Formation and Photodissociation of a Jet-Cooled Intramolecular Exciplex in the Bichromophoric EDA System: Multiconformations and Deuteration Effect

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The intramolecular exciplex formation and photodissociation in a supersonic free jet have been studied for deuterated anthryl bichromophoric EDA systems 1-(9-anthryl-d_8)-3-(*m*-(*N*,*N*-dimethylamino)phenyl)propanes (9-An-*d*-*m*-DMA) in comparison with the corresponding undeuterated compounds (9-An-*m*-DMA). Fluorescence hole burning depletion spectra in the anthryl deuterated 9-An-*d*-*m*-DMA suggests the presence of two distinct isomeric conformers. The S_1 vibrational energy thresholds for the exciplex formation in the two isomeric forms of the deuterated compounds are considerably smaller than those of the respective undeuterated compounds. The photodissociation of the exciplex leading to the formation of the excited-state anthryl moiety was observed in the excitation of the transient absorption band of the jet-cooled exciplex (S_n-S_1). The decay time of the photodissociation-induced anthryl fluorescence is shorter for 9-An-*d*-*m*-DMA than for 9-An-*m*-DMA. These deuteration effects of the anthryl moiety on the formation and photodissociation of the exciplex may be attributed to the role of the vibrational level density of the anthryl moiety in these excited-state reaction dynamics. The shorter decay time of the photodissociation-induced anthryl fluorescence of 9-An-*d*-*m*-DMA relative to 9-An-*m*-DMA is consistent with the conclusion that the emission originates from the vibrationally highly excited S_1 anthryl moiety.

Introduction

The intramolecular exciplex formation and excess vibrational energy dependence have been reported for several bichromophoric EDA systems in supersonic expansion,[1] following the pioneering work of Zewail and co-workers[2,3] on 1-(9-anthryl)-3-(*p*-*N*,*N*-(dimethylamino)phenyl)propane (abbreviated to 9-An-DMA). The existence of multiconformations of jet-cooled bichromophoric chain molecules has been demonstrated by fluorescence hole burning depletion spectra, and the vibrational energy thresholds for the exciplex formation have been found to depend on their ground-state conformations.[4−6] Very recently, Kurono, Takasu, and Itoh[6] have reported the fluorescence hole burning depletion spectra of jet-cooled bichromophoric EDA systems, 1-(1- and 9-anthryl)-3-(*m*-*N*,*N*-dimethylamino)-phenyl)propanes (abbreviated 1- and 9-An-*m*-DMA), which demonstrate the existence of two distinct ground-state conformations. The two conformational isomers exhibit different excess vibrational energy dependence for the intramolecular exciplex formation.

Saigusa, Sun, and Lim[7,8] reported the fluorescence depletion of the jet-cooled excimer generated from the naphthalene cluster in the excitation of the excimer state (B_{3g}) to its higher electronic state (B_{2u}). Very recently, we have reported the photodissociation of the exciplex in 9-An-DMA, leading to the simultaneous formation of the excited-state anthryl moiety.[9] This paper presents the supersonic jet spectroscopy of intramolecular exciplex formation and photodissociation in the deuterated anthryl bichromophoric EDA system 1-(9-anthryl-d_8)-3-(*m*-(*N*,*N*-dimethylamino)phenyl)propanes (abbreviated to 9-An-*d*-*m*-DMA) for comparison with the undeuterated compounds (9-An-*m*-DMA). Two distinct isomeric conformers were observed in the ground state of jet-cooled 9-An-*d*-*m*-DMA, and they exhibit a different excess vibrational energy dependence for the exciplex formation. The photodissociation of the exciplex leading to anthryl fluorescence with very short decay time was observed by excitation of the transient absorption band (S_n-S_1) in both deuterated and undeuterated compounds. The deuteration effect of the anthryl moiety on the formation and photodissociation dynamics of the exciplex was observed. The different features of the exciplex formation and photodissociation of the exciplex between the deuterated and the undeuterated compounds are discussed in terms of the role of vibrational level density in the excited-state reaction dynamics.

Experimental Section

Materials. The bichromophoric EDA compound with deuterium-substituted anthryl, 9-An-d_8-*m*-DMA, was synthesized from respective *m*-(*N*,*N*-dimethylamino)acetophenones and 9-anthryl-d_9-aldehyde by methods and procedures similar to those described in previous papers. The latter deuterated compound was prepared from anthracene-d_{10} (C/D/N Isotopes Inc., 99.5 atom % D) by *N*-methylformanilide and $POCl_3$ in *o*-dichlorobenzene. In the hydrogenation reaction of the carbonyl group of 1-(9-anthryl-d_9)-3-(*m*-*N*,*N*-(dimethylamino)phenyl)propan-1-ones by hydrazine in diethylene glycol, a deuterium atom at the 10 position of deuterated anthryl was substituted by a hydrogen atom. Then, 1-(9-anthryl-d_8)-3-(*m*-(*N*,*N*-dimethylamino)-phenyl)propane was obtained. The structure and purity of the compound were confirmed by elementary analysis and mass and NMR (270- and 500-MHz) spectroscopies before use. Elementary analysis and melting points are as follows: 1-(9-anthryl-d_8)-3-(*m*-(*N*,*N*-dimethylamino)phenyl)propane, mp 87.5−89.0 °C. Anal. Calcd for $C_{25}H_{17}D_8N$: C, 86.40; H, 4.93; D, 4.64; N, 4.03. Found: C, 86.53; H, 5.12; D, 4.55; N, 4.20.

General Procedures. The experimental setup and procedures for fluorescence spectroscopy in the pulsed supersonic free jet were completely the same as those described in the previous papers.[5,6,9] The 10-Hz pulsed supersonic free jet backed by He (2−3 atm) was excited at 10−12 mm downstream of a nozzle by an excimer laser pumped dye laser (Lambda Physik Compex

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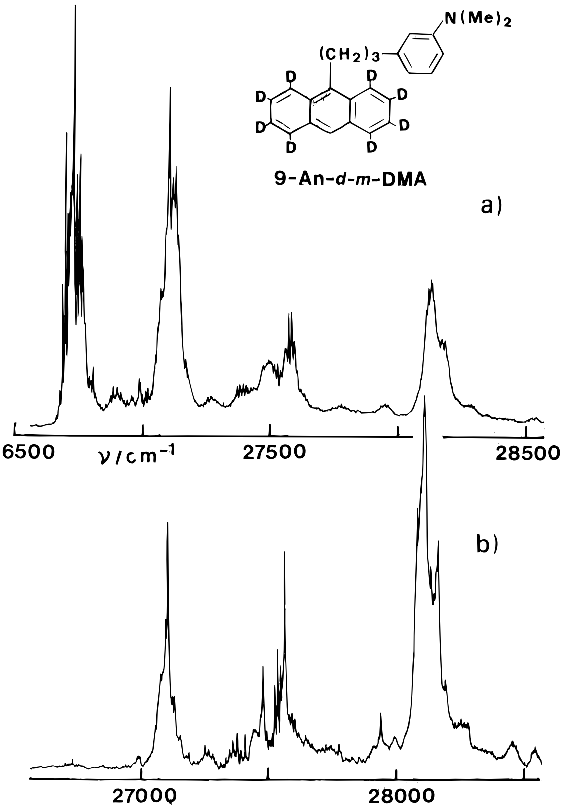

Figure 1. Fluorescence excitation spectra of jet-cooled 9-An-*d*-*m*-DMA. The spectra were monitored (a) at 395−400 nm and (b) at 470 nm.

102/FL 3002). The setup and procedures for the laser-induced fluorescence spectra and decay were the same as those described in the previous papers. The fluorescence hole burning depletion spectra were measured by a method essentially identical to those described previously.[6,9] An excimer laser pumped dye laser (Lambda Physik EMG 53MSC/FL 2002) was used as a probe laser. The hole-burning pump laser was the same as that used in the laser-induced fluorescence. The pump and probe lasers were counterpropagated and slightly focused through 50−60-cm lenses on the free jet 10−12 cm downstream from the nozzle. The pumping laser wavelength was scanned while detecting fluorescence by the probe laser excitation. Delay time between the two laser pulses was approximately 0.2−0.5 μs. The setup and procedures of the photodissociation of the exciplex were almost similar to those of the fluorescence hole burning depletion spectroscopy. Since time jitter between the two laser pulses was very important, a digital oscilloscope (Tektronix TDS 520) for detecting the photodissociation-induced fluorescence was triggered by a dissociation laser pulse, and the output of the signal was processed by a personal computer. The photodissociation experiment of the exciplex in solution was examined by the same setup as the two-step laser-induced fluorescence spectroscopy described in the previous papers.[9−11]

Results and Discussion

Excess Vibrational Energy Dependence of the Exciplex Formation in 9-An-*d*-*m*-DMA. Figure 1 shows UV and exciplex fluorescence excitation spectra of 9-An-*d*-*m*-DMA, which are very similar to those of the undeuterated compound (9-An-*m*-DMA) reported in the previous paper.[6] Strong bands with many vibrational structures at 373−375 (26 801−26 666 cm^{-1}) nm were observed only in the UV fluorescence excitation spectrum and not in the visible fluorescence excitation spectrum. The observation indicates that no exciplex formation takes place in the excitation of the lowest vibrational energy levels of the anthryl moiety of this compound. The anthryl vibronic bands show congested vibrational structures together with several sharp bands in both the UV and visible fluorescence excitation spectra. However, a careful inspection of these spectra indicates that the excitation spectra of the UV fluorescence exhibit considerably different vibrational structures from those of the exciplex fluorescence. These UV and visible fluorescence excitation spectra suggest involvement of two isomeric conformers in the ground state of the jet-cooled condition. Further, the different features between the UV and visible fluorescence excitation spectra suggest the different excess vibrational energy dependence of the exciplex formation between these isomers. Therefore, the fluorescence hole burning depletion spectra at the origin and low-energy vibronic band region were measured.

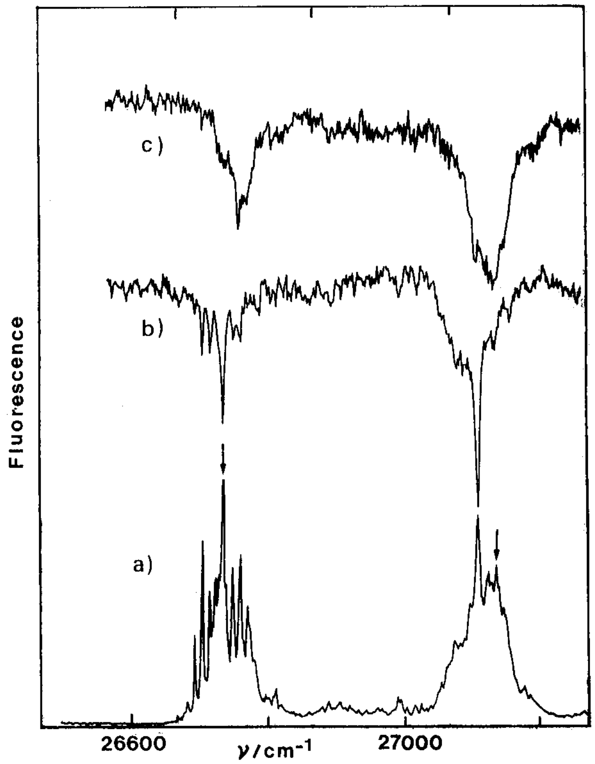

Figure 2. Fluorescence hole burning depletion spectra of 9-An-*d*-*m*-DMA in comparison with (a) UV fluorescence excitation spectrum. The pumping laser was scanned by tuning the probe laser to (b) 374.05 nm (28 737 cm^{-1}) and (c) 368.49 nm (27 137 cm^{-1}).

Figure 2 shows hole burning depletion spectra of 9-An-*d*-*m*-DMA obtained by scanning the pumping laser wavelength while detecting UV fluorescence produced by the probe laser excitations at (a) 374.05 nm (26 734 cm^{-1}) and (b) 368.49 nm (27 137.7 cm^{-1}). These hole burning depletion spectra clearly demonstrate the involvement of two components of spectra due to two ground-state isomers in this compound. The longer wavelength band series exhibits approximately 30−40 cm^{-1} redshift from the other. The former (abbreviated 9*dm*-a) shows considerably vibrationally resolved hole burning depletion spectra, while the other band series (9*dm*-b) is congested. The observation of hole burning depletion spectra of two band series due to the ground-state isomers in An-*d*-m-DMA is almost the same as that in the undeuterated compound An-*m*-DMA, reported in the previous paper.[6] The excess vibrational energy dependence of dispersed fluorescence spectra was examined by excitations of these two vibronic band series.

Figure 3 shows the dispersed fluorescence spectra obtained by excitations of vibronic bands of the two distinct isomers (9*dm*-a and 9*dm*-b). In nearly the same excess energy region

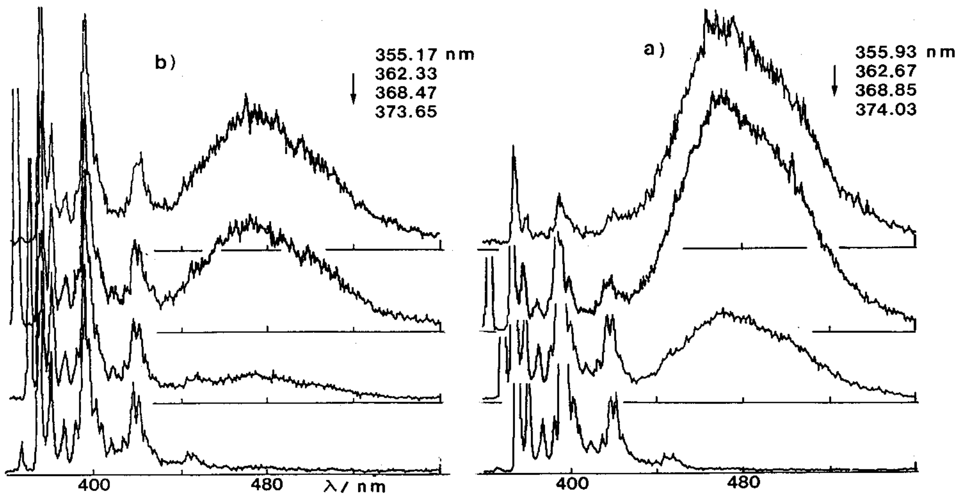

Figure 3. Dispersed fluorescence spectra in the origin and major vibronic band excitations of two isomeric band series of 9-An-*d*-*m*-DMA: (a) 9*dm*-a (an origin band, 27 137 cm^{-1}) and (b) 9*dm*-b (an origin band, 27 112 cm^{-1}).

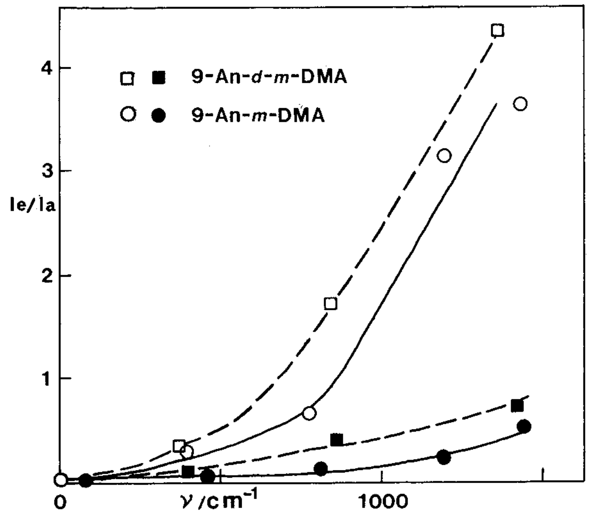

Figure 4. Ratio of relative fluorescence intensities for exciplex and anthryl moiety fluorescence of 9-An-*d*-*m*-DMA and 9-An-*d*-*m*-DMA vs the excess vibrational energy. The exciplex (I_e) and anthryl moiety fluorescence (I_a) were monitored at 470 nm and at a peak of 390−400 nm. The circle and the square represent the conformational isomers.

of the anthryl vibronic bands, the excess energy dependence for the exciplex fluorescence was more remarkable in 9*dm*-a than in 9*dm*-b. These spectral features are almost similar to those of the corresponding undeuterated compound, 9-An-*m*-DMA, reported previously.[6] At about the same excess vibrational energy, the intensity of the exciplex fluorescence was much greater in the 9*dm*-a band series than in 9*dm*-b. Figure 4 illustrates the ratio of relative intensities of the exciplex (I_e) and anthryl-like fluorescence (I_a) in 9-An-*d*-*m*-DMA vs the excess vibrational energy (ΔE), for comparison with those of the corresponding undeuterated compound 9-An-*m*-DMA. The excess energy threshold for the deuterated compound was estimated to be 450 cm^{-1} in 9*dm*-a, which is considerably less than that of the corresponding isomer (700−800 cm^{-1}) of the undeuterated compound (9*dm*-a), reported previously. However, the energy threshold for the exciplex formation in the second isomer, 9*dm*-b, was not estimated because of the small intensity ratios (I_e/I_a). The different features for the exciplex formation between two conformers and also their anthryl deuteration effect in 9-*d*-*m*-DMA were also observed in anthryl fluorescence decay times. Fluorescence decay times of the anthryl-d_8 moiety were considerably smaller than those of undeuterated 9-An-*m*-DMA. The fluorescence decay times of these anthryl moieties in the excitations of the origin band and major vibronic bands are summarized in Table 1.

TABLE 1: Fluorescence Decay Times of Anthryl Moieties of Origin and Low-Energy Vibronic Band Excitations of 9-An-*m*-DMA and 9-An-*d*-*m*-DMA[a]

	ΔE/cm^{-1}	τ/ns		ΔE/cm^{-1}	τ/ns
		9-An-*m*-DMA			
9*m*-a	0	19.0	9*m*-b	0	20.5
	398	13.8		408	15.9
	1165	12.7		1165	13.5
	1389	12.1		1400	12.2
		9-An-*d*-*m*-DMA			
9*dm*-a	0	14	9*dm*-b	0	12.0
	375	8.5		376	9.5
	837	8.5		836	9.0
	1359	7.8		1394	7.9

[a] Errors of decay times are approximately 5%.

In regular free jet condition (He pressure, 2−3 atms), the fluorescence hole burning depletion spectrum demonstrated that 9-An-DMA has only one chain conformation in the ground state and exhibits excess energy dependent exciplex fluorescence, as reported previously.[5] This chain conformation was ascribed to *trans* and *trans* conformations (*t/t*) associated with the anthryl−C_1−C_2− and −C_2−C_3−DMA torsional conformations. At considerably low He backing pressure (0.5−1 atm), however, red-shift (~50−60 cm^{-1}) and considerably congested fluorescence excitation spectra were observed. The new features were ascribed to *gauche* and *trans* conformations (*g/t*). The *trans/trans* and *gauche/trans* chain conformations were confirmed as two possible geometries of bichromophoric systems connected with trimethylene by the optimization of a simple AM-1 calculation, and the former was suggested to be more stable than the latter.[5] On the other hand, the fluorescence hole burning depletion spectra indicated that 9-An-*d*-*m*-DMA as well as nondeuterated An-*m*-DMA with a *m*-(*N*,*N*-dimethylamino)phenyl group consists of two ground-state conformers even in the regularly jet-cooled condition (2−3 He atm pressure). If the ground-state chain conformations in these compounds are the same *t/t* chain conformers as that of 9-An-DMA mentioned above, two ground-state conformers in these compounds may be attributable to the *m*-(*N*,*N*-dimethylamino)phenyl group. As mentioned in the previous paper, if the dihedral angle of the *m*-$N(CH_3)_2$−phenyl plane relative to a plane composed of C_1−C_2−C_3− bonding is perpendicular, there is only one conformer in these compounds. Therefore, conformations with a nonperpendicular dihedral angle of the phenyl ring relative to the

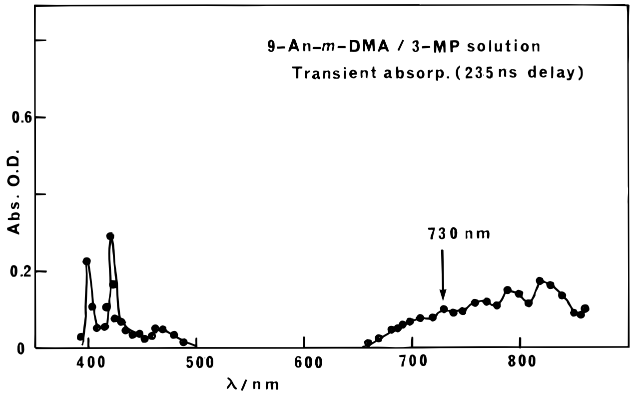

Figure 5. Transient absorption spectrum of 9-An-*m*-DMA in the deaerated 3-methylpentane solution at room temperature. The spectrum was depicted at 235-ns delay time in order to remove the exciplex fluorescence (450−500 nm), although decay time of the transient absorption was obtained to be 144 ns in this solution.

trimethylene may be required for the existence of two isomeric conformers in 9-An-*d*-*m*-DMA as well as the undeuterated compound. Two possible conformers concerned with rotations of $-C_3-$*m*-DMA and/or $-C_2-C_3-$ bondings were proposed (Figure 9 in ref 6). The different excess vibrational energy dependence of the exciplex formation between these conformers seems attributable to the consequence of the transformation dynamics from two distinct ground-state conformers to the optimum geometries for the excited-state charge transfer interaction. However, it is not obvious at the present stage if the exciplex with the same conformer is generated from the different ground-state conformations.

Photodissociation of the Intramolecular Exciplex in 9-An-*m*-DMA and 9-An-*d*-*m*-DMA. As mentioned in the introductory section, Saigusa *et al.* reported the excimer fluorescence depletion for jet-cooled naphthalene clusters following the excitation of the excimer state (B_{3g}) to the higher electronic state (B_{2u}). However, since the transient absorption spectrum of the exciplex is almost impossible to obtain in the supersonic jet, the spectra of both 9-An-*m*-DMA and 9-An-*d*-*m*-DMA were measured in deaerated solutions of 3-methylpentane at room temperature. Figure 5 shows the transient absorption spectrum of the 3-methylpentane solution of 9-An-*m-DMA.* The spectrum of the deuterated compound exhibits no significant difference from that of the undeuterated compound. Two transient absorption bands with rather long decay times at 700−800 and 460−475 nm in both compounds were observed. Since these bands were very similar to those of the anthryl anion and *N*,*N*-dimethylaniline cation radical, respectively,[13,14] these transient absorption bands in solution suggest considerable charge transfer character in the exciplex. The jet-cooled exciplex of these compounds was excited by the second laser pulse (730 nm) approximately 50−100 ns delayed from the first one. Figure 6 shows the time-resolved detection of the photodissociation of exciplex decay curves generated from two distinct isomers (359.00 nm, 27 855 cm^{-1} band of 9*m*-a and 359.18 nm, 27 841 cm^{-1} band of 9*m*-b) of 9-An-*m*-DMA. A pronounced depletion of the exciplex fluorescence was observed by excitation at 730 nm of the transient absorption band of the exciplex. The depletion of the exciplex fluorescence was approximately 70−90%, which was dependent on the depletion laser power and spatial alignments of the supersonic jet and the two laser beams. The anthryl fluorescence signal was observed simultaneously together with the depletion of the exciplex. The dependence of the exciplex depletion on the second laser wavelength (600−780 nm) was examined. The 700−750-nm dissociation laser pulse was most efficient for the exciplex depletion. The observation seems to suggest that the photodissociation of the exciplex may take place by the excitation of the exciplex (S_n-S_1). However, no accurate action spectrum of the photodissociation wavelength was presented in this paper, because of instability of the second laser pulse. Figure 7 shows typical anthryl fluorescence decay curves generated by the photodissociation of the exciplex in comparison with those obtained by the excitations of anthryl vibronic bands (27 855 and 27 841 cm^{-1}) leading to the exciplex formation. The anthryl decay time was 5.6 ns in the 27 855 cm^{-1} band excitation (9*m*-a), while the decay time was 11.8 ns in the 27 841 cm^{-1} band excitation (9*m*-b). These anthryl decay curves are shown in parts a and c of Figure 7. Since no significant difference of anthryl decay times between the two isomers (20.5−19 ns) was observed in the excitations of the origin band region, the different decay times (5.6 and 11.8 ns) of anthryl fluorescence between the two isomers in the vibronic band region (27 841−27 855 cm^{-1}, $\Delta E = 1168-1197$ cm^{-1}) indicate that the rate constant of the exciplex formation may be greater in 9*m*-a than in 9*m*-b, as reported in the previous paper. The anthryl fluorescence generated by the photodissociation of the exciplex exhibits markedly short decay times (2.3 and 6.0 ns) in comparison with the anthryl decay times (5.6 and 11.8 ns) in the exciplex formations. These anthryl decay curves observed in the exciplex dissociation are shown in parts b and d of Figure 7. It is noteworthy that very short decay times of the anthryl moiety were generated by the photodissociation of the jet-cooled intramolecular exciplex, and further these decay times were dependent on the different isomeric conformers. If the excitation of the exciplex to the higher electronic states leads to the conformational transformation of the closed exciplex state to the open form with the excited-state anthryl moiety, further exciplex formation might be expected again. However, no

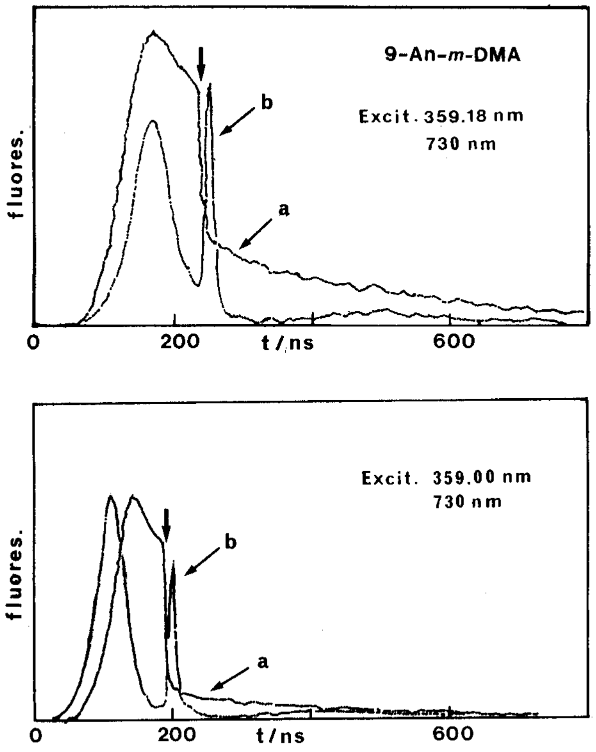

Figure 6. Time-resolved (a) depletions of the exciplex fluorescence and (b) fragment signals of anthryl fluorescence for two isomeric forms (9*m*-a and 9*m*-b) in jet-cooled 9-An-*m*-DMA. The times of dissociation laser pulse (730 nm, 5−10 mJ) are indicated by arrows. Neither depletion of the exciplex fluorescence nor of the anthryl fragment fluorescence was observed without simultaneous excitations by two laser pulses.

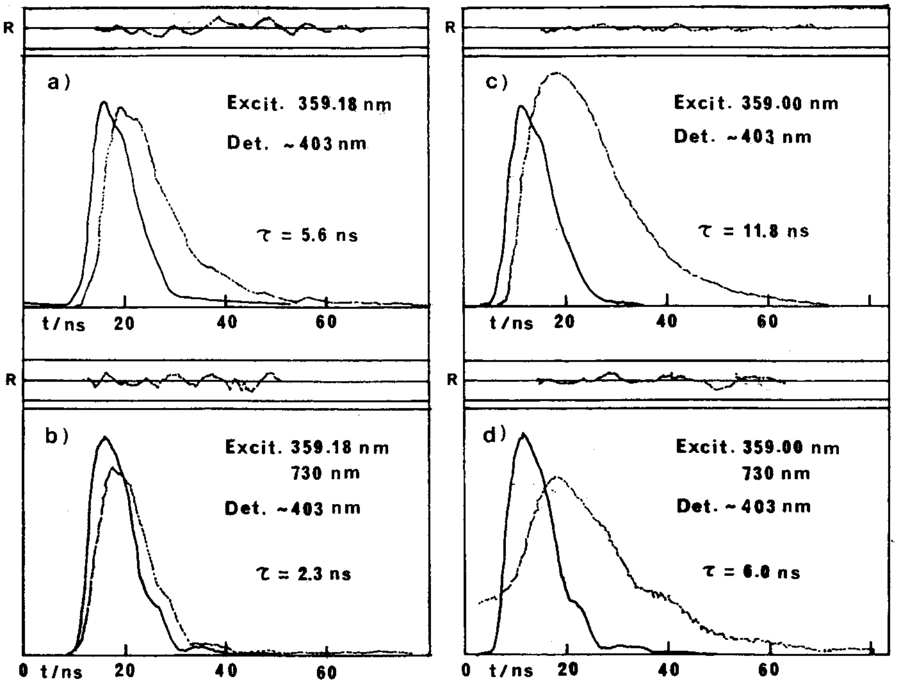

Figure 7. Time-resolved fluorescence decay curves of the anthryl moiety for the formation and photodissociation of the exciplex in 9-*m*-DMA: (a and b) anthryl fluorescence signal for the exciplex formation and anthryl fragment signal generated by the photodissociation of the exciplex in 9*m*-a; (c and d) those for the exciplex formation and for the exciplex photodissociation in 9*m*-b, respectively.

significant exciplex formation was observed in the time-resolved depletion curves of the exciplex, as shown in Figure 6.

The photodissociation dynamics of the exciplex leading to the anthryl fluorescence was also examined in the deuterated compound, 9-An-*d*-*m*-DMA, in supersonic expansion. The time-dependent exciplex depletions followed by the simultaneous formation of anthryl fluorescence were observed in this deuterated compound in the excitations (730 nm) of the exciplexes, as shown in Figure 6. The exciplexes were generated from levels with excess vibrational energy of ΔE = 860−870 cm^{-1} of the two isomers (9*dm*-a and 9*dm*-b) of 9-An-*d*-*m*-DMA. Remarkable depletion of the exciplex and formation of the excited-state anthryl of this compound are the same as those of the undeuterated compound, 9-An-*m*-DMA. The anthryl fluorescence decay curves were obtained by the photodissociation of the exciplexes, together with those of vibronic band excitations for the exciplex formations (ΔE = 850−860 cm^{-1}) of 9-An-*d*-*m*-DMA. Typical anthryl fluorescence decay curves of two isomeric forms of the deuterated compound in the exciplex formation and photodissociation are shown in Figure 8. Anthryl decay times (0.6 and 1.5 ns) by the photodissociation of the exciplex were remarkably smaller than those of the corresponding anthryl fluorescence (8.5 and 9.4 ns) in the exciplex formation. Typical fluorescence decay times of anthryl moieties and photodissociation data of the deuterated and undeuterated compounds are summarized in Table 2. These different features of the exciplex formation and photodissociation between deuterated and undeuterated compounds are discussed in terms of the role of level density in the reaction dynamics of the level crossing of the higher exciplex state (S_n) to the higher vibrational states of the anthryl S_1 state, as illustrated in Figure 9.

Saigusa *et al.*[7,8] reported an extensive study of the photodissociation of the excimer in jet-cooled naphthalene clusters as mentioned above. The photodissociation was attributed to the repulsive or weakly bound character of the B_{2u} excimer state to which the species is excited. However, in the photodissociation of the jet-cooled exciplex reported here, the mechanism of photodissociation may be considerably different from that of the excimer. Here, excitation of the exciplex to the upper state of the transient absorption band appears to lead to the higher vibrational continuum of the anthryl S_1 state through very fast intramolecular vibrational energy redistribution (IVR) and/or internal conversion. This results in the depletion of the exciplex fluorescence and concomitant appearance of the anthryl fluorescence with very short decay times.

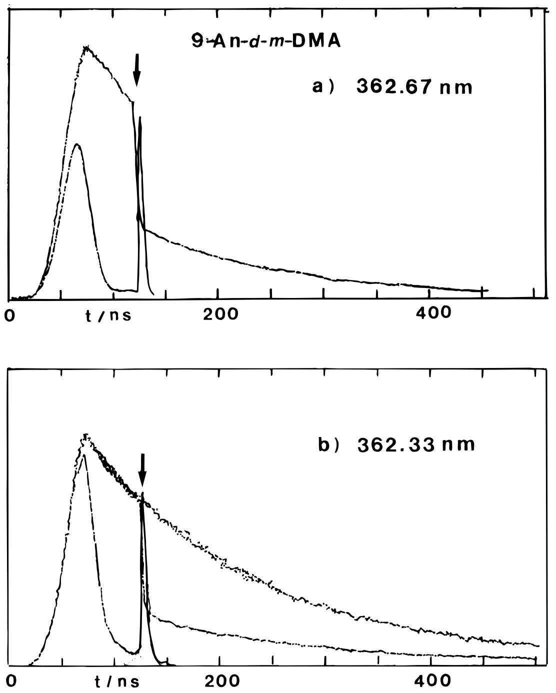

Figure 8. Time-resolved depletions of the exciplex fluorescence and fragment signals of anthryl fluorescence for two isomeric forms in jet-cooled 9-An-*d*-*m*-DMA: (a and b) 9*dm*-a and 9*dm*-b, respectively. The times of dissociation laser pulses are indicated by arrows.

Numerous investigations on the formation and dissociation of the inter- and intramolecular exciplex in solutions have been

TABLE 2: Typical Examples of Fluorescence Decay Times of Anthryl Moieties for the Exciplex Formation and Photodissociation[a]

	ΔE/cm^{-1}	exciplex formation (τ/ns)	exciplex photodissociation (τ/ns)
9-An-*m*-DMA			
9m-a	1197	5.6	2.3
9m-b	1168	11.8	6.0
9-An-*d*-*m*-DMA			
9*dm*-a	436	8.5	<0.6
9*dm*-b	487	9.5	1.5

[a] Errors of decay times are approximately 5%.

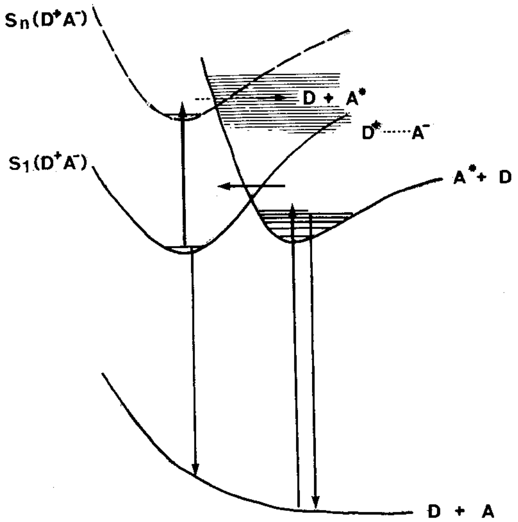

Figure 9. Schematic illustration of potential energy curves of the exciplex formation and photodissociation in a model of 9-An-DMA.

reported. However, the depletion of the exciplex fluorescence by the excitation of the exciplex to the higher electronic states has never been reported in the solution spectroscopy. Therefore, the photodissociation of the exciplex of 9-An-*m*-DMA and 9-An-*d*-*m*-DMA in solutions such as hexane and acetonitrile was examined by using the optical setup of the two-step laser-induced fluorescence (excitation wavelengths 308/730 nm). Further, the same experiment was also performed by picosecond depletion laser excitation (700-nm pulse, fwhm 10 ps, 0.5 mJ) and by using a streak camera (ns/ps TS-LIF).[11,12] However, neither depletion of the exciplex fluorescence nor increment of the anthryl moiety fluorescence was detected. This is because not only ionic dissociation of the exciplex and/or ion recombination but also internal conversion probably take place very fast within the pico- or femtosecond time domain in solutions.

Anthryl Deuteration Effects on Exciplex Formation and Photodissociation. Zewail and his co-workers proposed a simple theory to describe the excess energy dependence of the rate constant of the jet-cooled exciplex formation in 9-An-DMA.[2,3] From the excess vibrational energy dependence of the "electron transfer" rate, it was proposed that the folding of the two chromophores is crucial to bring about the intramolecular encounter necessary for the exciplex formation. This folding is the result of IVR from the anthryl moiety to the methylene chain, as pointed out by the groups of Zewail[3] and Itoh.[15] The rate of IVR is faster than the reaction rate at the excess energies, since no significant mode-selectivity of rate in the exciplex formation was observed at any given energy. Furthermore, Itoh *et al.*[15,16] reported excitation energy dependence of intramolecular exciplex/excimer formations in the static vapor of bichromophoric EDA systems. They proposed that the reaction rate constant of the intramolecular excimer formation in *N*,*N*,*N*,*N*-tetramethylpropanediamine vapor may be proportional to the product of transition probability and the calculated relative vibrational level density of the final excimer state.[16] Peng *et al.*[17] reported the dynamics of IVR in deuterated anthracene. They showed that the approximate density of states of S_1 in anthracene-d_{10} markedly increases with increasing excess vibrational energy (ΔE). The extent of the increase in the density of states at higher vibrational states was much greater for the deuterated anthracene than for the undeuterated one. The increase of the density of state in the deuterated anthryl moieties seems to promote the rate of IVR, leading to the folding of the methylene chain that is necessary for the exciplex formation.[3,5,15] On the other hand, Okajima and Lim[18] suggested an importance of the Franck–Condon factor associated with the transition from the uncomplexed to the complexed component molecules in the vibrational energy dependence of the formation rate constant associated with the intermolecular exciplex formation in the static vapor phase. Therefore, the smaller excess energy thresholds for the exciplex formation in the deuterated compounds may be qualitatively attributed to the higher density of states and differing Franck–Condon factors in the deuterated anthryl moieties.

Transient absorption spectra of the exciplex in solution indicate that the exciplex (S_1) has considerable anion and cation character of their component moieties, $(D^+,A^-)^*$, as mentioned above. This suggests that the upper states (S_n) of the transient absorption spectrum of the exciplex may have locally excited character of the cation and anion of the component moieties, the (D^{+*},A^-) and (D^+,A^{-*}) states. Another possibility for the upper excited states of the exciplex may be the involvement of the reverse charge transfer from the exciplex $(D^+,A^-)^*$ to (D_i^*,A) and (D,A_i^*), where (D_i^*,A) and (D,A_i^*) represent the higher singlet excited states of the DMA and anthryl moieties, respectively. Absorption bands that might be ascribed to transitions of the reverse CT states were reported in addition to the localized ionic transitions by Ottolenghi *et al.*[19] In solution spectroscopy, however, neither donor nor acceptor fluorescence has been observed in the excitation of the transient absorption band of the exciplex, as mentioned in the last section. This suggests the ionic recombination of anion and cation and/or internal conversion may be taking place within the pico- or femtosecond time domain, although the reverse CT might occur in solution.[20]

The remarkable depletion of the jet-cooled exciplex leading to the simultaneous formation of the excited-state anthryl with a very short decay time was observed in the excitation of the jet-cooled exciplex, as mentioned above. Furthermore, the anthryl decay times by the photodissociation was markedly decreased in the EDA compounds with deuterated anthryl, Table 2. The exciplex depletion and the appearance of anthryl fragment fluorescence suggest that the anthryl fluorescence relaxation takes place from the upper vibrational energy levels of the anthryl moiety. The higher degrees of vibrational excitation in the deuterated anthryl may be responsible for the shorter decay times of the deuterated anthryl in comparison with those of the undeuterated one. The transient absorption band excitation (730 nm) of the exciplex leads to the locally excited state with anthryl ionic character, (D^+,A^{-*}). The energy level of this state may correspond to the higher vibrational continuum of the exciplex and also probably to those of the reverse CT state (D,A^*). As shown in the potential energy curves of Figure 9, the IVR and/or internal conversion could lead the upper electronic states of the exciplex to the higher vibrational continuum states of the anthryl S_1 state. The short decay time of the photodissociation-induced anthryl fluorescence as well as the deuterium isotope effect thereon is entirely consistent with the emission that originates from the vibrationally highly excited S_1 anthryl moiety. It has been shown long ago by Lim and co-workers[21] that the $S_1 \rightarrow S_0$ internal conversion rate, and hence the fluorescence decay rate, of deuteriated aromatic compounds shows a larger increase with excess vibrational energy than the corresponding protic compound, so that the fluorescence decay rate of the ring-deuterated species exceeds that of the protic compound at high excess vibrational energies (inverse isotope effect).

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