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Anilide Linker Group as a Participant in Intramolecular Electron Transfer

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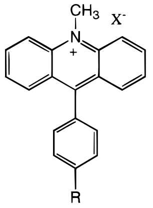
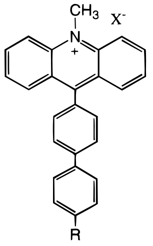
The photochemical properties of derivatives of 10-methylacridinium ion that have been modified by substitution with anilide moieties (e.g., $-C_6H_4NHCO-$) at the 9-position have been examined. Intramolecular electron transfer involving the anilide group as electron donor and the acridinium ring as electron acceptor was verified by observation of the quenching of fluorescence associated with the local acridinium chromophore and by the recording of electron transfer phototransient spectra in the picosecond time domain. The amidobiphenyl linkage was a superior electron donor and displayed rapid forward and reverse photoinduced electron transfer with rate constants for the latter reaching 5.2×10^{11} s^{-1} (CH_3CN solvent).

The combination of amide bonds and benzene rings has provided a common linkage (e.g., an anilide spacer, $-C_6H_4$-$NHCO-$) for a variety of systems in which electron or energy transfer agents are tethered together.[1,2] This assembly proves to be versatile in terms of synthesis of complicated arrays, since donors and acceptors can each carry unique amine and carboxylic acid functions that are reliably connected via condensation. Linkages involving porphyrins and other chromophores or redox active groups have been prominent among the examples of linked donor−acceptor systems that display this synthetic strategy. These arrays are frequently prepared for the study of photoinduced charge separation that in most cases occurs across the anilide link. The capacity of the amide link to function as a redox auxiliary can be assessed in part in terms of single-parameter substituent constants, which reveal that the NHCOR group is moderately electron withdrawing [0.22 and 0.08 for Hammett σ (meta) and σ (para) constants and 1.68 for the Taft σ^* parameter[3,4]]. Dual parameter analyses that take into account the electrostatic and covalent contributions to substituent constants[5] reveal a dominant "covalent" constant ($\Delta C_x = 0.26$), indicative of moderate electron donating capability for $NHCOCH_3$. Consistent with this finding is the reduction of the ionization potential of benzene (9.2 eV) on introduction of the amide group in acetanilide (8.4 eV)[6] which shows a pronounced stabilizing influence for NHCOR in radical cation formation.

As part of a photochemical study of linkages that involve the 10-alkyl acridinium ion as electron acceptor and a variety of substituent groups at the 9-position,[7,9] we have employed the benzanilide group ($-C_6H_4NHCO-$) as a molecular spacer. During these investigations, we have established that this common link can serve as a discrete electron donor. For a series of rigidly linked systems, we have determined the dependences of electron transfer rates on solvent and on changes in structure for the 9-aryl group, features that allow a better understanding of this linkage and its potential for photochemical reaction. The anilide link results in surprisingly fast nonradiative deactivation of excited species via reversible electron transfer. The results bear on the problem of the effectiveness of various bridges, particularly those carrying aromatic rings and π conjugation, in providing long-range communication for electron transfer via charge hopping or superexchange mechanisms.[10]



1, R = H
2, R = $NHCOC_6H_5$



3, R = H
4, R = $NHCOC_6H_5$

Experimental Section

Materials and General Procedures. Silica gel 40 μm (230−400 mesh, Baker) was employed as stationary phase for flash column chromatography (typically 2.5 cm (ID) × 32 cm for a 0.5−1.0 g of sample of crude product). Solvents composed of 5−30% acetone in chloroform, which gave an R_f for product of 0.2−0.3 on TLC (silica gel 60 F254), were used for elution of the acridinium salts. Half-wave potentials for acridinium PF_6^- salts were determined by cyclic voltammetry (nitrogen-purged acetonitrile solutions at 22 °C with tetrabutylammonium perchlorate serving as supporting electrolyte) using an EG&G Princeton Applied Research model 273 potentiostat/galvanostat and a platinum bead working electrode. Electron densities and optimum geometries were obtained by computation using the MOPAC algorithm (QCPE program no. 455, version 6.0) on a Silicon Graphics 4D/340 computer. A total charge of +1 was specified for calculations for ground (S_o) and first excited singlet (S_1) states for each acridinium species using the MNDO Hamiltonian (limited configuration interaction, four configurations, for S_1 calculations). For optimized geometries, the dihedral angles made by aromatic ring planes were found to be approximately 90° (±10°).

Corrected emssion spectra were recorded on an SLM 48000 phase-shift spectrofluorimeter. Fluorescence quantum yields

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were determined using methods previously described for Ar-purged samples, referenced to 10-methylacridinium chloride in water ($\Phi_f = 1.0$).[9] The transient absorption apparatus[11] consisted of a regeneratively amplified Ti:sapphire laser system that produced ca. 130 fs pulses which were frequency doubled to provide 1−5 μJ excitation pulses at 417 nm.

9-{4-[(Benzoylamino)phenyl]}-10-methylacridinium Hexafluorophosphate (2). To a stirred solution of benzoyl chloride (5.0 mL, 35 mmol) in 60 mL of acetonitrile at 0 °C was added 9-(4-aminophenyl)-10-methylacridinium hexafluorophosphate[12] (3.1 g, 7.2 mmol) in 40 mL of acetonitrile and an aqueous solution of K_2CO_3 (2.5 g in 30 mL). The resulting mixture was stirred at room temperature for 1 h. After CH_3CN was removed, a 5% HCl/H_2O solution (30 mL) was added. The aqueous solution was extracted with $CHCl_3$ (2 × 75 mL); the combined organic portions were dried with Na_2SO_4. The product was obtained by evaporation of the organic extracts in vacuo and purified by flash chromatography (acetone: chloroform = 1 : 4). Recrystallization from acetone:ethanol (1:7) gave 3.0 g (78%) of bright yellow crystals (mp 275−277°); ^1H NMR (400 MHz, acetone-d_6) δ 10.01 (s, 1H), 8.93 (d, $J = 9.2$ Hz, 2H), 8.54 (t, $J = 7.6$ Hz, 2H), 8.31 (d, $J = 8.4$ Hz, 2H), 8.26 (d, $J = 8.8$ Hz, 2H), 8.08 (d, $J = 8.0$ Hz, 2H), 8.03 (t, $J = 8.0$ Hz, 2H), 7.67 (t, $J = 8.8$ Hz, 2H), 7.58 (t, $J = 7.6$ Hz, 1H), 5.16 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 167.0, 162.7, 142.9, 142.6 (2C), 139.7 (2C), 136.0, 132.9, 132.0 (2C), 131.3 (2C), 129.5 (2C), 129.2 (2C), 128.8 (2C), 128.5 (2C), 127.3, 121.0 (2C), 119.7 (2C), 39.6; LRMS (EI, 70 eV) *m/z* (relative intensity) 390 ($(M + 1)^+$, 54), 389 (M^+, 43), 375 (100), 374 (43), 299 (121), 271 (66), 195 (24), 194 (88), 107 (19); HRMS (EI, 70 eV) *m/z* 389.1645 (M^+, calcd for $C_{27}H_{21}N_2O^+$ 389.1654).

9-[4-(4′-Benzoylamino)-4-biphenylyl]-10-methylacridinium Hexafluorophosphate (4). To a stirred solution of 9-(4′-amino-4-biphenylyl)-10-methylacridinium hexafluorophosphate[13] (1.0 g, 2.0 mmol) in 60 mL of acetonitrile at 0 °C was added benzoyl chloride (2 mL, 17 mmol) and aqueous Na_2CO_3 (1 g in 15 mL of water). The workup procedure followed that described for **2**. The crude product was purified by flash chromatography (acetone:chloroform = 1:3), followed by recrystallization from acetone:ethanol (1:5) to yield 1.2 g (96%) of yellow crystals (mp > 300 °C); ^1H NMR (400 MHz, acetone-d_6) δ 9.75 (s, 1H), 8.96 (d, $J = 9.2$ Hz, 2H), 8.56 (t, $J = 8.0$ Hz, 2H), 8.26 (d, $J = 8.8$ Hz, 2H), 8.14 (d, $J = 8.0$ Hz, 2H), 8.10 (d, $J = 8.4$ Hz, 2H), 8.05 (d, $J = 8.8$ Hz, 1H), 8.04 (t, $J = 6.8$ Hz, 2H), 7.92 (d, $J = 8.8$ Hz, 2H), 7.76(d, $J = 8.0$ Hz, 2H), 7.62 (t, $J = 7.6$ Hz, 1H), 7.56 (t, $J = 8.0$ Hz, 2H), 5.19 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 164.6, 162.4, 150.4, 149.3, 144.3, 141.8, 138.8 (2C), 131.9 (2C), 131.5, 130.8 (2C), 130.3 (2C), 129.5 (2C), 128.4 (2C), 127.9 (2C), 127.4 (2C), 127.3 (2C), 126.8 (2C), 126.2 (2C), 120.5 (2C), 118.8 (2C), 38.7; LRMS (EI, 70 eV) *m/z* (relative intensity) 466 ($(M + 1)^+$, 93), 465 (M^+, 45), 451 (79), 450 (96), 346 (52), 345 (42), 217 (32), 202 (52), 201 (79), 195 (70), 194 (100), 180 (28), 79 (58); HRMS (EI, 70 eV) m/z 465.1957 (M^+, calcd for $C_{33}H_{25}N_2O^+$ 465.1967).

Results and Discussion

The benzanilide derivatives, **2** and **4**, were prepared as PF_6^- salts by reaction of benzoyl chloride with, respectively, 9-(4-aminophenyl)-10-methylacridinium and 9-(4′-aminobiphenylyl)-10-methylacridinium salts (available, along with **1** and **2**, through procedures reported previously[8,12,13]). The absorption spectra for PF_6^- salts of **1** and **2** in various solvents were similar (long and short axis transitions associated with the acridinium chromophore at about 360 and 430 nm[8,9]), but for **2** a perturbation of the longer wavelength band due to the substituent in the 9-position was apparent. The change for **2** was more pronounced in less polar solvents such as CH_2Cl_2 ($\lambda_{max} = 453$ nm, $\epsilon = 8.1 \times 10^3$ M^{-1} cm^{-1}, see Figure 1). The red shift and increase in absorptivity for 9-substituted acridiniums (noted also for **4**, see Figure 1) has been discussed previously in terms of the imposition of an excited state having charge-transfer character.[8,9,12]

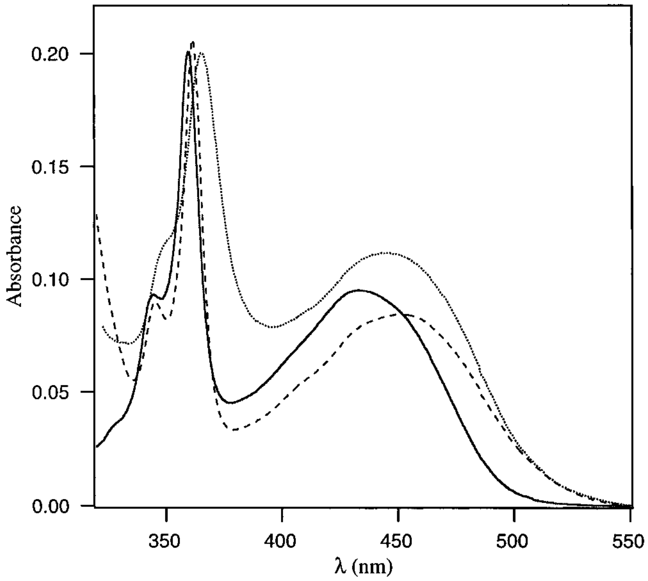


Figure 1. Absorption spectra for **2** in CH_3CN (—) and CH_2Cl_2 (− −) and for **4** in CH_2Cl_2 (···).

TABLE 1: Spectral Data, Fluorescence Quantum Yields and Phototransient Decay Times for Acridinium Salts

	CH_2Cl_2				CH_3CN			
compd	λ_a (nm)	λ_f (nm)	ϕ_f[a]	τ (ns)	λ_a (nm)	λ_f (nm)	ϕ_f[a]	τ (ns)
1	430	500	0.085	2.5[b]	424	496	0.063	1.5[b]
2	454	566	0.10	0.65	433	485	0.051	0.021
3	437	561	0.13	5.2	428	628	0.020	1.2
4	454	504	0.0006	0.072	431	~500	<0.0005	0.0019

[a] Deaerated solutions of 10 μM dye; fluorescence excitation at 360 nm. [b] Fluorescence lifetimes (ref 9).

The appearance of close-lying local (LE) and "charge-shift" (CSH) excited states was further confirmed on examination of fluorescence spectra (Figure 2). Notably, the emission from **2** (CH_3CN) peaked at 490 nm, similar to spectra assigned to local acridinium fluorescence for **1**,[9] but developed a noticeable tail that extended past 550 nm. The red-shifted fluorescence associated with the CSH state was more notable for **2** in less polar solvents such as benzene or CH_2Cl_2 (Figure 2A); the ensemble of spectra for different solvents was most readily interpreted in terms of mixtures, to varying degrees, of LE fluorescence (490−500 nm) and a CSH component of emission appearing at 525−610 nm. The fluorescence observed for **4** was weaker than that of **2** and and generally showed more of the longer wavelength CSH component (Figure 2B). Quantum yields of emission for both **2** and **4** are reported for two solvents in the Table 1, along with comparable data for **1** and **3** which have been previously reported.[8,9]

The trends can be rationalized in terms of the three state model that has been proposed for other donor-substituted acridinium ions (Scheme 1).[8,9,12] The local LE emission associated with the acridinium chromophore is quenched on introduction of an electron donor group in the 9-position. Local excited species produce CSH excited states on a sub-picosecond

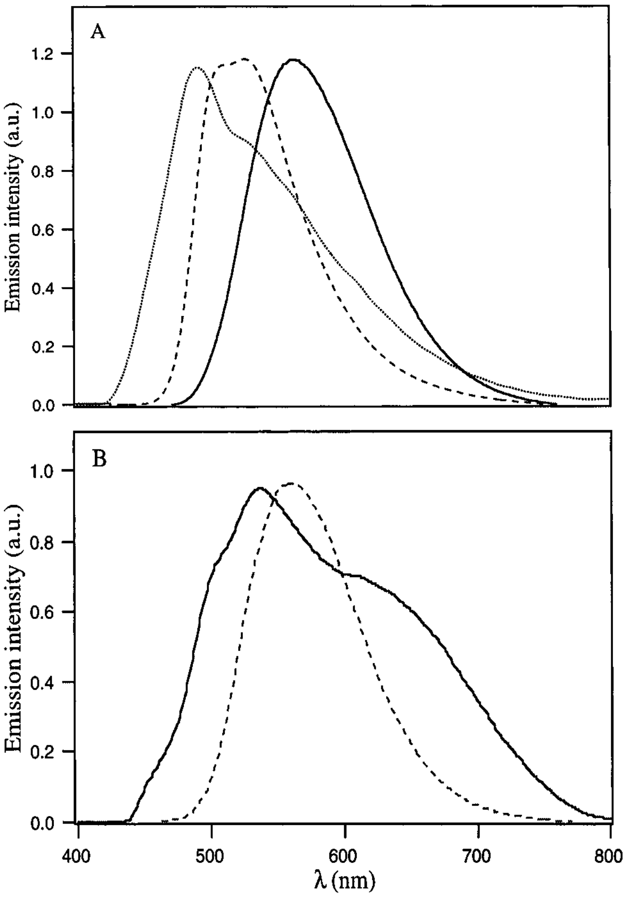
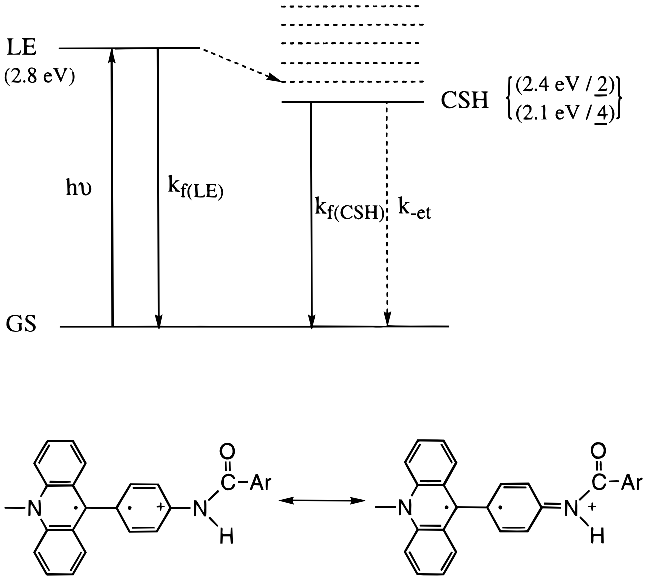


Figure 2. Fluorescence spectra for **2** (upper panel) and **4** (lower panel) in CH_3CN (•••), C_6H_6 (— —), and CH_2Cl_2 (—); excitation wavelength = 370 nm.

SCHEME 1



time scale;[8] the latter give rise to fluorescence that appears (when cleanly resolved) at 550−650 nm. According to the fluorescence data, the CSH species is spaced closely below the LE state for **2**. An assessment of the energetic placement of these states was made by measurement of redox potentials. Oxidation waves were observed by cyclic voltammetry and half-wave potentials recorded at scan rates of 50 mV/s (quasi-reversible behavior for **2**); for **2** and **4**, $E_{1/2}(\text{ox}) = 1.86$ and 1.58 V vs SCE, respectively. Reduction of the acridinium moiety is reversible with $E_{1/2} = -0.62$ V vs SCE for **4** in acetonitrile.

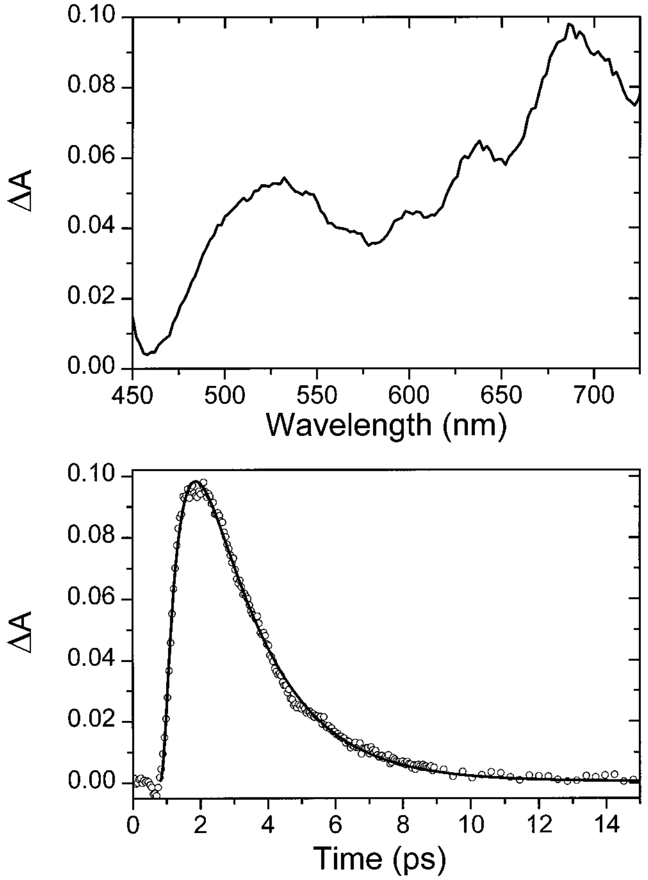


Figure 3. (a) Transient absorption spectrum at 1.0 ps time delay on excitation at 417 nm of **4** in CH_3CN, (b) decay profile for phototransient monitored at 700 nm.

The energy for the LE state was determined by the approximate placement of the 0−0 band from the intersection of absorption and LE fluorescence spectra. Since the biphenyl link serves as a better electron donor, the CSH state appears further below the LE state (Scheme 1), consistent with the observation of fluorescence for **4** that is further red-shifted compared to that for **2** (most notably for benzene solvent, see Figure 2). Stabilization of the CSH intermediates depends on delocalization of positive charge into the amide functionality (see Scheme 1, which includes resonance forms depicting the CSH state for **2**) and the interaction of an altered charge distribution with solvent.[14]

Calculations employing the MOPAC algorithm revealed a qualitative ordering for the changes in dipole moment that occur on photoexcitation. Charge density patterns resulted in μ values for ground and lowest excited states for **1** of 4.0 and 2.8 D, respectively (with positive charge localization in the acridinium ring). For **2,** a reversal and reduction in dipole moment is observed on proceeding from ground state (13.9 D) to the low-lying CSH state (5.74 D).[14] The red shift of CSH emission observed for **2** and **4** in less polar solvents is consistent with the larger size of the ground state dipole moment for these ions (i.e., relative destabilization of a more charge-localized ground state for lower polarity solvents).

The electron transfer characteristics for the acridinium derivatives were studied further, using fs laser flash photolysis methods. Flash excitation of **2** at 417 nm yielded a a transient at 520 nm, similar to that previously assigned to the reduced acridinyl radical species,[8,15] whereas photolysis of **4** resulted in a transient that absorbed with $\lambda_{\max} = 525$ and 685 nm (Figure 3). The longer wavelength phototransient is associated with the biphenyl radical cation and its simple derivatives.[16] The formation of radical (ion) transients, which grew in shortly following the laser pulse (rise times ranging 0.5−1.5 ps), was similar to the observations of distinct radical−ion absorption that have been previously associated with acridinium ions having substituents in the 9-position with moderate-to-strong electron donor properties.[8] The resolution of distinct bands in these spectra is consistent with a decoupling of the electron donor and acceptor groups that are joined at the meso position of the acridine ring, reminiscent of the arrays associated with twisted intramolecular charge transfer intermediates (TICT states).[7,17]

Measured decay times for **2** and **4** along with those reported for **1** and **3**,[8,9] showed significant variations (Table 1). Some comparisons further support a mechanism of intramolecular electron transfer and LE → CSH interconversion for the ions bearing the NHCOR group. The decay times are significantly shorter for **2** (Table 1) than the values recorded for **1** (a measurement of CSH fluorescence decay).[9,18] The decays observed in the ps regime for **4** contrast also with the ns decay times obtained for transients derived from the unsubstituted biphenyl derivative **3** in nonpolar and polar solvents.[8,9] We assume a mechanism of transient depletion for **2** and **4** that involves simple return of CSH intermediates to the ground state via back electron transfer ($k_{-\mathrm{et}}$, Scheme 1), although some population of a local triplet state is possible.[9] The faster return of the lower lying CSH state to the ground state for **4**, (in comparison with rates for **2**) is consistent with the proposed model in which the reverse charge shift for the acridiniums occurs in the inverted region of the dependence of electron transfer rate constant on driving force.[8,20]. The very fast decay rates for **2** and **4** may be due to the provision by the amide groups of high frequency (N−H and C=O) accepting vibrational modes[21] that facilitate the radiationless transition of CSH species to the ground state.[22]

In conclusion, it has been demonstrated that the common linker group, $-C_6H_4NHCO-$, can serve as a donor in electron transfer with a directly linked acceptor having an excited state reduction potential $[E_{1/2}(\mathrm{red}) + E_{00}]^{20} \geq 1.9$ V vs SCE. It would appear that a large number of chromophores having (0−0) transitions to low-lying excited states of about 2.5 eV (absorption < 500 nm) could engage in electron transfer with a closely linked (strongly coupled) anilide group. It is of some consequence as well to observe that the amide subunit (−NHCO−), also commonly found in conjunction with aromatic rings in various donor−acceptor arrays, may also play a special role in the control of electron transfer rates by providing (high-frequency) vibrations that enhance Franck−Condon factors for connecting initial and product states.

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References and Notes

(1) For example, see: Hermant, R. M.; Liddell, P. A.; Lin, S.; Alden, R. G.; Kang, H. K.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1993**, *115*, 2080. Gust, D.; Moore, T. A.; Moore, A. L.; Devadoss, C.; Liddell, P. A.; Hermant, R.; Nieman, R. A.; Demanche, L. J.; DeGraziano, J. M.; Gouni, I. *Ibid.* **1992**, *114*, 3590. Lindsey, J. S.; Brown, P. A.; Siesel, D. A. *Tetrahedron* **1989**, *45*, 4845.

(2) Kurreck, H.; Huber, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 849. Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198. Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.

(3) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Harper and Row Publishers: Cambridge, 1987; Chapter 2.

(4) Dean, J. A., Ed. *Lange's Handbook of Chemistry*, 12th ed.; McGraw Hill Book Co.: New York, 1979; Section 3.

(5) Drago, R. S. *Applications of Electrostatic-Covalent Models in Chemistry*; Surfside Scientific Publishers: Gainesville, 1994, Chapter 7.

(6) Franklin, J. L.; et al. *Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions; National Standard Reference Data Series*; National Bureau of Standards, U.S. Government Printing Office: Washington, DC, 1969.

(7) Jones, G., II; Farahat, M. S. In *Advances in Electron Transfer Chemistry*, Mariano, P. S., ed.; JAI Press: Greenwich, 1993; Vol. 3, Chapter 1.

(8) Jones, G., II; Farahat, M. S.; Greenfield, S. R.; Gosztola, D. J.; Wasielewski, M. R. *Chem. Phys. Lett.* **1994**, *229*, 40.

(9) van Willigen, H; Jones, G., II; Farahat, M. S. *J. Phys. Chem.* **1996**, *100*, 3312.

(10) Helms, A.; Heiler, D.; McLendon, G. *J. Am. Chem. Soc.* **1992**, *114*, 6227. Osuka, A.; Satoshi, N.; Maruyama, K.; Mataga, N.; Asahi, T.; Yamazaki, I.; Nishimura, Y.; Ohno, T.; Nozaki, K. *Ibid.* **1993**, *115*, 4577. Onuchic, J. N.; Beratan, D. N. *Ibid.* **1987**, *109*, 6771. Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440.

(11) Greenfield, S. R. Svec, W. A.; Gosztola, D.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 2041.

(12) Jonker, S. A.; Ariese, F.; Verhoeven, J. W. *Recl. Trav. Chim. Pays-Bas* **1989**, *108*, 109.

(13) Yan, D. X. Ph.D. Dissertation, Boston University, 1997.

(14) The effects of ion pairing for acridinium CSH systems in less polar media are presently under investigation, as well as direct determination using Stark spectroscopy of the changes in dipole moment on photoexcitation.

(15) Poulos, A. T.; Hammond G. S.; Burton, M. E. *Photochem. Photobiol.* **1981**, *34*, 169.

(16) Gould, I.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290.

(17) Rettig, W.; Baumann, W. *Prog. Photochem. Photophys.* **1992**, *6*, 79.

(18) The nonradiative decay feature that reduces the fluorescence yield and lifetime for **1**, compared with 10-methylacridinium ion[9] involves an interring twist or "free rotor" decay that has been established for a number of linked π systems.[19] On flash photolysis **1** displays weak LE state transient absorption at 480−500 nm, along with stimulated emission at 500−530 nm.

(19) Velsko, S. P.; Fleming, G. R. *J. Chem. Phys.* **1982**, *76*, 3553. Zimmerman, H. E.; Kamm, K. S., Wethemann, D. P. *J. Am. Chem. Soc.* **1975**, *97*, 3718.

(20) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(21) Jortner, J. *J. Chem. Phys.* **1976**, *64*, 4860. Chen, X. G.; Schweitzer-Stenner, R.; Krimm, S.; Mirkin, N. G.; Asher, S. A. *J. Am. Chem. Soc.* **1994**, *116*, 11141.

(22) The appearance of longer wavelength fluorescence for **4** is very solvent sensitive and perhaps indicative of other specific vibrational features (i.e., the imposition of two CSH intermediates, one less twisted and a second more twisted with regard to the biphenyl link, note maxima near 525 and 630 nm, CH_2Cl_2 solvent, Figure 2B).