

Donor–Acceptor Interaction and Photochemistry of Polymethylene-Linked Bichromophores in Solution

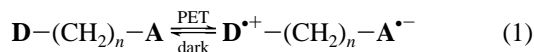
Song-lei Zhang, Matthew J. Lang, Steven Goodman,[†] Christopher Durnell, Vlastimil Fidler,[‡] Graham R. Fleming, and Nien-chu C. Yang*

Contribution from the Department of Chemistry, University of Chicago, Chicago, Illinois 60637

Received July 17, 1996[⊗]

Abstract: The ground-state and the excited-state spectroscopic properties of four series of polymethylene-linked anthracene–dialkylaniline bichromophores were compared as a probe to the relationship between energetics and distance in photoinduced electron transfer (PET). The results demonstrate that, when the energy level of the charge-transfer (CT) state is lowered below that of the localized excited state by appropriate substituents, there is a strong electron–donor–acceptor (EDA) interaction in the ground state which is absent in other bichromophores. Absorption and fluorescence excitation studies revealed that there is an unusually strong EDA interaction in the ground state of **A-2** which is absent in other members in the **A** series. When **A-2** is excited directly into this EDA absorption, it exhibits two CT emissions, one at 490 nm and the other at 605 nm. The quantum yield (τ_f) and the lifetime (Φ_f) of the two emissions are dependent on the viscosity of the alkane solvent. The Φ_f and the τ_f of the 490 nm emission increased when the solvent viscosity was increased; however, those of the 605 nm emission remained essentially unchanged. The risetime of the 605 nm emission is 420 ps, but that of the 490 nm emission is instrument-function limiting. The results suggest that the two CT emissions may be derived from the two different conformations of the CT state. The 490 nm emission may be derived from the trans conformer of **A-2**, which is the major conformer at equilibrium. The EDA interaction in the trans conformer of **A-2** may be treated as a type of through- σ -bond interaction via the spacer between the n orbital of the anilino nitrogen and the π orbital of the anthryl group. The direct excitation of **A-2** from its EDA ground state to the CT state indicates that PET may occur in a σ -linked bichromophoric system upon light absorption, thus reaching the limiting rate of a photochemical process.

Photoinduced electron transfer (PET) of organic compounds converts light energy into a chemical potential. It is the fundamental process in many photochemical and photobiological processes.¹ Since the back electron transfer from the radical ions generated in PET is a thermodynamically favorable process, the efficiency of PET depends on both the rate of PET and the rate of back-electron transfer. Therefore, for an efficient PET to occur, the rate of PET must be fast while the rate of the back electron transfer from radical ion products must be slow (eq 1). Contributions by Closs and Miller² showed that the rates



of electron transfer in the ground state of σ -linked bichromophoric systems vary with the free energy change of the process. The rate increases as the free energy becomes more favorable until it reaches a maximum. Beyond this point, the rate begins to decrease as the free energy change becomes more favorable, a theoretical prediction made by Marcus³ and known as the “inverted region” of rate dependence on the free energy change in chemical reactions. Therefore, the rate of back electron transfer may be controlled by varying the free energy change of the transfer. It has been suggested that, in contrast to the ground-state electron transfers, there is a lack of Marcus inverted region in PET, or charge separation (CS).

[†] National Science Foundation Undergraduate Research Participant, 1994.

[‡] On leave from the Charles University, Prague, Czech Republic.

[⊗] Abstract published in *Advance ACS Abstracts*, September 15, 1996.

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Weller and his co-workers have made pioneering and continuing contributions on intermolecular PET and PET in bichromophoric systems.⁴ Notable contributions in this area have been made in the laboratories of Gust,⁵ Mataga,⁶ Verhoeven,⁷ Paddon-Row,⁸ Wasielewski,⁹ and other scientists.¹⁰

The polymethylene-linked anthryl–dialkylanilino bichromophoric systems, **D** and **E**, are among the most intensively studied systems in photochemistry. Due to the flexibility of the polymethylene linkage, the localized excited state (LE) anthryl group may interact with the anilino donor after suitable conformational changes to form the charge-transfer (CT) state, which may decay with a red-shifted CT emission (Figure 1).

Verhoeven and Paddon-Row studied the PET in rigidly spaced and semirigidly spaced naphthyl–amino bichromophoric systems.^{7,8} They demonstrated that, under favorable energetic conditions, PET may occur in their systems prior to their conformational changes to yield a radical ion pair which

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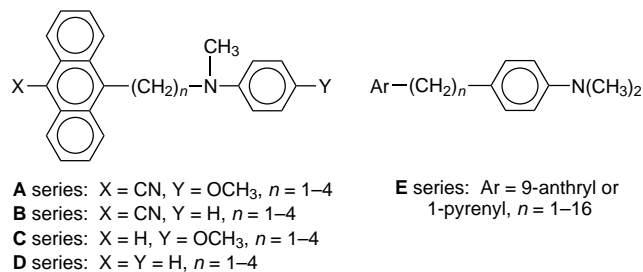
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undergoes “harpooning” via Coulombic interaction to form the product.⁷ Wasielewski, Yang, and co-workers studied a rigidly spaced anthryl–dimethylanilino system and demonstrated the ionic character of the emissive product from PET in their system.¹¹

The polymethylene-linked anthryl–dialkylanilino bichromophoric systems **A–D** offer many advantages for the study of intramolecular PET: (i) the free energy change in PET may be varied over a wide range (relative to **E**^{4,6}) by the introduction of substituents into either or both of its chromophores;¹⁰ (ii) the anthryl group is the simplest aromatic system having a low-lying L_a excited state with a more intense absorption and a larger substituent effect than the low-lying L_b state in other common aromatic systems;¹² (iii) anthryl groups absorb light at a wavelength substantially longer than that of the anilino donor and may thus be excited selectively; (iv) the conformation of lower members of the homologous series may be readily analyzed, and thus the conformation analysis will enable scientists to understand not only the conformation of the ground state of the substrates but also the conformation of radical ion products.¹³

Recent studies on the PET in the polymethylene-linked bichromophoric systems **C** and **D** in a supersonic jet indicate that when the energy level of the CT state of **C-2** is lowered by substitution to approximately the same level as that of the LE anthryl state, the ground state of **C-2** may mix with the CT state to form an electron–donor–acceptor (EDA) complex which may be photoexcited directly to the CT state; i.e., photoexcitation may become the rate-limiting step for PET (Figure 1).¹⁴ However, such mixing in **C-2** was very weak. This report deals with the photochemical and photophysical behaviors of two polymethylene-linked bichromophoric systems. Both systems contain a 10-cyano-9-anthryl acceptor, with one containing a 4-methoxy-*N*-methylanilino donor, **A**, and the other containing a *N*-methylanilino donor, **B**. Cyano substituents are known to increase the electron affinity (EA) of aromatic compounds appreciably. Introduction of a cyano substituent at the 9-position of anthracene is known to increase its EA by 0.67 eV¹⁵ and its $E_{1/2(\text{red})}$ in acetonitrile by 0.39 eV.¹⁶ This increase would enhance the mixing between the ground state and the CT state in **A-2** and would also extend the range of its PET.

Using the following literature values of ionization potential (IP) of 4-methoxy-*N,N*-dimethylaniline, 7.22 eV,¹⁷ and of its

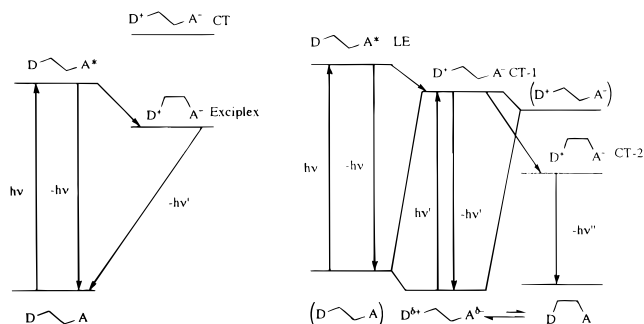


Figure 1. (a, left) Schematic representation of PET of bichromophoric systems involving conformational changes after initial excitation. (b, right) Schematic representation of PET of bichromophoric systems involving direct excitation of the EDA complex.

$E_{1/2(\text{ox})}$ in acetonitrile, 0.59 eV,¹⁸ we estimated that **A-2** may undergo PET over a distance of 5.4 Å in the gas phase and in alkanes (eqs 2 and 3).¹⁹ This value is appreciably longer than

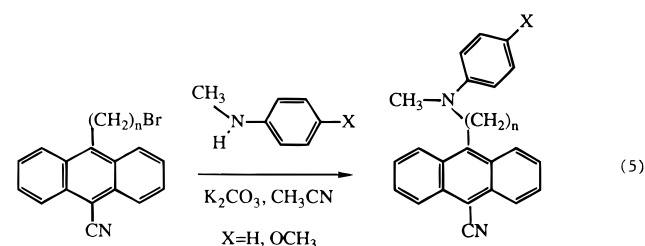
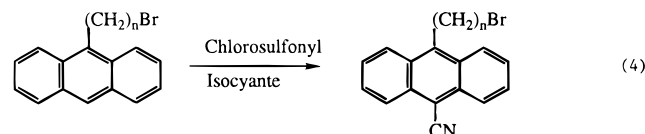
$$hv_{0,0} > e[\text{IP}(\text{D}) - \text{EA}(\text{A})] - e^2/r \quad (2)$$

$$hv_{0,0} > e[E_{1/2(\text{ox})}(\text{D}) - E_{1/2(\text{red})}(\text{A})] - e^2/\epsilon_s R_c - e^2(1/37 - 1/\epsilon_s)/r \quad (3)$$

the distance between the anilino N and the edge of the anthryl group (4.0 Å) of **A-2** in the trans conformation and is somewhat higher than the distance between anilino N and the center of the anthryl group in the same conformation (5.3 Å).

Experimental Section

General Procedures. 9-(*ω*-Bromoalkyl)anthracenes were synthesized by known methods,²⁰ and were converted into 9-(*ω*-bromoalkyl)-10-cyanoanthracenes by the direct cyanation using chlorosulfonyl isocyanate (reaction 4).²¹ Compounds **1** and **2** were synthesized from



the displacement of the corresponding bromide by either *N*-methylaniline or *N*-methylanisidine (reaction 5). All solvents used for the synthesis were the HPLC grade from Aldrich and used as they were received. THF was distilled from sodium benzophenone ketyl under N₂ immediately before use. Melting points were taken on a Fisher-Jones MP apparatus and were uncorrected. Proton NMR data were obtained on a custom constructed DS-1000 500 MHz NMR spectrometer. Carbon-13 NMR data were taken on a GE-300 NMR spectrometer at 75 MHz. IR spectra were taken on a Nicolet 20SX FTIR spectrometer. Mass spectra were taken on a VG mass spectrometer.

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UV-visible spectra were taken on a Perkin-Elmer Lambda-6 spectrometer. Elemental analysis were done by the Midwest Microlab, Indianapolis, IN.

Fluorescence Studies. All solvents used for the fluorescence studies were spectrophotometric grade purchased from Aldrich and were checked by fluorescence spectroscopy to make sure that they contained no fluorescent impurities before use. All steady-state fluorescence spectra were measured at 22 ± 1 °C on a Perkin-Elmer MPF-66 spectrofluorometer with an integrated electronic corrected spectra unit and a thermostatic sample compartment. Spectra were corrected below but not above 600 nm, which is the limit of the dye fluorescence. Wavelength resolution was determined by the excitation and emission monochromator slits, which were normally set at the same value.

The fluorescence quantum yields of the compounds were measured by using 9-methylanthracene as the secondary standard ($\Phi = 0.36$).²² A solution of 9-methylanthracene in methylcyclohexane was prepared with the same absorbance ($OD \sim 0.1$) as the samples at the (0–1) band of the anthryl chromophore absorption, and degassed for at least five freeze–pump–thaw cycles. Their fluorescence spectra were measured under the same operating conditions and settings. Quantum yields were determined by plotting the sample spectrum and the standard spectrum in wavenumbers (cm^{-1}) with the same frequency and intensity scales and by comparing the area underneath the spectrum of the sample with the standard by the “cut-and-weigh” method. When the fluorescence of compounds with low quantum efficiencies (~ 0.001) were measured, it was often necessary to use another compound with a known quantum yield comparable to the unknowns as a secondary standard. The spectra were then scanned 10–20 times to get the average in order to improve the signal-to-noise ratio. When the spectra consisted of overlapping fluorescence bands, they were plotted out and resolved by comparison with a model compound. Fluorescence excitation spectra were measured by setting the emission wavelength at the maximum of either the locally anthryl emission or the charge-transfer emission.

Fluorescence lifetimes were measured by using the time-correlated single-photon-counting technique previously described.²³ A 295 nm excitation pulse with fwhm of 8–10 ps is generated using a frequency-doubled, cavity-dumped Rhodamine 6G dye laser, synchronously pumped by an argon ion laser (Coherent Radiation), mode-locked at 514.5 nm. Sample fluorescence was monitored by a microchannel plate PMT (Hamamatsu R2809U) through a JY H20 monochromator (SA Instruments) with an 8 nm band-pass and a W335 cutoff filter. The instrument function was obtained by scattering the excitation light off an aqueous suspension of nondairy creamer and had a fwhm of 50 ps. Decays were collected up to 10 000 counts at the peak channels with a duration of 25 ps/channel. The variable-temperature experiments were performed by using a Neslab RTEA thermostat.

Synthesis of 1A, 1B, 2A, 2B, 3A, 3B, 4A, and 4B. To a solution of *N*-methylaniline or *N*-methyl-*p*-anisidine in CH_3CN was added Na_2CO_3 (2.0 equiv) and 9-(bromoalkyl)-10-cyanoanthracene (1.0 equiv). The mixture was kept under reflux for 24 h. The solvent was evaporated under reduced pressure. The mixture was purified by flash column chromatography over silica (hexane– CH_2Cl_2) and by recrystallization from methanol to yield **1A**, **1B**, **2A**, **2B**, **3A**, **3B**, **4A**, and **4B** (60%–80%).

9-[(*N*-Methyl-*N*-phenylamino)methyl]-10-cyanoanthracene (1B): mp 214–215 °C; FTIR (KBr) 2210 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.48 (d, 2H), 8.35 (d, 2H), 7.70 (t, 2H), 7.60 (t, 2H), 7.40 (t, 2H), 7.10 (d, 2H), 6.93 (t, 1H), 5.30 (s, 2H), 2.58 (s, 3H); ^{13}C NMR (CDCl_3) δ 149.5, 135.3, 131.9, 129.7, 128.6, 127.7, 126.3, 125.3, 124.3, 117.3, 116.4, 112.7, 106.0, 46.4, 34.5; LRMS (70 ev, EI) m/z (relative intensity, proposed ion) 322 (20, M^+), 216 (100, $\text{M}^+ - \text{C}_7\text{H}_8\text{N}$). Anal. Calcd for $\text{C}_{23}\text{H}_{18}\text{N}_2$: C, 86.7; H, 5.6; N, 8.7. Found: C, 85.43; H, 5.59; N, 8.86.

9-[[*N*-(4-Methoxyphenyl)-*N*-methylamino]methyl]-10-cyanoanthracene (1A): mp 207–209 °C; FTIR (KBr) 2209 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.48 (d, 2H), 8.43 (d, 2H), 7.70 (t, 2H), 7.58 (t, 2H), 7.05 (d, 2H), 6.93 (d, 2H), 5.20 (s, 2H), 3.85 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (CDCl_3) δ 152.3, 144.5, 135.8, 131.9, 129.7, 127.6, 126.1, 125.2,

124.4, 116.5, 115.6, 113.9, 105.8, 54.9, 48.2, 36.7; LRMS (70 ev, EI) m/z (relative intensity, proposed ion) 352 (20, M^+), 217 (80, $\text{M}^+ - \text{C}_8\text{H}_{10}\text{NO}$), 136 (100, $\text{C}_8\text{H}_{10}\text{NO}^+$), 120 (80, $\text{C}_8\text{H}_{10}\text{N}^+$). Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}$: C, 81.8; H, 5.7; N, 8.0. Found C, 81.57; H, 5.57; N, 8.03.

9-[2-(*N*-Methyl-*N*-phenylamino)ethyl]-10-cyanoanthracene (2B): mp 144–146 °C; FTIR (KBr) 2210, 1599, 1507, 1349, 749 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.45 (d, 2H), 8.33 (d, 2H), 7.70 (t, 2H), 7.60 (t, 2H), 7.33 (t, 2H), 6.83 (m, 3H), 3.98 (t, 2H), 3.83 (t, 2H), 2.90 (s, 3H); ^{13}C NMR (CDCl_3) δ 133.8, 130.2, 130.0, 129.2, 127.4, 127.1, 125.5, 118.6, 117.7, 113.2, 54.3, 39.3, 26.5; LRMS (70 ev, EI) m/z (relative intensity, proposed ion) 336 (10, M^+), 120 (100, $\text{C}_8\text{H}_{10}\text{N}^+$). Anal. Calcd for $\text{C}_{24}\text{H}_{20}\text{N}_2$: C, 85.7; H, 6.0; N, 8.3. Found C, 85.62; H, 5.96; N, 8.35.

9-[2-[[*N*-(4-Methoxyphenyl)-*N*-methylamino]ethyl]-10-cyanoanthracene (2A): mp 132–133 °C; IR (KBr) 2212, 1508, 1245, 756 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.45 (d, 2H), 8.29 (d, 2H), 7.70 (t, 2H), 7.60 (t, 2H), 6.91 (d, 2H), 6.80 (d, 2H), 3.88 (t, 2H), 3.82 (s, 3H), 3.70 (t, 2H), 2.90 (s, 3H); ^{13}C NMR (CDCl_3) δ 133.8, 130.2, 130.0, 129.2, 127.4, 127.1, 125.5, 118.6, 117.7, 113.2, 54.3, 39.3, 26.5; LRMS (70 ev, EI) m/z (relative intensity, proposed ion) 366 (5, M^+), 323 (20, $\text{M}^+ - \text{C}_3\text{H}_7$), 150 (100, $\text{C}_9\text{H}_{12}\text{NO}^+$), 135 (37, $\text{C}_9\text{H}_{13}\text{N}^+$), 120 (28, $\text{C}_8\text{H}_{10}\text{N}^+$). Anal. Calcd for $\text{C}_{25}\text{H}_{22}\text{N}_2\text{O}$: C, 82.0; H, 6.0; N, 7.7. Found C, 82.09; H, 6.05; N, 7.72.

9-[3-(*N*-Phenyl-*N*-methylamino)propyl]-10-cyanoanthracene (3B): mp 95–96 °C; FTIR (neat) 2211, 1599, 1443, 1372, 749 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.40 (d, 2H), 8.22 (d, 2H), 7.68 (t, 2H), 7.54 (t, 2H), 7.22 (t, 2H), 6.78 (d, 2H), 6.72 (t, 2H), 3.70 (t, 2H), 3.60 (t, 2H), 3.02 (s, 3H), 2.12 (m, 2H); ^{13}C NMR (CDCl_3) δ 26.84, 29.58, 39.66, 53.61, 113.49, 117.48, 125.59, 126.97, 127.23, 129.11, 129.42, 130.05, 133.75, 142.92; LRMS (EI) m/z (relative intensity, proposed ion) 350 (25, M^+), 146 (50, $\text{C}_{10}\text{H}_{12}\text{N}^+$), 120 (100, $\text{C}_8\text{H}_{10}\text{N}^+$). Anal. Calcd for $\text{C}_{25}\text{H}_{22}\text{N}_2$: C, 85.7; H, 6.3; N, 8.0. Found C, 85.49; H, 6.42; N, 8.15.

9-[3-[[*N*-(4-Methoxyphenyl)-*N*-methylamino]propyl]-10-cyanoanthracene (3A): mp 113–114 °C; FTIR (neat) 2213, 1511, 1443, 1345, 1179, 1048, 819, 759 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.40 (d, 2H), 8.20 (d, 2H), 7.64 (t, 2H), 7.56 (t, 2H), 6.84 (d, 2H), 6.80 (d, 2H), 3.78 (s, 3H), 3.64 (t, 2H), 3.48 (t, 2H), 2.96 (s, 3H), 2.04 (m, 2H); ^{13}C NMR (CDCl_3) δ 152.9, 143.2, 133.7, 129.4, 129.1, 127.2, 127.0, 125.7, 118.4, 116.2, 115.5, 56.5, 54.8, 40.6, 29.6, 26.9; LRMS (70 ev, EI) m/z (relative intensity, proposed ion) 380 (65, M^+), 150 (100, $\text{C}_9\text{H}_{12}\text{NO}^+$). Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}$: C, 82.1; H, 6.3; N, 7.4. Found C, 82.09; H, 6.33; N, 7.7.

9-[3-(*N*-Phenyl-*N*-methylamino)butyl]-10-cyanoanthracene (4B): mp 138–139 °C; FTIR (KBr) 2208 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.45 (d, 2H), 8.25 (d, 2H), 7.68 (t, 2H), 7.55 (t, 2H), 7.28 (m, 2H), 6.73 (m, 3H), 3.70 (m, 2H), 3.45 (m, 2H), 2.95 (s, 3H), 1.88 (m, 4H); LRMS (70 ev, EI) m/z (relative intensity, proposed ion) 364 (25, M^+), 216 (15, $\text{C}_{16}\text{H}_{10}\text{N}^+$), 133 (100, $\text{C}_9\text{H}_{11}\text{N}^+$), 120 (80, $\text{C}_8\text{H}_{10}\text{N}^+$). Anal. Calcd for $\text{C}_{26}\text{H}_{24}\text{N}_2$: C, 85.7; H, 6.6; N, 7.7. Found C, 85.64; H, 6.55; N, 7.73.

9-[3-[[*N*-(4-Methoxyphenyl)-*N*-methylamino]butyl]-10-cyanoanthracene (4A): mp 98–99 °C; FTIR (KBr) 2206 cm^{-1} ; ^1H NMR (CDCl_3) δ 8.45 (d, 2H), 8.25 (d, 2H), 7.68 (t, 2H), 7.55 (t, 2H), 6.83 (d, 2H), 6.73 (d, 2H), 3.80 (s, 3H), 3.65 (m, 2H), 3.30 (m, 2H), 2.88 (s, 3H), 1.88 (m, 4H); LRMS (70 ev, EI) m/z (relative intensity, proposed ion) 394 (35, M^+), 163 (100, $\text{C}_{10}\text{H}_{13}\text{NO}^+$), 150 (80, $\text{C}_9\text{H}_{12}\text{NO}^+$). Anal. Calcd for $\text{C}_{27}\text{H}_{26}\text{N}_2\text{O}$: C, 82.2; H, 7.0; N, 7.1. Found C, 81.1; H, 6.59; N, 7.17.

Results

a. Synthesis. We encountered considerable experimental difficulties in introducing a 10-cyano substituent into 9-alkylanthracene and their derivatives. Our original attempts to dehydrate the corresponding 9-carboxamide were found to be wanting due to difficulty in the synthesis of the amides and their low solubility. The synthesis was eventually achieved by the direct cyanation of 9-(haloalkyl)anthracene using chlorosulfuryl isocyanate²¹ followed by amination. All four members of homologs in both **A** and **B** series were thus synthesized.

b. Absorption Spectra of Compounds in A and B. The 10-cyano substituent in **A** and **B** causes a red-shift in the anthryl

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Table 1. Spectroscopic Properties of Bichromophores in Alkanes

compd	solvent	absorption 0-0 (nm)	LE emission		CT emission(s)		$2\mu_{\text{ex}}^2/hca^3$ (10^{-3} cm^{-1}) ^b
			0-0 (nm)	Φ_{LE}^a	max (nm)	Φ_{CT}^a	
A-1	mch ^c	406 ± 1	416 ± 2	0.015	nd ^d		
	hexadecane	407 ± 1	418 ± 2	0.02	nd ^d		
B-1	mch	406 ± 1	414 ± 2	0.011	nd ^d		
C-1 ^g	mch	386 ± 1	388 ± 2	0.014	nd ^e		-12.4 ± 1.3 ^f
D-1 ^g	mch	386 ± 1	388 ± 2	0.052	nd ^e		-11.6 ± 0.7 ^f
A-2	pentane	405 ± 1	412 ± 2	0.001	485 ± 2	0.001	
					600 ± 2	0.005	-4.9 ± 0.5
	mch	407 ± 1 ^h	415 ± 2	0.001	486 ± 2	0.001	
					605 ± 2	0.005	
					607 ± 2	0.005	
hexadecane	408 ± 1 ^h	416 ± 2	0.004	492 ± 2	0.004		
B-2	mch	408 ± 1 ^h	414 ± 2	0.02	516 ± 2	0.15	-16.1 ± 0.8
C-2 ^g	mch	388 ± 1	390 ± 1	0.05	522 ± 2	0.73	-11.4 ± 0.3
D-2 ^g	mch	388 ± 1	390 ± 1	0.08	448 ± 2	0.56	-15.1 ± 0.4
A-3	mch	410 ± 1	414 ± 2	0.002	610 ± 2	0.003	-4.9 ± 0.5
B-3	mch	410 ± 1	418 ± 2	0.03	555 ± 2	0.17	-9.3 ± 0.6
C-3 ^g	mch	389 ± 1	391 ± 1	0.01	530 ± 2	0.41	-10.5 ± 2.1
D-3 ^g	mch	389 ± 1	391 ± 1	0.08	487 ± 2	0.41	-7.6 ± 1.0
A-4	mch	409 ± 1	417 ± 2	0.012	612 ± 2	0.02	-5.3 ± 0.6
B-4	mch	408 ± 1	417 ± 2	0.18	541 ± 2	0.45	-16.1 ± 0.8
C-4 ^g	mch	389 ± 1	391 ± 1	0.05	525 ± 2	0.12	-8.2 ± 2.0
D-4 ^g	mch	389 ± 1	391 ± 1	0.35	470 ± 2	0.15	-9.8 ± 2.0

^a Range of uncertainty, ±10%; ±20% for $\Phi < 0.01$. ^b The slope of the Lippert–Mataga plot of V_{max} of CT emissions vs $f - 0.5 f'$. ^c Methylcyclohexane. ^d Not detected in all solvents. ^e Not detected in alkanes. ^f The slope of the Lippert plot was from solvents more polar than alkanes. ^g Values from ref 14. ^h From excitation.

absorption (0–0 band) from 387 ± 2 nm in **C** and **D** to 408 ± 2 nm (Table 1). With minor variations, **A-1**, **A-3**, and **A-4** exhibit an absorption spectrum which is not substantially different from that of the model compound, 10-methyl-9-cyanoanthracene (MCNA). However, the absorption spectrum of **A-2** appears to be the composite of a red-shifted broad featureless band superimposed on a weaker structured anthryl absorption. The red-shifted featureless band suggests that there may be a strong EDA-type of interaction in the ground state (Figure 2). A similar but weaker EDA-type of interaction is noted in the absorption spectrum of **B-2** but not in the other members of the **B** series. Although the fine structure of anthryl absorption may still be discerned in the spectrum of **B-2**, its 0–0 band is red-shifted to 418 nm (Figure 2). These features suggest that the absorption spectrum is also a composite of an anthryl absorption and an EDA-type of absorption.

The absorption in the 320–340 nm region is due to that *p*-anisidino group.

c. Fluorescence Studies. i. General Observations. In contrast to the negligible Stoke's shift in anthracenes, the presence of the 10-cyano group in **A** and **B** causes a red-shift of the 0–0 band in the LE fluorescence in methylcyclohexane of **C** and **D** from 390 ± 2 nm to 416 ± 2 nm, a Stoke's shift of $470 \pm 70 \text{ cm}^{-1}$, while its fine structure is maintained. A similar Stoke's shift of 415 cm^{-1} is noted in the model compound MCNA. The absorption spectrum of MCNA undergoes a minor red-shift of 2 nm when the solvent was changed from alkanes to methanol, but the fluorescence spectrum (0–0 band) undergoes a large red-shift from 414 to 434 nm. These observations suggest that the excited state of cyanoanthryl derivatives exhibit a substantial charge-transfer character with a dipole extending from the anthryl ring to the cyano group which causes both the Stoke's shift and the large red-shift of the fluorescence in polar solvents.

The slopes of Lippert–Mataga plots of the CT fluorescence of all compounds appear to be “normal”, i.e., within the range of $-(7-14) \times 10^3 \text{ cm}^{-1}$, excepting those in the **A** series. The Lippert–Mataga plots of **A-2**, **A-3**, and **A-4** exhibit the lowest slope of $\sim -5 \times 10^3 \text{ cm}^{-1}$ in spite of the low IP of its donor

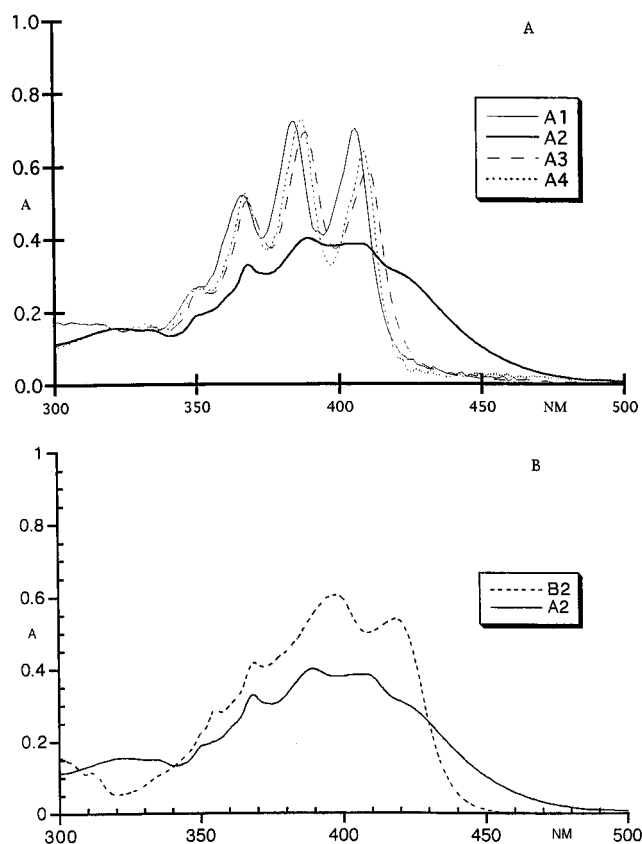


Figure 2. (A) UV–visible absorption spectra of **A-1**, **A-2**, **A-3**, and **A-4** in methylcyclohexane. (B) UV–visible absorption spectra of **A-2** and **B-2** in methylcyclohexane.

and the high EA of its acceptor. The spectral data collected from our fluorometer at >600 nm are uncorrected, and the sensitivity of our photomultiplier drops off sharply at longer wavelengths. Therefore, an uncorrected fluorescence spectrum will appear to be blue-shifted relative to a corrected spectrum at longer wavelength. Since CT fluorescence of **A-2**, **A-3**, and **A-4** occurs at >600 nm and only in nonpolar solvents, i.e., only

in alkanes and ethers, the anomalously low slopes of their Lippert–Mataga plots may also be the result of an artifact of our instrument function. The results are tabulated in Table 1.

Discussion

We carried out a systematic study on the relationship between PET and its free energy changes using polymethylene-linked anthryl–dialkylanilino bichromophoric systems. Since the linkages in our compounds are relatively short ($n = 1-4$), the number of conformers involved is limited. In our recent study in the gas phase, we detected an EDA complex in **C-2** which may be directly excited into the CT state. In our current study, the cyano substituent seem to cause a dramatic effect in the excited-state properties of **A-2**, as well as lesser effects in **B-2** and **A-3**, but no substantial effects in the excited-state properties of other compounds in our current study.

a. Compounds A-1 and B-1. In general, the 10-cyano group in the anthryl acceptor appears to have a larger effect than that of the 4-methoxy group in the anilino donor. The presence of the 4-methoxy group in **C-1** does not seem to have a major effect on its CT emission; i.e., like **D-1**, it does not exhibit CT emission from alkane solvents but still exhibits CT emissions in more polar solvents (Table 1). The presence of the 10-cyano substituent in **A-1** and **B-1** causes their CT emissions to disappear entirely, even in the more polar solvents. This may be attributed to the enhanced ionic character of the CT state by the polar cyano group. The enhanced ionic character may lead to the more rapid nonradiative decay of the CT state (*vide infra*).

The electronic transition spectrum of **A-1** or **B-1** is not appreciably different from their homologs with either a trimethylene or tetramethylene spacer (see Figure 2). *This observation indicates that there is no strong D–A interaction through the monomethylene spacer in the ground state.* Contributions from Weller's⁴ and Mataga's⁶ laboratories showed that related bichromophoric **D–A** systems **E-1** do not exhibit CT emissions in nonpolar solvents in spite of the relatively short distance between the chromophores. However, the Φ of the LE emission is greatly attenuated. We notice that there is a severe restriction on the rotation of the An–CH bond by the perhydrogens of anthryl group at the 1- and the 8-positions. The rotational barrier of this bond in **A-2** has been estimated to be 2.8–3.5 kcal/mol (*vide infra*). This restriction in **A-1** appears to be more severe than those in the higher homologs due to the proximity of the large anilino group to the anthracene ring. Because of this restriction, **A-1** may exist in two conformations, the major conformation in which the anilino N is in the proximity of the C-9 of anthracene, and the minor conformation where the anilino N is in the proximity of the C-1 and C-8 of anthracene. It has been suggested by Chandross on a related system that such systems may undergo rapid photocyclization via the radical ion pair to give a metastable intermediate **E** (eq 5) which reverts back to **A-1** in a nonradiative process.²⁵ This decay pathway would account for its excited-state behavior, while other nonradiative pathways such as intersystem crossing may also take part in this process. However, we are unable to analyze the relative proportions of these two conformers either in the ground state or in the excited state. The spatial separation between the anilino N and the C-9 of the anthryl group in the minor conformation prevents their chemical interaction to form **F**, and the minor conformer may thus decay by fluorescence, nonradiative decay, or a change in its conformation.

(24) Chandross, E. A.; Thomas, H. T. *Chem. Phys. Lett.* **1971**, *9*, 393–396.

(25) White, W. N. *J. Am. Chem. Soc.* **1959**, *81*, 2912–2913.

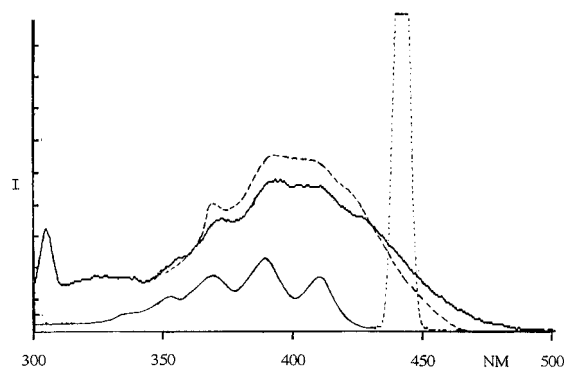


Figure 3. Fluorescence excitation spectra of **A-2** in methylcyclohexane: (heavy line) monitored at 442 nm and (—) monitored at 605 nm. Also shown is the UV–visible absorption spectrum of **A-2** in methylcyclohexane (---).

b. Compound A-2. i. Absorption Spectra and Ground-State Interactions. LE Absorption. When the excitation spectrum was monitored at the LE emission maximum (0–1 band, 440 nm), *only* a structured anthryl absorption spectrum was obtained (Figure 3). This observation suggests that the structured emission is the LE emission.

The relative proportions of various conformers at the equilibrium cannot be measured by the direct method. The proportions of the LE and CT conformers were estimated by comparing the fluorescence excitation spectra monitored at the maximum of LE emission, 440 nm, and at the maximum of a CT emission, 605 nm (Figure 3) in the corrected mode of our spectrofluorometer. Assuming all conformers have similar oscillator strength in their electronic transitions, the LE emission is derived from a minor conformer which comprises of ~25% of **A-2** at the equilibrium.

EDA Absorption. As shown in Figure 2, the electronic transition spectra of **A-2** is substantially different from that of the model compound MCNA. We attempted to study the possible EDA interaction between the **D** and the **A** groups by measuring the absorption spectrum of a model system of MCNA and 2 M *N,N*-dimethylanisidine in methylcyclohexane and found the spectrum to be identical to the mixture of MCNA and *N,N*-dimethylanisidine, i.e., we detected no intermolecular EDA complex under this condition. The fluorescence excitation spectra of **A-2** in alkanes monitored at the maximum of either one of the two CT emissions are, within experimental error, identical to the absorption spectrum in the same solvent (Figure 3). The slight broadening of the excitation spectra from the absorption spectrum may be attributed to the wider slit width (5 nm) used in the excitation measurements. Both spectra have the broad and featureless appearance of an EDA complex with some minor structural features in the shorter wavelength region.

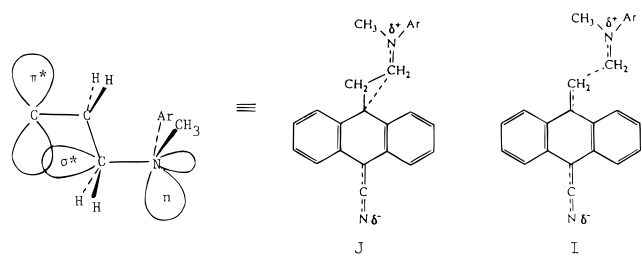
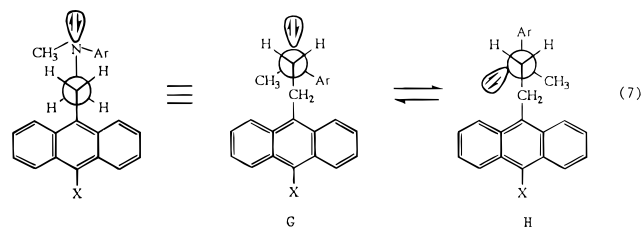
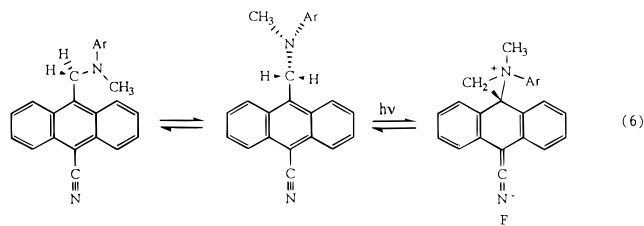
The EDA interactions in polymethylene-linked bichromophoric compounds were investigated by White²⁶ and his co-workers and reviewed by Foster.²⁷ Since both the *cis*- and the *trans*-1,2-disubstituted cyclopentanes containing appropriate donor and acceptor groups exhibit EDA interactions, both the through-bond and the through-space interactions between the chromophores may play a role in intramolecular EDA complex formations. The through-bond EDA interaction of **A-2** will be elaborated in the next section.

The donor and the acceptor in **A-2** are linked by three σ bonds, C–C–C–N, and may exist in a number of staggered

(26) For a review on intramolecular EDA complexes, see: Foster, R. *Organic Charge-Transfer Complexes*; Academic Press: New York, 1969; pp 78–82.

(27) For a compilation of bond lengths and bond angles, see: March, J. *Advanced Organic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1992; pp 20–23.

conformations resulting from the rotation of the C–C bond as well as from the rotation of the C–N bond. In examining molecular models, there is an appreciable steric interaction between the bulky anthryl group and the *N*-anilino group. It is reasonable to assume that **A-2** exists mainly as the *trans* conformer around the C–C bond (eq 7).¹⁴ A C–N bond (1.47



Å) is slightly shorter than a C–C bond (1.54 Å), and the difference exerts only a minor effect on the relative stability between the *anti* and the *gauche* conformers. If we assume that only the conformer **G**, which has the nonbonding lone pair of the anilino nitrogen aligned in an antiparallel orientation with the anthryl group, has the favorable through-bond EDA interaction between the donor and the acceptor groups, this favorable through-bond interaction will be attenuated by the *gauche* interaction between the N substituents on the anilino N and the bulky anthrylmethyl group on the C-2 carbon (eq 7). A *gauche* interaction may destabilize the conformation of a system by ~1–1.5 kcal/mol. Since the EDA conformer is still the major conformer at the equilibrium in spite of the two *gauche* interactions, the EDA interaction may have stabilized the system by ~2–2.5 kcal/mol.

Photoexcited **A-2** in the noninteracting conformations **H** may undergo either a conformational change to the EDA conformer **G** or undergo radiative and nonradiative decays in the LE mode to **A-2**. Since EDA complexes may be excited directly into the CT states, photoexcitation of **A-2** from its EDA complex to its CT state indicates that PET of **A-2** has attained the theoretical limiting rate for a photochemical process.

ii. Fluorescence Spectroscopy. Steady-state fluorescence study of **A-2** in pentane or methylcyclohexane reveals that the fluorescence of **A-2** depends on the wavelength of excitation. When it is excited at 390 nm, the maximum of the absorption, **A-2** yields three groups of emissions: a structured anthryl LE emission with 0–0 band at 414 ± 2 nm, a broad CT-type emission with a maximum at 490 nm, and another broad CT-type emission with a maximum at 605 nm. When **A-2** is excited selectively into the EDA band at a longer wavelength, 420 nm, it yields only the two CT emissions (Figure 4). Since **A-2**

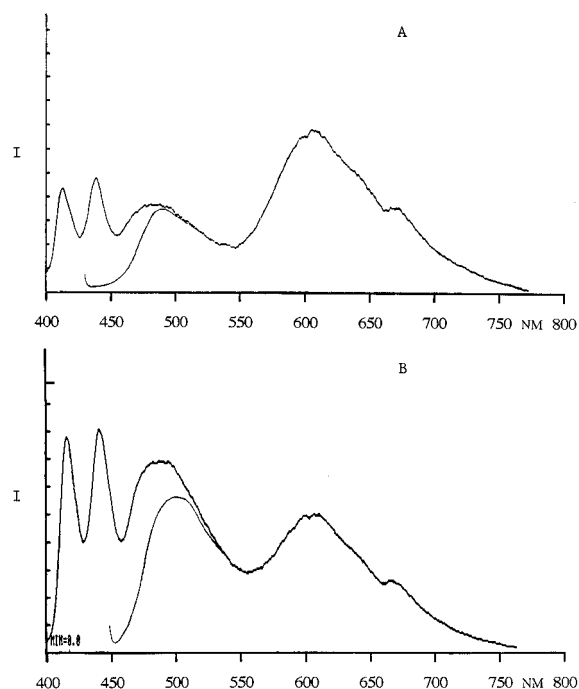


Figure 4. Steady-state fluorescence spectrum of **A-2** in alkanes. (A) In methylcyclohexane: upper curve, excitation wavelength, 389 nm; lower curve, excitation wavelength 425 nm. (B) In hexadecane: upper curve, excitation at 390 nm; lower curve, excitation at 440 nm. The shoulders at 660 nm in these spectra are artifacts due to a change in the program of the spectrometer.

exhibits two groups of absorption, one by the EDA conformer **G** and the other by the noninteracting conformer(s) **H**, the LE emission must be derived from the noninteracting conformer(s) only.

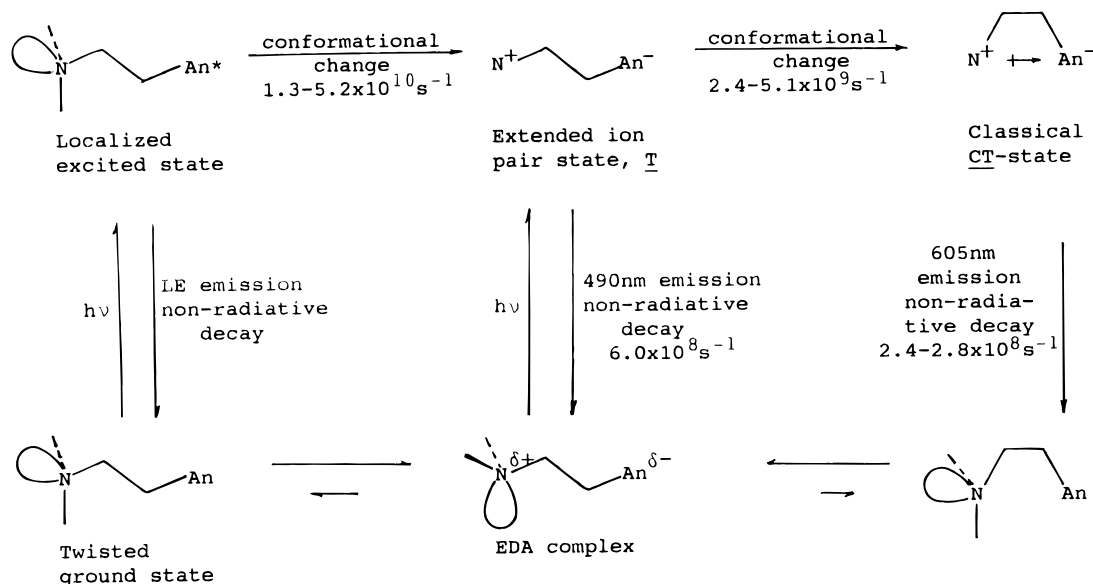
It is noteworthy that the quantum yields of the two CT emissions are the same when **A-2** is excited at either wavelength region (Figure 4). The result suggests that the major decay mode of the LE state is in its conversion to the CT states via a rapid conformational change at almost unit efficiency (Scheme 1).

LE Emission. The intensity of the LE emission increases appreciably with the viscosity of the alkane solvent, from 0.001 in methylcyclohexane to 0.004 in hexadecane (Table 1). Since the fluorescence quantum yield of MCNA does not vary substantially in these two solvents (0.55 ± 0.06 in methylcyclohexane and 0.61 ± 0.06 in hexadecane), the increase in LE emission in a more viscous solvent is most likely an inherent property of **A-2** and not due to its contamination with a fluorescence impurity. However, we encountered experimental difficulties in our attempts to determine the fluorescence lifetime of the LE emission by time-resolved fluorescence spectroscopy, particularly in less viscous solvents. The difficulties are likely due to both the low quantum yields of the LE emission (~0.001) and the interference caused by the nearby 490 nm CT emission. Assuming the fluorescence properties of compounds in **A** series are similar to those of their model compound MCNA, we may estimate the lifetime of the LE emission of **A-2** from the lifetime of MCNA emission (10.6 ns in methylcyclohexane) according to eq 8. The values obtained are 19.3 ps in methylcyclohexane

$$\tau_f = \tau_{\text{MCNA}} \left(\frac{\Phi_f}{\Phi_{\text{MCNA}}} \right) \quad (8)$$

and 77 ps in hexadecane. The result clearly indicates that there is an extremely rapid process or processes competing against the fluorescence emission. The calculated rates of the competing process(es) in alkanes are viscosity dependent, varying from

Scheme 1



$5.2 \times 10^{10} \text{ s}^{-1}$ in methylcyclohexane to $1.3 \times 10^{10} \text{ s}^{-1}$ in hexadecane. The rates correspond to an activation energy barrier of 2.8–3.5 kcal/mol at 25 °C for a unimolecular process. The results suggest that the emitting species of **A-2** may be different conformers; i.e., they may interconvert to one another by the rotation of a σ bond, and we conclude that only one conformer of **A-2**, the conformer **G**, exhibits the EDA-like absorption and gives rise to the CT emissions.

CT Emissions. The classical CT emissions or the exciplex emissions of analogous bichromophoric compounds are related to one another by the substituent effect. The introduction of a 10-cyano substituent into **D-2** to form **B-2** causes its CT emission to shift from 450 to 522 nm, or a 3065 cm^{-1} red-shift. We may estimate the classical CT emission of **A-2** from that of **C-2** by assuming that the cyano group will cause the same red-shift as that **D-2** to **B-2**. The calculated value for the classical CT emission from **A-2** is $16\,390 \text{ cm}^{-1}$ or 610 nm. Since CT emissions are broad peaks, the calculated value is within the experimental uncertainty of our observed CT emission at 605 nm. Therefore, we assign the CT-2 emission at 605 nm to the classical CT emission in the overlapping conformation.

It is predicted that **A-2** may undergo PET in the trans conformation. Therefore, the 490 nm emission may be the CT state of **A-2** in the trans conformation, **G**, which has a larger charge separation than the classical CT state and will undergo a conformational change via Coulombic interaction to the classical CT state in the overlapping conformation (Figure 1). If this is the case, the energy difference between the two CT states is that between the Coulombic interactions of two conformations. However, by using the literature values of bond lengths and bond angles,²⁷ and assuming ϵ of alkanes to be 2, the value obtained, 0.68 eV, appears to be only in qualitative agreement with the observed difference between 490 and 605 nm of 0.48 eV, or 11.1 kcal/mol. Since the overlapping CT-2 state is destabilized relative to the Franck–Condon ground state and the extended CT-1 state is not, the observed energy difference between the two CT states may well be in good agreement with our explanation; i.e., the 490 nm emission is derived from the CT state in the **G** conformation, which undergoes a conformational change via Coulombic interaction to the classical CT state. The classical CT state decays back to the ground state by emitting at 605 nm. This conformational change is related to the “harpooning” in PET first proposed by Verhoeven in his

Table 2. Lifetimes of Excited **A-2** in Solution

	solvent		
	<i>n</i> -pentane	methylcyclohexane	<i>n</i> -hexadecane
viscosity (cps, T) ^a	0.23 (19 °C)	0.73 (20 °C)	3.45 (20 °C)
CT-1 (V_{max} , nm) ^b	485	486	492
Φ	0.001	0.001	0.004
τ	<i>c</i>	22 °C, 136 ps 32 °C, 118 ps 40 °C, 105 ps 50 °C, 91 ps	22 °C, 335 ps 32 °C, 261 ps 40 °C, 212 ps 50 °C, 176 ps
CT-2 (V_{max} , nm) ^b	600	605	607 ^d
Φ	0.004	0.004	0.005
τ (22–50 °C)	<i>c</i>	$4.20 \pm 0.04 \text{ ns}$	$3.52 \pm 0.02 \text{ ns}$

^a Viswanath, D. S.; Natarajan, G. *Data Book on the Viscosity of Liquids*; Hemisphere: New York, 1989. ^b Excitation at 295 nm. ^c Not measured. ^d Rise time, $420 \pm 50 \text{ ps}$.

PET studies on rigid or semirigid systems⁷ and to the “loose” exciplex observed in the time-resolved studies of **E-3** by Mataga in polar solvents.⁶

Since the rate of conformational change of a molecule by a σ -bond rotation may be retarded by a more viscous solvent, and methylcyclohexane ($\eta = 0.73 \text{ cps}$) has virtually the same dielectric constant ($\epsilon = 2.02$) as hexadecane ($\eta = 3.45 \text{ cps}$, $\epsilon = 2.05$),^{28,29} any change in the spectroscopic behaviors of **A-2** in these two solvents may be related to the difference in their viscosity alone (Tables 1 and 2). Changes in the fluorescence behaviors of **A-2** are immediately noticeable when the solvent is changed from methylcyclohexane to hexadecane (Figure 3). When **A-2** is excited at its absorption maximum of 390 nm, the Φ 's of both the LE emission and the 490 CT emission increase appreciably as the solvent viscosity increases, while the Φ of the 605 nm emission remains unchanged. The intensification of the 490 nm emission caused by this solvent change agrees with our postulate that the two CT emissions may be derived from two CT states related to one another by a conformational change (Figure 1).

This explanation is verified by time-resolved fluorescence spectroscopy at temperatures ranging from 22 to 50 °C at picosecond resolution (Table 2). The τ_f of the 490 nm emission

(28) Viswanath, D. S.; Natarajan, G. *Data Book on the Viscosity of Liquids*; Hemisphere: New York, 1989.

(29) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Wiley-Interscience: New York, 1986.

of **A-2** in methylcyclohexane decreases from 136 ps at 22 °C to 91 ps at 50 °C. The τ_f of the 490 nm emission of **A-2** in hexadecane at the same temperature range is much longer, decreasing from 335 ps at 22 °C to 176 ps at 50 °C. However, the τ_f of the 605 nm emission remains unchanged at 3.52 ns in hexadecane and at 4.20 ns in methylcyclohexane over the same temperature range (Table 2).

The relationship between the CT emissions was also analyzed by the rise times of their emissions. Although we were unable to resolve the rise time of the 605 nm emission in methylcyclohexane, we found the rise time in hexadecane to be 420 ps at 22 °C. Since the excited EDA conformer in the **T** conformation does not necessarily decay entirely via the conformational change (Scheme 1), the time-resolved spectroscopy results clearly agree with our explanation that the excited EDA conformer decays by a conformational change to the classical CT state. The Arrhenius activation energy, ΔE^\ddagger , for the decay of the 490 nm emission may be calculated from the temperature dependence of its lifetime to be 2.71 ± 0.05 kcal/mol in methylcyclohexane and 4.78 ± 0.02 kcal/mol in hexadecane. We also attempted to determine the rise time of the CT-1 emission and were unable to obtain meaningful results. The experimental difficulty may be related to the following factors: (1) the major portion of the CT-1 state (vide supra) may be accessed by direct excitation of the EDA conformer in the ground state and the remaining portion via a rapid decay from the LE state ($\tau = 19\text{--}77$ ps, depending on the solvent viscosity); (2) the limitation of our instrument function (~ 25 ps); and (3) the overlap between CT-1 and the LE emissions.

The relative population of an emitting species at the steady state is directly proportional to its lifetime. The lifetime of the classical CT emission of **A-2** (3.52 ns) in hexadecane is much longer than the 490 nm emission derived from the EDA conformer of **A-2** (335 ps) at 22 °C, yet the quantum yields of the two CT emissions are comparable. If there were an appreciable concentration of **A-2** in the overlapping conformation stabilized by a **D-A** through-space interaction, the overlapping conformer would be excited directly into the classical CT-2 state. We would have observed a faster rise time and higher quantum efficiency of the CT-2 emission. Coupled with our observations that the rise time of the classical CT-2 emission corresponds to the decay of the EDA conformer and that there was no detectable intermolecular interaction in the model system, we may conclude that the **D:A** through-space interaction in the overlapping conformation makes an insubstantial contribution to the EDA interaction in **A-2**.

Furthermore, it is well-known empirically that the mobility or the reciprocal of viscosity (η^{-1}) of many solvents exhibits Arrhenius-type behavior.³⁰ The associated activation energy of methylcyclohexane and hexadecane may be estimated from the temperature dependence of their viscosity to be 2.2 kcal/mol for methylcyclohexane and 3.9 kcal/mol for hexadecane. Since the conformation change between the two CT states must also overcome the rotational barrier of the central C-C bond, these values are in general agreement with our observed barrier for the conformational change. This renders additional support for the assertion that the two CT states are related to one another by a change in conformation.

In the classical theory of through- σ -bond interaction between chromophores, the effect is transmitted through the σ^* level of the bond and is characterized by a transmission constant β for each bond.³¹ However, when the energy level of the CT state of a bichromophoric system has been lowered by substituents

below the LE state, we observed a strong EDA interaction in **A-2** through three σ bonds which does not exist in **A-1** through two σ -bonds (Figure 2). Since **A-2** contains an n donor and a π acceptor, the interaction between the donor and the acceptor in the ground state may be formulated by a canonical resonance structure **I**. In **I**, the n donor electron is successively relayed through the σ^* orbitals of dimethylene linkage between the donor and the acceptor. This relay requires the antialignment between the donor and acceptor and weakens the middle σ -link. The canonical formula **I** is analogous to the classical formulation of hyperconjugation in organic compounds by a β substituent to a chromophore.³² The PET of **A-2** involves the promotion of an n electron from the anilino donor into the π^* orbital of anthryl acceptor. This promotion may also occur via the σ^* orbital of the α -N-C bond, formula **J**. In either case, EDA interaction involves the n orbital of the N donor and the π^* orbital of the C acceptor via the σ^* level of the spacer, and it may be visualized as a form of nitrogen-carbon hyperconjugation. We can offer no other explanation at this moment. In the meantime, an X-ray structural analysis will be performed on **A-2** and **D-2** in collaboration with Professor Michael Garavito in order to achieve better understanding in our work.

The fluorescence of **A-2** was also studied in a few other solvents. Since the CT emissions from ion pair states are known to undergo much larger red-shifts than exciplex emissions in polar solvents,^{11,33} we estimated that the CT emission at 490 nm in alkanes may undergo a red-shift to 580 ± 20 nm in *n*-butyl ether. The CT emission at 490 nm of **A-2** does undergo noticeable red-shift in more polar solvents. Since CT emissions are broad and weak emissions, we were unable to resolve two overlapping CT emissions into their individual components in ethereal solvents. Both CT emissions become nondetectable in solvents more polar than ethyl acetate (vide supra, Table 1). Therefore, we were unable to extract valuable information about the dipole moments and charge separation of the CT emission at 490 nm.

c. Compound B-2. Like **A-2**, **B-2** also exhibits a broadened red-shifted absorption spectrum with some fine structure and a 0-0 band at 418 nm (Figure 2). The fluorescence excitation spectra of **B-2** is also similar to those of **A-2**, i.e., they are dependent on the wavelength of emission at which the excitation spectrum is monitored. In methylcyclohexane, when the excitation spectrum is monitored at the maximum of the LE emission of 439 nm, **B-2** exhibits a structured excitation with a 0-0 band at 408 nm (shoulder at 422 nm). When the excitation spectrum is monitored at the maximum of the CT emission of 514 nm, **B-2** exhibits a broadened structured excitation with a 0-0 band at 422 nm, or a 813 cm^{-1} red-shift (Figure 5). The shoulder in the excitation spectrum monitored at 439 nm may well be due to a low-intensity CT emission at 439 nm. A similar red-shift in the excitation spectrum monitored at different excitation wavelengths is also noted in hexadecane and in ethereal solvents, expecting the red-shifting of the CT emission. Since it is theoretically impossible for a compound to exhibit a 0-0 band of absorption or excitation to the red of the 0-0 band of emission, the results suggest that the novel **D-A** interaction through a bis-methylene linkage may also exist in **B-2**, but to a lesser extent than **A-2**. By selectively exciting **B-2** at 423 nm, 5 nm to the red of the 0-0 band, a weak CT emission, which

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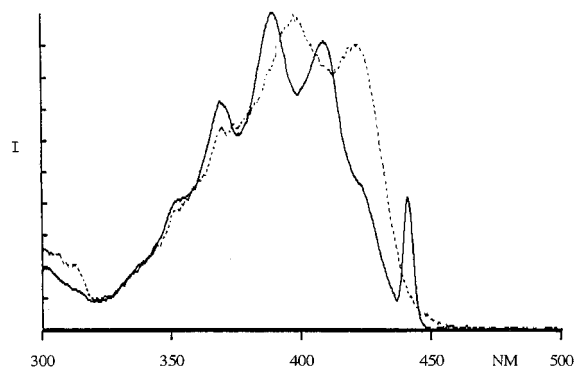


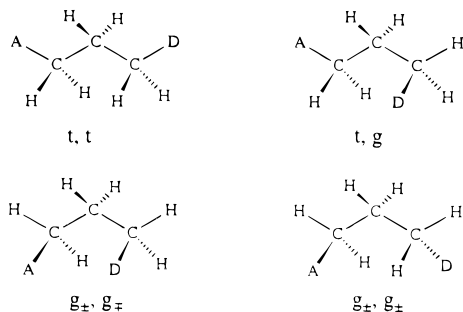
Figure 5. Fluorescence excitation spectra of **B-2** in methylcyclohexane: (—), monitored at 439 nm; (---), monitored at 516 nm.

overlaps with the LE emission when **B-2** is excited at shorter wavelength, becomes resolved with an estimated maximum at 440 nm (Figure 6). This result, coupled with our data from **A-2**, is in agreement with our suggestion (*vide supra*) that there is also a novel **D-A** interaction in **B-2**. Furthermore, the results suggest that the emission at 440 nm is derived from the extended conformer via the novel through bond interaction as in **A-2**. Such an interaction is not detected in **C-2** under similar conditions which indicates that the EDA interaction is weaker in **C-2**. However, the cyano substituent in **B-2** exerts a lesser effect in causing the red-shift of the CT emission from **D-2** at 448 nm, a 68 nm or 2942 cm^{-1} shift, than the methoxy substituent in **C-2**, a 74 nm or 3164 cm^{-1} shift (Table 1).

Since the substituent effect on the CT emission of a 10-cyano group on the anthryl group becomes larger than that of a *p*-methoxy group on the anilino group in the trimethylene and the tetramethylene derivatives (*vide infra*), the effect may be related to other factors which will be treated in the next section.

d. Compounds A-3, A-4, B-3, and B-4. The dependence of fluorescence excitation spectrum of **A-3** in methylcyclohexane on the wavelength of emission is also observed but to a lesser degree than in **A-2** and **B-2** (Figures 7 and 8). When the excitation spectrum is monitored at the maximum of the LE emission of 437 nm, it exhibits a structured excitation with a 0-0 band at 406 nm. When the excitation was monitored at the maximum of the CT emission of 610 nm, it also exhibits a structured excitation but its 0-0 band is red-shifted by 200 cm^{-1} to 409 nm. Both emissions are weaker than those of **C-3**, and the emissions of **A-3** become almost nondetectable in ethereal solvents.

Compound **A-3** may exist in four different staggered conformations: *t, t, t, g, g_±, g_±, and g_±, g_∓*. All of these conformations interconvert readily from each other under our



experimental conditions. The excitation spectrum monitored at the LE emission is most likely derived from the conformers whose **D-A** distance exceeds the energetic limit for the PET; whereas the excitation spectrum monitored at the CT emission is a composite of absorption spectra of different conformers from

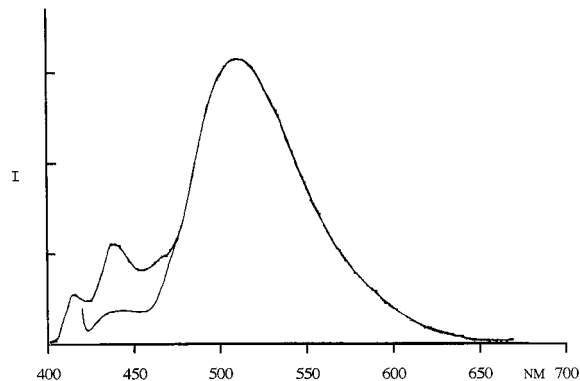


Figure 6. Steady-state fluorescence spectra of **B-2** in methylcyclohexane: upper curve, excitation at 386 nm; lower curve, excitation at 423 nm.

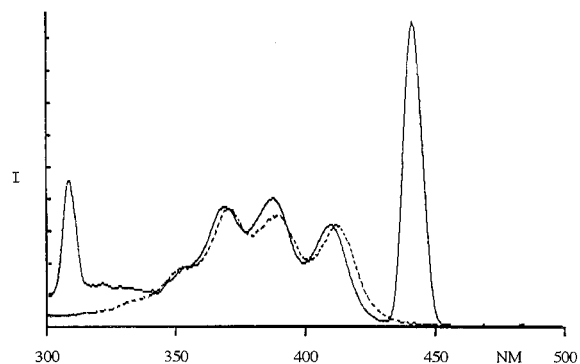


Figure 7. Fluorescence excitation spectra of **A-3** in methylcyclohexane: (—), monitored at 437 nm; (---), monitored at 610 nm.

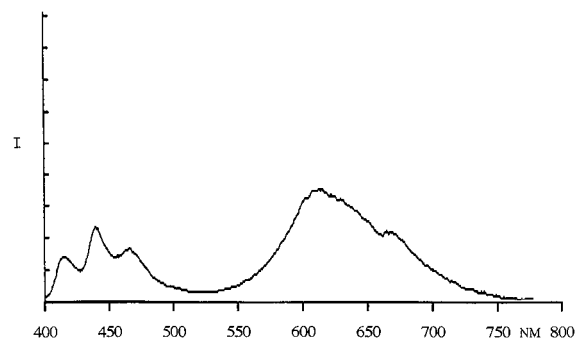


Figure 8. Steady-state fluorescence spectrum of **A-3** in methylcyclohexane.

which the CT state is derived. Since the **D-A** distance in the overlapping conformer, or the g_{\pm}, g_{\mp} conformer, and that in the g_{\pm}, g_{\pm} conformer are within the range of PET, the contribution of these conformers in the excitation spectrum will be amplified relative to the other conformers. Due to the strong through-space **D-A** interaction in the overlapping conformer, it is expected to exhibit a broad structureless red-shifted absorption spectra. Since the absorption spectrum of **A-3** is "normal" and similar to those of **A-1** and **A-4** in the homologous series (Figure 2), the result indicates that the overlapping conformer makes an insignificant contribution in the ground state. The g_{\pm}, g_{\pm} conformer is a minor conformer of **A-3** at the equilibrium, and its orientation between the **D** and the **A** groups precludes both a strong through-bond and a strong through-space interaction. The presence of a minor amount of this conformer cannot be excluded by its absorption spectrum, yet its presence may be amplified in the excitation spectrum resulting in the observed red-shift. The validity of such an explanation may be resolved, as in the case of **C-2**, by a gas-phase photochemical study of compounds in the **A** series.

Such anomalous excitation spectra in alkane solvents were not observed in **A-4**, **B-3**, and **B-4**. This is apparently due to the larger average distance between the **D** and the **A** groups at its conformational equilibrium.

The CT emission in the unsubstituted series of **D-3** and **D-4** is at 487 and 470 nm, respectively. A 10-cyano substituent in the anthryl group in **B-3** and **B-4** causes a red-shift in the CT emission to 555 and 541 nm, respectively, an average shift of ~ 70 nm or 2650 ± 140 cm^{-1} , which is larger than the shift caused by a 4-methoxy substituent in the anilino group in **C-3** and **C-4** to 530 and 525 nm, respectively, an average of ~ 50 nm or 1950 ± 289 cm^{-1} (Table 1).¹⁴ The larger effect of the cyano substituent may be related to its larger effect in stabilizing the CT state. However, the observed substituent effect in the CT emission in **B-2** and **C-2** is reversed from the observed effect in the **3** and **4** series, in which the cyano substituent in **B-2** causes a 68 nm or 2942 cm^{-1} red-shift, and in which the methoxy substituent in **C-2** causes a 74 nm or 3164 cm^{-1} red-shift (Table 1). A unique feature of our anthryl-dialkylanilino bichromophores in compounds **A-D** is that the nitrogen atom in the dialkylanilino group is oriented to face the anthryl acceptor. In the related molecules **E** studied in other laboratories, the phenyl group in the dialkylanilino group is oriented to face the anthryl acceptor. The dimethylene spacer in the **2** series prevents the two aryl groups in **E** from achieving the parallel overlap between them. As the result, **E-2** only exhibits CT emissions in solvents more polar than hydrocarbons. However, molecular modeling shows that the nonbonding pair on the nitrogen of **C-2** can come into contact with the anthryl π system. The most stable configuration for the CT state or the exciplex is where the **D** and the **A** groups have attained a parallel alignment with the maximum overlap between them. This is possible for trimethylene and tetramethylene derivatives but not possible in the dimethylene derivatives **B-2**. Sterically, the nonparallel **D-A** alignment may reduce the effect of the 10-cyano group to the anthryl π acceptor on the CT state to a greater extent than the effect of the 4-methoxy group to the

anilino donor. This may be the cause for the lesser effect of the cyano substituent in **B-2** relative to the methoxy substituent on **C-2**.

Conclusions

In order to further our understanding of both the ground-state EDA interaction and the PET of σ -linked bichromophoric compounds, we plan to carry out the following: (i) an all-valence electron calculation of the structure of **A-2** in the ground state in collaboration with Dr. John Miller of the Argonne National Laboratory; (ii) syntheses of analogous compounds containing other donors, acceptors, and spacers in between them; and (iii) physical studies of these compounds in collaboration with Professor D. H. Levy, Professor M. Garavito, and other scientists.

In conclusion, although polymethylene-linked bichromophores may exist in a number of conformations, our studies of the lower members of the homologous series, $n = 4$ or less, revealed novel behaviors in the $n = 2$ homologs as well as predictable behaviors following the conformational analysis. We also confirm that, when the energy level of the CT state of our compounds is lowered below that of the LE state, there is a ground-state interaction between the **D** and **A** groups. These compounds may be excited directly into the CT state; i.e., the photoinduced electron transfer in **A-2** and related compounds apparently occurs upon light excitation, thus reached the limiting rate of a photochemical process.

Acknowledgment. The authors thank the National Science Foundation for the financial support, Professor Donald H. Levy for his initial and continuing stimulation and valuable discussions, Professor Hansen Shou for the synthesis and preliminary studies of compounds in the **C** and **D** series, and Professor Professor M. Garavito and Professor Jerry Berson for many valuable discussions.

JA9523698