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PHOTOCHEMISTRY OF POLYCHROMOPHORIC ARYLAMINES

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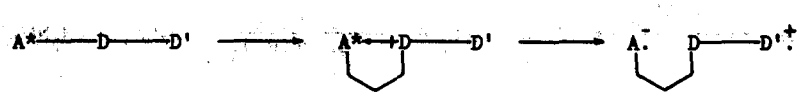
Abstract: Rates and yields of intramolecular exciplex formation and electron transfer in polychromophoric arylamines may be modified dramatically by varying the nature of the aryl or the amino group as well as the nature and length of the chain between the two groups. In trichromophoric systems 1 containing one aryl and two amino groups, photoinduced electron transfer may be affected between the aryl group and one of the amino groups in fairly non-polar solvents.

The primary process in photosynthesis involves photoinduced electron transfer in an ordered multicomponent system[1] which catalyzes a great deal of activity in the photochemistry of polychromophoric molecules as models for photosynthesis.[2] Photoexcited aromatic hydrocarbons may react with an amine donor to undergo exciplex formation in non-polar media or electron transfer in polar solvents yielding a radical ion pair (reaction 1).[3] However, these radical ions tend to undergo rapid back electron transfer to yield the substrates in their ground state or triplet state (reaction 2).[4] In order to convert light energy into chemical energy in an efficient manner, the rate of this back electron transfer must be retarded. We have found that exciplexes may be deactivated by another ground state molecule.[5-7] In a preliminary study, we have discovered that such a process may take place intramolecularly in a trichromophoric system to yield radical ions in dichloromethane (reaction 3).[8] This work demonstrates the generality of this electron transfer and the lifetimes of ions generated in such systems are substantially longer than the lifetimes of ions from analogus electron transfers in polar media.

$$A^* + D \xrightarrow[\text{polar solvents}]{\text{encounter distance}} A^{\cdot -} + D^{\cdot +} \qquad (1)$$

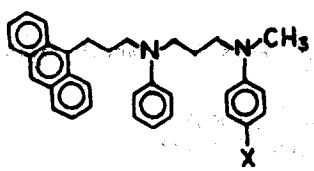
$$A^{\cdot -} + D^{\cdot +} \longrightarrow {}^3A \text{ or } A + D \qquad (2)$$



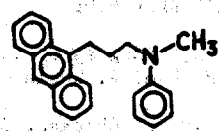
(3)

Polynuclear aromatic hydrocarbons form well-characterized exciplexes with anilines.[3] Among polynuclear aromatic hydrocarbons, both anthracene and pyrene exhibit distinct and well-defined spectroscopic properties and are known to exhibit desirable physiological properties.[9] Therefore, both derivatives of anthracene and pyrene were synthesized. Since compounds in the 9-anthryl series (A series) exhibit markedly different lifetimes

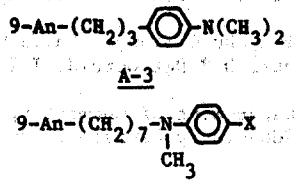
between their excited state and their exciplex while compounds in the 1-pyrenyl series (P series) do not,[10,11] compounds in the A series were investigated first.[5] These include the trichromophoric compounds A-1a-c, as well as dichromophoric compounds A-2 and A-3. Subsequently, compounds P-1a-c and P-2 were also synthesized, and the excited state behaviors of both series of compounds were analyzed by spectroscopic techniques. An investigation of these compounds enables us to study the dependence of the nature of the donor and the excited acceptor on the exciplex induced electron transfer.



A-1

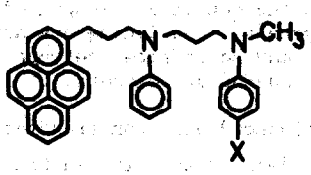


A-2

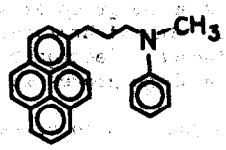


A-3

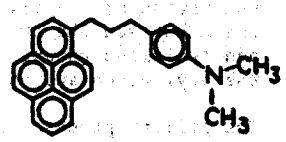
A-4



P-1



P-2



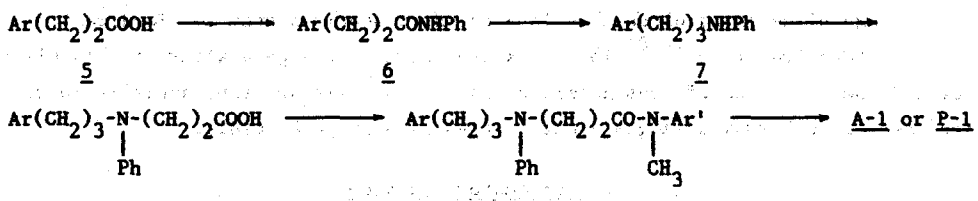
P-3

a series, X = H; b series, X = CH_3

c series, X = OCH_3

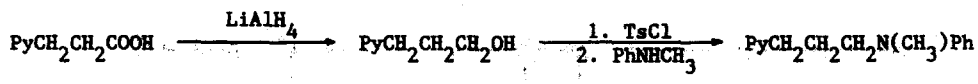
SYNTHETIC SCHEMES

A-1 or P-1 (Ar = 9-anthryl or 1-pyrenyl, Ar' = phenyl or substituted phenyl)



5 6 7 8 9

P-2 (Py = 1-pyrenyl)



P-5 P-10 P-2

EXPERIMENTAL PART

All solvents used were the spectroscopic grade solvents purchased from the Aldrich or Eastman Kodak Co., tetrahydrofuran was distilled first from lithium aluminum hydride and then sodium benzophenone ketyl immediately prior to use. If the solvent was not available in the reagent grade, it was purified by fractional distillation just before use. All analytical spectra were taken from a variety of modern instruments. Fluorescence spectra were recorded either on a Perkin-Elmer MPF-4 or MPF-66 spectrofluorimeter with a thermostatic sample compartment. Samples were prepared at a concentration with an o.d. of approximately 0.1 at the excitation wavelength and degassed by multiple freeze-thaw cycles at a pressure <0.1 Torr. The instruments used for the kinetic spectroscopy have been described previously.[12] Both the system and the samples were carefully flushed with nitrogen before the measurements were made, and the sample was circulated through the cell in a flow system in order to assure the transients had decayed between the laser pulses.

Compounds A-2,[13], A-3[14], P-3[15], A-5[16] and P-5[17] are synthesized by known methods.

N-Phenyl-3-(9-anthryl)-1-aminopropane (A-7). To a solution of xylene (50 ml) and aniline (50 ml) was added 3-(9-anthryl)propionic acid (A-5, 10.0 g, 0.040 mole). The system was fitted with a Dean Stark trap and reflux condenser, and the solution was refluxed for 12 hrs. The reaction mixture was cooled to 0°C causing a solid to precipitate. The solid was collected on a filter and washed with ether (100 ml), yielding A-6 (9.2 g, 0.028 mole, 70%), mp 250-252°C; m/e 325. To a solution of LAH (0.76 g, 0.02 mole) in THF (50 ml) was added A-6 thus prepared (5.0 g, 0.020 mole) over a period of 1 hr under dry nitrogen. The reaction mixture was refluxed for 12 hrs following the addition. The excess LAH was destroyed by the method of Steinhardt.[18] The precipitate was removed by filtration and the filtrate was diluted with ether (50 ml) and dried over $MgSO_4$. The drying agent was then removed by filtration and the filtrate was concentrated under reduced pressure. The concentrated solution was cooled to yield A-7 in form of yellow crystals, mp 75-76°C; ir(KBr) 1608 and 1507cm^{-1}; nmr($CDCl_3$), δ 2.15 (p, 2H, J = 8Hz), 3.34 (t, 2H, J = 8Hz), 3.67 (broad s, 1H), 3.74 (t, 2H, J = 8Hz), 6.63 (d, 2H, J = 8Hz), 6.72 (t, 1H, J = 8Hz), 7.18 (t, 2H, J = 8Hz), 7.42-7.49 (m, 4H), 8.00-8.04 (m, 2H), 8.24 (d, 2H, J = 9Hz) and 8.35ppm (s, 1H); uv(CH_3OH) λ_{max}(ε) 387(12200), 367(12500), 349(7350), 332(3380), 312(1920), 298(2510), 256 (254000) and 249nm(140000); Anal. for $C_{23}H_{21}N$, Found: C, 88.53%; H, 6.76%.

3-N-Phenyl-N-[3-(9-anthryl)-1-propyl]aminopropionic Acid (A-8). A-7 (2.0 g, 6.4 mmol) was added to a mixture of acrylic acid (5.0 ml) and acetic acid (5.0 ml) and the mixture was stirred at 21°C under nitrogen for 3 hrs. Excess acetic acid and acrylic acid were removed under reduced pressure, and the residue was dissolved in dichloromethane and washed with water. The organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure, giving A-8 as a yellow powder which was used for the next step without purification (1.3 g, 3.4 mmol, 53%); mp 65-66°C; ir(CH_2Cl_2) 1710 and 1600cm^{-1}; nmr($CDCl_3$) δ 2.05 (p, 2H, J = 8Hz), 2.59 (t, 2H, J = 8Hz), 3.46 (t, 2H, J = 8Hz), 3.57 (t, 2H, J = 8Hz), 3.63 (t, 2h, J = 8Hz), 6.71-6.73 (m, 3H), 7.19 (t, 2H, J = 7Hz), 7.37-7.44 (m, 4H), 7.81 (d, 2H, J = 8Hz), 8.12 (d, 2H, J = 8Hz) and 8.27ppm (s, 1H).

3-N-Phenyl-N-[3-(9-anthryl)-1-propyl]amino-N'-methylpropionanilide (A-9). A-8 (1.0 g, 2.6 mmol) was added to a solution of dicyclohexylcarbodiimide (0.60 g, 2.9 mmol) and N-methylaniline (1.0 g, 9.3 mmol) in THF (50 ml). This mixture was stirred for 12 hrs at 21°C. The precipitate was removed by filtration, the filtrate was concentrated under reduced pressure, and the excess N-methylaniline was removed with the aid of an oil pump. The residue was purified by chromatography over silica gel and eluted with dichloromethane/pet ether (1:1). This yielded A-9 as a yellow oil (0.74 g, 1.6 mmol, 60%); ir(neat) 1670, 1600 and 1520cm^{-1}; nmr($CDCl_3$) δ 2.01 (p, 2H, J = 8Hz), 2.40 (t, 2H, J = 8Hz), 3.24 (s, 3H), 3.44 (t, 2H, J = 8Hz), 3.56 (t, 2H, J = 8Hz), 3.67 (t, 2H, J = 8Hz), 6.46 (d, 2H, J = 7Hz), 6.60 (t, 1H, J = 7Hz), 6.68 (d, 1H, J = 7Hz), 7.03-7.09 (m, 4H), 7.24 (t, 2H, J = 7Hz), 7.41-7.47 (m, 4H), 7.98 (d, 2H, J = 8Hz), 8.15 (d, 2H, J = 8Hz) and 8.31ppm (s, 1H). This material is used for the preparation of A-1 without further purification.

N-Phenyl-N-[3-(9-anthryl)-1-propyl]-N'-methyl-N'-phenyl-1,3-diaminopropane (A-1a). A solution of A-9 (0.5 g, 1.1 mmol) in 10 ml of THF was added to a stirred suspension of LAH (0.1 g, 2.6 mmol) in 10 ml of THF under dry nitrogen at a rate sufficient to maintain gentle reflux. The mixture was stirred for 12 hrs at 21°C following the addition. The excess reducing agent was destroyed as in the preparation of A-7. The precipitate was removed by filtration and the filtrate concentrated under reduced pressure. The residue was purified by chromatography over silica gel. The product A-1a was recrystallized from ether to yield yellow prisms (0.20 g, 0.44 mmol, 40%); mp 99-100°C, ir(KBr) 1585 and 1490 cm^{-1}; nmr($CDCl_3$) δ 1.88 (p, 2H, J = 8Hz), 2.10 (p, 2H, J = 8Hz), 2.86 (s, 3H), 3.33-3.40 (m, 4H), 3.50 (t, 2H, J = 8Hz), 3.62 (t, 2H, J = 8Hz), 6.64-6.69 (m, 6H), 7.15-7.21 (m, 4H), 7.43-7.47 (m, 4H), 7.97-8.00 (m, 2H), 8.16-8.19 (m, 2H) and 8.32ppm (s, 1H); uv (CH_3OH) λ_{max}(ε) 388(10400), 367(10600), 350(5400), 333(2700), 312(2200), 305(2300), 256 (252000) and 248 nm(12800); m/e 459 (protonated parent); Anal. for $C_{33}H_{34}N_2$, Found: C, 86.18%; H, 7.54%; N, 6.02%.

N-Phenyl-N-[3-(9-anthryl)-1-propyl]-N'-methyl-N'-4-tolyl-1,3-diaminopropane (A-1b). A-1b was prepared as in the case of A-1a, mp 78-79°C, ir(KBr) 1586 and 1492 cm^{-1}; nmr($CDCl_3$) δ 1.84 (p, 2H, J = 8Hz), 2.07 (p, 2H, J = 8Hz), 2.21 (s, 3H), 2.81 (s, 3H), 3.25 (t, 2H, J = 8Hz), 3.33 (t, 2H, J = 8Hz), 3.47 (t, 2H, J = 8Hz), 3.60 (t, 2H, J = 8Hz), 6.60-6.68 (m, 5H), 6.99 (d, 2H, J = 8Hz), 7.13 (t, 2H, J = 8Hz), 7.43-7.47 (m, 4H), 7.97-8.00 (m, 2H) and 8.31 ppm (s, 1H); uv(CH_3OH) λ_{max}(ε) 388(10400), 367(10600), 350(5400), 333(2700), 311 (2250), 305(2200), 256(251500) and 248nm (128000); Anal. for $C_{34}H_{36}N_2$, Found: C, 86.04%; H, 7.81%; N, 5.83%.

N-Phenyl-N-[3-(9-anthryl)-1-propyl)-N'-methyl-N'-4-anisyl-1,3-diaminopropane (A-1c). A-1c was prepared as in the case of A-1a, mp 78-79°C, ir(KBr) 1587 and 1495cm^{-1}; nmr($CDCl_3$) δ 1.84 (p, 2H, J = 8Hz), 2.09 (p, 2H, J = 8Hz), 2.79 (s, 3H), 3.21 (t, 2H, J = 8Hz), 3.26 (t, 2H, J = 8Hz), 3.49 (t, 2H, J = 8Hz), 3.61 (t, 2H, J = 8Hz), 3.73 (s, 3H), 6.64-6.69 (m, 5H), 6.79 (d, 2H, J = 8Hz), 7.16 (t, 2H, J = 8Hz), 7.43-7.47 (m, 4H), 7.97-8.00 (m, 2H), 8.16-8.19 (m, 2H) and 8.32ppm (s, 1H); uv(CH_3OH) λ_{max}(ε) 388(10300), 367(10500), 350(5300), 332(2700), 312(2150), 305(2250), 255(251000) and 248nm(127000); Anal. for

$C_{34}H_{36}N_2O$, Found: C, 83.58%; H, 7.63%; N, 5.69%.

N-Phenyl-3-(1-pyrenyl)proprionamide (P-6). P-6 was prepared as in the case A-6 in 86% yield, mp 211-212°C; ir(KBr), 1655, 1533, 1444 and 841cm^{-1}; nmr($CDCl_3$) δ 2.90 (t, 2H, J = 7Hz), 3.83 (t, 2H, J = 7Hz), 7.10 (t, 1H, J = 7Hz), 7.27 (m, 2H), 7.36 (d, 2H, J = 8Hz) and 7.9-8.4ppm (m, 9H); Anal. for $C_{25}H_{20}N_2O$, Found: C, 85.33%, H, 5.61%; N, 3.87%.

N-Phenyl-3-(1-pyrenyl)-1-aminopropane (P-7). P-7 was prepared as in the case of A-7 and was recrystallized from EtOAc-hexane, mp 92-94°C; ir(KBr), 1600, 1510, 744 and 690cm^{-1}; nmr($CDCl_3$) δ 2.20 (p, 2H, J = 7Hz), 3.36 (t, 2H, J = 7Hz), 3.47 (t, 2H, J = 7Hz), 6.62 (d, 2H, J = 7Hz), 6.70 (t, 1H, J = 7Hz), 7.17 (t, 2H, J = 7Hz) and 7.8-8.3ppm (m, 9H); Anal. for $C_{25}H_{22}N_2$, Found: C, 89.80%; H, 6.31%; N, 4.07%.

3-N-Phenyl-N-[3-(1-pyrenyl)-1-propyl]aminopropionic Acid (P-8). P-8 was prepared by a method similar to that for A-8, except the stirring was prolonged to 15 hrs. The crude product was recrystallized from toluene giving P-8 in 47% yield, mp 142-143°C; ir(KBr), 1701, 1599, 1505, 842 and 749cm^{-1}; nmr($CDCl_3$) δ 2.20 (p, 2H, J = 7Hz), 2.60 (t, 2H, J = 7Hz), 3.20 (t, 2H, J = 7Hz), 3.40 (t, 2H, J = 7Hz), 3.45 (t, 2H, J = 7Hz), 6.60 (m, 3H), 7.30 (m, 2H), 7.80-8.30ppm (m, 9H); Anal. for $C_{28}H_{26}N_2O_2$, Found: C, 82.83%; H, 6.23%; N, 3.33%.

General Procedure for the Synthesis of 3-N-Phenyl-N-[3-(1-pyrenyl)-1-propyl]amino-N'-aryl--N'-methylpropionamide (P-9). To a solution containing 1 eq. of P-8 and 3.5 eq. of the appropriate N-methyl-N-arylamine in dry dichloromethane cooled in an ice-bath was added a solution of 1.2 eq. of dicyclohexylcarbodiimide in dichloromethane with stirring. The solution was allowed to warm up to the room temperature (21°C) and stirred for 12 hrs. The precipitate was removed by filtration and the solvent was evaporated under reduced pressure from the filtrate to yield a pale yellow oil. The crude product was purified by chromatography over silica gel (hexane/ethyl acetate). Typical yield was 50%. This material was used directly for the preparation of P-2.

General Procedure for the Synthesis of N-Phenyl-N-[3-(1-pyrenyl)-1-propyl]-N'-aryl-N'-methyl-1,3-diaminopropanes (P-1). P-9 was reduced to the corresponding P-1 by diborane using a reported procedure.[19] The crude product was purified by chromatography over silica gel (hexane/dichloromethane/ethyl acetate) to yield a pale yellow oil which solidifies upon standing. The product was further purified by recrystallization from ethyl acetate/methanol.

P-1a, mp 74-76°C; ir(KBr) 1601, 1505, 1189, 840cm^{-1}; nmr($CDCl_3$) δ 1.74 (p, 2H, J = 7Hz), 2.02 (p, 2H, J = 7Hz), 2.71 (s, 3H), 3.15-3.45 (4 overlapping triplets, 8H), 6.56 (m, 6H), 7.08 (m, 4H), 7.8-8.2 (m, 9H); uv(CH_2Cl_2) λ_{max}(ε) 345.5(38000), 329(28000), 315(16000), 277(51000), 266(50000) and 244nm(81000); m/e: Calcd for $C_{35}H_{34}N_2$: p 482, p+1 483(39.1 of p); Found: p, 482, p+1 483(39.9 of p).

P-1b, mp 63-65°C; ir(KBr) 1598, 1519, 1503, 1369, 1241, 846cm^{-1}; nmr($CDCl_3$) δ 1.84 (p, 2H, J = 7Hz); 2.15 (p, 2H, J = 7Hz), 2.23 (s, 3H), 2.81 (s, 3H), 3.2-3.5 (4 overlapping triplets, 8H), 6.58-6.70 (m, 5H), 6.98 (d, 2H, J = 8Hz), 7.16 (t, 2H, J = 8Hz), 7.8-8.3ppm (m, 9H); uv(CH_2Cl_2) λ_{max}(ε) 345.5(38000), 333(28000), 315(16000), 277(52000), 266

(50000) and 244nm(81000); Anal. Found for $C_{36}H_{36}N_2$: C, 87.11%; H, 7.43%; N, 5.59%.

P-1c, mp 50-51°C; ir(neat) 1597, 1511, 1244, 1037, 843cm^{-1}; nmr($CDCl_3$) δ 1.81 (p, 2H, J = 7Hz), 2.15 (p, 2H, J = 7Hz), 2.76 (s, 3H), 3.20 (t, 2H, J = 7Hz), 3.25-3.55 (3 overlapping triplets, 6H), 3.73 (s, 3H), 6.60-6.72 (m, 5H), 6.78 (d, 2H, J = 8Hz), 7.16 (t, 2H, J = 8Hz) and 7.8-8.3ppm (m, 9H); uv(CH_2Cl_2) λ_{max}(ε) 345.5(39000), 329(30000), 315 (17000), 277(53000), 266(50000) and 244(85000); Anal. Found for $C_{36}H_{36}N_2O$: C, 84.21%; H, 7.11%; N, 5.41%.

3-(1-Pyrenyl)-1-propanol (P-10). A solution of 3-(1-pyrenyl)propionic acid (P-5, 4 g, 14.6 mmol) in 15 ml of absolute THF was added dropwise with stirring to a suspension of of 0.7 g of LAH in 100 ml of absolute THF under nitrogen. The mixture was refluxed for 3 hrs following the addition. The mixture was worked up as in the case of A-7 yielding 3.2 g of P-10 (84%) as pale yellow crystals, mp 67-70°C; nmr($CDCl_3$) δ 2.15 (p, 2H, J = 7Hz), 3.28 (t, 2H, J = 7Hz), 3.45 (t, 2H, J = 7Hz) and 7.8-8.3ppm (m, 9H). The material was used without further purification for the preparation of P-2.

N-Methyl-N-Phenyl-3-(1-pyrenyl)-1-aminopropane (P-2). To a cooled solution of P-10 (3 g) in 70 ml of dry pyridine at 0°C, 4.4 g of tosyl chloride were added with stirring. The solution was stored overnight in a refrigerator at 4°C. The entire mixture was poured into a mixture of ice and water and extracted with ether. The ethereal extract was washed twice with cold 1N HCl, twice with cold water, dried over anhydrous potassium carbonate and evaporated, yielding 3.1 g (65%) of the tosylate as a yellow oil. The material was shown to be homogeneous by nmr and used without further purification.

The tosylate thus prepared (2.9 g) was added to 25 ml of N-methylaniline. The mixture was stirred and heated at 100°C for 4 hrs. Most of the unreacted N-methylaniline was removed with the aid of an oil pump leaving a dark brown oil. The oil was purified by chromatography over silica gel (hexane/dichloromethane/ethyl acetate), yielding 1.3 g of P-2 52%) as a pale yellow oil which solidified upon standing, mp (CH_3OH) 72-73°C; ir(neat) 1594, 1506, 1353, 1180, 840cm^{-1}; nmr($CDCl_3$) δ 2.15 (p, 2H, J = 7Hz); 2.95 (s, 3H), 3.37 (t, 2H, J = 7Hz), 3.48 (t, 2H, J = 7Hz), 6.68 (m, 3H), 7.20 (t, 2H, J = 8Hz), 7.8-8.3ppm (m, 9H); uv(CH_2Cl_2) λ_{max}(ε) 345(38000), 329(27000), 315(14000), 277(47000), 266(36000) and 244nm(72000); high resolution ms: m/e calcd. for $C_{26}H_{21}N$: 349.1830; found, 349.1785; Anal. Found for $C_{26}H_{21}N$: C, 89.22%; H, 6.77%; N, 3.95%.

RESULTS

The excited state behaviors of 1-3 were analyzed by steady state fluorescence spectroscopy in a variety of solvents for the detection and characterization of the exciplex formed, time-resolved fluorescence spectroscopy for the analysis of exciplex emission, and time-resolved absorption spectroscopy for the detection and analysis of transients formed. The formation and decay of anthryl radical anion are followed by its absorption at 680-700nm region,[20] pyrenyl radical anion at 492nm,[21] anilino radical cation at 470nm,[21,22] anthryl triplet at 425nm,[23] and pyrenyl triplet at 415nm.[20] A typical transient absorption spectrum, that of A-1a, is given in Figure 1. For trichromophoric compounds in both

the anthryl and pyrenyl series, only A-1a and A-1b, as A-2,[5] exhibit an appreciable monomeric aromatic emission in saturated hydrocarbon solvents. On the other hand, none of them exhibit an appreciable exciplex emission in solvents more polar than dichloromethane. The results are tabulated in Tables 1-3.

Table 1. Fluorescence Maxima of Polychromophoric Arylamines in Different Solvents.

	Compound(cm^{-1})							
Solvents(f - 1/2f')	A-2	A-1a	A-1b	A-1c	P-2	P-1a	P-1b	P-1c
pentane(0.090)	20600	20530	20530	19960	23150	23090	21880	20200
Mecyclohexane(0.106)	20530	20490	20530	19920	23250	23090	22170	20200
C_2HCl_3(0.197)	19920	20000	19920	18520	22320	22030	20830	19600
ethyl ether(0.256)	19760	19920	19650	17700	21740	21650	20410	18520
ethyl acetate(0.293)	19050	19050	18180	16500	20530	20410	19490	17540
CH_2Cl_2(0.319)	18870	18870	17860	---[a]	20410	20200	18730	17090
$-\mu_{ex}^2/hca^3(10^{-3}cm^{-1})$	7.6±1.0	7.0±1.0	5.2±0.6[b] 15.5±1.3[c]	16.5±1.5	12.5±1.5	12.7±1.5	13.5±1.6	13.6±1.8

[a]Too weak to be evaluated. [b]For solvents from pentane to ether. [c]For more polar solvents.

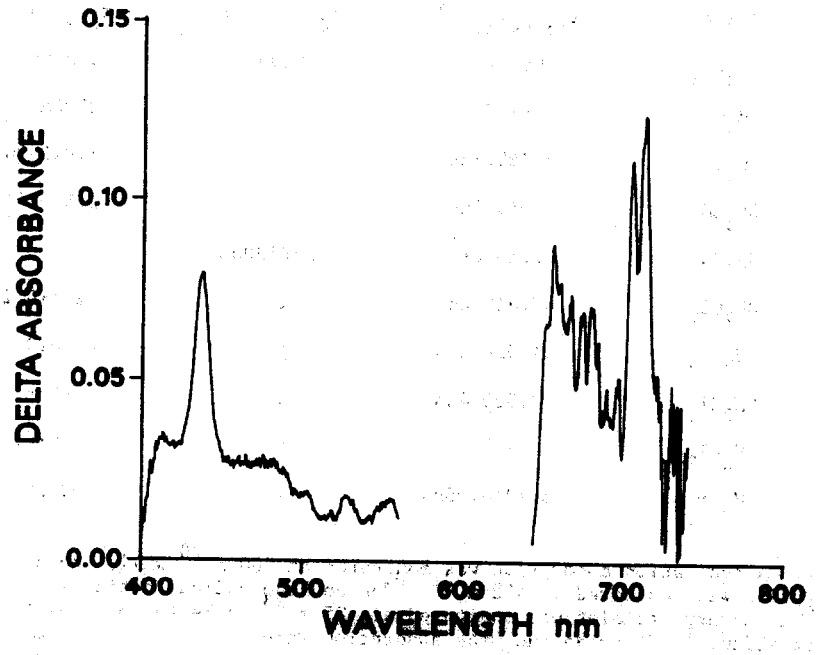


Figure 1. Transient Absorption Spectrum of A-1a.

Table 2. Exciplex Quantum Yields and Lifetimes from Polychromophoric Arylamines.[a,b]

Compound	Pentane		CH_2Cl_2	
	Φ_{ex}	τ_{ex}(ns)	Φ_{ex}	τ_{ex}(ns)
A-1a	0.44	79	<0.01	<2
A-1b	0.44	82	--[c]	--[c]
A-1c	0.13	59	--[c]	--[c]
A-2	0.46	80	0.12	28
P-1a	0.62	48[d]	0.11	25
P-1b	0.36	48[d]	0.07	48
P-1c	0.10	26	<0.01	--[c]
P-2	0.70	54	0.19	27

[a]The range of uncertainty of experimental values given is ±10%. [b]The lifetime values given are the average of a minimum of two runs. [c]Too weak to be measured. [d]The decay is double exponential with a longer lifetime component.

Table 3. Transient Absorptions from Photoexcited Polychromophoric Arylamines.

Compound	Solvent	$\tau_{decay(Ar.^-)}$[a]	$\tau_{decay(\equiv N.^+)}$[b]	$\tau_{rise(^3Ar)}$[c]
A-1a	CH_2Cl_2	20±1ns	19±3ns	20±2ns
A-2	CH_2Cl_2	---[d]	e	27±2ns
A-1a	CH_3CN	2.0±0.3ns	f	1.8±0.3ns
A-2	CH_3CN	1.6±0.4ns	f	2.5±0.4ns
A-3	CH_3CN	270±30ps	270±30ps	f
P-1a	CH_2Cl_2	47.4±0.4ns	g	42.1±0.2ns
P-1b	CH_2Cl_2	44.5±0.1ns	g	43.0±0.1ns
P-1c	CH_2Cl_2	18.3±0.4ns	g	<5ns
P-2	CH_2Cl_2	---[h]	e	13.0±0.6ns
P-2	CH_3CN	6.10±0.05ns	g	5.30±0.05ns

[a]The anthryl radical anion absorption was monitored at 700nm,[20] while the pyrenyl radical anion absorption was monitored at 492nm.[21] [b]The aniline radical cation was monitored at 470nm.[22] [c]The anthryl triplet was monitored at 425nm,[23] while the pyrenyl triplet was monitored at 415nm.[21] [d]A broad and weak absorption which is different from the anthryl radical anion absorption was detected at 700nm. This may be due to the exciplex absorption. [e]None detected. [f]Not measured. [g]A broad shoulder at 450-470nm was detected. Due to its overlap with the pyrenyl radical anion absorption at 492nm, it was not analyzed. [h]Too weak to be analyzed.

DISCUSSION

The basic object of our investigation is to study the interaction between [arene*:amine] exciplexes and another amine donor as a model for the photochemical interaction in multicomponent systems. Since such interactions would have taken place between three or more different molecules in intermolecular systems, in order to alleviate the unfavorable entropy factor in such interactions, we synthesize trichromophoric systems A-1 and P-1 containing one aryl group and two amines as our entries for such an investigation in an intramolecular system. When we initiated our investigation, there were two commonly known bichromophoric systems, 2 and 3, for the studies on intramolecular exciplexes.[24] In principle, either of them may be modified to a trichromophoric system. In practice, modification of 3 to a trichromophoric system would result in a trisubstituted aniline derivative via a ring-substitution or the incorporation of a rigid phenyl group with a considerable amount of steric restraint in the exciplex:amine interaction via an N-substitution. None of this complication will occur in the modification of A-2 and P-2 to A-1 and P-1. These compounds were thus synthesized according to the Synthetic Scheme. It is interesting, perhaps significant, to note that the methodology used in the synthesis of 1 may be readily modified for the synthesis of multichromophoric systems of even higher order.

A goal of our investigation is to show that light-induced electron transfer may be facilitated in the exciplex:amine interaction. This phenomenon was demonstrated in a preliminary study where A-1a underwent electron transfer in dichloromethane while A-2 did not (Table 3).[8] The formation of both an anthryl radical anion and an anilino radical cation was demonstrated by kinetic absorption spectroscopy (Figure 1). The absorptions of these radical ions correspond well to the known values of these ions formed in the excitation of bichromophoric 2 and 3 in a polar solvent, acetonitrile.[24] The lifetimes of these radical ions are within the experimental error of the risetime of the anthryl triplet absorption. The results demonstrate that these radical ions annihilate to form the anthryl triplet as in the case of these radical ions formed from 2 or 3 in acetonitrile (equation 2). However, the lifetime of radical ions formed from A-1a in dichloromethane is approximately one order of magnitude longer than those formed from 2 and related systems in acetonitrile (Table 3). Our results thus offer us an entry to construct polychromophoric arylamines which may yield radical ions of even longer lifetimes such that they may be trapped by chemical means to affect the storage of light energy in the form of chemical energy.

$$D^{+\cdot} + A^{-\cdot} \longrightarrow D + {}^{3}A \text{ or } A \qquad (2)$$

Since excited pyrenyl systems are known to have longer lifetimes than the corresonding anthryl systems, compounds in the P-1 series were thus synthesized and studied. The results were tabulated in Tables 1-3.

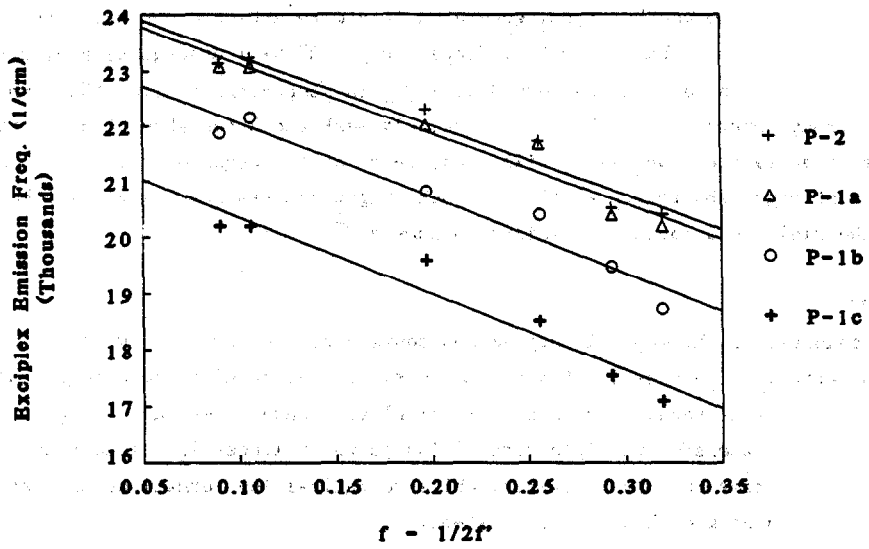
A. Intramolecular Exciplex Formation

By comparing the fluorescence maxima of exciplexes derived from compounds in P-1 and

P-2 to the corresponding compounds in A-1 and A-2, we find that they are generally blue-shifted (Table 1), e.g., 23090cm^{-1} for P-1a vs 20530cm^{-1} for A-1a. Furthermore, when the polarity of solvents is changed from pentane to dichloromethane, the red shift of the exciplex emission is larger in the pyrenyl series, e.g., the shift is 2890cm^{-1} in P-1a vs. 1660cm^{-1} in A-1a. The blue-shift in exciplex fluorescence is in agreement with the higher the IP and EA of pyrenyl compounds,[25] which increase the energy gap between the LUMO of the aryl system and HOMO of the anilino donor. The bigger energy gap also increases the charge-transfer character in the exciplex which results in the larger shift in exciplex fluorescence with increasing solvent polarity.

We have shown that intramolecular exciplex formation occurs only to a minimal extent between the photoexcited anthryl group and the anilino function in N-methyl-N-phenyl-7-(9-anthryl)-1-heptylamine, A-4a.[26] Although it is known that the σ-bonds in these compounds may undergo rotation during the lifetime of the excited anthryl group, the groups are still too far apart for an interaction to occur to an appreciable extent when they are linked by 8 σ-bonds. Independent work by Zachariasse indicated that intramolecular exciplex formation does take place between the photoexcited 7-(1-pyrenyl) group and the 1-anilino group in an analogus compound.[27] This may be due to the much longer lifetime of excited pyrenyl groups (>200ns) vs. that of a 9-anthryl group (≈5ns),[10] although the higher LUMO of pyrenyl derivatives over that of anthryl derivatives may also play a role in this interaction. This interaction may also account for the red-shift of exciplex emission from P-1a to P-1b in hydrocarbon solvents while such a shift does not occur from A-1a to A-1b (Table 1). Both anilino functions in P-1a and P-1b may interact with the excited pyrenyl group in hydrocarbon solvents while only the nearer anilino group does in A-1a and A-1b. The interaction between the p-tolidino group and the excited pyrenyl group in P-1b causes the red-shift in its exciplex emission. This interpretation is supported by our experimental observation that exciplexes from both A-1a and A-1b undergo single exponential decay in hydrocarbon solvents, while those from P-1a and P-1b undergo a more complex decay (Table 2). The charge-transfer interaction between components in an exciplex may be analyzed quantitatively by the dependence of its fluorescence maximum (λ_{max}) on the solvent polarity ($f - 1/2f'$).[28] We found that the slopes of such plots, $-\mu_{ex}^2/hca^3$, from P-1a, P-1b, P-1c and P-2 are within experimental errors of each other (Table 1 and Figure 2). These results differ markedly from those obtained from the analogus compounds in the anthracene series. We have noted previously that exciplexes from A-1a and A-2 possess similar charge-transfer characters, 7.0±1.0 and 7.6±1.0x10^{-3}cm^{-1} respectively, that from A-1c possess a much higher charge-transfer character, 16.5±1.5x10^{-3}cm^{-1}, while that from A-1b exhibits a variable charge-transfer character depending on the range of solvent polarity, 5.2±0.6 and 15.5±1.3x10^{-3}cm^{-1} (Table 1).[5] This variation of charge-transfer character provides support for the existence of two different types of exciplexes, and one of them being the ternary systems. The absence of such a variation strongly suggests that only binary exciplexes are formed in the pyrenyl series and two different binary exciplexes may be formed from P-1a and P-1b in hydrocarbon solvents.

Figure 2. Exciplex Emission Freq. vs. (f - 1/2f') for P-1 and P-2.



B. Exciplex Induced Electron Transfer.

We found that the photoexcited dichromophoric P-2, as in the case of A-2, readily yields the radical ions in acetonitrile which annihilate to yield the pyrenyl triplet, while it undergoes no detectable electron transfer in the less polar solvent, dichloromethane. Among the trichromophoric pyrenyl compounds, both P-1a and P-1b yield well-defined pyrenyl radical anion absorption at 492nm[21] as well as the anilino radical cation absorption at 450-470nm[22] as a shoulder to the stronger pyrenyl radical ion absorption. Due to the overlap between these two absorptions, only the decay of the stronger pyrenyl absorption was monitored. Once again the lifetime of the exciplex corresponds well with the risetime of pyrenyl triplet absorption, and this observation agrees with the well-known behavior of radical-ion pairs which annihilate to yield the corresponding triplet (equation 2). Although the lifetimes of radical ions generated from the pyrenyl series are longer than those from the anthryl series, the difference, approximately a factor of two, is judged to be not substantial enough to affect the efficient trapping of these photo-generated radical ion-pairs chemically.

In the trichromophoric anisidine derivatives, A-1c and P-1c, neither compound yields appreciable exciplex emission in dichloromethane. Since an anisidino group may undergo direct photoinduced electron transfer over 8 σ-bonds to a 9-anthryl group in A-4c,[26] it is possible for the excited aryl group in A-1c and P-1c to interact with both nitrogen atoms in these compounds. Since the rotation of σ-bonds will occur during the lifetime of excited aryl groups, it is probable that the electron transfer may occur from

the anisidino group to the excited aryl may take place in two or more conformations. One type of radical ion pairs generated from one of the conformation is in a close proximity from each other, while another type, generated in a more extended conformation, is further apart from each other. The "intimate radical ion pairs" will undergo back electron transfer at a rate comparable to those formed from P-2 in acetonitrile, i.e. ≈5ns, which, due to their strong interaction, exhibit a relatively weak and broad absorption at the 492nm, while the "free radical ion pairs" will decay decay at the observed rate of 18.3ns yet exhibits a stronger absorption at 492nm. Such suggestion has been given by other scientists in the field to account for similar phenomena.[24]

CONCLUSION

Photoexcited trichromophoric arylamines containing one aryl and two amino groups may undergo a variety of interesting transformations. In saturated hydrocarbons, they may form either binary or ternary exciplex. In dichloromethane, they may undergo exciplex promoted electron transfer to yield radical ion pairs of longer lifetimes than those from analogus systems in polar solvents, while no radical ion formations are detected from the corresponding dichromophoric systems.

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