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INTRAMOLECULAR PHOTO-INDUCED ELECTRON TRANSFER IN A RIGID ANTHRACENE-N,N-DIMETHYLANILINE SYSTEM. POSSIBLE RÔLE of EDA COMPLEX FORMATION

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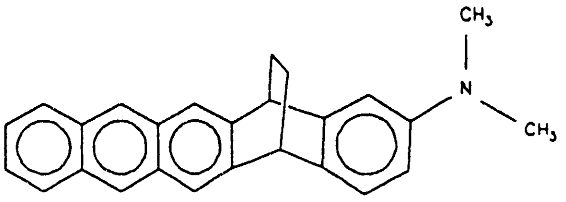
ABSTRACT

2-(N,N-Dimethylamino)-5,14-ethanopentacene (1) was synthesized and spectroscopic behaviors investigated. The results suggest that 1 undergoes photoinduced electron transfer (PET) in solvents more polar than saturated hydrocarbons. The resulting charge-transfer (CT) state undergoes CT fluorescence efficiently in solvents of low dielectric constants. Fluorescence excitation studies of the CT emission reveal the existence of an EDA interaction in the ground state. The implications of these results will be discussed.

INTRODUCTION

Through the classical contribution of Weller and his coworkers [1], it has been demonstrated that excited aromatic hydrocarbons may interact with amines to undergo either exciplex formation or photo-induced electron transfer (PET) depending on the experimental conditions. 2-(N,N-Dimethylamino)-5,14-ethanopentacene (1) was synthesized [2], in which the excited anthracene electron acceptor, A*, and N,N-dimethylanilino donor, D, are held rigidly in a spatial configuration such that they are prevented from undergoing large structural changes before or after photoexcitation. The rigidity would prevent the D and A* moieties to align themselves in a classical face-to-face exciplex-like conformation, and presumably, would allow the moieties to undergo PET which may require a less-restricted geometry. Since both phenomena exhibit marked solvent dependence, fluorescence of 1 was examined in a variety of solvents of different polarity. The results suggested that PET had occured in 1 in solvents more polar than methylcyclohexane. Independent contribution by Verhoeven and coworkers indicate that a similar event had taken place in their systems [3]. The emission from the ion-pair state is now commonly known as the charge-transfer (CT) emission.



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EXPERIMENTAL PART

The synthesis of 1 has been outlined previously [2] and will be published elsewhere. Steady state fluorescence measurements were carried out on a Perkin-Elmer MPF-66 spectrofluorimeter, and quantum yields were determined by using 9,10-diphenylanthracene as the secondary standard. The instruments used in measuring fluorescence lifetimes, fluorescence risetimes, and absorption lifetimes have been described previously [4].

RESULTS AND DISCUSSIONS

1. Steady State Fluorescence. The fluorescence spectroscopy of 1 was investigated in solvents of differing polarity in order to probe for electron transfer from the N,N-dimethylaminophenyl donor to the excited anthracene acceptor, and the results are tabulated in Table 1.

Table 1. Fluorescence quantum yields of localized anthracene emission (Φ_{LE}) and charge-transfer emission (Φ_{CT}) of 1.

Solvent	$\varepsilon_s{}^a$	$f - 0.5f'^{b}$	$_{CT}$(nm)^c	$\Phi_{LE}{}^d$	$\Phi_{CT}{}^d$
Methylcyclohexane	2.02	0.106	---^{e}	0.25	---^{f}
Benzene	2.28	0.116	438	0.04	0.57
Toluene	2.38	0.126	433	0.05	0.54
n-Butyl ether	3.05	0.192	430	0.14	0.26
Trichloroethylene	3.41	0.197	440	0.02	0.43
Ethyl ether	4.22	0.256	460	0.01	0.69
n-Butyl acetate	5.01	0.267	507	---^{f}	0.39
Ethyl acetate	6.00	0.293	522	---	0.38
Tetahydrofuran	7.39	0.307	520	---	0.39
Dichloromethane	8.93	0.319	530	---	0.29
2-Propanol	18.3	0.370	575	---	0.06
Acetonitrile	37.5	0.393	605	---	0.03

[a] Static dielectric constant. [b] $[(\varepsilon_s-1)/(2\varepsilon_s+1)]-0.5(\varepsilon_{op}-1)/(2\varepsilon_{op}+1)]$.

[c] ±2nm. [d] ±10%. [e] Not detected. [f] <0.001.

From the dependence of the emission maximum on the solvent polarity factor [1], a line with a slope of $-33.5\pm0.24\cdot10^3$ cm^{-1} and an intercept of 29430cm^{-1} is obtained. The points of benzene and toluene are excluded because $\varepsilon_{op}\approx\varepsilon_s$, which lowers the CT emission in aromatic solvents relative to alkanes with similar ε_s. Assuming a solvent cavity diameter of 10Å and the model as described by Weller [1], the results suggest that the dipole moment of the system is greater than 20D, which in turn suggests that complete charge separation may have occured in excited 1 in solvents more polar than alkanes.

Intramolecular exciplex formation and electron transfer from acyclic systems linked by one carbon atom have been noted previously by Chandross and Thomas [5] as well as by Okada et al. [6]. In addition, these processes have also been reported for rigid molecules possessing naphthalene donors and dicyanoethylene acceptors [3]. The low quantum yield of locally excited anthracene emission from 1 in solvents more polar than diethyl ether, Table 1, suggests that another state is formed rapidly from the initial locally excited anthracene singlet. The low Φ_{LE}'s in these solvents indicate that this process should occur with a rate constant $>7\times10^{10}$ s^{-1} (vide infra), which is in agreement with our observation that the risetime of CT emission from 1 in ethyl ether or ethyl acetate is at the limit of our instrumental resolution of <15ps.

2. Dynamic Spectrocopies.

Since steady-state fluorescence study of 1 suggests that extensive charge-separation has occured in excited 1, time-resolved fluorescence and transient absorption spectroscopic studies of 1 were carried out in a number of solvents in order to probe further into this phenomenon. The decay of fluorescence in these solvents was monitored at their respective maxima, and transient absorption was monitored at 700nm attributed to the anthracene radical anion [7]. Attempts were also made to monitor the decay of N,N-dimethylanilino radical cation at 470nm [8] as well as the risetime of anthracene triplet absorption at 425nm [9]. Although the decay of N,N-dimethylanilino absorption qualitatively parallels to that of anthracene radical anion, the quantitative analysis of this absorption as well as the rise of anthracene triplet failed, due to the interference between these two absorptions. The results of dynamic spectroscopies are given in Table 2.

Table 2. Absorption and Fluorescence Decay Lifetimes of 1.

Solvent	$\tau_{ab}(ns)^a$	$\tau_{CT}(ns)^b$	$k_d(10^7 s^{-1})^c$
Methylcyclohexane	3.6	---	---
Toluene	11.2	11.4	9.1
Ethyl ether	22.2	20.8	4.8
Ethyl acetate	21.6	24.0	4.2
Dichloromethane	14.8	15.3	6.7
Acetonitrile	5.7	4.2	23.0

[a] Monitored at 700nm, ±1,0ns. [b] Monitored at the maximum, ±1,0ns.
[c] Rate of decay of the CT state or back electron transfer.

Dynamic spectroscopic studies are in agreement with our assignment that the photoexcited 1 is the CT state in solvents more polar than alkanes. They decay via back-electron transfer, and their rates are dependent upon their free energy change. In non-aromatic solvents, the rate increases as the solvent becomes more polar. We estimated from the polarographic data [1] that free energy changes in the back electron transfer are 2.05, 2.34, 2.37 and 2.69eV in acetonitrile, dichloromethane, ethyl acetate and ethyl ether respectively. The rate decreases qualitatively as the free energy becomes more favorable. This correlation suggests that the dependence of rates of back-electron transfer in different solvents on free energy changes take place in the Marcus's inverted region as originally proposed by Closs and Miller [10].

The dramatic dependence of the excited state behvaiors of 1 on the solvent polarity, i.e., local excitation occurs in methylcyclohexane while PET occurs in more polar solvents, may be rationalized qualitatively in terms of the energetics of PET of 1 in solvents of different polarity which is given in equation 1 [1].

$$\Delta G = e[E_{ox}(D) - E_{red}(A)] - E_{o,o} - e^2/\varepsilon_s R_c - e^2/r(1/37 - 1/\varepsilon_s) \qquad (1)$$

where $E_{ox}(D)$, $E_{red}(A)$ and $E_{o,o}$ are the polarographic oxidation potential of D, polarographic reduction potential of A, excitation energy of the system respectively, ε_s is the static dielectric constant of the solvent, R_c is the the center to center distance between A and D, and r is the average ionic radius. Using 2,3-dimethylanthracene as the model for A, it has an E_{red} of -2.13V [10]. The value of E_{ox} for N,N-dimethyl-3,4-xylidine, the model for D, is not known and is estimated to be 0.70V [11], and the value of $E_{o,o}$ may be calculated from its absorption spectrum to be 3.30eV. Assuming a value of R_c of 7Å for the initial non-adiabatic PET and 4.5Å for the average ionic radius, ΔG would be slightly unfavorable by approximately 0.05eV in an alkane of ε_s of 2.0, while it would become favorable in n-butyl ether which has an ε_s of 3. It is also likely that the molecular conformation of 1 would be modified in the ion-pair after PET, owing to the strong coulombic interaction between the charges.

3. EDA Interaction in Ground State.

In intramolecular PET of flexible molecules, the molecule may undergo extensive conformational changes both before and after excitation. Radical ion pairs derived from PET may thus assume a face-to-face conformation and become exciplexes. In such cases, radical ion pairs are intermediates in the reaction pathway for the formation of exciplexes, and have been characterized using transient and kinetic spectroscopy [12].

As given in the energy-level diagram (Figure 1), when the level of ion-pair CT state is lowered by solvation in solution below the local excited (LE) level, the CT state may interact with the ground state in an EDA type of interaction. The extent of this interaction will depend on the distance and the orientation between the D and A groups. Although 1 is quite rigid, it may still undergo minor vibrational distortions. When the C_1-C_2 and C_6-C_1 as well as the C_3-C_4

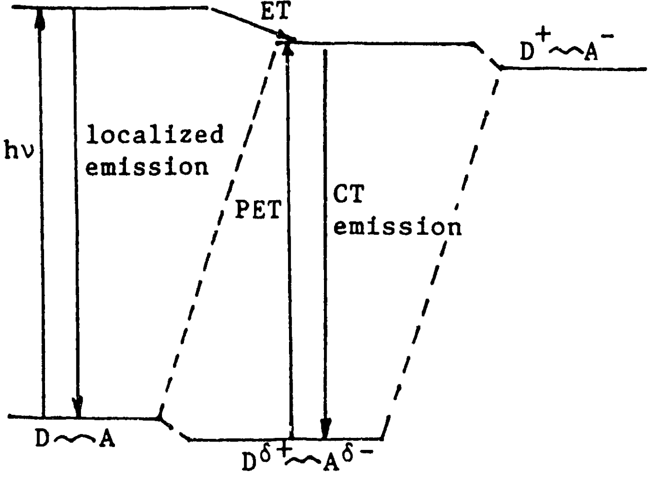


Figure 1. A schematic diagram on the role of ground state complexation in PET.

and C_5-C_4 bonds in the cyclooctadienyl ring system undergo the scissoring in-plane bending vibrations, the motion may bring the D and A groups a bit closer together causing an appreciable edge-to-edge EDA type of interaction. The EDA interaction may introduce a partial polar character to the ground state allowing its direct excitation into the CT state. The PET of 1 may thus be reached by two alternative pathways: (a) the direct excitation from the EDA level, and (b) the ET from the LE level. After it has undergone PET in an appropriate solvent to form a radical ion pair, the coulombic interaction between the charges may distort the molecule further by bending the D and A groups toward each other. Although the conformational restraint would prevent the radical ion pair to come to a face-to-face exciplex-type of configuration, the D-A distance in the radical ion pair would be closer than that in the ground state of 1. An effort was thus made to detect the intramolecular EDA type of interaction in 1.

A careful examination of the electronic absorption spectra in a variety of solvents failed to detect definitive EDA type of interaction in 1 owing to the interference by the strong low-lying L_a absorption of the anthryl group. Since the PET in 1 via ET from the locally excited state is competitive against a number of radiative and non-radiative decay processes, while the PET via the direct excitation from the EDA surface is not, the EDA absorption may be amplified relative to that of the localized L_a state by examining the fluorescence excitation spectrum of the CT emission in a variety of solvents. After the excitation spectra in different solvents have been normalized with respect to the intensity of the 0-0 band of the anthryl absorption, the results are given in Figure 2. A clearly discernible difference was noticed between the excitation spectrum of 1 in methylcyclohexane monitored at the maximum of localized emission

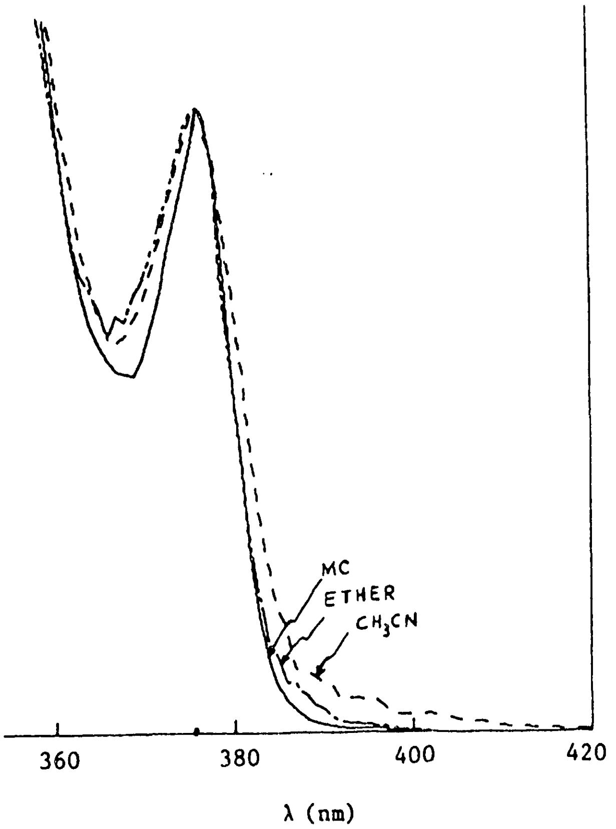
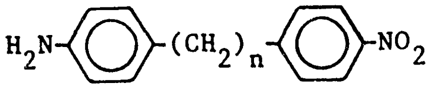


Figure 2. Fluorescence excitation spectrum of 1 in different solvents.

and the excitation spectrum in acetonitrile monitored at the maximum of CT emission. An additional group of bands extended approximately by 20nm from the red-edge of the spectrum in methylcyclohexane was detected. Judging from the relative intensities of two groups of absorption in the excitation spectrum, we concluded that the indirect pathway for PET via the local excited state appears to be the major one. It may appear to be surprising that two non-parallel π-systems may undergo EDA-type of interaction. However, such interactions have been noted previously in several instances [14]. They include not only polymethylene-linked D-A systems [14], such as 2, but also D-A systems having the two groups occupying vicinal cyclopentyl positions in both cis- and trans-orientations [15], 3 and 4. The role of ground state EDA interaction in PET exhibited by 1 was also detected in the fluorescence excitation spectra of three related intramolecular systems, the PET of N-p-methoxyphenyl-N-methyl-2-[9-anthryl]ethylamine 5 in solution and in a supersonic jet [16], the PET of N-phenyl-N-methyl-2-[10-cyano-9-anthryl]ethylamine 6 in solution [17], and the PET of N-p-dimethylaminobenzyl-10-cyano-9-anthramide 7 in solution [18]. Factors governing the two pathways in intramolecular PET, the direct pathway via the EDA excitation and the indirect pathway via the local excited state (Figure 2) will be pursued actively in our laboratories.



n = 1 to 3

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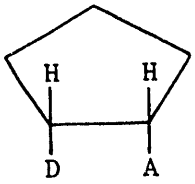

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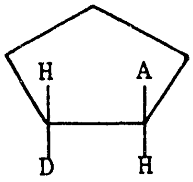

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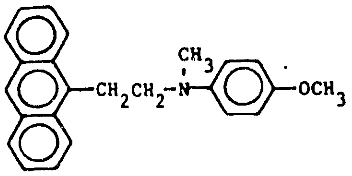

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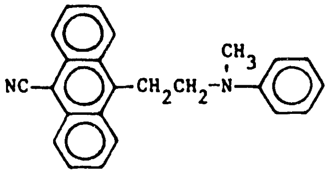

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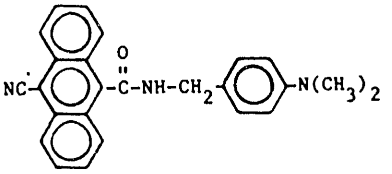

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