

Synthesis and Electrochemical Properties of Intramolecular Multi-electron Transfer Probe Compounds

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ABSTRACT

The absorption spectra of diquinone pentacene-5,7,12,14-tetrone (PDQ), have been studied and it was found that the long wavelength absorption of the neutral quinone and of the semiquinone anion radicals were different. For example, $\lambda_{\max}(\text{PDQ}) = 375 \text{ nm}$, $\lambda_{\max}(\text{PDQ}^-) = 1350 \text{ nm}$, $\lambda_{\max}(\text{PDQ}^{2-}) = 850 \text{ nm}$. PDQ can be used as an electron acceptor which can accept up to four electrons. Investigations of absorption spectra readily determines how many electrons have been transferred. We have now synthesized a series of compounds containing PDQ as acceptor and carbazole as donor, linked by a chain of variable length.

The intramolecular multi-electron transfer 'probe' compounds prepared can be reduced chemically or electrochemically to give the corresponding anion radicals. The reduction potentials for these compounds were estimated by cyclic voltammetry at a mid point between the anodic and cathodic peak potentials. The reduction of the quinones to the semiquinone anion radicals was carried out using 0.1 M tetrabutylammonium tetrafluoroborate in CH_3CN under a N_2 atmosphere.

1 INTRODUCTION

Polyacenediquinones are of interest since they provide rigid rods with long delocalization lengths. Our initial investigations showed that these compounds exhibited unusual physical properties and we have reported the near-infrared absorption spectra of anion radicals and dianions, and also triplet state absorption and its decay kinetics.^{1,2} The synthesis of compounds of this type was developed by Miller *et al.*^{3–6} IR, ESR, and electrochemical

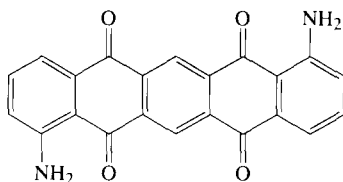
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data which characterize the anion radicals and dianions have also been reported.^{2,5,6} We initially prepared such compounds as part of a study directed toward molecular electronics, e.g. as 'molecular conducting wire'. However, the conductivity and solubility in organic solvents of the compounds were not ideal, but in view of their unusual absorption properties, further investigations seemed of interest. The λ_{max} of the anions and dianions are quite different from those of the neutral diquinones, which absorb in the UV region, and this factor offers the possibility to test quantitatively the one to four electron reduction processes in the diquinones.

Most investigations on photosynthetic systems have focused on one-photon-induced one-electron transfer processes.⁷ However, in order to mimic natural photosynthesis, multi-photon-induced multi-electron transfer needs to be evaluated. In order to conveniently study multi-electron transfer processes, it is necessary to find a multi-electron transfer 'probe' compound, which could then be used to test the degree of electron transfer which takes place. In this present study, we utilized the absorption properties of diquinones as a test method, and diquinones as probe compounds for multi-electron transfer. The diquinones were linked with two electron donors *via* a non-conjugated bridge to form D—A—D systems. In D—A—D systems such as these, multi-electron transfer can occur from the donor to the acceptor (i.e. diquinones), and absorption spectra can then be used to determine how many electrons are involved in the transfer.

2 EXPERIMENTAL

2.1 Synthesis of 1,8-diamino-5,7,12,14-pentacenetetrone



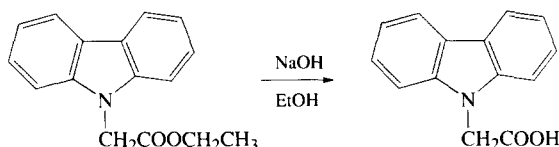
5,7,12,14-Pentacenetetrone (5 g, 0.015 mol) was dissolved in 98% H_2SO_4 (100 ml) at 65°C and to the stirred solution 10% fuming nitric acid (20 ml) was slowly added. After stirring for 10 min and then standing overnight, the liquor was filtered and the residue (6 g) recrystallized from nitrobenzene to give 3.2 g (51%) of the 1,8-dinitro compound, m.p. > 300°C.

This compound (1 g) was stirred into water (200 ml) and reduced at room temperature by addition of NaHS solution (obtained by passing H_2S into 50% aq. NaOH). After reacting for 6 h, and then leaving for 20 h at room temperature, air was blown in overnight and the product filtered, washed

neutral and dried. The crude product was finely ground, boiled with dilute HCl for 20 min, filtered, washed with alcohol, ether and CS₂, and finally recrystallized from nitrobenzene as purple needles (0.6 g), yield 69%.

MS (EI) M_z^+ : 368 (M^+), 353 (-15). IR: 3300, 1675, 1250 cm⁻¹.

2.2. Synthesis of carbazole-*N*-acetic acid

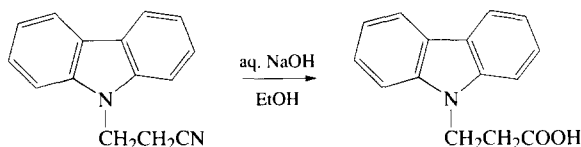


A mixture of carbazole (16.7 g, 0.1 mol) and powdered KOH (5.6 g, 0.1 mol) in toluene (70 ml) was heated to reflux and water azeotropically distilled over 3 h. The mixture was then cooled to room temperature, filtered and the product recrystallized from tetrahydrofuran to give 19 g (93%) of the potassium salt of carbazole. This (12.9 g, 0.06 mole) was stirred into *N*-methyl-2-pyrrolidone (30 ml) and after cooling to 0–5°C ethyl chloroacetate (6.7 g, 0.06 mol) was added dropwise. The mixture was stirred overnight, and then poured into water. The product was filtered and recrystallized from ethanol to give carbazole-*N*-ethyl acetate (6.4 g, 42%) m.p. 94–95°C.

A mixture of carbazole-*N*-ethyl acetate (5.6 g), 50% NaOH (25 ml), H₂O (25 ml) and ethanol (25 ml) was refluxed for 6 h, the reaction liquor filtered hot and the filtrate acidified with HCl. The product was filtered, washed neutral and recrystallized from ethanol to give white needles (3.5 g, 70%) m.p. 190–192°C.

C₁₄H₁₁NO₂ requires: C, 74.67; H, 4.89; N, 6.22. Found: C, 74.46; H, 4.90; N, 6.11. IR: 1710, 1326, 3000, 750, 725 cm⁻¹.

2.3 Synthesis of carbazole-*N*-propionic acid



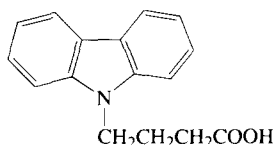
Carbazole (16.7 g, 0.1 mol) and acrylonitrile (25 ml) were cooled to 0–5°C and 40% benzyltrimethylammonium hydroxide (Triton B) (0.5 ml) was dropped in and the mixture heated on a steam bath for 1 h. White needles were obtained on cooling, and these were filtered and recrystallized from acetone to give 18.8 g (yield 85.4% of carbazole-*N*-propionitrile), m.p. 154–155°C.

The mixture of this (20 g), 95% ethanol (60 ml) and 3*N* NaOH (30 ml) was refluxed for 4 h, and then filtered. The filtrate was acidified with HCl,

filtered and the product recrystallized from benzene to give white needles, m.p. 173–174°C of carbazole-*N*-propionic acid.

$C_{15}H_{13}NO_2$ requires: C, 75.31; H, 5.44; N, 5.86. Found: C, 75.31; H, 5.41; N, 5.72. IR: 1710, 1326, 3000, 750, 725 cm^{-1} . MS (EI): M/z 239 (M^+), 180 ($M-CH_2COOH$).

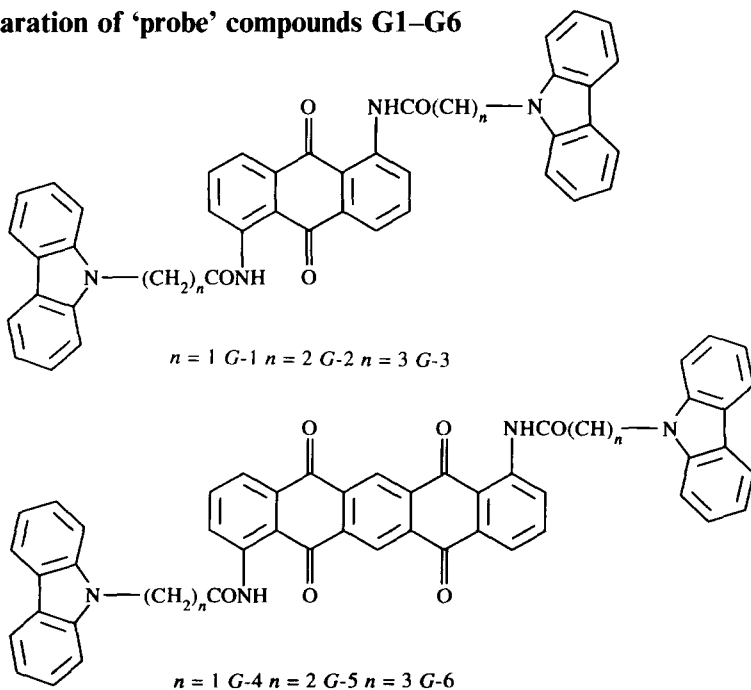
2.4 Synthesis of carbazole-*N*-butyric acid



A solution of carbazole (10 g, 0.06 mol) in *N*-methyl-2-pyrrolidinone (30 ml) was added to a sodium ethoxide solution prepared by adding sodium metal to ethanol (20 ml). γ -Butyrolactone (18 ml) was added and the mixture heated for 4 h at 160°C. The reaction mixture was then poured into water, filtered, and the filtrate acidified with HCl. The residue was collected, dried in vacuo at 100°C and recrystallized from benzene to give carbazole-*N*-butyric acid as white needles (8.6 g, 56%) m.p. 155°C.

IR: 1710, 1326, 2950, 750, 725 cm^{-1} . 1H NMR ($CDCl_3$): 1.89–2.47 ppm 4H; 4.43 ppm, 2H; 7.05–7.69, 6H; 8.18 ppm, 2H.

2.5 Preparation of 'probe' compounds G1–G6



A mixture of nitrobenzene (35 ml), carbazole-*N*-acetic acid (0.25 g, 2 mmol) and NaOH (0.09 g, 2 mmol) was heated to 120–130°C and water removed over 30 min. The temperature was lowered to 60–70°C and 1,5-diaminoanthraquinone (1 mmol) was stirred in, followed by dropwise addition of PCl_3 . The mixture was then heated at 130–140°C for 2 h, ethanol added and the mixture allowed to stand overnight. The product was filtered, washed with acetone, dried and recrystallized from DMF giving yellow needles of **G-1** (0.1 g, 13%) m.p. > 300°C.

IR: 3400, 3200, 1680, 1550, 650, $\sim 750\text{ cm}^{-1}$.

Compounds **G-2** to **G-6** were prepared by the same method.

G-2 Yield 20%. Elemental analysis:

Calculated: C, 77.64; H, 4.71; N, 8.23. Found: C, 77.82; H, 4.70; N, 8.41.

MS (EI): M/e 680 (M^+), 460, 180.

IR: 3400, 3200, 1680, 1550, 650–750 cm^{-1} .

G-3 Yield 20%.

MS (EI): M/e 708 (M^+), 474, 180.

IR: 3400, 3200, 1670, 1560 cm^{-1} .

G-4 Yield 15%.

IR: 3400, 3200, 1680, 1560 cm^{-1} .

G-5 Yield 15%.

Elemental analysis: Calculated: C, 77.03; H, 4.19; N, 6.91. Found: C, 76.55; H, 4.23; N, 6.85.

^1H NMR ($\text{CF}_3\text{ COOD}$): 3.5 ppm, 4H (COCH_2); 4.5–5.0 ppm, 4H (NCH_2); 7.0–10.0 ppm, 24H (aromatic H).

IR: 3200, 2900, 1680, 1580 cm^{-1} .

G-6 Yield 10%.

IR: 3300, 3000, 1680, 1560 cm^{-1} .

2.6 Electrochemistry

A simple two-compartment cell was used with a medium-porosity glass frit dividing the two chambers. The characteristic potentials of anion radical and dianion formation were obtained by cyclic voltammetry. All potential measurements were referred to a saturated calomel electrode. The data were obtained with degassed DMF and 0.1 M tetrabutylammonium tetrafluoroborate as electrolyte. The solutions were deaerated with nitrogen. 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 (0.3 μm first, then 0.05 μm alumina). The counter electrode was platinum. The solution was again purged with nitrogen prior to initiation of the voltammetry experiment. Voltammograms were generally recorded at a sweep rate of 100–150 mV sec^{-1} . The E^0 values were

taken from cyclic voltammetry peak potential as $(E_{\text{anode}} + E_{\text{cathode}})/2$. All experiments were carried out at room temperature.

3 RESULTS AND DISCUSSIONS

In the compounds synthesized, the carbazole moiety is an electron donor and the quinones and diquinones are electron acceptors, and the systems were used to explore the possibility of probing multi-electron transfer. Figure 1 shows the voltammograms with two reduction potential peaks for monoquinones (**G-1**, **G-2**, **G-3**). Figure 2 shows the voltammograms with four reduction potential peaks for diquinones (**G-4**, **G-5**, **G-6**). The voltammogram for 1,8-diamino-polyacenediquinone is also shown for comparison. Table 1 lists the reduction potentials for the mono- and diquinones.

In comparison with diquinones, the monoquinones show a shift of both the first and second E^0 to more negative values. This implies that diquinones reduce more easily than monoquinones. The diquinones D—A—D systems, compared with 1,8-diamino-polyacene diquinone, show all

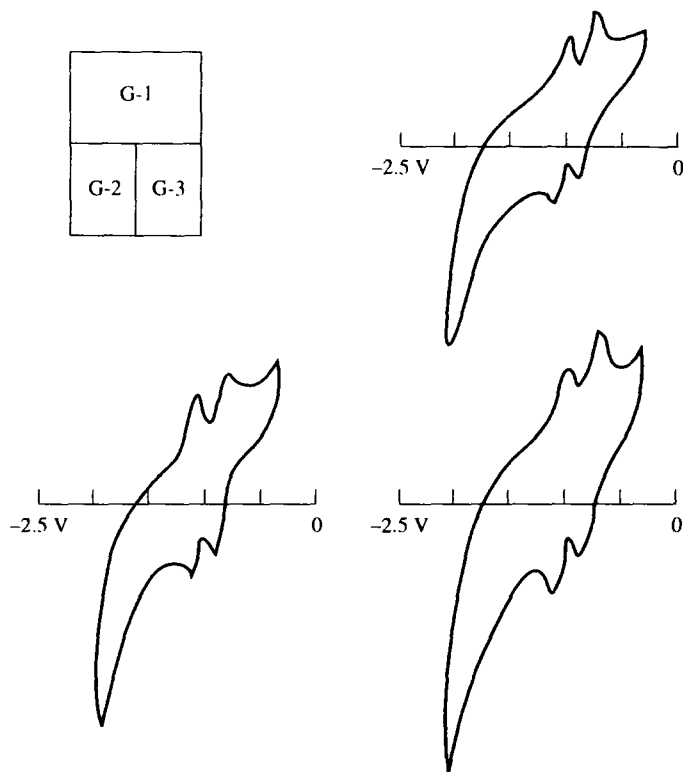


Fig. 1. Voltammograms with two reduction potential peaks for mono-quinones (**G-1**, **G-2**, **G-3**).

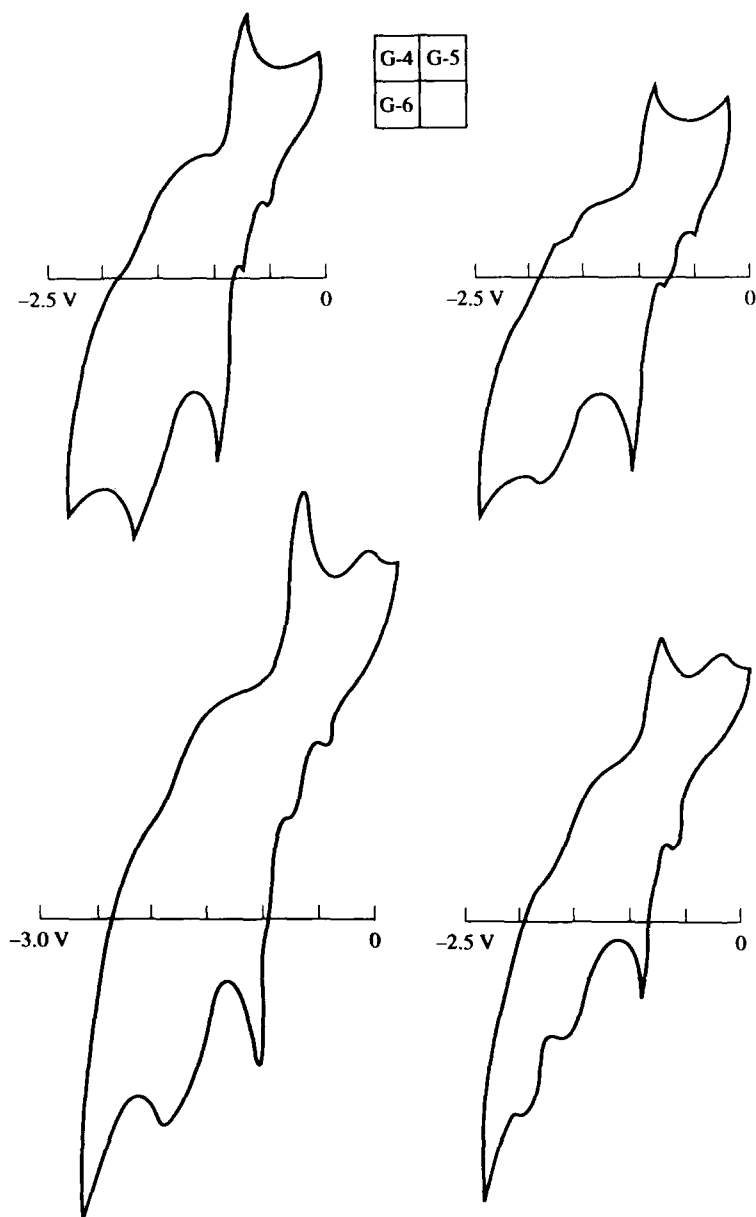


Fig. 2. Voltammograms for the diquinones (G-4, G-5, G-6).

four reduction potential peak values shifted to less negative values and it can be concluded that when the 1- and 8-positions are substituted by electron donors, the polyacencediquinone is more easily reduced.

Table 2 shows the absorption spectra data of the compounds. Data for the anion and dianion were recorded in degassed DMF on a Shimadzu UV-

TABLE 1
Reduction Potential of the Compounds

Compound	E^0 (V, SCE)			
	Dye^{1-}	Dye^{2-}	Dye^{3-}	Dye^{4-}
1,5-Diaminoanquinone	-0.92	-1.48		
G-1	-0.84	-1.12		
G-2	-0.82	-1.14		
G-3	-0.86	-1.10		
PDQ (CH_3CN)	-0.43	-0.92	-1.93	-2.44
1,8-Diamino-PDQ	-0.68	-0.98	-1.74	-2.04
G-4	-0.48	-0.70	-1.12	-1.84
G-5	-0.48	-0.72	-1.06	-1.78
G-6	-0.52	-0.72	-1.04	-1.82

VIS-NIR 365 spectrometer. Samples of anions from the electrosynthesis were syringed into the argon-purged cuvette (quartz) directly from the electrochemical cell, by use of a gas-tight syringe and the spectrum was recorded immediately, since the anions are unstable in the presence of oxygen. As seen in Table 2, the λ_{max} values of the anions and dianions are quite different from those of the neutral diquinones, which absorb in the UV. This offers a possibility of using the diquinones to determine the number of electrons involved in the reduction process. When induced by multi-photons, in D—A—D systems such as those synthesized in this work, there may exist multi-electron transfer from the donor to the acceptor (i.e. diquinones). Absorption spectrometry could then be used to confirm how

TABLE 2
 λ_{max} of the Compounds in DMF

Dyes	$\lambda_{\text{max}}(\text{nm})$				
	Dye^0	Dye^{1-}	Dye^{2-}	Dye^{3-}	Dye^{4-}
AQ	327*	553*			
1,5-Diamino-AQ	480				
PDQ	340	1335*	825*	1070*	715*
2,9-Dichloro-PDQ	378 (H_2SO_4)	1410*	833*	1150*	700*
1,8-Diamino-PDQ	509				
G-1	430				
G-2	432				
G-3	434				
G-4	431				
G-5	426				
G-6	430				

*Data from Ref. 2.

many electrons are involved in the intramolecular transfer. Time-resolved experiments for these compounds are being carried out and will be reported later.

ACKNOWLEDGMENT

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