Articles

Electrochemistry and Near-Infrared Spectra of Anion Radicals Containing Several Imide or Quinone Groups

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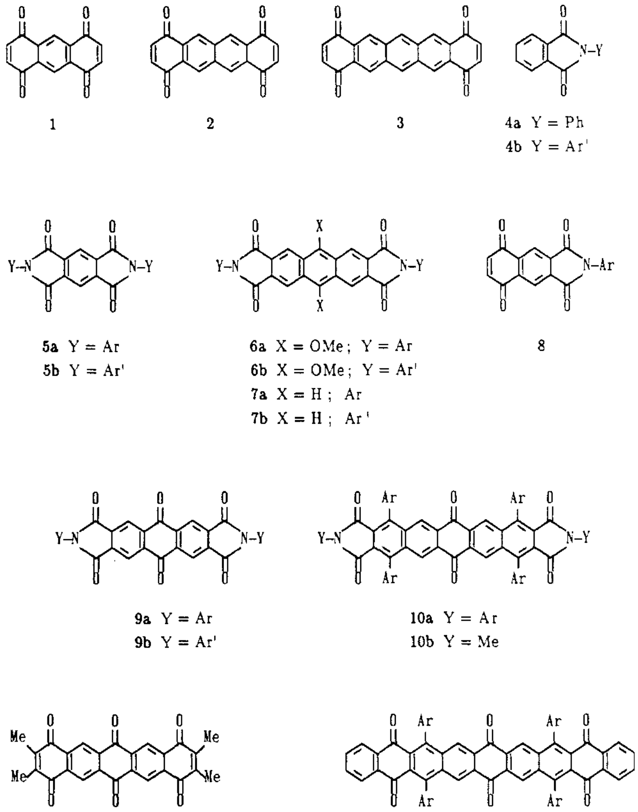
A series of aromatic compounds possessing imide and quinone electron-acceptor groups were prepared using Diels–Alder reactions. These linear, aromatic compounds were studied using cyclic voltammetry and reduced electrochemically to produce solutions of the corresponding anion radicals. The anion radical near-infrared spectra were recorded and showed bands over the range 700–1700 nm (log ϵ 3.8–4.6). Most of the spectra are interpreted to arise from π^*-π^* transitions. The spectra and $E°$ values are consistent with ground states in which the odd electron is delocalized over two electrophores.

There have been few reports on the electronic absorption spectra of anion radicals, and these have been limited to rather simple compounds.[1] Even so, the results are interesting because the ions absorb at long wavelengths in the visible or near-infrared (NIR). NIR absorbers are of growing interest because of applications in communications and optical storage,[2] and it is appropriate to study some more complex anion radicals in order to understand their optical properties.

In recent publications from this laboratory, the unusual NIR spectra of the anion radicals of conjugated diquinones have been revealed.[3-5] These species absorb at much longer wavelengths than the anion radicals of monoquinones. For example, the diquinone anion radical, $1^{\bullet-}$, has a sharp band at 1560 nm (ϵ = 16 000 cm^{-1} M^{-1}),[3,5] while 1,4-anthraquinone has λ_{max} = 510 nm. Molecular orbital calculations as well as substituent and solvent effects on the spectra suggested that the long-wavelength band for $1^{\bullet-}$ originated from a π^*-π^* transition, i.e. SOMO → LUMO, from a delocalized ground state.[5]

In surprising contrast to the spectrum of $1^{\bullet-}$, the anion radicals, $2^{\bullet-}$ and $3^{\bullet-}$, where the two quinones are separated by two and three rings, give extraordinarily broad, featureless absorptions extending from 600 to 2200 nm.[4,5] Based upon molecular orbital calculations, it was suggested that these two anion radicals have mixed valence structures and are not completely delocalized. IR spectra of $1^{\bullet-}$ and $2^{\bullet-}$ were consistent with these interpretations.

Chart I


1 2 3

4a Y = Ph
4b Y = Ar'

5a Y = Ar
5b Y = Ar'

6a X = OMe; Y = Ar
6b X = OMe; Y = Ar'
7a X = H; Ar
7b X = H; Ar'

8

9a Y = Ar
9b Y = Ar'

10a Y = Ar
10b Y = Me

11

12

Ph = –C$_6$H$_5$ Ar = 4-tert-butylphenyl Ar' = 2,5-di-tert-butylphenyl

The unusual aspects of these spectra and the hypothesized mixed-valence ground-state structures for $2^{\bullet-}$ and $3^{\bullet-}$ have led us to explore the scope of these phenomena. In this paper, we report on the electrochemistry and the vis–NIR spectra of several anion radicals containing two imide functional groups. We also extend our studies to several anion radicals containing three electrophores.[6] The

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(1) (a) Ortho and para semiquinones: Iida, Y. *Bull. Chem. Soc. Jpn.* **1974**, *44*, 1777. Mikhailov, G.; Trifonov, A. *Izv. Otd. Khm. Nauki, Bulg. Nauk.* 1971, *4*, 533. Mitzner, R.; Dorst, H.; Frosch, D. *Z. Chem.* **1975**, *15*, 400. Staples, T. L.; Szwarc, M. *J. Am. Chem. Soc.* **1970**, *92*, 5022. (b) Aromatic and unsaturated aliphatic carbonyl-substituted anion radicals: Shida, T.; Iwata, S.; Imamura, M. *J. Phys. Chem.* **1974**, *78*(7), 741. (c) Aromatic hydrocarbon ion radicals: Shida, T.; Iwata, S. *J. Am. Chem. Soc.* **1974**, *95*, 3473. (d) Aromatic nitro-substituted anion radicals: Shida, T.; Iwata, S. *J. Phys. Chem.* **1971**, *75*(17), 2591.

(2) (a) Fabian, J.; Zahradnik, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1. (b) Emmelius, M.; Pawlowski, G.; Vollmann, H. W. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1445. (c) Agrawal, G. P.; Dutta, N. K. *Long Wavelength Semiconductor Lasers*; Van Nostrand and Reinhold: New York, 1986.

(3) (a) Jozefiak, T. H.; Miller, L. L. *J. Am. Chem. Soc.* **1987**, *109*, 6560. (b) Ph.D. Thesis of T. H. Jozefiak, University of Minnesota, 1989.

(4) Almlof, J.; Jozefiak, T. H.; Feyereisen, M. W.; Miller, L. L. *J. Am. Chem. Soc.* **1989**, *111*, 4105.

(5) Almlof, J.; Jozefiak, T. H.; Feyereisen, M. W.; Miller, L. L. *J. Am. Chem. Soc.* **1990**, *112*, 1206.

(6) For a definition of the term "electrophore", see: Miller, L. L.; Jacoby, L. J. *J. Am. Chem. Soc.* **1969**, *91*, 1130.

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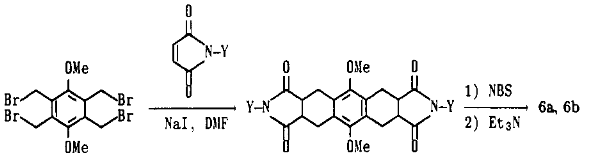
synthesis of these ions allowed a comparison of electrochemical and NIR data for a series of anion radicals with different functional groups and conjugation lengths. The results are self-consistent and lead to some insight into the origin of the spectra, the structure of the ions, and, in general, expand our knowledge of NIR absorbers.

Results and Discussion

We have studied a set of diimides, quinone–imides, and triquinones where the electrophores are held apart by one or more aromatic rings. In addition to general synthetic constraints, the major problem faced in this work was that these long, flat compounds are not very soluble. For imides this problem was addressed using *N*-(*tert*-butylphenyl) or *N*-(2,5-di-*tert*-butylphenyl) derivatives.

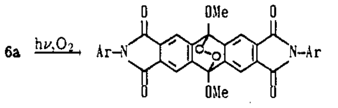
Synthesis. Of the compounds 4–12 that were studied (see Chart I), **4a**, **10a,b**, and 12 were previously synthesized.[7,8] Compounds **4b** and **5a,b** were obtained from phthalic anhydride and pyromellitic dianhydride employing the appropriate aniline derivative. With the intention of spacing two imide groups farther apart, compounds **6a** and **6b** were prepared. The methoxy groups on **6a,b** were used because they often improve solubility and they can provide a route to the corresponding quinones, **9a,b**. Bis-Diels–Alder addition was employed to build the desired framework from a tetrabenzyl bromide in one step (eq 1).[9] The diadducts **13a,b** were then aromatized using *N*-bromosuccinimide, followed by triethylamine. Compounds **6a,b** fluoresce highly in solution, but the bright yellow color dissipates readily in room light to quantitatively yield a new product. The photoproduct of **6a** was isolated by chromatography and identified as endoperoxide 14 (eq 2). When 14 is heated as a solid to 250 °C, **6a** is regenerated. Refluxing in toluene, however, gave quinone **9a**. A better synthesis of **9a** (and similarly of **9b**) utilized ceric ammonium nitrate (CAN) oxidation of **6a,b**.[10]



Eq. 1

13a Y = Ar

13b Y = Ar'



Eq. 2

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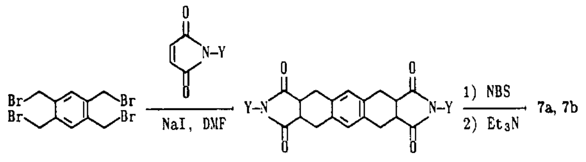
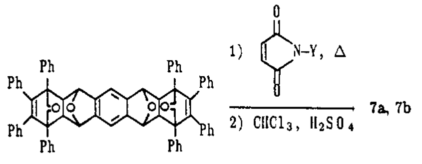
Compounds **7a,b** were also obtained by bis-Diels–Alder addition followed by aromatization (eq 3). The desired aromatized products **7a,b** were unexpectedly accompanied by brominated side products (as shown by FAB mass spectrometry). Purification of **7a,b** proved to be difficult by recrystallization and chromatographic techniques. Therefore, another method was employed for the syntheses of **7a,b** utilizing a benzodifuran precursor (**16**),[11] which was heated with the appropriate maleimide derivative (eq 4). The presumably formed dioxy intermediate was then aromatized with H_2SO_4 to give **7a,b**. Purification could then be accomplished with conventional hot filtration and chromatographic techniques. **7a,b** proved to be more stable to photoxidation than **6a,b**.



15a Y = Ar

15b Y = Ar'

Eq. 3



Eq. 4

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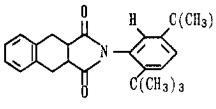
The intermediates **13a,b** and **15a,b** were isolated, and based upon their NMR spectra, are assigned to be the trans-bis-endo adducts. Special attention should be given to the ^{1}H NMR of **13b** and **15b** possessing the 2,5-di-*tert*-butylphenylimide functionality. These spectra show a doublet of ca. δ 5.3 ppm, which is assigned to the ortho hydrogens on the di-*tert*-butylphenyl rings. A 2D COSY spectrum of **13b** confirms the assignment. Following a literature interpretation for similar adducts[12] this unusual shift results from a confluence of two conformational factors: (1) the *o*-*tert*-butyl group locks the phenyl ring orthogonal to the imide plane and (2) the phenyl rings of interest are held over (and under) the central benzene ring. This brings the ortho hydrogens of interest into the shielding region of the central benzene ring. Compound 17 was synthesized and also displayed a doublet (1 H) at δ 5.3 ppm. This is consistent with the interpretation and it makes it unlikely that the peak at δ 5.3 ppm in the ^{1}H NMR spectra of **13b** and **15b** is due to an interaction between two 2,5-di-*tert*-butylphenyl groups located in a syn configuration.



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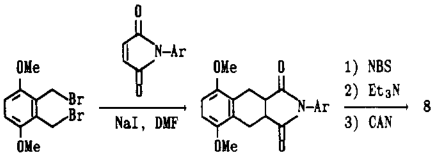
Via the Diels–Alder strategy the quinone–imide 8 was prepared (eq 5).



Eq. 5

It was of interest to study a triquinone like 11 as a trielectrophore. This derivative was studied because the analogue without the four methyl groups was too insoluble to use. Via a protocol which we have previously established,[4,5] the appropriate benzocyclobutenol was reacted

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[8] Chiba, T.; Kenny, P. W.; Miller, L. L. *J. Org. Chem.* **1987**, *52*, 4327.

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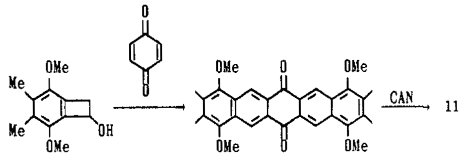
Table I. Reduction Potentials[a]

compd	$-E°$, mV		
1	0.26	0.74	
2	0.50	0.75	
3	0.72	0.84	
4a	1.36	2.22	
4b	1.40	2.30[b]	
5a	0.72	1.38	
5b	0.71	1.43	
6a	1.01[c]	1.45[c]	
6b	1.03	1.52[d]	
7a	1.07	1.47[d]	
7b	1.07	1.53	
8	0.32	1.04	
9a	0.27	0.82	1.72[d]
9b	0.28	0.82	1.80[d]
10a	0.68	1.19	1.62[d]
11	0.26	0.60	1.02
12	0.66	0.98	1.26

[a] Measured in DMF, 0.1 M Bu_4NBF_4, scan rate 150 mV s^{-1}, glassy carbon working electrode, SCE reference. $E° = (E_p{}^a + E_p{}^c)/2$. [b] This value represents $-E_p{}^c$. No anodic peak observed for dianion. [c] CV wave was recorded on a solution of **6a**$^{\bullet-}$, which was more soluble than **6a**. [d] ΔE_p anodic–cathodic 70–85 mV.

with benzoquinone ($^1/_2$ equiv) in a Diels–Alder reaction followed by ceric ammonium nitrate oxidation (eq 6).



Eq. 6

Electrochemistry. Cyclic voltammetry was used to estimate reduction potentials for the compounds of interest (Table I). The electrolyte solution was degassed DMF, 0.1 M Bu_4NBF_4, the working electrode was a polished glassy carbon disk, and the reference electrode, SCE. An apparent $E°$ was taken as the midpoint between anodic and cathodic peak potentials. In general the peak separation was 60 ± 5 mV, but a few ΔE_p values were larger. Extensive work was not performed to see if these larger values could be made closer to the expected 59 mV using slower sweep rates or other changes. Since the relative peak currents were as required, it will be assumed that all the apparent $E°$ values represent thermodynamic equilibrium.

All the two-electrophore compounds gave two reversible couples. At more negative potentials, irreversible peaks were observed. The three-electrophore compounds (**9–12**) all gave three reversible couples with further irreversible process at more negative potentials.

A number of observations and generalizations can be made concerning relative $E°$ values. (i) Like diquinones compared to quinones, diimides reduce easier than imides. Compare **5a** (−0.72, −1.38 V) with *N*-phenylphthalimide (−1.37, −2.22 V). (ii) Diquinones reduced easier than quinone-imides, which reduce easier than diimides. Compare 1 (−0.26, −0.74 V), 8 (−0.32, −1.05 V), and **5a** (−0.72, −1.38 V). (iii) Triquinones reduce slightly more easily than quinone–dimides. Compare 11 (−0.26, −0.60, −1.02 V) with **9a** (−0.27, −0.82, −1.72 V), or compare 12 (−0.67, −0.98, −1.27 V) with **10a** (−0.68, −1.19, −1.62 V).

The data in i–iii are self-consistent. They indicate that a higher density of electrophores gives a more positive reduction potential and that a quinone will accept an electron more readily than an imide. The literature is consistent with these conclusions.[13] Especially pertinent are the gas-phase electron affinities of naphthoquinone (1.81 eV) and *N*-phenylphthalimide (1.16 eV).

Table II. Absorption Spectral Data of Radical Anions[a]

compd	λ_{max}, nm (log ϵ)
4b$^{\bullet-}$	820 (2.74), 419 (3.54)
5a$^{\bullet-}$	719 (4.29), 656 (3.68), 416 (3.23)
5b$^{\bullet-}$	718 (4.62), 652 (3.99), 406 (3.43)
6b$^{\bullet-}$	785 (4.03), 634 (3.91), 568 (3.95), 507 (4.28), 476 sh (4.10)
7b$^{\bullet-}$	784 (4.34), 585 sh (4.10), 548 (427), 485 (4.66), 453 (4.39)
8$^{\bullet-}$	846 broad (3.86), 435 (3.82)
9a$^{\bullet-}$	1088 (4.15), 936 (4.11), 420 (3.65)
9b$^{\bullet-}$	1090 (4.20), 937 (4.13), 417 (3.76)
10a$^{\bullet-}$	1155 (4.41), 1000 sh (4.20), 450 sh (4.23)
10b$^{\bullet-}$	1125 (4.18), 980 (3.93), 426 (4.07), 405 (4.06)
11$^{\bullet-}$	1720 (4.38)
12$^{\bullet-}$	1730 (4.43), 485 (4.11), 435 (4.17)

[a] Spectra recorded in DMF containing 0.1 M Bu_4NBF_4.

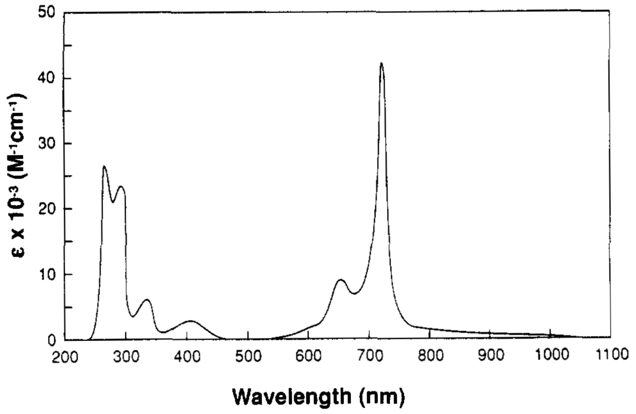


Figure 1. Spectrum of **5b**$^{\bullet-}$ in DMF, 0.1 M Bu_4NBF_4.

In a previous study[4] it was shown that the $E°$ values for 2 and 3 were consistent with localization of the added electron on one quinone unit. The difference between diquinones and diimides can be illustrated by comparison of $E°$ for a pair of quinones with a structurally similar pair of diimides; naphthoquinone with **3**, and phthalimide **4b** with **7b**. The diquinone **3** (−0.72 V) is *more difficult* to reduce than the monoquinone (−0.61 V). This leads to localization on one quinone unit. In contrast, the diimide **7b** (−1.07 V) is *easier* to reduce than the monoimide (−1.40 V). This suggests that for **7b** the extra electron is delocalized onto the anthracene unit and second imide moiety.

Anion Radical Spectra. Because of the paucity of information about both NIR absorbers and anion radical absorption spectra, the data collected (Table II) on compounds **4–12** form an unusual set. They document the spectral effect of change in electrophore (quinone to imide), change in number of electrophores (mono-, di-, and trielectrophores), and change in the spacing between electrophores (or length of conjugation). The results show absorption bands over the range 700–1700 nm, demonstrating that the "color" of these anions can be controlled and varied over a wide range. It is suggested that the NIR color comes from π^*-π^* (SOMO → LUMO) transitions of the odd-electron.

Preparative reductions were performed in DMF, 0.1 M Bu_4NBF_4 at a carbon sponge cathode. The potential was set just negative of the cathodic E_p and typically 1.1 Faradays/mol were passed to form anion radicals. Of central interest are the spectra of the pyromellitic diimide anions, **5a,b**$^{\bullet-}$, which show a sharp band at 719 and 718 nm, respectively. Less intense bands are found at 656 and 652 nm, respectively (Table II, Figure 1). The difference in energy between the two peaks in the **5a** spectrum is 1336 cm^{-1}, which corresponds closely to the vibrational splitting

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[13] (a) Kebarle, P.; Chowdhury, S. *Chem. Rev.* **1987**, 513. (b) Paul, G.; Kebarle, P. *J. Am. Chem. Soc.* **1989**, *111*, 464.

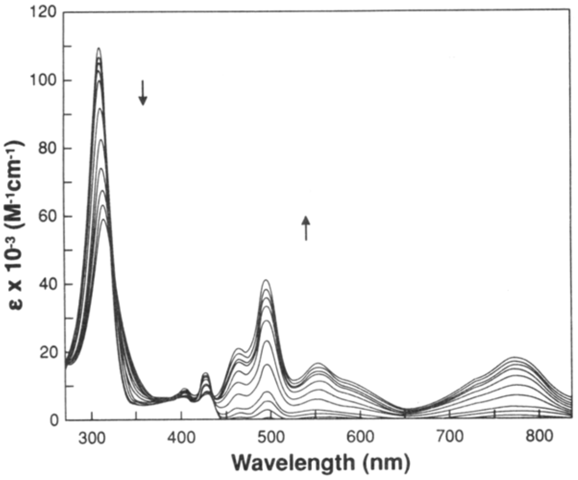


Figure 2. Spectroelectrochemical data taken as **7b** was reduced in DMF, 0.1 M Bu_4NBF_4. The time zero spectrum has no absorption beyond 450 nm. Eleven spectra taken at 10-s intervals show the build up of bands in the vis–NIR.

found for $1^{\bullet-}$ as well as simple aromatic hydrocarbons.[14] When $\mathbf{5a}^{\bullet-}$ was formed using DMF, $LiClO_4$ and $\mathbf{5b}^{\bullet-}$ was formed using THF, Bu_4NBF_4, the peak positions were unchanged. Over the range of concentrations 7×10^{-4} to 2×10^{-4} M, the spectra followed Beers Law. All these observations correspond to those for the model anion $1^{\bullet-}$, and it is proposed that like $1^{\bullet-}$, $\mathbf{5a,b}^{\bullet-}$ have a delocalized ground state, with a SOMO to LUMO π^*-π^* transition of the odd electron accounting for the 719-nm band. This band is at much shorter wavelength than the 1560 nm π^*-π^* band for $1^{\bullet-}$. This can be understood by considering that the change in structure amounts to replacement of the two "outside" C–C double bonds of $1^{\bullet-}$ with two nitrogen atoms in $\mathbf{5a,b}^{\bullet-}$. The double bonds have π^* orbitals which act to delocalize the odd electron. Indeed in the excited state of $1^{\bullet-}$ there is a significant amount of electron density on these outside double bonds.[5] The nitrogen atoms of $\mathbf{5a,b}^{\bullet-}$ do not offer this possibility. Therefore, the excited state of $\mathbf{5a,b}^{\bullet-}$ is destabilized, and the band is at a shorter wavelength.

These conclusions concerning the structure and spectra of $\mathbf{5a,b}^{\bullet-}$ are in agreement with literature reports of the visible spectrum of (pyromellitic dianhydride)$^{\bullet-}$,[1b] thin films of (polyimide)$^{\bullet-}$ derived from pyromellitic dianhydride[15] and the ESR spectrum of (pyromellitic diimide)$^{\bullet-}$.[16]

To make the connection between quinones and imides, the quinone–imide **8** was studied. Prepared electrochemically, $8^{\bullet-}$ showed a broad absorption band at 846 nm. This is at longer wavelength than the band for $5^{\bullet-}$ or the band for a model monoquinone$^{\bullet-}$ like 1,4-anthraquinone$^{\bullet-}$ which absorb near 500 nm.[4,5] Again, a π^*-π^* transition is indicated.

It was of great interest to see if the anion radicals of the "stretched" diimides **6a,b** and **7a,b** would exhibit sharp bands or the broad, featureless absorptions found for the quinone analogues, $2^{\bullet-}$ and $3^{\bullet-}$. The diimides reduced smoothly, but the anion radicals were only marginally stable (as was previously found for $3^{\bullet-}$). Normal anaerobic transfer techniques often led to absorption spectra possessing bands due to the neutral as well as those due to the anion radical. Therefore, an in situ spectroelectrochemical approach was employed. A thin-layer electrochemical cell[17] allowed spectra to be taken every 10 s and allowed the anion radicals to be fully formed in 2 min. $\mathbf{6b}^{\bullet-}$ and $\mathbf{7b}^{\bullet-}$ were studied. Each showed bands throughout the visible region into the NIR (Figure 2). Electrochemical reoxidation was successful, and isosbestic points were observed as the reduction and reoxidation proceeded. Vis–NIR spectra of transferred samples were very similar and showed no other peaks beyond 900 nm.

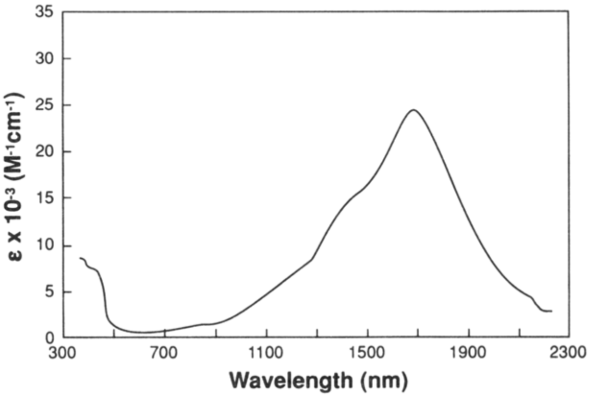
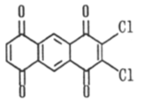


Figure 3. Spectrum of $11^{\bullet-}$ in DMF, 0.1 M Bu_4NBF_4.

The spectra are more intense and not as broad as those from $2^{\bullet-}$ and $3^{\bullet-}$, but more complex than the spectra of $\mathbf{5a,b}^{\bullet-}$. They are qualitatively consistent with spectra expected for delocalized ions. Since the energy of an anthracene π^*-orbital (anthracene $E_A = 0.60$)[13a] is not too different from that of an imide π^* orbital (*N*-phenylmaleimide $E_A = 1.36$ eV)[13b] the half-filled π^* orbital of $6^{\bullet-}$ and $7^{\bullet-}$ may have substantial anthracene character. This in turn suggests that both π^*-π^* and π-π^* (from a high lying anthracene-like π-orbital) will occur. This will give intense, complex spectra like that for anthracene$^{\bullet-}$;[1c] spectra more intense than those for $2^{\bullet-}$ and $3^{\bullet-}$ where localization dramatically diminishes the intensity of the long wavelength π^*-π^* band. These expectations for $6^{\bullet-}$ and $7^{\bullet-}$ are fulfilled. The bands occur in the same region as those for anthracene$^{\bullet-}$, and they are about 10 times as intense as those for $2^{\bullet-}$ and $3^{\bullet-}$.

Trielectrophore Anion Radical Spectra. Consider now the spectra of anion radicals of the trielectrophores **9**–**12**. Here one electron reduction proceeded smoothly, and the ions were quite stable. Figure 3 shows the five ring $11^{\bullet-}$ (formed by 1 Faraday/mol reduction) which absorbs at 1720 nm ($\epsilon = 23\,000$ cm^{-1} M^{-1}). The band has the familiar vibrational splitting (separation 1366 cm^{-1}) like $1^{\bullet-}$ and shows no solvent shift when CH_2Cl_2 is used as solvent instead of DMF. The peak is somewhat broadened as expected if $11^{\bullet-}$ is considered an unsymmetrical analogue of $1^{\bullet-}$, like $18^{\bullet-}$.[5] The peak for $11^{\bullet-}$ is similar in wavelength to that for $18^{\bullet-}$ and is at a longer wavelength than that for $1^{\bullet-}$. This is expected[5] if the "third quinone" stabilizes the π^*-π^* excited state more than the ground state. Electrochemically (Table I) **11** behaves very similarly to **1**, suggesting that the lowest π^* orbital of **11** is similar in energy to that of **1**.



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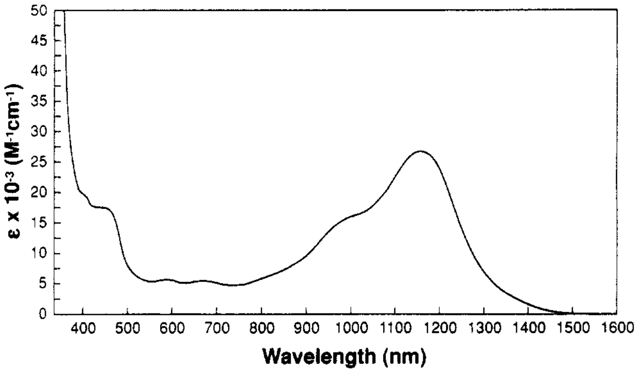
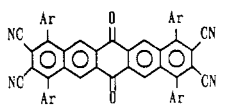


Figure 4. Spectrum of **10a**$^{\bullet-}$ in DMF, 0.1 M Bu_4NBF_4.

Consider next the corresponding quinone–diimides, **9a,b**. **9a**$^{\bullet-}$ has bands at 1088 (ϵ = 14 000 cm^{-1} M^{-1}) and 936 (ϵ = 13 000 cm^{-1} M^{-1}). **9b**$^{\bullet-}$ gives similar results (Table II). By analogy, we compare this with quinone–imide **8**$^{\bullet-}$ with a peak at 846 nm. Addition of the third electrophore again leads to a shift to longer wavelength but does not give a spectrum like that of the stretched diimides **6b**$^{\bullet-}$ and **7b**$^{\bullet-}$. **8** is also a good model for the electrochemistry of **9a,b**$^{\bullet-}$ since the $E°$ values for **9a,b** are just positive of the $E°$ for **8**. Again it is suggested that the addition of the third electrophore has only a small stabilizing effect on the π^* orbitals.

10a,b$^{\bullet-}$ are also quinone–diimides, but here the electrophores are spaced apart by diarylnaphthyl groups. The long-wavelength absorptions of **10a,b**$^{\bullet-}$ (Table II, Figure 4) are rather similar in width, intensity, and wavelength to the spectra of **8**$^{\bullet-}$ and **9a,b**$^{\bullet-}$. A shoulder in the spectrum of **10a**$^{\bullet-}$ with an inflection point at about 1000 nm may correspond to a peak with the vibrational splitting of about 1340 cm^{-1}. We conclude that **10a,b**$^{\bullet-}$ fall in the class of **1**$^{\bullet-}$, **5**$^{\bullet-}$, **8**$^{\bullet-}$, **9**$^{\bullet-}$, and **11**$^{\bullet-}$. Anion radical **19**$^{\bullet-}$ which three electrophores, is also in this class.[18]



19

The nine ringed triquinone **12**$^{\bullet-}$ also gives a spectrum with one intense (ϵ = 25 000), well defined peak at 1730 nm. The wavelength, intensity, and peak width are very similar to that for the other triquinone$^{\bullet-}$, **11**$^{\bullet-}$, and for unsymmetrical diquinone **18**$^{\bullet-}$. Studied in methylene chloride, **12**$^{\bullet-}$ absorption was at the same wavelength as in DMF. This independence from solvent effects was also found for **1**$^{\bullet-}$ and **11**$^{\bullet-}$. It is concluded that **12**$^{\bullet-}$ has a long wavelength π^*-π^* transition. These spectral characteristics are not similar to those of **2**$^{\bullet-}$, which has a very similar structure to one side of **12**$^{\bullet-}$.

As indicated above, we suggest that this may arise because **2**$^{\bullet-}$ is localized while **12**$^{\bullet-}$ is not. One difference between **2** and **12** is that **12** has a naphthoquinone electrophore on the end, while **2** has benzoquinone. Benzoquinone has a higher electron affinity and may, therefore, localize the odd electron better than naphthoquinone. A second difference is that **2** has a naphthalene bridge while **12** has a diarylnaphthalene. It is expected that diarylnaphthalene will have a higher electron affinity[19] and may, therefore, delocalize the charge better than naphthalene. Both these effects will tend to explain the observations. One must be concerned here with geometry differences induced by the aryl groups as well, but these effects are not clear to us.

In this light consider the $E°$ values for the trielectrophores **10a** (−0.68 V) and **12** (−0.66 V), which are quite similar to monoquinone models like naphthoquinone (−0.61 V). This certainly would allow the possibility that the extra electron is localized on one or two of the three electrophores in **10** and **12**. If this electron was localized on one end, it might be expected that the second electron would be added at almost the same potential as is found for **3**$^{\bullet-}$, where ΔE_p = 120 mV. The ΔE_p for **10a** (−0.51 V) and **12** (−0.32 V) are larger than the value for **3** and provide no convincing evidence in favor of a localized structure.

Summary

NIR absorptions from organic compounds are rather unusual.[2a] Here, however, we have found examples of anion radicals with bands at positions throughout the region 700–1700 nm. For the anions **5**$^{\bullet-}$, **8**$^{\bullet-}$, **9**$^{\bullet-}$, **10**$^{\bullet-}$, **11**$^{\bullet-}$, and **12**$^{\bullet-}$ these bands are assigned as π^*-π^*. For the stretched diimide anion radicals **6**$^{\bullet-}$ and **7**$^{\bullet-}$ the long-wavelength band may be either π^*-π^* or π-π^*. In these latter cases the electrochemical $E°$ and spectral data did not give convincing evidence for localization as previously postulated for certain diquinone anion radicals, like **3**$^{\bullet-}$. The difference between **3**$^{\bullet-}$ and diimide **7**$^{\bullet-}$ is postulated to arise because quinone π^* orbitals are lower in energy than imide π^* orbitals. This tends to give more localization for quinones than for imides.

The spectral results on dielectrophore$^{\bullet-}$ can be referenced to data reported by Shida.[1b,d] For example, the nitro group is an excellent electrophore, and it was found that 1,4-dinitrobenzene$^{\bullet-}$ (926 nm), 4,4′-dinitrobiphenyl$^{\bullet-}$ (1163 nm), and trans 4,4′-dinitrostilbene$^{\bullet-}$ (1220 nm) have sharp NIR bands, while nitrobenzene$^{\bullet-}$ absorbs in the visible region. A hydrocarbon, 1,1-diphenylethylene$^{\bullet-}$, also shows sharp NIR absorption. In this case, the two phenyls could be considered the electrophores.

The trielectrophore anion radicals studied here give electrochemical and spectral results (bands between 1 and 2 μm) that are similar to those from two-electrophore analogues.

Experimental Section

General Methods. Infrared spectra were recorded on a Perkin-Elmer 1600 Fourier transform instrument. ^{1}H NMR and ^{13}C NMR were measured using an IBM-NR-300-AF (300 MHz) or IBM-IR-200-AF (200 MHz) FT-NMR spectrometers. Chemical shifts are reported in δ units with respect to the $CDCl_3$ protonic impurity peak at 7.257 ppm. Fast atom bombardment (FAB) mass spectra were recorded on a high-resolution VG-7070E-HF instrument. Electron-impact mass spectra were recorded using a AEI MS-30 mass spectrometer. Elemental analyses were performed by M-H-W laboratories of Phoenix, AZ. Cyclic voltammograms were recorded on a BAS 100 electrochemical analyzer. Bulk electrolyses were performed with a Princeton Applied Research (Model 173) potentiostat. Absorption spectra were recorded on a Shimadzu UV-160 or Cary-17 spectrophotometers.

Materials. Chemicals purchased (Aldrich Chemical Co.) included 4-*tert*-butylaniline, 1,2,4,5-tetrakis(bromomethyl)benzene, 2,5-di-*tert*-butylaniline, and anhydrous DMF. Tetrabutylammonium tetrafluoroborate (electrometric grade) was purchased from Southwestern Analytical Chemicals Inc., recrystallized from water/methanol, 3:1, and dried in vacuo. Lithium perchlorate was recrystallized from water/methanol, 1:1, and dried in vacuo. The anhydrous DMF was used fresh or after temporary storage over 4-Å sieves while under nitrogen. The syntheses of **10a,b** and **12** were described previously.[7,8]

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

[19] Santhanam, K. S. V.; Bard, A. J. *J. Am. Chem. Soc.* **1966**, *88*, 2669. House, H. O.; Koepsell, D. G.; Campbell, W. J. *J. Org. Chem.* **1972**, *37*, 1003.

Electrochemistry. Voltammetry,[5] bulk electrolysis,[5] and spectroelectrochemical[17] cells and methods have been described.

***N*-(4-*tert*-Butylphenyl)maleimide and *N*-(2,5-di-*tert*-butylphenyl)maleimide** were prepared from the appropriate aniline derivative and maleic anhydride by following the literature procedure for the analogous *N*-phenylmaleimide.[20] The properties of *N*-(4-*tert*-butylphenyl)maleimide have already been reported.[21] The *N*-(2,5-di-*tert*-butylphenyl)maleimide was purified by chromatography over silica gel ($CHCl_3$ eluent) to give a white solid (74% yield), mp 198.5–199.5 °C. ^{1}H NMR ($CDCl_3$): δ 7.50 (d, J = 8.4 Hz, 1 H), 7.41 (dd, J_1 = 8.4 Hz, J_2 = 2.3 Hz, 1 H), 6.88 (s, 2 H), 6.83 (d, J = 2.2 Hz, 1 H), 1.28 (broad s, 18 H). ^{13}C NMR ($CDCl_3$): δ 171.01, 150.33, 146.27, 135.02, 128.71, 128.39, 128.14, 127.06, 35.08, 34.26, 31.64, 31.19. MS (EI, 70 eV) m/e (relative abundance) 270 (100), 285 (19). Molecular ion calcd for $C_{18}H_{23}NO_2$, $M^{\bullet +}$ 285.1726, found 285.1724.

***N*-(2,5-Di-*tert*-butylphenyl)phthalimide (4b).** Phthalic anhydride (0.65 g, 4.38 mmol) and 2,5-di-*tert*-butylaniline (0.90 g, 4.38 mmol) were placed in 50-mL round-bottom flask containing dry DMAc (6 mL). The flask was equipped with a magnetic stirbar, reflux condenser, and N_2 inlet. The reactants were stirred for 5 min, and then the solution was heated to a gentle reflux for 19 h. The red-brown solution was allowed to cool to room temperature, and the white precipitate that formed upon cooling was collected by filtration. The white solid was recrystallized from EtOH (50 mL) to give 0.81 g (2.41 mmol, 55% yield) of shiny-white flakes, mp 250–1 °C. ^{1}H NMR ($CDCl_3$): δ 7.95 (m, 2 H), 7.81 (m, 2 H), 7.55 (d, J = 8.5 Hz, 1 H), 7.44 (dd, J_1 = 8.5 Hz, J_2 = 2.2 Hz, 1 H), 6.94 (d, J = 2.2 Hz, 1 H), 1.30 (s, 9 H), 1.29 (s, 9 H). IR (KBr, cm^{-1}): 2958, 1775, 1762, 1716, 1405, 1375, 1356, 728. MS (EI, 30 eV) m/e (relative abundance) 320 (100), 335 (29). Molecular ion calcd for $C_{22}H_{25}NO_2$, $M^{\bullet +}$ 335.1884, found 335.1885. Anal. Calcd: C, 78.77; H, 7.51; N, 4.18. Found: C, 78.80; H, 7.62; N, 4.22.

***N*,*N*′-Bis(4-*tert*-butylphenyl)-1,2,4,5-benzenetetracarboxylic 1,2:4,5-Diimide (5a).** 1,2,4,5-Benzenetetracarboxylic 1,2:4,5-diianhydride (0.50 g, 2.3 mmol) and *p*-*tert*-butylaniline (0.94 g, 6.3 mmol) were placed in a 200-mL round-bottom flask containing dry DMAc (88 mL). The flask was equipped with a magnetic stirring bar, reflux condenser, and N_2 inlet. The solution was heated to reflux for 12 h. During this time, the reaction mixture turned a red color. After achieving room temperature, the yellow precipitate was collected by filtration and washed well with MeOH. The shiny-yellow platelets were dried in vacuo, giving 0.72 g (65% yield) of quite pure **5a**. Further purification was performed by recrystallization from DMF, mp >300 °C. ^{1}H NMR ($CDCl_3$): δ 8.49 (s, 2 H), 7.56 (d, J = 8.7 Hz, 4 H), 7.38 (d, J = 8.7 Hz, 4 H), 1.36 (s, 18 H). IR (KBr, cm^{-1}): 2955, 1774, 1713, 1515, 1370, 1089, 822. MS (EI, 70 eV) m/e (relative abundance) 106 (100), 184 (94), 465 (27), 480 (8). Molecular ion calcd for $C_{30}H_{28}N_2O_4$ ($M^{\bullet +}$) 480.2046, found 480.2052. Anal. Calcd: C, 74.98; H, 5.87; N, 5.83. Found: C, 74.81; H, 5.86; N, 5.82. UV-Vis (CH_2Cl_2) λ_{nm}, (log ϵ): 266 (4.43), 230 (4.67).

***N*,*N*′-Bis(2,5-di-*tert*-butylphenyl)-1,2,4,5-benzenetetracarboxylic 1,2:4,5-Diimide (5b).** **5b** was prepared in a similar procedure to that used for **5a**, employing 2,5-di-*tert*-butylaniline. The isomeric composition of the major product was not investigated. A fine white solid was obtained in 76% yield, mp >300 °C. ^{1}H NMR ($CDCl_3$): δ 8.52 (s, 2 H), 7.58 (d, J = 8.5 Hz, 2 H), 7.48 (dd, J_1 = 8.5 Hz, J_2 = 2.2 Hz, 2 H), 6.94 (d, J = 2.2 Hz, 2 H), 1.30 (broad s, 36 H). ^{13}C NMR ($CDCl_3$): δ 166.64, 150.54, 145.79, 137.79, 128.71, 128.53, 127.79, 127.48, 119.42, 35.29, 34.34, 31.71, 31.18. IR (KBr, cm^{-1}): 2955, 1782, 1725, 1406, 1376, 1355, 1111, 836. HRMS (FAB, H_2SO_4 matrix) calcd for $C_{38}H_{45}N_2O_4$ (M + H$^+$) 593.3379, found 593.3428. Anal. Calcd: C, 77.00; H, 7.48; N, 4.73. Found: C, 76.75; H, 7.53; N, 4.73. UV–vis (CH_2Cl_2) λ_{nm} (log ϵ): 320 (3.49), 237 (4.80).

***N*,*N*′-Bis(4-*tert*-butylphenyl)-9,10-dimethoxy-1,2,3,4,5,6,7,8-octahydro-2,3,6,7-anthracenetetracarboxylic 2,3:6,7-Diimide (13a).** 1,4-Dimethoxy-2,3,5,6-tetrakis(bromomethyl)benzene[9b] (500 mg, 0.98 mmol), *N*-(4-*tert*-butylphenyl)maleimide (674 mg, 2.94 mmol), and dry NaI (11.20 g, 9.81 mmol) were placed in a 25-mL pear-shape flask containing 5 mL of dry DMF. The flask was equipped with a magnetic stirring bar, reflux condenser, N_2 inlet, and a thermometer. The reactants were heated to 85–90 °C for 36 h. The reaction mixture had turned a dark red/black color during the course of the reaction. The product mixture was cooled to room temperature, and an aqueous sodium bisulfite solution was added. A brown solid was collected by filtration and washed well with H_2O. The crude product was recrystallized from EtOH/C_6H_6 (1:1) and washed with cold EtOH. The desired product was obtained as a white powder (420 mg, 0.65 mmol, 66% yield). The collected product appeared to be that of a single isomer, mp >300 °C. ^{1}H NMR ($CDCl_3$): δ 7.36 (d, J = 8.5 Hz, 4 H), 6.89 (d, J = 8.5 Hz, 4 H), 3.66–3.61 (m, 10 H), 3.46 (broad s, 4 H), 1.96 (broad d, J = 7.1 Hz, 4 H), 1.27 (s, 18 H). HRMS (FAB, MNBA matrix) calcd for $C_{40}H_{44}N_2O_6$ ($M^{\bullet +}$) 648.3199, found 648.3217.

***N*,*N*′-Bis(2,5-di-*tert*-butylphenyl)-9,10-dimethoxy-1,2,3,4,5,6,7,8-octahydro-2,3,6,7-anthracenetetracarboxylic 2,3:6,7-Diimide (13b).** The syntheses of octahydroanthracenes **13b** and **15a,b** closely paralleled the procedure described for **13a** using the appropriate tetrakis(bromomethyl)benzene derivative and maleimide precursor. The desired product was a white solid, 29% yield, mp >300 °C. ^{1}H NMR ($CDCl_3$): δ 7.37 (d, J = 8.5 Hz, 2 H), 7.24 (dd, J_1 = 8.2 Hz, J_2 = 2.2 Hz, 2 H), 5.37 (d, J = 2.1 Hz, 2 H), 3.82 (d, J = 14.6 Hz, 4 H), 3.65 (s, 6 H), 3.51 (s (broad), 4 H), 2.51 (d (broad), J = 13.4 Hz, 4 H), 1.24 (s, 18 H), 1.06 (s, 18 H). HRMS (FAB, MNBA matrix) calcd for $C_{48}H_{60}N_2O_6$ ($M^{\bullet +}$) 760.4451, found 760.4440.

***N*,*N*′-Bis(4-*tert*-butylphenyl)-1,2,3,4,5,6,7,8-octahydro-2,3,6,7-anthracenetetracarboxylic 2,3:6,7-Diimide (15a).** The desired product was obtained as a white solid, 35% yield, mp > 300 °C. ^{1}H NMR ($CDCl_3$): δ 7.35 (d, J = 8.6 Hz, 4 H), 7.00 (s, 2 H), 6.81 (d, J = 8.6 Hz, 4 H), 3.44 (s (broad), 4 H), 3.22 (d, J = 14.4 Hz, 4 H), 2.90 (d (broad), J = 13.7 Hz, 4 H), 1.26 (s, 18 H). HRMS (FAB, MNBA matrix) calcd for $C_{38}H_{41}N_2O_4$ (M + H$^+$) 589.3066, found 589.3057.

***N*,*N*′-Bis(2,5-di-*tert*-butylphenyl)-1,2,3,4,5,6,7,8-octahydro-2,3,5,6-anthracenetetracarboxylic 2,3:5,6-Diimide (15b).** A white solid believed to be the trans-bis-endo isomer was isolated, 21% yield, R_f = 0.27 (silica gel, $CHCl_3$), mp >300 °C. ^{1}H NMR ($CHCl_3$): δ 7.36 (d, J = 8.5 Hz, 2 H), 7.22 (dd, J_1 = 8.5 Hz, J_2 = 2.2 Hz, 2 H), 7.13 (s, 2 H), 5.21 (d (Ar), J = 2.2 Hz, 2 H), 3.48 (s (broad), 4 H), 3.33 (d, J = 14.5 Hz, 4 H), 2.82 (d (broad), J = 14.3 Hz, 4 H), 1.23 (s, 18 H), 1.05 (s, 18 H). A 2D COZY NMR spectrum verified the coupling between aromatic protons. HRMS (FAB, MNBA matrix) calcd for $C_{46}H_{57}N_2O_4$ (M + H$^+$) 701.4318, found 701.4274. ^{1}H NMR ($CDCl_3$): δ 8.99 (s, 4 H), 7.58 (d, J = 8.6 Hz, 4 H), 7.44 (d, J = 8.6 Hz, 4 H), 4.27 (s, 6 H), 1.38 (s, 18 H). HRMS (FaB; MNBA: *m*-cresol matrix) calcd for $C_{40}H_{37}N_2O_6$ (M + H$^+$) 641.2652, found 641.2614.

***N*,*N*′-Bis(4-*tert*-butylphenyl)-9,10-dimethoxy-2,3,6,7-anthracenetetracarboxylic 2,3:6,7-Diimide (6a).** *N*,*N*′-Bis(4-*tert*-butylphenyl)-9,10-dimethoxy-1,2,3,4,5,6,7,8-octahydro-2,3,6,7-anthracenetetracarboxylic 2,3:6,7-diimide (200 mg, 0.308 mmol), *N*-bromosuccinimide (554 mg, 3.08 mmol), and benzoyl peroxide (7 mg, 1%) were placed in a 25-mL pear-shaped flask containing CCl_4 (50 mL). The stirred reaction mixture was purged with nitrogen and then refluxed in the dark for 13.5 h. The reaction mixture turned a yellow color during the course of the reaction. After the mixture was cooled to room temperature, 1 mL of Et_3N was added, and stirring was continued. The resulting yellow precipitate was collected by filtration and washed with H_2O followed by 75 mL of hot EtOH. The bright yellow powder (176 mg, 0.28 mmol, 89% yield) was quite pure. Milligram portions of **6a** were purified further by chromatography (silica gel prep plate; $CHCl_3$ as eluent) in the dark prior to electrochemical experiments. ^{1}H NMR ($CDCl_3$): δ 8.99 (s, 4 H), 7.58 (d, J = 8.6 Hz, 4 H), 7.44 (d, J = 8.6 Hz, 4 H), 4.27 (s, 6 H), 1.38 (s, 18 H). IR (KBr, cm^{-1}): 2964, 1767, 1720, 1517, 1365, 1351, 1130. HRMS (FAB; MNBA: *m*-cresol matrix) calcd for $C_{40}H_{37}N_2O_6$ (M + H$^+$) 641.2652, found 641.2614.

Endoperoxide 14. 6a (15 mg) was suspended in 1 mL of $CDCl_3$ in a standard ^{1}H NMR tube. The heterogeneous mixture was a highly fluorescent yellow/green color. The sample was observed by ^{1}H NMR at various times over a 4-day period with occasional shaking. The yellow solid (**6a**) suspended in solution diminished over time, and the peaks from the endoperoxide grew into the

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[20] Cava, M. P.; Deana, A. A.; Muth, K.; Mitchell, M. J. *J. Org. Synth.* **1973**, *5*, 944.

[21] Fletcher, H. R.; Little, J. R. U.S. Patent 3153014, 1964.

NMR spectrum. The appearance of the endoperoxide was correlated to the time of the sample's exposure to room lights. **6a** persists in the absence of either light or oxygen. Purification of the crude product by chromatography (silica gel prep plate; $CHCl_3$ eluent) gave **14** as a white solid that is formed quantitatively. ^1H NMR ($CDCl_3$): δ 8.14 (s, 4 H), 7.52 (d, *J* = 8.6 Hz, 4 H), 7.32 (d, *J* = 8.6 Hz, 4 H), 4.08 (s, 6 H), 1.34 (s, 18 H). ^{13}C NMR ($CDCl_3$): δ 166.58, 151.56, 144.59, 131.86, 128.64, 126.30, 125.98, 117.06, 101.75, 54.84, 34.82, 31.34. IR (KBr, cm^{-1}): 2961, 1779, 1729, 1517, 1380, 1307. HRMS calcd for $C_{40}H_{37}N_2O_8$ ($M + H^+$) 673.2549, found 673.2545. UV–vis (CH_2Cl_2) λ_{nm} (log ε): 300 sh (3.61), 247 (4.74).

Thermal Decomposition Studies of 14. Several milligrams of **14** were placed between two cover slides and heated to 250 °C with a melting point apparatus. Above 190 °C the white solid gradually turned a pale yellow/brown color, but it never melted. The ^1H NMR spectrum of the major decomposition product was studied before and after purification (chromatography) and shown to match the spectrum of **6a**.

In a separate experiment, **14** (2.8 mg) was heated in 2 mL of refluxing toluene for 70 h in the dark. After the yellow product mixture was allowed to cool to room temperature the toluene was removed under reduced pressure, and the products were dried in vacuo. ^1H NMR analysis of the crude material showed that some starting material remained. The major product recovered following purification (chromatography on silica gel) was the quinone, **9a**.

***N*,*N'*-Bis(2,5-di-*tert*-butylphenyl)-9,10-dimethoxy-2,3,6,7-anthracenetetracarboxylic 2,3:6,7-Diimide (6b).** The general NBS aromatization procedure used for the synthesis of **6a** was also used for the formation of **6b** and **7a,b** (method A). The desired bright yellow solid was obtained following chromatography (silica gel, $CHCl_3$; R_f = 0.63) in 81% yield. The isomeric composition was not investigated. ^1H NMR ($CDCl_3$): δ 9.01 (s, 4 H), 7.60 (d, *J* = 8.6 Hz, 2 H), 7.49 (dd, J_1 = 8.5 Hz, J_2 = 2.1 Hz, 2 H), 7.01 (d, *J* = 2.1 Hz, 2 H), 4.28 (s, 6 H), 1.35 (s, 18 H), 1.33 (s, 18 H). ^{13}C NMR ($CDCl_3$): δ 167.86, 154.49, 150.40, 145.67, 129.36, 128.59, 128.29, 127.79, 127.26, 121.57, 65.30, 35.31, 34.32, 31.72, 31.19. IR (KBr, cm^{-1}): 2963, 1773, 1720, 1406, 1351, 1194, 1129. HRMS (FAB, MNBA matrix) calcd for $C_{48}H_{53}N_2O_6$ ($M^{\bullet+}$) 752.3825, found 752.3851. UV–vis (CH_2Cl_2) λ_{nm} (log ε): 448 (4.24), 421 (4.10), 402 sh (3.77), 311 (5.07), 232 (4.53).

***N*,*N'*-Bis(2,5-di-*tert*-butylphenyl)-2,3,6,7-anthracenetetracarboxylic 2,3:6,7-Diimide (7b). Method A.** The crude product was purified by flash chromatography (silica gel, grade 60, 230–400 mesh; $CHCl_3$). The desired product was accompanied by another product with a slightly higher R_f which is believed to be a monobromonated (1-position) anthracene derivative. Thus, several separations were often required to achieve a high purity of **7b**. The isomeric composition of **7b** was not investigated. ^1H NMR ($CDCl_3$): δ 8.96 (s, 2 H), 8.74 (s, 4 H), 7.59 (d, *J* = 8.5 Hz, 2 H), 7.48 (dd, J_1 = 8.5 Hz, J_2 = 2.2 Hz, 2 H), 7.01 (d, *J* = 2.2 Hz, 2 H), 1.34 (s, 18 H), 1.32 (s, 18 H). ^{13}C NMR ($CDCl_3$): δ 167.73, 150.36, 145.64, 134.12, 133.20, 129.32, 128.84, 128.59, 127.77, 127.23, 126.37, 35.31, 34.31, 31.70, 31.18. IR (KBr, cm^{-1}): 2962, 1773, 1718, 1585, 1404, 1355, 1121. HRMS (FAB; MNBA matrix) calcd for $C_{46}H_{48}N_2O_4$ ($M^{\bullet+}$) 692.3614, found 692.3652.

***N*,*N'*-Bis(2,5-di-*tert*-butylphenyl)-1-bromo-2,3,6,7-anthracenetetracarboxylic 2,3:6,7-Diimide.** ^1H NMR ($CDCl_3$): δ 9.46 (s, 1 H), 8.95 (s, 1 H), 8.84 (s, 1 H), 8.76 (s, 1 H), 8.70 (s, 1 H), 7.60 (d, *J* = 8.6 Hz, 2 H), 7.48 (dd, J_1 = 8.4 Hz, J_2 = 2.1 Hz, 2 H), 7.00 (m, 2 H), 1.34 (s, 18 H), 1.32 (s, 18 H). High-resolution MS (FAB; MNBA matrix) calcd for $C_{46}H_{47}N_2O_4Br$ ($M^{\bullet+}$) 770.2719, found 770.2696.

7b, Method B. The benzodifuran precursor **16**[11] (100 mg, 0.10 mmol) and *N*-(2,5-di-*tert*-butylphenyl)maleimide (120 mg, 0.42 mmol) were ground together and placed in a constricted glass tube which was then flame sealed under vacuum. The reactants were heated to 200 °C for 20 min. Gas evolution was apparent. The product mixture was allowed to cool to room temperature and then suspended in hexane (30 mL). The white solid was collected by filtration and transferred to a 25-mL flask; 3 mL of $CHCl_3$ were added to the sample flask followed by 3 mL of concentrated H_2SO_4. The sample was stirred vigorously in the dark for 5 h. The yellow/brown product mixture was poured over crushed ice, stirred well, and extracted with 40 mL of $CHCl_3$. The organic layer was washed 2 × 50 mL with saturated $NaHCO_3$ followed by 2 × 100 mL with H_2O, dried over Na_2SO_4, and filtered, and the solvent was removed under reduced pressure. Purification by chromatography (silica gel, CH_2Cl_2; R_f = 0.50) gave 48 mg (69%) of the yellow product **7b**.

***N*,*N'*-Bis(4-*tert*-butylphenyl)-2,3,6,7-anthracenetetracarboxylic 2,3:6,7-Diimide (7a). Method A.** The crude product was placed in hot $CHCl_3$ (10 mL), and the remaining solid was collected by filtration. A 67% yield of the pale yellow product was collected. Further purification was performed by recrystallization from $CHCl_3$ and chromatography, but the limited solubility of **7a** made these techniques difficult. The solubility of **7b** was greater than that of **7a**. A ^{13}C spectrum of **7b** could be readily recorded in $CDCl_3$ but TFA-*d* must be added as a solubility enhancer to obtain a ^1H spectrum of **7a** in $CDCl_3$. ^1H NMR ($CDCl_3$ (0.5 mL) containing TFA-*d* (1 drop)): δ 9.06 (s, 2 H), 8.83 (s, 4 H), 7.61 (d, *J* = 8.6 Hz, 4 H), 7.34 (d, *J* = 8.5 Hz, 4 H), 1.38 (s, 18 H). IR (KBr, cm^{-1}): 2964, 1768, 1708, 1586, 1517, 1372, 1129, 1112. HRMS (FAB; MNBA: *m*-cresol matrix) calcd for $C_{38}H_{33}N_2O_4$ ($M + H^+$) 581.2440, found 581.2417. UV–vis (CH_2Cl_2) λ_{nm} (log ε): 423 (4.00), 399 (3.81), 305 (4.87), 233 (4.30).

7a, Method B. The synthesis of **7a** via method B was similar to that of **7b** via method B. More $CHCl_3$ (10×) was required in the workup due to the lower solubility. The crude product was purified by heating in refluxing EtOH and then collecting the solid in a hot filtration. An 83% yield of the yellow solid **7a** was obtained.

***N*-(4-*tert*-Butylphenyl)-5,8-dimethoxy-1,2,3,4-tetrahydro-2,3-naphthalenedicarboximide.** 1,4-Dimethoxy-2,3-bis(bromomethyl)benzene[9a] (610 mg, 1.9 mmol), *N*-(4-*tert*-butylphenyl)maleimide (648 mg, 2.8 mmol), and dry NaI (1.42 g, 9.4 mmol) were reacted (DMF), and the product was worked up in a similar manner as described for **13a**. The crude product was purified by chromatography (silica gel; $CHCl_3$ as the eluent), giving the desired product as a white solid (R_f = 0.21, 455 mg, 62% yield), mp 173–5 °C. ^1H NMR ($CDCl_3$): δ 7.38 (d, *J* = 8.4 Hz, 2 H), 6.89 (d, *J* = 8.4 Hz, 2 H), 6.72 (s, 2 H), 3.76 (s, 6 H), 3.53 (d, *J* = 15.2 Hz, 2 H), 3.38 (broad s, 2 H), 2.78 (broad d, *J* = 14.6 Hz, 2 H), 1.27 (s, 9 H). MS (EI, 70 eV) *m*/*e* (relative abundance) 393 (100), 378 (75), 175, (52), 189 (48). Molecular ion calcd for $C_{24}H_{26}NO_4$, $M^{\bullet+}$ 393.1892, found 393.1908.

***N*,*N'*-Bis(4-*tert*-butylphenyl)-5,8-dimethoxy-2,3-naphthalenedicarboximide.** *N*-(4-*tert*-Butylphenyl)-5,8-dimethoxy-1,2,3,4-tetrahydro-2,3-naphthalenedicarboximide (150 mg, 0.38 mmol), NBS (309 mg, 1.72 mmol), and benzoyl peroxide (6 mg) were reacted in a similar manner as described for the synthesis of **6a**. The crude product was purified by chromatography (silica gel prep plate, $CHCl_3$; R_f = 0.67) and then recrystallized from EtOH (100 mL), giving 83 mg (2.13×10^{-4} mol, 56% yield) of yellow needles. ^1H NMR ($CDCl_3$): δ 8.84 (s, 2 H), 7.55 (d, *J* = 8.7 Hz, 2 H), 7.42 (d, *J* = 8.7 Hz, 2 H), 6.89 (s, 2 H), 3.98 (s, 6 H), 1.36 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ 167.43, 151.10, 150.92, 129.38, 128.34, 127.13, 126.17, 126.14, 119.78, 107.36, 56.06, 34.80, 31.39.

***N*-(4-*tert*-Butylphenyl)-1,4-dioxo-6,7-naphthalenedicarboximide (8).** *N*-(4-*tert*-Butylphenyl)-5,8-dimethoxy-2,3-naphthalenedicarboximide (80 mg, 0.21 mmol) was placed in a 200-mL round-bottom flask containing CH_3CN (30 mL). Ceric ammonium nitrate (CAN) (281 mg, 0.51 mmol) dissolved in 4 mL of a 1:1 H_2O–CH_3CN mixture was added dropwise over several minutes, and stirring was continued for 45 min. The product mixture was taken up in 100 mL of $CHCl_3$ and washed with H_2O. The organic layer was dried over Na_2SO_4 and decanted, and the solvent was removed under reduced pressure. The crude product was purified by chromatography (silica gel prep plate; $CHCl_3$ as the eluent), and the band with a R_f = 0.48 was collected. The desired product was a cream-colored solid (36 mg, 49% yield) that turns a yellow/brown color upon standing. ^1H NMR ($CDCl_3$): δ 8.67 (s, 2 H), 7.55 (d, *J* = 8.6 Hz, 2 H), 7.39 (d, *J* = 8.7 Hz, 2 H), 7.16 (s, 2 H), 11.35 (s, 9 H). ^{13}C NMR ($CDCl_3$): δ 183.13, 165.53, 151.85, 138.98, 136.57, 135.48, 128.36, 126.34, 125.86, 122.30, 34.82, 31.30. IR (KBr, cm^{-1}): 2956, 1782, 1716, 1670, 1623, 1516, 1383, 1320, 1098. MS (EI, 70 eV), *m*/*e* (relative abundance) 344 (100), 359 (20). Molecular ion calcd for $C_{22}H_{17}NO_4$, $M^{\bullet+}$ 359.1155, found 359.1159. UV–vis (CH_2Cl_2) λ_{nm} (log ε): 334 (3.58), 266 (4.46), 231 (4.57).

***N*-(2,5-Di-*tert*-butylphenyl)-1,2,3,4-tetrahydro-2,3-naphthalenedicarboximide (17).** α,α'-Dibromo-*o*-xylene (0.62

g, 2.34 mmol), *N*-(2,5-di-*tert*-butylphenyl)maleimide (1.0 g, 3.5 mmol), and dry NaI (2.1 g, 14 mmol) were reacted in DMF, and the product was worked up in a similar manner as described for **13a**.[9] The crude product was first chromatographed (silica gel, $CHCl_3$) to give 0.82 g of a white solid; 0.67 g of the white solid was recrystallized for EtOH (40 mL), giving 0.41 g (1.05 mmol, 61% yield) as rods. The isolated product is believed to be the endo adduct. ^1H NMR ($CDCl_3$): δ 7.35 (d, J = 8.5 Hz, 1 H), 7.24–7.19 (m, 6 H), 5.31 (d, J = 2.2 Hz, 1 H), 3.47 (m, 2 H), 3.33 (d, J = 14.2 Hz, 2 H), 2.94 (dm, J = 14.2 Hz, 2 H), 1.23 (s, 18 H), 1.05 (s, 18 H). ^1H NMR (C_6D_6): δ 7.27 (d, J = 8.5 Hz, 1 H), 7.14–6.96 (m, 6 H), 5.66 (d, J = 2.2 Hz, 1 H), 3.11 (d, J = 14.1 Hz, 2 H), 2.70 (m, 2 H), 2.29 (dm, J = 13.9 Hz, 2 H), 1.30 (s, 18 H), 1.03 (s, 18 H). ^{13}C NMR ($CDCl_3$): δ 179.82, 150.12, 144.46, 135.44, 130.20, 128.04, 127.85, 127.57, 127.36, 126.51, 40.57, 35.07, 33.97, 31.56, 30.97, 30.17. MS (EI, 70 eV), *m/e* (relative abundance) 374 (100), 389 (52), 318 (35), 128 (24). Molecular ion calcd for $C_{26}H_{31}NO_2$, $M^{\bullet+}$ 389.2354, found 389.2364.

***N*,*N*′-Bis(4-*tert*-butylphenyl)-9,10-dioxo-2,3,6,7-anthracenetetracarboxylic 2,3:6,7-Diimide (9a).** The CAN oxidation of **6a** to **9a** follows the related procedure for the synthesis of **8**. The reaction was performed in the dark, and solubility limitations required the use of a $CHCl_3$–CH_3CN solvent mixture. During the course of the reaction, the bright yellow color of the reaction mixture turned to a pale yellow color. After 3 days, the solvent was removed under reduced pressure. The product mixture was suspended in H_2O and sonicated for several minutes, and a yellow solid was collected by filtration. The crude product was recrystallized from $CHCl_3$ to give the desired product in 43% yield. ^1H NMR ($CDCl_3$ (0.5 mL) and TFA-*d* (2 drops)): δ 8.99 (s, 4 H), 7.58 (d, J = 8.7 Hz, 4 H), 7.35 (d, J = 8.5 Hz, 4 H), 1.37 (s, 18 H). IR (KBr, cm^{-1}): 2963, 1783, 1724, 1679, 1618, 1518, 1388, 1315, 1209, 1127, 713. HRMS (FAB; H_2SO_4 matrix) calcd for $C_{34}H_{31}N_2O_6$ ($M + H^+$) 611.2182, found 611.2122. UV–vis (CH_2Cl_2) λ_{nm} (log ϵ): 340 (3.79), 276 (4.59), 240 (4.80).

***N*,*N*′-Bis(2,5-di-*tert*-butylphenyl)-9,10-dioxo-2,3,6,7-anthracenetetracarboxylic 2,3:6,7-Diimide (9b).** The CAN oxidation of **6b** to **9b** also follows the related procedure for the synthesis of **8**. The crude product was purified by heating in CCl_4 and allowed to cool, and the pale yellow solid was collected by filtration, 31% yield. R_f = 0.59 (CH_2Cl_2). ^1H NMR ($CDCl_3$): δ 8.98 (s, 4 H), 7.58 (d, J = 8.6 Hz, 2 H), 7.49 (dd, J_1 = 8.6 Hz, J_2 = 2.1 Hz, 2 H), 6.96 (d, J = 2.1 Hz, 2 H), 1.31 (s, 18 H), 1.30 (s, 18 H). IR (KBr, cm^{-1}): 2963, 1786, 1719, 1685, 1675, 1309, 719. HRMS (FAB, MNBA matrix) calcd for $C_{46}h_{46}N_2O_6$ ($M^{\bullet+}$) 722.3356, found 722.3288.

1,4,8,11-Tetramethoxy-2,3,9,10-tetramethyl-6,13-pentacenedione. 3,6-Dimethoxy-4,5-dimethylcyclobuten-1-ol (34 mg, 0.16 mmol)[4,5] was placed in a 25-mL round-bottom flask containing benzoquinone (8.6 mg, 0.08 mmol) and toluene (15 mL). The flask was equipped with a magnetic stirring bar, reflux condenser, and N_2 inlet. The solution was purged with N_2 and heated to reflux for 4 days. The solution was cooled overnight in a refrigerator and the bright yellow precipitate that formed was collected by filtration, washed several times with toluene, and dried in vacuo. The pentacene quinone (19 mg, 0.04 mmol, 25% yield) can be purified in small quantities by chromatography over silica gel with $CHCl_3$ eluent. ^1H NMR ($CDCl_3$): δ 9.14 (s, 4 H), 3.94 (s, 12 H), 2.44 (s, 12 H). IR (KBr, cm^{-1}): 1674, 1606, 1453, 1424, 1322, 1272. HRMS (EI, 70 eV) calcd for $C_{30}H_{28}O_6$ 484.1878, found 484.1880.

2,3,9,10-Tetramethyl-1,4,6,8,11,13-pentacenehexone (11). **11** was prepared by the CAN oxidation of 1,4,8,11-tetramethoxy-2,3,9,10-tetramethyl-6,13-pentacenedione in a similar procedure as in the formation of **8**. The reaction mixture was stirred for 30 min, and the solution was then added to water and filtered over a small frit. A pale yellow solid was collected and washed with water. The product was dried in vacuo. **11** was obtained in 89% yield and found to be only sparingly soluble in organic solvents. ^1H NMR ($CDCl_3$): δ 9.07 (s, 4 H), 2.27 (s, 12 H). HRMS (EI, 70 eV) calcd for $C_{26}H_{16}O_6$, $M^{\bullet+}$ 424.0958, found 424.0963.

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A [4 + 1] Annulation Approach to Nitrogen Heterocycles Using 2,3-Bis(phenylsulfonyl)-1,3-butadiene and Primary Amines

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The reaction of amines with 2,3-bis(phenylsulfonyl)-1,3-butadiene affords pyrrolidines in high yield. The formation of the nitrogen heterocycle involves initial conjugate addition and this is followed by a 5-*endo-trig* cyclization of the resulting amine onto the adjacent vinyl sulfone. Treatment of these pyrrolidines with sodium methoxide induces elimination of benzenesulfinic acid, producing the 3-pyrroline ring system. Heating a sample of the resulting 3-pyrroline in the presence of DDQ smoothly affords 3-(phenylsulfonyl)-substituted pyrroles. Treatment of these pyrroles with *tert*-butyllithium readily generates 2-lithiated pyrroles, which can be quenched with electrophiles such as methyl iodide, benzaldehyde, benzoyl chloride, dimethylformamide, and methyl acrylate. In all cases high yields of *N*-alkyl-2,3-disubstituted-pyrroles were obtained. The ability of these 3-(phenylsulfonyl)-substituted pyrroles to undergo lithiation and subsequent alkylation in high yield was further illustrated by the synthesis of the pyrrolizidine–pyrrole system. Finally, the reaction of 2,3-bis(phenylsulfonyl) diene with *N*,*N*′-dimethylethylenediamine was investigated. The reaction proceeds by two competitive pathways leading to both six- and eight-membered rings under kinetic conditions. Upon stirring for longer periods of time, the eight-membered ring undergoes a ring contraction to give the thermodynamically more stable piperazine system.

The occurrence of five-membered nitrogen heterocycles in many natural products continues to contribute to the development of new synthetic methodologies.[1-3] The preparation of pyrrolidines has received extensive attention from synthetic chemists in recent years, in part due to the

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