(69) All melting points and boiling points are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, Ga. The infrared absorption spectra were determined on a Perkin-Elmer Model 137 Infracord spectrophotometer. The ultraviolet absorption spectra were measured with a Cary Model 14 recording spectrophotometer using 1-cm matched cells. The proton magnetic resonance spectra were determined at 100 MHz using a Varian XL-100 and a Jeolco MH-100 spectrometer. Mass spectra were determined with a Perkin-Elmer RMU6 mass spectrometer at an ionizing voltage of 70 eV. All irradiations were carried out using a 450-W Hanovia medium-pressure mercury arc lamp.

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Chemistry of Exciplexes. 9.
Viscosity Effect on Intramolecular Exciplex Formation in Saturated Hydrocarbons

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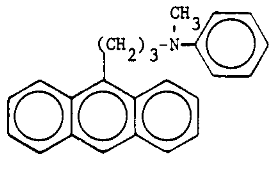
Abstract: The relative intensities of the anthracene-like fluorescence and the intramolecular exciplex fluorescence of *N*-phenyl-*N*-methyl-3-(9-anthryl)-1-aminopropane in saturated hydrocarbons are dependent on the solvent viscosity. Both the rates of exciplex formation and dissociation are retarded in more viscous solvents, but the solvent viscosity has only little effect on the equilibrium of intramolecular exciplex formation.

Photoexcited anthracenes form exciplexes with tertiary amines.[1] Since exciplexes are more polar than the uncomplexed excited aromatic hydrocarbons, it is well known that the polarity of solvent exerts a marked effect on the properties of exciplexes.[2] Bichromophoric molecules containing both an aromatic group and a tertiary amino substituent may form intramolecular exciplexes.[3-9] Recently these phenomena have been applied to study the macroscopic environment in polymers.[10] Anthracene–dimethylaniline exciplex will undergo interesting chemical reactions with another molecule of the amine.[11] In connection with our interest in the chemistry of exciplexes, we synthesized *N*-phenyl-*N*-methyl-3-(9-anthryl)-1-aminopropane (**1**)[7] and are investigating the chemical interaction between its intramolecular exciplex with a variety of amines.[12] When the fluorescence of **1** was examined carefully in a variety of solvents including several saturated hydrocarbons, we found that the emission varies from one hydrocarbon to another. The results were analyzed by kinetic spectroscopy and it was found that both the rates of exciplex formation and dissociation are retarded in a more viscous solvent, but the solvent viscosity has little effect on the equilibrium of exciplex formation.[13]



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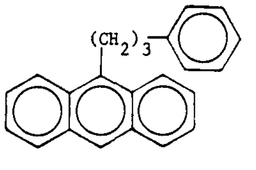

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Experimental Methods

All solvents used were the spectroscopic grade solvents purchased from the Aldrich Co. *N*-Phenyl-*N*-methyl-3-(9-anthryl)-1-aminopropane (**1**) was prepared according to a known procedure.[7] 3-(9-Anthryl)-1-phenylpropane (**2**) was prepared from 9-anthranilydene acetophenone in two steps.

3-(9-Anthryl)-1-phenyl-1-propanone. A solution of 9-anthranilydene acetophenone[14] (4.0 g) in tetrahydrofuran (250 mL) was hydrogenated in the presence of 800 mg of Pd/C (10%) catalyst at room temperature (21 °C) and atmospheric pressure. The pale green residue solidified upon trituration with ether. An analytical sample was prepared from this solid by recrystallization from ether: mp 116–117 °C; NMR ($CDCl_3$), δ 3.44 (t, 2 H), 4.08 (t, 2 H), 7.48 (m, 7 H), 7.94 (d, 2 H), 8.12 (d, 2 H), 8.26 (d, 2 H), 8.34 ppm (s, 1 H). Anal. Calcd for $C_{23}H_{18}O$: C, 89.00; H, 5.85. Found: C, 88.60; H, 6.00.

3-(9-Anthryl)-1-phenylpropane (2). A mixture of 3-(9-anthryl)-1-phenylpropanone (1 g), anhydrous hydrazine (1 mL), NaOH (0.9 g), and diethylene glycol (10 mL) was heated gradually to 200 °C and was maintained at 200–205 °C for 3.5 h. After cooling, the mixture was poured into water and extracted with benzene. The benzene extract was washed, dried, and evaporated under reduced pressure. The yellow semicrystalline residue was chromatographed over silica gel packed in benzene. The product **2** was isolated from the benzene eluant by evaporation and recrystallization from petroleum ether: mp 79–80 °C; NMR ($CDCl_3$) δ 2.19 (quintet, 2 H), 2.92 (t, 2 H), 3.62 (t, 2 H), 7.17 (m, 5 H), 7.52 (m, 4 H), 7.98 (d, 2 H), 8.12 (d, 2 H), 8.30 ppm (s, 1 H). The overall yield from 9-anthranylidene acetophenone was 40–45%. Anal. Calcd for $C_{23}H_{30}$: C, 93.20; H, 6.80. Found: C, 89.95; H, 6.98.

All fluorescence spectra were measured at 22.0 ± 0.5 °C on a Perkin-Elmer MPF-4 spectrofluorimeter with an integrated electronic corrected spectra unit and a thermostatic sample compartment. Samples were prepared at 1.5×10^{-5} M concentration in **1** or **2** and were degassed by multiple freeze–thaw cycles at a pressure <0.01 Torr.

The instrument used for the kinetic spectroscopy had been described previously.[15,16] The excitation source was an acousto-optically mode-locked argon ion laser with a synchronously pumped doubled dye laser system. The excitation wavelength was arbitrarily set at 2941.5 Å. The fluorescence signals from the PMT were processed via a timing filter amplifier to a constant fraction discriminator, a biased time to pulse height converter, and a multichannel pulse height analyzer successively. The data were collected at the teletype and analyzed by an IBM 370-168 or PDP 11/03 computer according to a known procedure.[16] The resolution in lifetime measurements was estimated to be >0.2 ns.

Results

The fluorescence spectra of **1** in four hydrocarbons, *n*-pentane, *n*-heptane, methylcyclohexane, and *n*-hexadecane, are given in Figure 1. The spectra consist of two discernable but overlapping groups of emissions, a structured anthracene-like emission (emission A*) at 391 and 412 nm, and broad structureless emission (emission E*) with a maximum at 487

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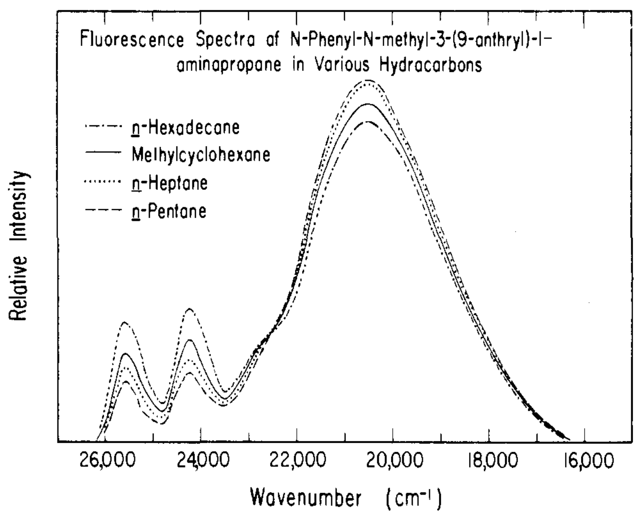


Figure 1. Fluorescence spectra of *N*-phenyl-*N*-methyl-3-(9-anthryl)-1-aminopropane (**1**) in various hydrocarbons.

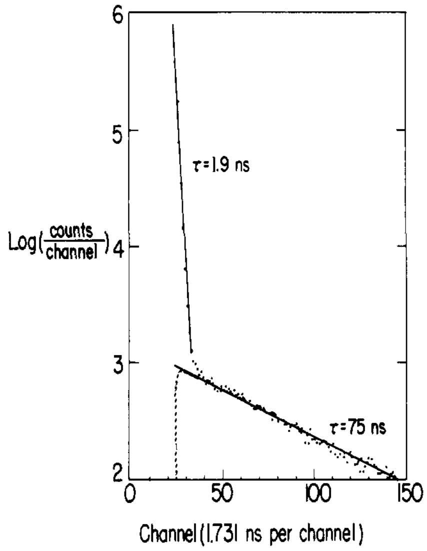


Figure 2. Decay of intramolecular exciplex fluorescence of **1** in *n*-hexadecane.

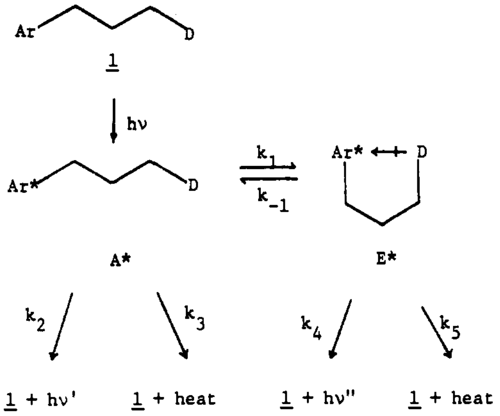
nm, which are assigned to be those of the uncomplexed excited **1** and the intramolecular exciplex of **1**, respectively. Since the profile of emission A* is virtually identical with the fluorescence of **2** in the short wavelength region, the emission is resolved artificially into two separate groups of emissions by assuming that the remaining portion of emission A* which overlaps with emission E* is identical with that of the model compound **2**. The quantum yields of these two emissions, Φ_{A^*} and Φ_{E^*}, are calculated from the relative areas underneath the respective emissions using both quinine sulfate and diphenylanthracene as the secondary standard.[17]

The lifetimes of these two emissions were analyzed according to the method of Hui and Ware.[18] The emission A* at 391 nm exhibits a two-component decay, a short-lived component corresponding to the lifetime of A* (τ_{A^*}) and a long-lived component corresponding to the lifetime of E* (τ_{E^*}). The long-lived component of emission A* results from A* regenerated from the dissociation of E* (vide infra). The result from a typical run on the decay of fluorescence of **1** at 391 nm in *n*-hexadecane is given in Figure 2. The emission E* at 487 nm exhibits a fast rise time corresponding to τ_{A^*} followed by a slow single-component decay with a lifetime corresponding to τ_{E^*}. Both τ_{A^*} and τ_{E^*} obtained from these two measurements are in excellent agreement with each other indicating the reliability of our experiments, e.g., the values of τ_{E^*} in methylcyclohexane obtained from the decay of emission of E* in five different runs were 74.6, 74.6, 73.5, 73.2, and 76.2 ns and those from the long-lived component of emission A* in a duplicate run were 75.2 and 76.6 ns. Similarly, the values of τ_{A^*} in *n*-pentane obtained from the rise time of emission E* were 0.76 and 0.92 ns and those from the decay of short-lived component of emission A* were 0.78 and 0.81 ns. The relative emission intensities of emission A* from the short-lived component to the long-lived component (Φ_{A^*S}/Φ_{A^*L}) were estimated from the area under the respective components in a plot of emission intensities vs. time. The results of these measurements are tabulated in Table I.

Calculation of Rates and Equilibrium Constants

Judging from the results summarized in Table I, photophysical behaviors of **1** depends markedly on the viscosity of hydrocarbon media. Kinetically, the behavior of photoexcited **1** may be expressed by Scheme I where k_1 and k_{-1} are the rate of formation of the intramolecular exciplex, E*, from the localized excited A* and the rate of dissociation of E* to A*, respectively; k_2 and k_3 are the rates of radiative and nonradiative decays of A*, respectively; k_4 and k_5 are the rates of radiative and nonradiative decays of E*, respectively; *hν′* and *hν″* are the fluorescence of A* and E*, respectively.

Scheme I



Since E* has a much longer lifetime than A* and E* formation is a reversible process, the fluorescence of A* will decay nonexponentially. It will decay initially with a rate equivalent to the reciprocal of τ_{A^*} and subsequently with a rate equivalent to the reciprocal of τ_{E^*}. Such a phenomenon is well known in the intermolecular exciplex formation and dissociation between aromatic compounds and amines.[18] Under our experimental conditions when A*, E*, and **1** are all present in very low concentrations, all bimolecular processes are insignificant. τ_{E^*} may be given by the following expression:

$$\tau_{E^*}^{-1}[E^*] = (k_{-1} + k_4 + k_5)[E^*] - k_1[A^*] \qquad (1)$$

Since A* decays so much faster than E*, during the lifetime measurement of E*, virtually all A* formed by initial excitation has already decayed and the concentration of A* in solution may be adequately represented by the A* regenerated from the intramolecular dissociation of E*. The regenerated A* decays with a lifetime of τ_{E^*}, as has been shown experimentally. Thus,

$$\tau_{E^*}^{-1}[A^*] = (k_1 + k_2 + k_3)[A^*] - k_{-1}[E^*] \qquad (2)$$

Since τ_{E^*} is much longer than τ_{A^*}, or k_1 is much larger than k_{-1}, $\tau_{A^*}^{-1}$ may be adequately represented by the sum of k_1, k_2, and k_3, and substituting ($k_1 + k_2 + k_3$) by $\tau_{A^*}^{-1}$ in eq 2 and transposing the terms containing [A*] to one side of the

Table I. Fluorescence Properties of **1** and **2** in Solution[a]

	solvent			
	n-pentane[b]	*n*-heptane[b]	methylcyclohexane[b]	*n*-hexadecane[b]
η, cP	0.22	0.39	0.73	3.34
ϵ	1.84	1.97	2.02	2.06
$\lambda_{A*}(0\rightarrow0)$, nm	390 ± 1	390 ± 1	391 ± 1	391 ± 1
$\lambda_{E*}(\max)$, nm	486 ± 2	486 ± 2	487 ± 2	488 ± 2
Φ_{A*}	0.048 ± 0.005	0.061 ± 0.006	0.081 ± 0.008	0.105 ± 0.010
Φ_{E*}	$0.45_4 \pm 0.02$	$0.45_0 \pm 0.02$	$0.41_1 \pm 0.02$	$0.38_0 \pm 0.02$
τ_{A*}, ns	0.82 ± 0.10[c]		1.10 ± 0.15[c]	1.90 ± 0.20[d]
τ_{E*}, ns	79.3 ± 2.0[c]		74.6 ± 2.0[c]	75.0 ± 0.5[d]
Φ_{A*F}/Φ_{A*S}	6.0 ± 0.3		9.7 ± 0.5	21.5 ± 1.0
τ_2, ns	4.32 ± 0.20[e]		5.99 ± 0.20[e]	7.20 ± 0.20[e]
Φ_2	0.30 ± 0.03		0.44 ± 0.04	0.50 ± 0.05

[a] At 22.0 ± 0.5 °C. [b] Values of viscosity and dielectric constant are obtained from "Landolt-Börnstein Zehlenwerte Funktionen"; Springer-Verlag: Berlin; Band II, Teil 5 and 6. [c] Average and range of values obtained from multiple runs of both experimental methods. [d] Average and experimental uncertainties of values obtained from a single run of both experimental methods. [e] Values and experimental uncertainties obtained from a single run.

Table II. Rates and Equilbrium Constant of Photoexcited **1** at 22 °C

	solvent		
	n-pentane	methylcyclohexane	*n*-hexadecane
k_1, s^{-1}	9.88 ± 10^8	7.42×10^8	3.87×10^8
k_{-1}, s^{-1}	2.59×10^6	1.69×10^6	8.43×10^5
K	382	439	459
k_2 or k_{2f}, s^{-1}	6.94×10^7	7.35×10^7	6.94×10^7
k_3 or k_{2nr}, s^{-1}	1.62×10^8	9.35×10^7	6.94×10^7
k_4, s^{-1}	7.07×10^6	6.73×10^6	6.89×10^6
k_5, s^{-1}	5.03×10^6	6.33×10^6	6.21×10^6

equation, we have

$$(\tau_{A*}{}^{-1} - \tau_{E*}{}^{-1})[A^*] = k_{-1}[E^*] \tag{3}$$

or

$$[A^*] = \frac{k_{-1}[E^*]}{(\tau_{A*}{}^{-1} - \tau_{E*}{}^{-1})} \tag{4}$$

Substituting eq 4 into eq 1, we have

$$\tau_{E*}{}^{-1}[E^*] = (k_{-1} + k_4 + k_5)[E^*] - \left[\frac{k_1 k_{-1}[E^*]}{(\tau_{A*}{}^{-1} - \tau_{E*}{}^{-1})}\right]$$

or

$$\tau_{E*}{}^{-1} = (k_4 + k_5) + k_{-1}[1 - k_1(\tau_{A*}{}^{-1} - \tau_{E*}{}^{-1})^{-1}] \tag{5}$$

In other words, since the intramolecular exciplex formation and its dissociation back to A* are reversible processes while both A* and E* undergo independent radiative and nonradiative decays, the lifetime of E* is determined not only by k_4 and k_5 but also by a fractional value of k_{-1} represented by the last term in eq 5. This term represents the fraction of A* in the steady state which will eventually contribute to the decay of E*.

Since the values of k_2 and k_3 cannot be evaluated directly from our measurements, we synthesized 1-(9-anthryl)-3-phenylpropane (**2**) as the model compound for the uncomplexed anthracene component of **1**. Compound **2** was selected as the model for **1** over other simple 9-alkylated anthracenes because they are similar in structure and thus have similar modes of vibrations. We found that both the fluorescence quantum yield (ϕ_{2f}) and fluorescence lifetime of **2** (τ_2) are variable with the hydrocarbon solvent used in this study (Table I).[19] The ϕ_{2f} increases from 0.30 ± 0.03 to 0.50 ± 0.05 and τ_2 increases from 4.32 ± 0.20 to 7.20 ± 0.20 ns when the solvent was changed from *n*-pentane to *n*-hexadecane. Since the fluorescence lifetime is the reciprocal of the sum of both radiative and nonradiative decays, or $\tau_2 = k_{2f} + k_{2nr}$, when our results were analyzed according to this expression, it was found that this variation of ϕ_{2f} and τ_2 in different hydrocarbon solvents is indeed due to the variation of k_{2nr} only (Table II). We subsequently found that this variation of fluorescence quantum yield and lifetime with solvent viscosity is common for several other 9-substituted anthracenes while not for anthracene itself and 9,10-dimethylanthracene.[20] This phenomenon will be treated in detail in a separate communication. Based on these experimental results, values of k_{2f} and k_{2nr} are taken to be the values of k_2 and k_3, respectively, for **1**, and values of k_1 in different solvents are calculated according to

$$k_1 = \tau_{A*}{}^{-1} - (k_2 + k_3) = \tau_{A*}{}^{-1} - \tau_2{}^{-1} \tag{6}$$

We found that the value of k_1 decreases successively from 9.87 × 10^8 s^{-1} in *n*-pentane, to 7.42 × 10^8 s^{-1} in methylcyclohexane, and to 3.87 × 10^8 s^{-1} in *n*-hexadecane.

Alternatively, if a simple 9-alkylated anthracene, such as 9-methylanthracene or 9-ethylanthracene, was chosen as the model for the uncomplexed anthracene component of **1**, although the calculated values of k_1 would be slightly different from those obtained above, the same conclusion would be reached for the effect of solvent viscosity on the rates and equilibria of intramolecular exciplex formation and dissociation of **1**.[20]

Since the fluorescence of A* exhibits a two-component decay, a fast component derived from A* formed by the direct excitation of **1** and a slow component from A* regenerated from the dissociation of E*, the ratio of fluorescence quantum yields of the fast component to the slow component, Φ_{A*F}/Φ_{A*S}, is a direct measure of the relative concentrations of A* formed in these two processes. Since the fraction of A* which will undergo intramolecular exciplex E* formation is $k_1\tau_{A*}$ and the fraction of E* which will eventually undergo dissociation to regenerate A* is $k_{-1}\tau_{E*}$, the ratio Φ_{A*F}/Φ_{A*S} may be analyzed by the following expression:

$$\Phi_{A*F}/\Phi_{A*S} = (k_1 k_{-1}\tau_{A*}\tau_{E*})^{-1}$$

or

$$(\Phi_{A*F}/\Phi_{A*S})k_{-1} = (k_1\tau_{A*}\tau_{E*})^{-1} \tag{7}$$

Using experimental values listed in Table I and calculated values of k_1, we may evaluate the value of k_{-1} in different solvents. These are 2.59 × 10^6, 1.69 × 10^6, and 8.43 × 10^5 s^{-1} in *n*-pentane, methylcyclohexane, and *n*-hexadecane, respectively. From the values of k_1 and k_{-1} in different solvents, the equilibrium constant for the intramolecular exciplex formation and dissociation, K, may be readily calculated. The values are 382, 439, and 459 in *n*-pentane, methylcyclohexane, and *n*-hexadecane, respectively.

Substituting respective values of k_1, τ_{A^*}, and τ_{E^*} in eq 5, we have, in *n*-pentane,

$$\tau_{E^*}^{-1} = (k_4 + k_5) + 0.181k_{-1} \qquad (8)$$

in methylcyclohexane,

$$\tau_{E^*}^{-1} = (k_4 + k_5) + 0.171k_{-1} \qquad (9)$$

in *n*-hexadencane,

$$\tau_{E^*}^{-1} = (k_4 + k_5) + 0.246k_{-1} \qquad (10)$$

The fluorescence quantum yield of intramolecular exciplex, Φ_{E^*}, is the product of the fraction of E* formed originally from A*, $k_1\tau_{a^*}$, and the fraction of E* which will eventually undergo radiative decay, $k_4\tau_{E^*}$, or $\Phi_{E^*} = k_1k_4\tau_{A^*}\tau_{E^*}$. Since all values in this expression except k_4 are now known, k_4 may be readily evaluated according to

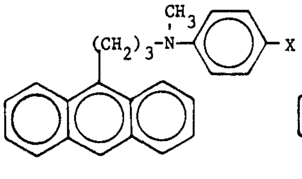
$$k_4 = \Phi_{E^*}(k_1\tau_{A^*}\tau_{E^*})^{-1} \qquad (11)$$

Substituting appropriate values of k_{-1} and k_4 into eq 8, 9, and 10, we may calculate for the values of k_5. These are, in *n*-pentane, $k_4 = 7.07 \times 10^6$, $k_5 = 5.03 \times 10^6$ s^{-1}; in methylcyclohexane, $k_4 = 6.73 \times 10^6$, $k_5 = 6.33 \times 10^6$ s^{-1}; in *n*-hexadecane, $k_4 = 6.89 \times 10^6$, $k_5 = 6.21 \times 10^6$ s^{-1}.

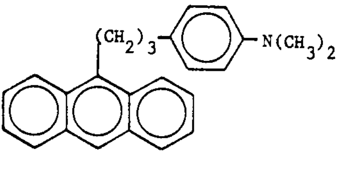
All calculated rates and equilibrium constants are tabulated in Table II.

Discussions and Conclusions

The intramolecular exciplexes derived from two types of substituted anthracenes, **1a** and **3**, have been investigated by several groups of investigators.



1a



3

The exciplex formation is affected by the substituent X in **1a**,[7] the polarity of solvent,[5,7] and the temperature.[7] We have observed for the first time that the Φ_{A^*} of **1** increases and Φ_{E^*} decreases as the viscosity of the hydrocarbon solvent increases. These observations suggest that the rate of E* formation is retarded in a more viscous solvent. Such a conclusion is in agreement with the observation of Williams and his co-workers that **3** fails to form the intramolecular exciplex in a polystyrene matrix,[8] in apparent disagreement with a report by Gnädig and Eisenthal.[21] Gnädig and Eisenthal reported that the rate of intramolecular exciplex formation of **3** is exceptionally rapid (rise time ≃ 40 ps) and is independent of the solvent viscosity. However, subsequent investigations in laboratories of Eisenthal,[5] Williams,[8] and Mataga[22] showed that the rate of intramolecular exciplex formation of **3** is only of the order of 10^8 s^{-1}. We also found that the emission profile of **3** is dependent on solvent viscosity as in the case of **1**, indicating that the rate of intramolecular exciplex formation of **3** is also dependent on the solvent viscosity.[12]

In all previous reports, no attempts were made to evaluate the rate of dissociation of intramolecular exciplex E* (k_{-1}) or the equilibrium constant for the exciplex formation and dissociation, *K*. By using **2** as the model compound for the aromatic component of **1** and the experimental results listed in Table I, we were able to solve for all of the rates in Scheme I in three hydrocarbon solvents, *n*-pentane, methylcyclohexane, and *n*-hexadecane. Since as many as three quantum yield determinations and three kinetic measurements were necessary to solve for the rates, the cumulative experimental uncertainties in these values may be quite large. Particularly, the accuracy of our lifetime measurement is ±0.2 ns while the lifetime of A* ranges from 0.82 to 1.90 ns only; therefore, we have to exercise caution in the interpretation of our experimental results. In spite of this limitation, valuable information in accordance with physical principle were obtained for intramolecular exciplex formation.

(1) In saturated hydrocarbons of approximately same dielectric constants, the rate of intramolecular exciplex formation decreases as the solvent viscosity increases. The most stable conformation of an aliphatic chain in the ground state is the extended trans conformation in which the bulky anthryl group and the amino function will be well separated from each other in **1**. Since the rate of vibrational relaxation of initial excited **1** is of the order of 10^{12} s^{-1},[23] during this time A* is unlikely to undergo appreciable changes in conformation from that of the ground state. The rate of formation of E* from A*, k_1, may involve the rotation around the aliphatic chain in order to bring the anthryl group and amino function in contact with each other. Our results clearly indicate that the rotation of a carbon chain with bulky substituents is retarded by a more viscous solvent. The rate of E* formation decreases approximately by a factor of 2.6 as the solvent viscosity increases by a factor of 15. There is apparently no simple quantitative relationship between the rate of formation of E* and the solvent viscosity as the case between the rate of diffusion and the solvent viscosity.[24]

(2) The rate of intramolecular exciplex dissociation, k_{-1}, is also retarded in a more viscous solvent. It decreases by a factor of ~3.1 from *n*-pentane to *n*-hexadecane. The decrease in k_{-1} is approximately of the same magnitude as that in k_1.

(3) The equilibrium constant for intramolecular exciplex formation and dissociation, *K*, varies by ~20% and has the value of 382, 439, and 459 in *n*-pentane, methylcyclohexane, and *n*-hexadecane, respectively (Table II). Since $\Delta G = -RT \ln K$, these values of *K* reflect only a small change in ΔG which have values of −3.47, −3.55, and −3.59 kcal/mol, respectively. The minor increase in ΔG may be attributed to the stabilization of E* relative to A* in a solvent of slightly higher dielectric constant (Table I) which increases slightly as the hydrocarbon becomes more viscous. Although the value of *K* in *n*-pentane is smaller than those in the other two solvents, it is still within experimental uncertainty of each other. Since the experimental uncertainty in our lifetime measurement is ±0.2 ns and τ_{A^*} in *n*-pentane is 0.82 ns, and the actual values of τ_{A^*} may range from 0.62 to 1.02 ns while our experimental values range from 0.76 to 0.92 ns. If τ_{A^*} has a value of 0.72 ns, the value of *K* would be 461. Equation 6 would be $\tau_{E^*} = (k_4 + k_5) + 0.160\,k_{-1}$, and values of k_1, k_{-1}, k_4, and k_5 would be 1.16×10^9, 2.52×10^6, 6.85×10^6, and 5.35×10^6 s^{-1}, respectively. In other words, they would be in almost perfect fit with values in other two solvents! Therefore, the equilibrium constant for the intramolecular exciplex formation and dissociation is only slightly affected or unaffected by the solvent viscosity as would be expected if the relative energies of the equilibrium configurations of A* and E* do not change appreciably. However, it is approximately one order of magnitude smaller than that of the intermolecular (anthracene*–dimethylaniline) exciplex.[11] The results indicate that the intramolecular exciplex formation of **1** is less favored than the intermolecular exciplex formation in spite of a more favorable entropy factor. The difference may be attributed to a small strain existing in the intramolecular exciplex, possibly the conformation strain.

(4) The rates of radiative and nonradiative decays of E*, k_4, and k_5 remain constant within experimental uncertainties in all three solvents (Table II) and are apparently unaffected by the solvent viscosity. The values of k_4 and k_5 are within the same order of magnitude as those of the (anthracene*–di-

methylaniline) exciplex indicating similar nature of their electronic structure.[11,25]

(5) Since the intramolecular exciplex formation and dissociation is a reversible process, k_{-1} only makes a partial contribution to the lifetime of E*, τ_{E^*} (eq 8-10). Since values of $k_4 + k_5$ are appreciably larger than those of k_{-1} in different solvents (Table II), it is apparent that exciplex dissociation makes only a small contribution of τ_{E^*}. Therefore, in contrast to τ_{A^*}, τ_{E^*} does not vary appreciably with the solvent viscosity as we have observed experimentally.

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Nucleophilic Addition to Activated Olefins. 3.[1] Reactions of Piperidine and Morpholine with Benzylidenemalononitrile in 50% Dimethyl Sulfoxide-50% Water. Intrinsic Barriers in Nucleophilic Additions

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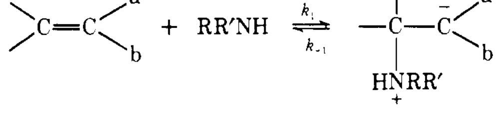
Abstract: The reactions of piperidine and morpholine with benzylidenemalononitrile give rise to two observable kinetic processes. The first is measurable by the stopped-flow temperature-jump technique and is associated with the formation of a zwitterionic addition complex ($T^{\pm}$ in Scheme I) and subsequent deprotonation to form the anionic complex T^-. The second process, which was monitored in the stopped-flow apparatus, refers to the cleavage of the addition complex T^- into benzaldehyde and malononitrile (Scheme II). In the first process nucleophilic attack is rate limiting for the piperidine reaction but proton transfer is partially rate limiting in the morpholine reaction at low amine concentrations. This result implies that base catalysis in nucleophilic vinylic substitutions by amines might be a consequence of rate-limiting proton transfer in some cases. For a given equilibrium constant for nucleophilic addition to an activated olefin the rate constants are higher for benzylidenemalononitrile (cyano activation) than for olefins activated by alkoxycarbonyl groups or the nitro group, implying a lower intrinsic barrier to nucleophilic attack in the former. The similarity of these results with findings on proton transfers involving carbon acids activated by the same substituents is discussed and related to a common origin. Analysis of the data referring to the cleavage of T^- shows that protonation of T^- on carbon, to form T^0, is rapid, while cleavage of T^0 into the iminium ion, $PhCH{=}N^+R_2$, and malononitrile anion is rate limiting.

Nucleophilic addition to the double bond of activated olefins is an important elementary process in organic chemistry.[2] Recently we have started a systematic study[3-5] of the reactions of amines with olefins bearing different electron-withdrawing substituents a and/or b (eq 1). In a preliminary report[3] we



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