

# Photofragmentation in Linked Donor-Acceptor Molecules. Intramolecular Single Electron Transfer Induced Cleavage of a 1,2-Diamine

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Received June 29, 1992

**Abstract:** Two intramolecular donor-acceptor molecules which fragment by a single electron transfer initiated cation radical carbon-carbon bond cleavage have been synthesized and their photoreactivity studied. The intramolecular "diads" consist of a 1,2-diamine linked via an ester bond to either an anthraquinone or a 9,10-dicyanoanthracene electron-acceptor chromophore. As the covalent linkage between the donor and acceptor chromophores prevents solvent separation of the photogenerated radical ion pair, these systems provide a "clock" to examine directly competition between fragmentation and back electron transfer. The linked anthraquinone molecule fragments efficiently, with quantum yields approaching 80%, despite the inability of the photoproduced radical ions to separate. These high yields may be attributed to a slow, spin-forbidden back electron transfer and a rapid fragmentation. In contrast, the quantum yields for the dicyanoanthracene diad (reactive singlet) are markedly lower, less than 0.001 in benzene. The reactivity of comparable intermolecular donor-acceptor combinations is also reported.

## Introduction

There is much interest in the development of clean, efficient, photoinduced electron transfer initiated reactions, and research in this field has led to the development of many novel and useful photoreactions.<sup>1-5</sup> The diverse array of products afforded by such processes includes organic compounds that cannot be easily made by conventional even-electron reactions. In addition, the mechanistic intricacies of the interconversion of even- and odd-electron species offer insights into such basic and fundamental areas as photosynthesis and solar energy conversion and storage.

Often, the efficiency of photoinduced electron transfer processes is limited by the rapid return electron transfer, and the main challenge in designing efficient reactions lies in circumventing this energy-wasting process so as to optimize the amount of useful chemistry that can be derived. Several of the strategies that have been utilized toward this end include the facilitation of solvent cage escape to provide increased yields of free radical ions, from which return electron transfer is greatly inhibited. This has been accomplished through cosensitization<sup>6-10</sup> (particularly with biphenyl), the use of polar solvents,<sup>11-13</sup> and the use of charged reagents.<sup>14,15</sup> The donors and acceptors involved can also be

judiciously chosen so as to drive the return electron transfer into the Marcus inverted region, hence slowing the process through manipulation of the energetics.<sup>16</sup> It has been found that the use of a triplet system will result in a spin-forbidden return electron transfer, significantly slowing this process.<sup>17-21</sup> In addition, many of the multiple-component "relay" systems developed to mimic photosynthesis<sup>22-24</sup> have produced radical ion pairs with unusually long lifetimes.

For intramolecular electron transfer systems involving covalently linked donors and acceptors, the inability of the photoproduced radical ions to diffuse apart prevents the use of many of these strategies. Though many such linked systems have been made,<sup>25-28</sup> they have primarily been used for photophysical studies, and only a few have involved actual bond breaking and bond-forming reactions.<sup>29,30</sup>

We are interested in the development of rapid fragmentation reactions<sup>31-37</sup> induced by electron transfer, particularly for

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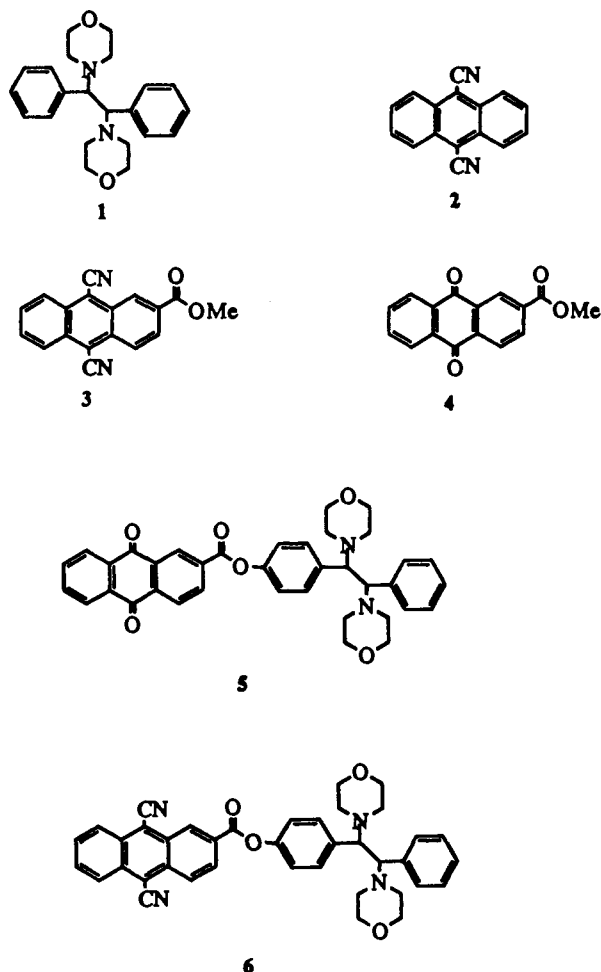


Figure 1. Donors and acceptors used.

1,2-diamines.<sup>34-36</sup> In this paper we report studies of two intramolecular "diads" containing electron acceptor chromophores linked to reactive diamine donors which can undergo unimolecular fragmentation in competition with back electron transfer. As radical ion separation cannot occur due to the covalent linkage, these molecules may serve as a "clock" with which to probe back electron transfer rates. These systems are compared to their analogous intermolecular systems consisting of free, unlinked donors and acceptors, so as to ascertain the role of radical ion pair separation in these reactions. Interestingly, we find the intramolecular donor/acceptor molecule, where electron transfer is initiated by the quenching of an excited-state singlet acceptor, to be significantly less reactive than the corresponding intermolecular counterpart. In contrast, the linked molecule reacting via quenching of a triplet acceptor shows highly efficient photoreaction, despite the inability of the photogenerated radical ions to charge-separate.

## Results

The molecules used in this study are shown in Figure 1. The syntheses are described in detail in the Experimental Section. The diamine donor used, *erythro*-1,2-dimorpholinyl-1,2-diphenylethane (**1**), was synthesized from previously prepared 2-morpholinyl-1,2-diphenylethanol<sup>31</sup> by the conversion of the amino alcohol to the corresponding amino mesylate, followed by nucleophilic displacement of the mesylate by morpholine. This reaction is thought to occur by a neighboring group participation mechanism involving an aziridinium ion intermediate to give

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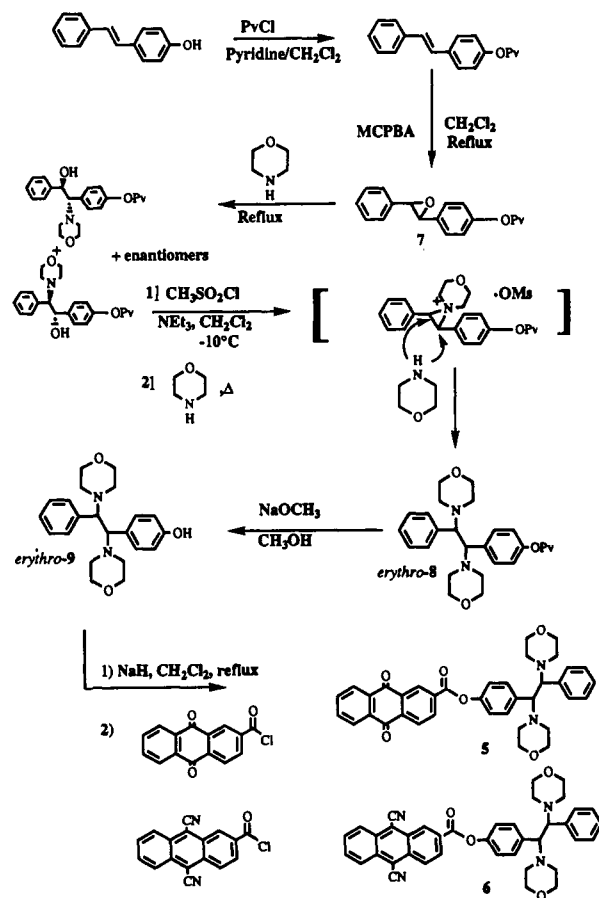


Figure 2. Synthesis of diads **5** and **6**.

retention of stereochemistry.<sup>38</sup> Indeed, the only isolated product was the meso diastereomer, as determined by X-ray crystal structure.

The linked donor/acceptor "diads" **5** and **6** (see Figure 2) were both made by an acid chloride/phenol esterification involving the acid chloride of the electron acceptor (either anthraquinone-2-carbonyl chloride or 9,10-dicyanoanthracene-2-carbonyl chloride) with 1,2-dimorpholinyl-1-(*p*-hydroxyphenyl)-2-phenylethane. This hydroxy diamine was synthesized starting from *trans*-4-hydroxystilbene. The stilbene was protected as the pivalate, epoxidized, ring-opened by reflux in morpholine, and then converted to the diamine by the same method used for **1**, and finally deprotected.

9,10-Dicyanoanthracene-2-carbonyl chloride, and the acceptor, 2-(methoxycarbonyl)-9,10-dicyanoanthracene (**3**) were prepared from 9,10-dibromoanthracene-2-carboxylic acid, which was synthesized by a known procedure.<sup>39</sup> This compound was esterified with methanol/H<sub>2</sub>SO<sub>4</sub>, and the bromines were displaced by cuprous cyanide in refluxing dimethylformamide to afford the dicyanoanthracene methyl ester **3**, which was then hydrolyzed and heated in thionyl chloride to afford the acid chloride.

Three acceptors with similar redox characteristics were chosen for the study of the fragmentation of **1** initiated by intermolecular photoinduced electron transfer: 2-(methoxycarbonyl)anthraquinone (**4**), 9,10-dicyanoanthracene (**2**), and 2-(methoxycarbonyl)-9,10-dicyanoanthracene (**3**). **4**, a nonfluorescent chromophore with a highly efficient intersystem crossing,<sup>40</sup> has an excited-state (triplet) redox potential of 1.99 V,<sup>41</sup> the same as the excited-

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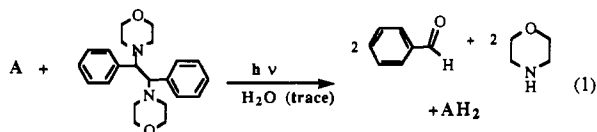
(41) Determined by cyclic voltammetry.

Table I. Intermolecular Quantum Yields

acceptor	CH <sub>3</sub> CN	CH <sub>2</sub> Cl <sub>2</sub>
4	1.02 ± 0.06	0.81 ± 0.05
2	0.078 ± 0.006	0.012 ± 0.001
3	0.086 ± 0.001	

state singlet 2.<sup>42</sup> The other dicyanoanthracene derivative used, 3, has a slightly higher excited state redox potential of 2.15 V.<sup>41</sup> The singlet acceptors, upon photoreduction, afford corresponding 9,10-dihydro-9,10-dicyanoanthracenes. 4 is photoreduced to 9,10-dihydroxy-2-(methoxycarbonyl)anthracene, which in the presence of oxygen is rapidly reoxidized back to the quinone.

Diamine 1 undergoes a cation radical fragmentation, the general mechanism of which has been previously reported.<sup>34-36</sup> Upon oxidation by a photoexcited electron acceptor, the diamine fragments to yield an iminium cation and a benzylamine radical. The radical is rapidly oxidized, presumably by a dark (ground state) electron transfer, to yield a second equivalent of iminium ion. The iminium ion is then rapidly hydrolyzed to give 2 equiv of morpholine and 2 equiv of benzaldehyde with the stoichiometry shown in eq 1. The cation radical, once formed, fragments

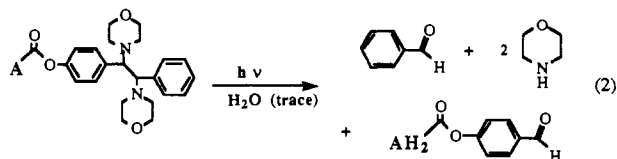


A = 2,3,4

independently of the acceptor.<sup>35</sup> Although it would be expected that the fragmentation rate would be influenced at least somewhat by solvent, this effect seems relatively small.

The diamine donor in irradiated acceptor solution fragments with the quantum yields shown in Table I. In acetonitrile, chosen as a moderately polar solvent, the quantum yields range from 1 using the triplet anthraquinone ester 4 to 0.078 with 2. In methylene chloride (chosen as a nonpolar solvent due to the high solubility of the diamine), the quantum yields for the reaction decrease, but by less than one order of magnitude. 3 gave a complex reaction in this solvent, and the quantum yield was found to drop off sharply with time.

The intramolecular diads 5 and 6 are both yellow compounds. Diad 6 shows a very weak fluorescence and has an excited-state lifetime of 334 ps as measured by single-photon counting experiments. The triplet molecule 5 shows no fluorescence, as is characteristic of the anthraquinone chromophore. The unlinked dicyanoanthracene ester 3 shows a lifetime of 17.8 ns. Both linked compounds undergo photoreactions which are analogous to their intermolecular counterparts. In both cases, the products consist of 2 equiv of morpholine, 1 equiv of benzaldehyde, and 1 equiv of the ester-linked reduced acceptor-aldehyde (eq 2). 5 was found



A = 2, anthraquinone

to give a remarkably clean reaction, yielding the expected products, in all of the solvents indicated in Table II and in chloroform, a notoriously bad photochemical solvent. Interestingly, in the unlinked anthraquinone ester case, significant amounts of the chloroform adduct are obtained. The reaction is not appreciably

(42) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794.

suppressed by oxygen and gives the same products, the only difference being that the dihydroquinone reduction product is rapidly reoxidized by oxygen, thus regenerating the anthraquinone. The anthraquinone acceptor, in the presence of oxygen, thus essentially acts as a catalyst. This behavior is also seen in the intermolecular case. 6 photoreacts cleanly in benzene, butyronitrile, and acetonitrile but yields an unidentified product with a red-shifted absorbance (480 nm) in dimethylformamide. In methylene chloride, 6 shows the same complex behavior as the intermolecular dicyanoanthracene system 3 in this solvent.

The quantum yields for the intramolecular photoreaction are shown in Table II. The reaction was found to be very efficient for diad 5 in all solvents used, ranging from 0.33 in benzene to 0.78 in dimethylformamide. Similarly, diad 6 showed the slowest reaction in benzene, a barely measurable quantum yield of less than 0.001.

## Discussion

The main mechanistic difference between the intermolecular and intramolecular systems lies in the role of solvent separation of the photogenerated radical ions (Figure 3). For the unlinked, intermolecular reactions, the photogenerated radical ion pair has three pathways available. First, it can undergo return electron transfer, and hence no further reaction will occur. Second, the donor can fragment, and the previously indicated oxidation and reduction products will be formed. Alternately, the radical ions can diffuse apart. From the free ions, chemistry can occur without competition from the return electron transfer.<sup>43</sup>

For the linked molecules, solvent separation cannot occur, and hence there is a direct competition between return electron transfer and fragmentation. From the kinetic schemes in Figure 3, eqs 3 and 4 can be derived relating the intra- and intermolecular quantum yields to the rate constants for reaction ( $k_r$ ), solvent separation ( $k_{sep}$ ), and return electron transfer ( $k_{-et}$ ).

$$\phi_{inter} = \frac{k_r + k_{sep}}{k_r + k_{sep} + k_{-et}} \quad (3)$$

$$\phi_{intra} = \frac{k_r}{k_r + k_{-et}} \quad (4)$$

It is reasonable to assume that  $k_r$  will show little intrinsic difference between the linked and unlinked systems. As the donor and acceptor redox potentials will be nearly the same in both cases and only slight differences can be expected in the Weller Coulombic and solvation terms,<sup>44</sup> it is reasonable to likewise assume that in acetonitrile, the return electron transfer rates will not differ much between the intermolecular and intramolecular reactions.<sup>45</sup> Hence eqs 3 and 4 can be solved simultaneously as a system of two equations with two variables, to give  $k_r$  and  $k_{-et}$ . The solvent separation rate constant of  $k_{sep} = 8 \times 10^8 \text{ s}^{-1}$  has been reported by Farid<sup>46</sup> for 9,10 dicyanoanthracene photoredox systems in acetonitrile. Using this value and the quantum yields of 0.010 and 0.086 for the linked and unlinked dicyanoanthracene systems (diad 6 and acceptor 3, with diamine 1, respectively), eqs 3 and 4 give  $k_r = 9.6 \times 10^7 \text{ s}^{-1}$  and  $k_{-et} = 9.5 \times 10^9 \text{ s}^{-1}$ .

(43) Given  $k_r > 10^7 \text{ s}^{-1}$ , the low steady state concentration of free ions would not give recombination rates that could be competitive with fragmentation.

(44) Weller, A. *Z. Phys. Chem. N. Eve. Folge.* **1982**, *133*, 183.

(45) Given the steric and conformational restraints on the linked molecules, it is unlikely that they can assume the required "face to face" donor/acceptor orientation so as to be treated as a contact radical ion pair. The solvent separated radical ion pair seems a better model for these compounds. In polar solvents, such as acetonitrile, the intramolecular systems will likewise form the solvent separated radical ion pair directly upon photolysis. Both types of radical ion pair, consequently, show Marcus curves of markedly different shape. This phenomenon is documented in Gould, I. R.; Young, R. H.; Moody, R. E.; Farid, S. *J. Phys. Chem.* **1991**, *95*, 2068.

(46) Farid, S., private communication.

Table II. Intramolecular Quantum Yields

compound	benzene	C <sub>3</sub> H <sub>7</sub> CN	CH <sub>3</sub> CN	CH <sub>2</sub> Cl <sub>2</sub>	DMF
5	0.33 ± 0.09	0.53 ± 0.05	0.75 ± 0.02	0.75 ± 0.02	0.78 ± 0.07
6	<0.001	0.014 ± 0.004	0.010 ± 0.001		

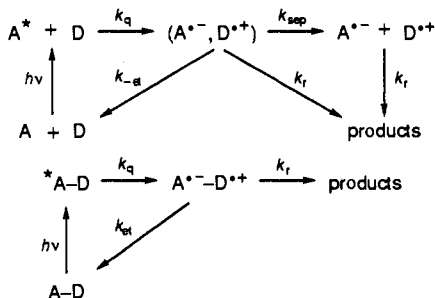


Figure 3. Schemes for inter- and intramolecular reactions.

Alternately, we may estimate  $k_{-et}$  using Marcus plots generated for similar reactions of **2** in acetonitrile. From the curves of Gould, Moody, and Farid<sup>47</sup> generated for **2** with alkylbenzene donors, we can estimate a  $k_{-et}$  of slightly greater than  $10^{10} \text{ s}^{-1}$ . Using  $k_{-et} = 1 \times 10^{10} \text{ s}^{-1}$ ,  $k_{sep} = 8 \times 10^8 \text{ s}^{-1}$ , and the quantum yield of 0.078 for the reaction of **2** in acetonitrile, we arrive at a value of  $k_r = 4.6 \times 10^7 \text{ s}^{-1}$ , though it would be expected that this value might be slightly higher, since the  $k_{-et}$  derived from the curves is a lower limit.

With the assumption that the fragmentation rate will change only slightly from solvent to solvent, the value of  $k_r = 9.6 \times 10^7 \text{ s}^{-1}$  can be used with eq 3 to ascertain the back electron transfer rates for the other intermolecular systems. Using this number for **2**,  $k_{-et}$  is found to be  $1.1 \times 10^{10} \text{ s}^{-1}$ , slightly higher than the value of  $9.5 \times 10^9 \text{ s}^{-1}$  calculated for the dicyanoanthracene ester **3**.<sup>48</sup> This is not surprising, given the differences in back electron transfer exothermicities for **2** and **3** (1.95 and 1.82 eV, respectively).<sup>49</sup> Since the quantum yield is higher for **3**, which has a slightly more exothermic return electron transfer, it can be assumed that the back electron transfer occurs in the Marcus normal region. The Marcus curves of Gould et al. would place this return electron transfer directly on the top of the curve. Given the differences in electron donors used, however, a return electron transfer occurring slightly into the normal region is not unreasonable. As the quantum yield for the photoreaction with **4** is 1 in acetonitrile, a numerical value for  $k_{-et}$  cannot be calculated. This quantity, however, must be significantly less than  $10^8 \text{ s}^{-1}$  for this quantum yield to be obtained.

In order to calculate the return electron transfer rates in methylene chloride, a  $k_{sep}$  value of  $1 \times 10^5 \text{ s}^{-1}$  can be estimated from a semi-empirical formula by Weller.<sup>50</sup> Using eq 3 and  $k_r = 1 \times 10^8 \text{ s}^{-1}$ , the return electron transfer rates for the reactions with acceptors **2** and **4** in methylene chloride are calculated to be  $8 \times 10^9$  and  $2 \times 10^7 \text{ s}^{-1}$ , respectively. This gives a difference of roughly three orders of magnitude between the singlet and triplet return electron transfer rates, a difference significant enough to increase the quantum yields to near 1.

Using the calculated  $k_r$  and eq 4, the back electron transfer rates can similarly be calculated for the intramolecular systems. For the triplet diad **5**,  $k_{-et}$  has a maximum value of  $2 \times 10^8 \text{ s}^{-1}$  in benzene and a minimum of  $3 \times 10^7 \text{ s}^{-1}$  in acetonitrile, methylene chloride, and DMF. A similar difference with solvent is shown for diad **6**, wherein the  $k_{-et}$  decreases from  $1 \times 10^{11} \text{ s}^{-1}$  in benzene

to  $1 \times 10^{10} \text{ s}^{-1}$  in butyronitrile and acetonitrile. This difference of approximately one order of magnitude upon going from solvents of low to high polarity is similar to that of other linked donor/acceptor molecules found in the literature. Most of the other systems examined, however, have involved much larger separation distances and rigid spacers such as a steroid skeleton or a rigid hydrocarbon assembly.<sup>25,26</sup> Such an increase of  $k_{-et}$  with decreasing solvent polarity is consistent with a return electron transfer in the Marcus normal region.

From the singlet lifetimes of **3** and diad **5**, the Stern-Volmer quenching constant for diad **6** was calculated to be  $2.9 \times 10^9 \text{ s}^{-1}$ . This is surprising, since the unlinked system has a  $k_q$  of  $7.5 \times 10^9 \text{ s}^{-1}$ . The fact that the linked system shows a lower value is suggestive that there may exist an optimum donor/acceptor orientation which the linked molecule is not able to adopt.

In summary, we have designed linked donor/acceptor molecules which may be used as probes of back electron transfer rates in various solvents. The quinone-based system undergoes a very efficient photofragmentation reaction despite the inability of the photogenerated radical ions to diffuse apart. We attribute this high reactivity to a relatively slow  $k_{-et}$  in the triplet radical ion pair combined with a rapid fragmentation. In addition to exhibiting high reactivity in solution, preliminary results suggest that the fragmentation also occurs in the solid state for a number of quinone linked diamines. Studies are underway to construct photodegradable polymers consisting of alternating anthraquinone and diamine monomers.

## Experimental Section

(a) **Preparation of Materials.** Anthraquinone-2-carbonyl chloride was obtained from TCI America and used without further purification. 9,10-Dicyanoanthracene was obtained from Kodak and was recrystallized three times from pyridine. All other reagents were obtained from Aldrich. The 4-hydroxystilbene pivalate was prepared by the pyridine-catalyzed reaction of *trans*-4-hydroxy stilbene with trimethylacetyl chloride.<sup>51</sup> 2-(Methoxycarbonyl)anthraquinone was similarly prepared from methanol and anthraquinone-2-carbonyl chloride. 9,10-Dibromoanthracene-2-carboxylic acid was prepared from a known procedure.<sup>39</sup> Morpholine was distilled twice, at which point no yellow color remained. Silica gel used for flash chromatography was 70–230 mesh. Monitoring of reactions by thin-layer chromatography was performed using Kodak Chromatogram silica gel TLC sheets. All NMR analyses were conducted at room temperature using a General Electric/Nicolet QE 300-MHz spectrometer. Proton chemical shifts are relative to tetramethylsilane and were referenced to the residual deuterium lock solvents, i.e., CDCl<sub>3</sub>, 7.27 and DMSO-*d*<sub>6</sub>, 2.50. All IR spectra were recorded on a Matheson Galaxy 6020 spectrometer. Melting points were taken on a Mel-Temp apparatus and are uncorrected. Cyclic voltammetry measurements were performed on a BAS 100B electrochemical analyzer, and redox potentials are reported relative to SCE. Elemental analyses were performed by Galbraith Labs. FAB mass spectra were performed at the Midwest Center for Mass Spectrometry.

**meso-1,2-Dimorpholinyl-1,2-diphenylethane (1)** was prepared via nucleophilic displacement by morpholine of the mesylate derivative of previously prepared *erythro*-2-morpholino-1,2-diphenylethanol. This amino alcohol (10.00 g, 0.035 mol) was combined with triethylamine (7.5 mL, 0.054 mol) in 150 mL of freshly distilled CH<sub>2</sub>Cl<sub>2</sub> in a 250-mL round-bottomed flask fitted with a low-temperature thermometer, N<sub>2</sub> inlet, magnetic stirrer, and 50-mL addition funnel protected with a calcium chloride drying tube. Moderate stirring was initiated, and the reaction vessel was flushed with dry nitrogen for 30 min and then placed on an ice-salt bath until a solution temperature of -10 °C was obtained. Methanesulfonyl chloride (3.4 mL, 0.044 mol) in 15 mL of CH<sub>2</sub>Cl<sub>2</sub> was then added dropwise via an addition funnel over 20 min such that the

(47) Gould, I. R.; Moody, R.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 7242.

(48) For both of these values, the calculated error is less than 1%.

(49) Back electron transfer exothermicities are given by  $E^{\text{oxD}} - E^{\text{redA}}$ . The redox potentials of **3** and **1**, as determined by cyclic voltammetry, are -0.77 and 1.05 V, respectively. The redox potential for **2** (-0.90 V) is reported in ref 42. As the voltammetry curve for **1** is irreversible, the reported value of 1.05 V must be seen as a lower limit. Hence, it is possible that the calculated exothermicities are larger.

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solution temperature never rose to over  $-5\text{ }^{\circ}\text{C}$ . The yellowish solution was allowed to stir for 30 min, at which point silica gel TLC analysis (with 2:1 hexanes/ethyl acetate) showed complete conversion to the mesylate. Next, the ice bath was removed and replaced with a heating mantle. Morpholine (30 mL, excess) was added all at once and the addition funnel was removed. The nitrogen flow was increased and gentle heating was applied until the volume was reduced by half. After 5 min, a white precipitate could be seen. The reaction was allowed to stir at room temperature for another hour, at which point the mesylate no longer appeared on TLC. The reaction mixture was poured into 200 mL of  $\text{CH}_2\text{Cl}_2$  and washed five times with equal volumes of water. Upon drying of the  $\text{CH}_2\text{Cl}_2$  over anhydrous magnesium sulfate, the solvent was removed on a rotary evaporator to give a yellow slurry. The crude product was recrystallized three times from 450 mL of acetone to yield 8.51 g of white, crystalline powder (69%, mp  $250\text{--}252\text{ }^{\circ}\text{C}$ ).  $^1\text{H NMR}$  (300 MHz) in  $\text{CDCl}_3$ :  $\delta$  2.27 (m, 4H), 2.40 (m, 4H), 3.27 (m, 4H), 3.40 (m, 4H), 4.12 (s, 2H), 7.21 (d,  $J = 7\text{ Hz}$ , 4H), 7.27–7.39 (m, 6H). Anal. Calcd for  $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_2$ : C, 74.96; H, 8.01; N, 7.94. Found: C, 74.85; H, 8.10; N, 7.91. (Meso stereochemistry confirmed by X-ray structure.)

**trans-4-Pivaloxystilbene oxide (7).** To the 4-hydroxystilbene pivalate (6.39 g, 0.025 mol) dissolved in 20 mL distilled  $\text{CH}_2\text{Cl}_2$  was added 3-chloroperoxybenzoic acid (4.91 g, 0.028 mol) over 10 minutes via addition funnel. The solution was heated at a steady reflux for 4 h and then cooled to room temperature and allowed to stir overnight. The large amount of white precipitate (3-chlorobenzoic acid) which had formed was filtered off using a fritted glass funnel, and the solution was extracted four times with 70 mL of 5% sodium bicarbonate. After being dried over anhydrous magnesium sulfate, the solution was stripped of solvent using a rotary evaporator to yield 6.41 g of a viscous, clear oil which solidified upon standing overnight (95%, mp  $53\text{--}54\text{ }^{\circ}\text{C}$ ). IR (KBr):  $\nu$  1751 (s, C=O)  $^1\text{H NMR}$  (300 MHz) in  $\text{CDCl}_3$ :  $\delta$  1.38 (s, 9H), 3.88 (d,  $J = 9\text{ Hz}$ , 2H), 7.09 (d,  $J = 9\text{ Hz}$ , 2H), 7.38 (m, 7H).

**erythro-1,2-Dimorpholinyl-1-(p-pivaloxyphenyl)-2-phenylethane (8).** The epoxide **7** (6.07 g, 0.021 mol) and morpholine (35 mL, excess) were combined in a 100-mL round-bottom flask with magnetic stirrer and heated at reflux for 3 h, at which point the complete disappearance of epoxide can be seen by silica gel TLC (2:1 hexanes/ethyl acetate). The reaction solution was poured into 200 mL of ethyl acetate and was extracted four times with 100 mL of water and once with 100 mL of brine. After being dried over anhydrous magnesium sulfate, the solvent was removed via rotary evaporation to yield 6.19 g of a viscous, yellow oil that solidified upon standing. This crude mixture of regioisomers was converted to the diamine through the amino alcohol-to-diamine conversion reported above for **1** (60.4%, mp  $146\text{--}147\text{ }^{\circ}\text{C}$ ). IR (KBr):  $\nu$  1745 (s, C=O).  $^1\text{H NMR}$  (300 MHz) in  $\text{CDCl}_3$ :  $\delta$  2.29 (m, 4H), 2.40 (m, 4H), 3.26 (m, 4H), 3.41 (m, 4H), 4.08 (d,  $J = 10\text{ Hz}$ , 1H), 4.13 (d,  $J = 11\text{ Hz}$ , 1H), 7.08 (d,  $J = 8\text{ Hz}$ , 2H), 7.21 (t,  $J = 7\text{ Hz}$ , 2H), 7.35 (m, 5H).

**erythro-1,2-Dimorpholinyl-1-(p-hydroxyphenyl)-2-phenylethane (9).** The pivalate-protected diamine **8** (3.90 g,  $8.63 \times 10^{-3}$  mol) and sodium methoxide (0.90 g, 0.017 mol) were dissolved in 100 mL of absolute ethanol in a 250-mL round bottom flask with a magnetic stirrer and a calcium chloride drying tube. The reaction solution was allowed to stir at room temperature for 2 h. A small amount of water ( $\sim 1\text{ mL}$ ) was added, and  $\text{CO}_2$  was vigorously bubbled into the solution until neutrality was achieved, at which point the solution grew cloudy. The solvent was then stripped off by rotary evaporation. The white powder obtained was mixed with 20 mL of EtOAc and washed with EtOAc through a short silica flash column. The collected solvents were removed through rotary evaporation to yield 2.95 g of a fine, white powder (92.9%, mp  $176\text{--}178\text{ }^{\circ}\text{C}$ ). IR (KBr):  $\nu$  3279 (br, PhOH).  $^1\text{H NMR}$  (300 MHz) in  $\text{DMSO}-d_6$ :  $\delta$  2.12 (m, 4H), 2.22 (m, 4H), 3.06 (m, 4H), 3.19 (m, 4H), 4.16 (d,  $J = 12\text{ Hz}$ , 1H), 4.21 (d,  $J = 12\text{ Hz}$ , 1H), 6.71 (d,  $J = 8\text{ Hz}$ , 2H), 7.08 (d,  $J = 8\text{ Hz}$ , 2H), 7.27 (m, 5H), 9.15 (s, 1H, ArOH).

**Diad 5.** The hydroxy diamine (0.22 g,  $5.98 \times 10^{-4}$  mol) was combined with sodium hydride (0.0234 g,  $9.75 \times 10^{-4}$  mol) in 5 mL freshly distilled  $\text{CH}_2\text{Cl}_2$ . The solution was heated at a gentle reflux for 1 h. Anthraquinone-2-carbonyl chloride (0.33 g,  $1.22 \times 10^{-3}$  mol) was added all at once, and the reaction was allowed to stir overnight in the dark. The reaction solution was then run directly through a 3-cm  $\times$  20-cm silica column with 1:1 hexanes/EtOAc as eluent. The first fraction was collected, and the solvent was stripped on a rotary evaporator to yield a fine, yellow powder. The product was left overnight in a vacuum oven at  $50\text{ }^{\circ}\text{C}$ . Yellow powder (0.18 g) was collected (49.6%, mp  $234\text{--}236\text{ }^{\circ}\text{C}$ ). IR (KBr):  $\nu$  1738 (s, C=O), 1677 (s, C=O) UV/vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  (nm) = 330.  $^1\text{H NMR}$  (300 MHz) in  $\text{CDCl}_3$ : 2.33 (m, 4H), 2.42 (m, 4H), 3.33 (m, 4H), 3.45 (m, 4H), 4.12 (d,  $J = 12\text{ Hz}$ , 1H), 4.20 (d,  $J = 12\text{ Hz}$ , 1H),

7.21–7.41 (m, 9H), 7.88 (t,  $J = 4\text{ Hz}$ , 2H), 8.40 (m, 2H), 8.50 (d,  $J = 8\text{ Hz}$ , 1H), 8.63 (d,  $J = 8\text{ Hz}$ , 1H), 9.17 (s, 1H).  $^{13}\text{C NMR}$  (300 MHz) in  $\text{CDCl}_3$ :  $\delta$  49.76, 67.08, 68.82, 69.46, 120.44, 127.00, 127.44, 127.50, 127.74, 129.06, 129.13, 130.06, 133.34, 133.38, 133.67, 134.48, 134.55, 134.68, 134.97, 135.89, 136.44, 149.53, 163.48, 182.16, 182.45. Mass spectrum (FAB, positive ion, nitrobenzyl alcohol matrix):  $m/z$  603.2 (M+H), 516.1 (M+ - morpholine).

**2-(Methoxycarbonyl)-9,10-dibromoanthracene.** 9,10-Dibromoanthracene-2-carboxylic acid (2.80 g,  $7.78 \times 10^{-3}$  mol) was combined with 200 mL of DMSO, 100 mL of methanol, and 20 mL of  $\text{H}_2\text{SO}_4$  in a 1-L round bottom flask. The solution was heated at reflux for 48 h and then poured into 1 L of  $\text{H}_2\text{O}$  and extracted twice with 500 mL of  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were extracted twice with water and dried over  $\text{MgSO}_4$ , and the solvent was stripped by rotary evaporation. The crude, yellow powder was recrystallized twice from benzene to afford 2.20 g of fine, yellow powder (91.1%, mp  $208\text{--}210\text{ }^{\circ}\text{C}$ ). IR (KBr):  $\nu$  1725 (s, C=O); UV/vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) = 338, 354, 374, 394, 418.  $^1\text{H NMR}$  (300 MHz) in  $\text{CDCl}_3$ :  $\delta$  4.06 (s, 3H), 7.70 (m, 2H), 8.16 (d,  $J = 9\text{ Hz}$ , 1H), 8.63 (m, 3H), 9.38 (s, 1H).

**2-(Methoxycarbonyl)-9,10-dicyanoanthracene.** 2-(Methoxycarbonyl)-9,10-dibromoanthracene (1.50 g, 0.004 mol) was combined with 100 mL of DMF and 0.92 g (0.01 mol) of CuCN. The solution was heated at reflux for 1 h, and the deep red, translucent solution was quickly poured into a solution of 3 mL of concentrated HCl and 6.50 g of  $\text{FeCl}_3$  in 250 mL of water. A yellow precipitate instantly formed, and the mixture was allowed to stir for 10 min. The precipitate was then filtered off and washed three times with 50 mL of water. The crude product was then dissolved in 100 mL of  $\text{CHCl}_3$  and passed through a nylon filter, and the solvent was removed in a rotary evaporator. The product was recrystallized from 1:1 benzene/acetone to afford 0.85 g of a fine, bright yellow, crystalline powder (74%, mp  $226\text{--}240\text{ }^{\circ}\text{C}$  dec). IR (KBr):  $\nu$  2219 (w, CN), 1727 (s, C=O). UV/vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) = 364, 382, 404, 428.  $^1\text{H NMR}$  (300 MHz) in  $\text{CDCl}_3$ :  $\delta$  4.09 (s, 3H), 7.92 (t,  $J = 4\text{ Hz}$ , 2H), 8.42 (d,  $J = 9\text{ Hz}$ , 1H), 8.58 (m, 3H), 9.26 (s, 1H).  $^{13}\text{C NMR}$  (300 MHz) in  $\text{CDCl}_3$ :  $\delta$  53.00, 111.66, 113.41, 115.42, 115.53, 126.26, 126.45, 126.65, 128.26, 128.81, 128.97, 129.06, 130.34, 130.87, 131.14, 132.56, 133.22, 165.63. Mass spectrum (EI):  $m/z$  286 (M<sup>+</sup>), 255 (M<sup>+</sup> -  $\text{CH}_3\text{O}$ ), 227 (M<sup>+</sup> -  $\text{CO}_2\text{CH}_3$ ).

**Potassium 9,10-Dicyanoanthracene-2-carboxylate.** 2-(Carboxymethyl)-9,10-dicyanoanthracene (0.46 g,  $1.61 \times 10^{-3}$  mol) was combined in a 100-mL round-bottom flask with 0.22 g ( $3.92 \times 10^{-3}$  mol) of KOH and 60 mL of 2:1 acetone/water. The mixture was heated at reflux for 4 h and cooled to room temperature. The solid, undissolved product was filtered off, washed once with 30 mL of water and once with 30 mL of cold acetone, and dried overnight in a vacuum oven. Fine, yellow needles (0.46 g) were collected (92.1%, mp  $> 300\text{ }^{\circ}\text{C}$ ). IR (KBr): 1589 (s,  $\text{CO}_2^-$ ), 1390 (s,  $\text{CO}_2^-$ ), 2221 (w, CN). UV/vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) = 388, 406, 438, 476; ( $\text{CH}_3\text{CN}$ , acidified)  $\lambda_{\text{max}}$  (nm) = 364, 382, 404, 428.  $^1\text{H NMR}$  (300 MHz) in  $\text{DMSO}-d_6$ :  $\delta$  7.98 (m, 2H), 8.35 (d,  $J = 9\text{ Hz}$ , 1H), 8.43 (m, 3H), 8.88 (s, 1H).

**9,10-Dicyanoanthracene-2-carbonyl chloride** was prepared by heating 0.40 g ( $1.29 \times 10^{-3}$  mol) of potassium 9,10-dicyanoanthracene-2-carboxylic acid in 20 mL of  $\text{SOCl}_2$  at reflux for 3 h, at which point all of the starting material had dissolved. The  $\text{SOCl}_2$  was then distilled off, and the product (a mixture of the acid chloride and KCl) was placed in a vacuum oven overnight to remove residual  $\text{SOCl}_2$ . The crude product was used without further purification; 0.48 g collected (100%). IR (KBr):  $\nu$  1751 (s, CO), 2220 (w, CN). UV/vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) = 364, 384, 414, 436.  $^1\text{H NMR}$  (300 MHz) in  $\text{CDCl}_3$ :  $\delta$  7.98 (m, 2H), (d,  $J = 9\text{ Hz}$ , 1H), 8.62 (m, 3H), 9.42 (s, 1H).

**Diad 6.** Hydroxy diamine **9** (0.35 g,  $9.5 \times 10^{-4}$  mol) and 0.0248 g ( $1.03 \times 10^{-3}$  mol) of NaH were heated for 30 min in 10 mL refluxing  $\text{CH}_2\text{Cl}_2$ . The cloudy solution was added dropwise via addition funnel over 10 min to a solution of 0.35 g ( $9.58 \times 10^{-4}$  mol) of 9,10-dicyanoanthracene-2-carbonyl chloride and 0.3 mL ( $2 \times 10^{-3}$  mol) of triethylamine and was allowed to stir at room temperature overnight. The deep yellow solution was then run directly through a 3-cm  $\times$  20-cm florisil column with 1:1 ethyl acetate/hexanes eluent. The solvent was stripped on a rotary evaporator, and the product was recrystallized once from 1:1 chloroform/heptane and once from benzene. The microcrystalline yellow powder was dried overnight in a vacuum oven; 0.28 g collected (48.5%, mp  $240\text{--}260\text{ }^{\circ}\text{C}$  dec). IR (KBr): 1738 (s, CO), 2220 (w, CN). UV/vis ( $\text{CH}_3\text{CN}$ ):  $\lambda_{\text{max}}$  (nm) = 364, 382, 406, 430.  $^1\text{H NMR}$  (300 MHz) in  $\text{CDCl}_3$ :  $\delta$  2.35 (m, 4H), 2.45 (m, 4H), 3.36 (m, 4H), 3.45 (m, 4H), 4.13 (d,  $J = 11\text{ Hz}$ , 1H), 4.20 (d,  $J = 12\text{ Hz}$ , 1H), 7.21–7.43 (m, 9H), 7.88 (m, 2H), 8.53–8.70 (m, 4H), 9.48 (s, 1H).  $^{13}\text{C NMR}$  (300

MHz) in  $\text{CDCl}_3$ :  $\delta$  49.80, 67.07, 68.89, 69.50, 111.73, 113.56, 115.31, 115.43, 120.53, 126.25, 126.46, 126.87, 127.03, 127.58, 128.83, 129.06, 129.70, 130.10, 130.41, 130.69, 131.02, 132.60, 133.30, 133.36, 134.56, 135.88, 149.57, 163.65. Mass spectrum (FAB, positive ion, nitrobenzyl alcohol matrix):  $m/z$  623.3 ( $\text{M}+\text{H}$ ), 536.2 ( $\text{M}^+$  - morpholine).

**(b) General Methods, Photolyses, and Quantum Yield Determinations.** Spectroscopic grade solvents were used for all photolyses, except for butyronitrile (98%), which was fractionally distilled three times, each time discarding the first and last fractions. Methylene chloride and benzene were "dampened" by shaking in a separatory funnel with a small amount of water. All irradiations were carried out in vacuum-degassable sample tubes (vacuum-degassed through 6-8 freeze/pump/thaw cycles until a pressure of  $3 \times 10^{-6}$  Torr was reached, and sealed with a torch). A similar apparatus for NMR experiments was made by fusing an NMR tube onto a reservoir cell (5-10-mL round-bottom flask). All solution preparation, degassing, and detection was performed in a darkroom under dim red light.

Photoredox products were analyzed using  $^1\text{H}$  NMR and IR as previously described. UV/vis absorbance measurements were performed on a Hewlett-Packard 8451A diode array spectrometer. High-pressure liquid chromatography was performed on a Waters 990 HPLC with photodiode array detection. A normal phase column (silica packed) was used with 60:40 chloroform/hexane eluent. GC/MS analysis was carried out on a Hewlett-Packard HP 5890 gas chromatogram with an HP 590 series mass selective detector.

**Photolysis.** Irradiations for qualitative purposes were performed using a 200-W high pressure mercury lamp with a monochromator set at 313 (anthraquinone acceptors) or 436 nm (dicyanoanthracene acceptors). Irradiations for quantum yield determinations were carried out in a merry-go-round with a 450-W mercury lamp. For anthraquinone systems, a Corning 0-52 filter (340 nm cutoff) was used. A combination of Corning filters 3-73 and 7-59 was used for photolyses of **2** and **3** to isolate the 436-nm spark.

**Quantum Yield Determinations.** For the anthraquinone methyl ester (**4**) sensitized systems, vacuum degassed solutions were prepared

containing  $1 \times 10^{-4}$  M **4** and concentrations of **1** which varied from  $1 \times 10^{-4}$  to  $5 \times 10^{-3}$  M in acetonitrile and  $1 \times 10^{-4}$  to  $5 \times 10^{-2}$  M in methylene chloride. These Solutions were irradiated in parallel in a merry-go-round with vacuum degassed solutions of anthraquinone  $1 \times 10^{-4}$  M in ethanol as a secondary actinometer.<sup>52</sup> Reactions were monitored by periodically measuring the acceptor absorbances on a UV/Vis spectrometer. The extent of reaction was measured as a function of the bleaching of the acceptor  $\lambda_{\text{max}}$  ( $n-\pi^*$ ) at  $\sim 330$  nm.<sup>53</sup> Samples were irradiated to  $\sim 10\%$  conversion. Double reciprocal plots ( $1/\phi$  vs  $1/[\text{diamine}]$ ) were prepared and the quantum yields were extrapolated to infinite concentration of donor. Solutions of the linked compound **5** ( $1 \times 10^{-4}$  M) in the various solvents were similarly photolyzed. The quantum yields in this case were assumed to be for 100% quenching, and no further corrections were used.

For the cyanoanthracene systems, solutions of **1** ( $4.5 \times 10^{-3}$  M) and **2/3** ( $3.5 \times 10^{-5}$  M) were degassed and photolyzed in a merry-go-round in parallel with ferrioxalate actinometers.<sup>54</sup> Bleaching of the dicyanoanthracene absorbance was monitored periodically, and the reactions were driven to  $\sim 10\%$  conversion. Fluorescence quenching experiments were then performed using a SPEX 111CM Fluorolog fluorimeter with a 150-W xenon lamp on solutions containing  $1 \times 10^{-5}$  M **2** or **3**, degassed by bubbling with argon for 20 min. The quantum yields were corrected to 100% quenching.

**Acknowledgment.** This work was supported by the Department of Energy (Grant No. DE-FG02-86ER13504). We are grateful for the helpful suggestions of Drs. Hong Gan, Samir Farid, Joseph Dinnocenzo, Joshua Goodman, and Jack Kampmeier.

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