt bridge was used to connect the two. This was composed of a course glass frit at the end of a 10-cm tube (0.5-cm diameter) containing a DMF (0.50 M $TBABF_4$)/methylcellulose gel. Directly above this was an aqueous agar (1 M KCl), and above this, a saturated aqueous KCl solution in which the SCE was suspended. A simple one-compartment cell was used for voltammetry experiments. The working electrode was a glassy carbon disk set into a Teflon tube. Prior to a voltammetry experiment, the working electrode was polished with alumina paste on a micro polishing cloth (Buehler), by first using 0.30- and then 0.05-μm alumina (Buehler). The electrode was then sonocated in distilled water for 5 min and wiped dry. The electrode was installed into the voltammetry cell along with a platinum wire counter electrode and the reference. The solvent and electrolyte were then put into the cell and degassed with nitrogen. The working electrode was cycled many times between the anodic and cathodic limits of interest until there was no change in the charging current. The substrate was then introduced (1–5 mM), and the solution again was purged with nitrogen before the voltammetry experiment was initiated. Voltammograms were generally recorded at a sweep rate of 100 mV/s. After several voltammograms were obtained on the substrate in solution, a small amount of ferrocene was added, and the voltammogram was repeated, this time including the anodic couple of ferrocene along with the cathodic quinone couples. The $E°$ values of the quinone compound of interest were then determined placing the ferrocene couple at +0.47 V vs SCE.

Bulk Electrolysis. The bulk electrolyses of quinone compounds both in dilute solutions for spectroscopic analysis and in more concentrated solution for the preparation of solid samples were performed under similar constant potential conditions. A simple two-compartment cell was used, with a medium-porosity glass frit dividing the two chambers. For large-scale electrolysis, which usually required several hours, this glass frit was covered with a layer of the nonaqueous methylcellulose salt bridge material to hinder diffusion of substrate between the two chambers. The cell was then charged with solvent/supporting electrolyte (SSE). The auxiliary chamber was fitted with a carbon rod electrode. The working chamber was sealed with a flat Teflon cap through which the reference electrode and the glassy carbon voltammetry electrodes were suspended. Also suspended from the cap was a platinum wire, which held a large surface area carbon-felt electrode. This Teflon cap also provided a small hole through which a syringe needle introduced a flow of dry nitrogen through or above the solution. After a stir bar was placed into the working chamber, the Teflon cap was installed, and the solution was purged with nitrogen. The voltammetry electrode was used to measure a voltammogram on the blank SSE. The substrate was then introduced, and again voltammetry was used to check that the electrochemical response of the substrate was as expected. The BAS-100 used for voltammetry was disconnected from the cell, and a Princeton Applied Research (PAR) potentiostat Model 173 was connected to the cell. With good stirring in the working chamber, the carbon-felt synthesis electrode was stepped to the desired potential. A PAR-179 coulometer, connected to the potentiostat, measured the cathodic current passed. When 1-equiv of electrons had been passed, the current level had decreased to a very small value. At this point, the electrolysis was considered to be complete, and the resulting anion solution was sampled.

UV-Vis-Near-IR Absorbance Spectra. UV-vis-near-IR spectra were recorded with a Cary 14 spectrometer interfaced to an IBM compatible microcomputer. The computer interface allowed the subtraction of background absorbances and the storage of spectra on magnetic disks. Quartz cuvettes (Helma) of 1-cm and 0.1-cm path length were adapted for work in an inert atmosphere by the installation of a ground glass joint and a stopcock. Samples of anions from electrosynthesis were syringed into the argon-purged cuvette directly from the electrochemical cell, by use of a gas-tight syringe, and the spectrum was recorded immediately.

EPR Spectra. EPR spectra were recorded on a Varian E4 X-band spectrometer at room temperature. EPR samples were prepared in an inert atmosphere box under an argon atmosphere. A DMF solution of electrogenerated anion was diluted to the 1×10^{-5} M concentration range. The diluted solution was syringed into Pyrex tubes 8 in. in length and with an inner diameter of 1 mm. Several samples were prepared, including one from the concentrated solution. The tubes were sealed with small septa, removed from the dry box, and sealed with a torch. The EPR spectra were recorded within hours of sample preparation.

Infrared Spectra. IR spectra of anion radicals in DMSO solution were measured with a Perkin-Elmer 7100 FT-IR instrument. A 0.1 mm path length cell with calcium fluoride windows was used, because this material is resistant to DMSO solutions. Spectra were recorded in DMSO solution, 0.1 M in $LiClO_4$ and 5 mM in substrate, in the absence of oxygen. Background absorbances due to the DMSO solvent were subtracted from the spectra.

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Systematic Study of a Series of Highly Fluorescent Rod-Shaped Donor–Acceptor Systems

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Abstract: The synthesis and emissive properties of bichromophoric molecules **1–11** are reported. All systems contain an anilino group as a one-electron donor (D) and various substituted ethylene moieties as electron acceptor (A) separated by a rod-shaped alicyclic framework provided by a piperidine ring. From the emissive properties it is concluded that in these molecules the electronic coupling between D and A is sufficient to allow complete charge transfer upon excitation (if thermodynamically feasible). The dipolar charge-transfer (CT) excited state thus populated displays a very strong fluorescence, which is highly solvatochromic (i.e., undergoes a large wavelength shift in response to changes of the solvent polarity), making these systems of interest as a new class of fluorescent probes. Variation of the acceptor group is found to allow design of such probes, with quantum yield vs solvent polarity profiles optimized for any particular polarity range.

1. Introduction

Recently we reported[1a] about the rod-shaped[1b] donor–acceptor systems **1** and **2** (see Figure 1), which show intense charge-transfer (CT) fluorescence in solution. In these molecules a dialkyl anilino moiety is acting as a one-electron donor (D) and a 1-vinyl-4-cyanonaphthyl (**1**) or a 2-vinylnaphthyl (**2**) moiety as a one-electron acceptor (A).

Neglecting the dipole moment in the ground state μ_0 relative to that of the excited (charge-transfer) state μ_e, Lippert[2] and Knibbe[3] derived relation 1. In equation 1, $\nu_{ct}(0)$ denotes the

$$\nu_{ct} = \nu_{ct}(0) - (2\mu_e^2/hc\rho^3)\Delta f \qquad (1)$$

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