J. Am. Chem. Soc. 1993, 115, 4799–4807

Intramolecular Exciplex Formation in Jet-Cooled Bichromophoric Chain Molecules: Torsional Conformations and Excess Vibrational Energy Dependence

Noriyuki Kizu and Michiya Itoh*

Contribution from the Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-Machi, Kanazawa 920, Japan, and Department of Physical and Chemical Biodynamics, Graduate School, Kanazawa University, Kanazawa 920, Japan

Received November 30, 1992

Abstract: Intramolecular exciplex formation and excess vibrational energy dependence were investigated in the bichromophoric EDA systems of several 1-(4-(dialkylamino)phenyl-3-(1- and 9-anthryl)propanes in a supersonic free jet. Fluorescence excitation spectra suggest that two types of ground-state conformers are involved at low He backing pressure (750 Torr). These conformers were tentatively ascribed to *trans* (*t*) and *gauche* (*g*) conformers concerning the C_1–C_2 conformation of trimethylene-substituted anthryl. Fluorescence excitation spectra of the *t* conformer show well-resolved vibrational structures of the S_1 state, while those of *g* were considerably congested. The dispersed fluorescence spectra of the *t* conformer exhibit large Stokes shifted exciplex fluorescence depending on the excess vibrational energy above the zero-point level of the S_1 state. However, no significant exciplex formation was observed in the *g* conformers up to an excess vibrational energy of <2000 cm^{-1}. The energy thresholds for the exciplex formation in the *t* conformers in 1-(4-(dimethyl- and diethylamino)phenyl)-3-(9-anthryl)propanes were determined to be 900 and 700 cm^{-1}, respectively. Those for 1-(4-(dimethyl- and diethylamino)phenyl)-3-(1-anthryl)propanes were 500 and 1400 cm^{-1}. The remarkably different features of exciplex formation between *t* and *g* conformers and also the energy threshold for the exciplex formation in the *t* conformers will be discussed in terms of intramolecular conformations of the ground and exciplex states.

Introduction

Zewail and his co-workers[1,2] reported the intramolecular exciplex formation in the jet-cooled 1-(9-anthryl)-3-(4-(dimethylamino)phenyl)propane (9-An-DMA) and a remarkable excess vibrational energy dependence corresponding to the activation energy of the intramolecular exciplex formation. The activation energy was ascribed to the energy for intramolecular collisional dynamics between the ground and excited state moieties. On the other hand, we reported the first observation of the exciplex formation from the excited state van der Waals (vdW) complex in the 1-cyanonaphthalene and triethylamine systems in a supersonic free jet. In the exciplex formation from the vdW complex, a remarkable excess vibrational energy dependence was observed.[3-5] The electronic relaxation from the locally excited state (LE or resonance state) to the charge-transfer (CT) state takes place leading to exciplex formation in the excitation of vibronic bands with excess vibrational energy higher than the threshold, which is probably attributable to the activation energy of exciplex formation. Similar jet-cooled exciplex formations were reported by other research groups.[6,7] The intramolecular exciplex formation mentioned above is completely distinguishable from the intermolecular exciplex formation in the jet-cooled vdW complex.[3-8] The former is attributable to intramolecular collision between the ground and excited state moieties, while the latter is attributable to the excited state transformation of the vdW complex (LE state) to the exciplex (CT state).

Hopkins, Powers, and Smalley[8] proposed the rotational isomers of *trans* (*t*) and *gauche* (*g*) conformations in jet-cooled *n*-propylbenzene. For *n*-alkylbenzenes with a chain length of three or higher, spectra of two distinct conformations are observed in roughly equal intensity. These conformations are distinguished by their configuration about the C_1–C_2 bond of the alkyl chain. In the *t* conformation, the alkyl chain extends away from the phenyl group, leaving both sides of the ring free. In the *g* conformation, the alkyl chain partially covers one side of the phenyl ring, which produces a small red-shift of the fluorescence excitation spectrum (48.8 cm^{-1} for *n*-propylbenzene). Further, Song et al.[9,10] reported similar extended (*anti*) and folded (*gauche*) conformations in *p*-*n*-propylaniline. Very recently, Takahashi and Kimura[11] have reported cation vibrational spectroscopy of *t* and *g* *n*-propylbenzene rotational isomers. However, Syage et al.[2] failed to observe any obvious doubling pattern in the excitation spectra of 9-An-DMA, and they suggested that the exciplex formation takes place from one ground state conformer in jet-cooled 9-An-DMA, though there is some indication of a weak second conformer in the jet-cooled condition. On the other hand, Syage et al.[12] reported the role of alkylation on the intramolecular vibrational redistribution (IVR) in jet-cooled 9-methyl- and 9-hexylanthracenes.

---

* Address correspondence to this author at the Faculty of Pharmaceutical Sciences.

[1] Felker, F. M.; Syage, J. A.; Lambert, W. R.; Zewail, A. H. *Chem. Phys. Lett.* **1982**, *92*, 1.

[2] Syage, J. A.; Felker, P. M.; Zewail, A. M. *J. Chem. Phys.* **1984**, *81*, 2233.

[3] Saigusa, H.; Itoh, M. *Chem. Phys. Lett.* **1984**, *106*, 391; *J. Chem. Phys.* **1984**, *81*, 5682.

[4] Saigusa, H.; Itoh, M.; Baba, H.; Hanazaki, I. *J. Chem. Phys.* **1987**, *86*, 2528.

[5] (a) Itoh, M.; Sasaki, M. *J. Phys. Chem.* **1990**, *94*, 6544. (b) Ito, A.; Fujiwara, Y.; Itoh, M. *J. Chem. Phys.* **1992**, *96*, 7474.

[6] Castella, M.; Prochorow, J.; Tramer, A. *J. Chem. Phys.* **1984**, *81*, 2511.

[7] Anner, O.; Haas, Y. *Chem. Phys. Lett.* **1985**, *119*, 199.

[8] (a) Hopkins, J. B.; Powers, D. E.; Mukamel, S.; Smalley, R. E. *J. Chem. Phys.* **1980**, *72*, 5049. (b) Hopkins, J. B.; Powers, D. E.; Mukamel, S.; Smalley, R. E. *J. Chem. Phys.* **1980**, *72*, 5049.

[9] Song, X.; Willkinson, C. W., Jr.; Lucia, J.; Pauls, S.; Reilly, J. P. *Chem. Phys. Lett.* **1990**, *174*, 377.

[10] Song, X.; Pauls, S.; Lucia, J.; Du, P.; Davidson, E. R.; Reilly, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 3202 and references therein.

[11] Takahashi, M.; Kimura, K. *J. Chem. Phys.* **1992**, *97*, 2920.

[12] Syage, J. A.; Felker, P. M.; Semmes, D. H.; Al Adel, F.; Zewail, A. H. *J. Chem. Phys.* **1985**, *82*, 2896.

0002-7863/93/1515-4799$04.00/0

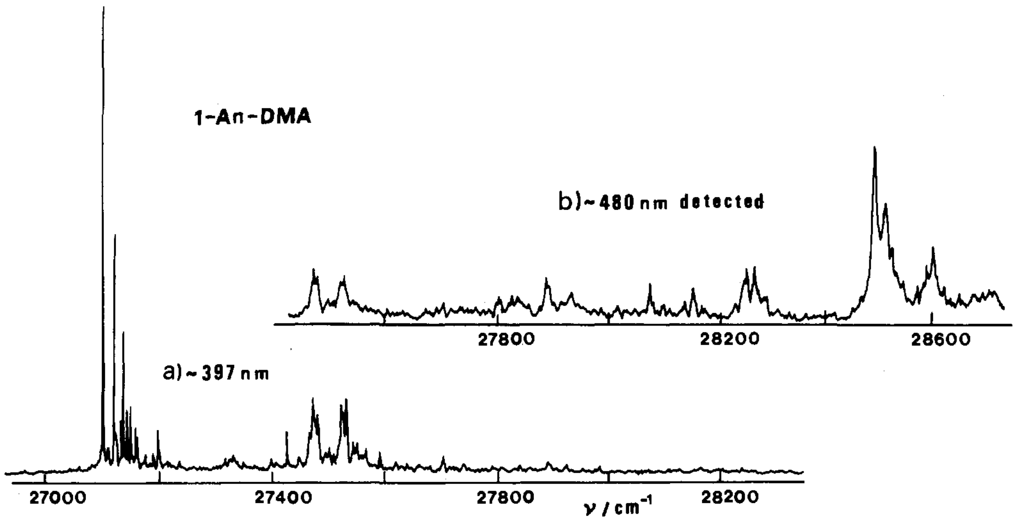
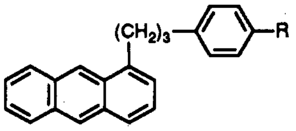
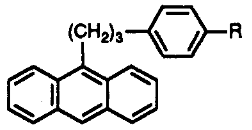


Figure 1. Fluorescence excitation spectra of jet-cooled 1-An-DMA: fluorescence was detected at 397 nm (a) and 480 nm (b).

Taking account of investigations on these jet-cooled inter- and intramolecular exciplex formations, some crucial questions arise in the exciplex formation of bichormophoric EDA systems such as 9-An-DMA in supersonic expansion. (1) How is the ground state conformation concerned with the exciplex formation dynamics? (2) How does the threshold of excess vibrational energy for the intramolecular exciplex formation depend on electron donor and acceptor moieties in the bichromophoric systems? Therefore, this paper presents the intramolecular exciplex formation in several bichormophoric EDA systems composed of 1- and 9-anthryl and (dialkylamino)phenyl moieties connected by trimethylene in a supersonic free jet. The fluorescence excitation and dispersed fluorescence spectra indicate the existence of two types of ground state conformations. These are *t* and *g* torsional conformations concerning the C_1–C_2 bonding of the 1-propylanthryl moiety of these compounds. Remarkably different energy features between these two conformations were observed for the exciplex formation. Further, the vibrational energy threshold for the exciplex formation was demonstrated to depend on the dialkylamino group and on the 1- and 9-positions of the anthryl group substituted by trimethylene. These results were discussed in terms of the intramolecular vibrational redistribution (IVR) of the anthryl group and torsional conformational consideration of trimethylene in the bichromophoric EDA systems.



1-An-DMA (R = $N(CH_3)_2$)
1-An-DEA (R = $N(C_2H_5)_2$)



9-An-DEA (R = $N(CH_3)_2$)
9-An-DEA (R = $N(C_2H_5)_2$)

Experimental Section

Materials. The synthesis and purification of bichromophoric compounds used in this paper were done by methods and procedures similar to those described in previous papers. Structure and purity of these compounds were confirmed by elementary analysis and mass and NMR (200 and 500 MHz) spectroscopies before use. Elementary analysis and melting points follow. **1-(9-Anthryl)-3-phenylpropane**: mp 74.5–75.7 °C. Anal. Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80. Found: C, 93.25; H, 6.87. **1-(1-Anthryl)-3-(4-(dimethylamino)phenyl)propane**: mp 94.0–96.1 °C. Anal. Calcd for $C_{25}H_{25}N$: C, 88.45; H, 7.42; N, 4.12. Found: C, 88.43; H, 7.67; N, 4.06. **1-(1-Anthryl)-3-(4-(diethylamino)phenyl)propane**: mp 79.2–80.6 °C. Anal. Calcd for $C_{27}H_{29}N$: C, 88.24; H, 7.95; N, 3.81. Found: C, 88.33; H, 8.07; N, 3.77. **1-(9-Anthryl)-3-(4-(dimethylamino)phenyl)propane**: mp 101.5–102.5 °C. Anal. Calcd for $C_{25}H_{25}N$: C, 88.45; H, 7.42; N, 4.12 Found: C, 88.59; H, 7.36; N, 4.13. **1-(9-Anthryl)-3-(4-(diethylamino)phenyl)propane**: mp 89.2–90.5 °C. Anal. Calcd for $C_{27}H_{29}N$: C, 88.24; H, 7.95;, N, 3.81. Found: C, 88.29; H, 7.95; N, 3.65. Structure and purity of these compounds were confirmed by UV, NMR (500 MHz), and mass spectroscopies.

General Procedures. The experimental setup and procedures of a pulsed supersonic free jet are similar to those described in previous papers.[5,13] The 10-Hz pulsed supersonic free jet backed by He (2–0.5 atm) was excited at 10–12 mm down stream of a nozzle (700 μm) by an excimer laser pumped dye laser (Lambda Phys EMG 53 MSC/FL 3002). The He backing pressure is 2 atm (approximately 1520 Torr) except when indicated otherwise. The pressure in the vacuum chamber was 5–8 × 10^{-4} Torr during experiments. The laser induced fluorescence excitation and dispersed fluorescence spectra were determined by a photomultiplier (Hamamatsu R1246) through a grating monochromator (Nikon G-250). Detected spectral widths for fluorescence excitation spectra were approximately 3–5 nm, and that for dispersed fluorescence spectra was <3 nm. The output signal was processed by a boxcar integrator (Par M162/164). Fluorescence decay was determined by a digital oscilloscope (Tektronix 2430) and processed by computer-simulated convolution.

Results

Fluorescence Spectroscopy of Jet-Cooled 1-(1-Anthryl)-3-(4-(dimethyl- and diethylamino)phenyl)propanes. The UV fluorescence excitation spectrum of jet-cooled 1-An-DMA exhibits considerably well-resolved vibrational structures starting from an origin band at 27 122 cm⁻¹ (368.70 nm) in the He backing pressure. The vibrational structures seem essentially consistent with those of fluorescence excitation spectra of alkyl-substituted anthracenes. The spectra show a remarkable decrease in intensity with an increase in vibrational energy, as shown in Figure 1a. In the visible fluorescence excitation spectrum of this compound, no significant spectrum was observed in the origin band region, but a gradually increasing number of bands were observed in the vibronic band region with an excess vibrational energy of 500–600 cm⁻¹ above the origin band level. Since a nonpolar solution of 1-An-DMA exhibits intramolecular exciplex fluorescence in the 430–500-nm region, the UV and visible fluorescence excitation spectra of jet-cooled 1-An-DMA shown in Figure 1 suggest that excitations of vibronic bands in a higher vibrational energy region afford a large Stokes shifted exciplex fluorescence.

Figure 2 illustrates the dispersed fluorescence spectra of 1-An-DMA in supersonic expansion which are remarkably dependent on the excess vibrational energy from the energy level of the origin band. The spectra demonstrate intramolecular exciplex fluorescence at 400–500 nm in the excitations of the vibronic bands with an excess vibrational energy larger than approximately 500 cm⁻¹. Further, the UV fluorescence due to the anthryl moiety

---

(13) Itoh, M.; Takamatsu, M.; Kizu, N.; Fujiwara, Y. *J. Phys. Chem.* **1991**, *95*, 9682.

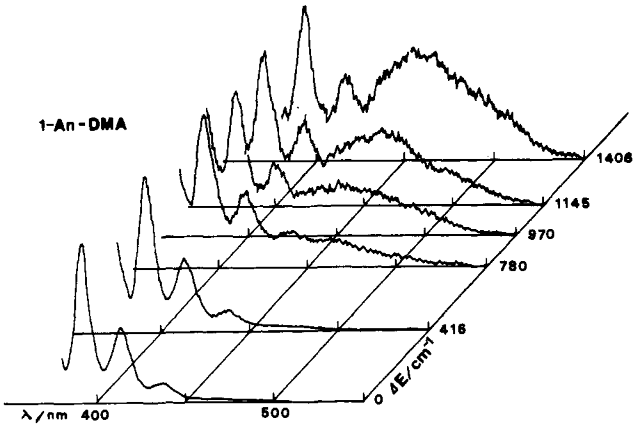


Figure 2. Excess vibrational energy dependence of the dispersed fluorescence spectra of jet-cooled 1-An-DMA. The fluorescence intensities were normalized at 397 nm and ΔE are excess vibrational energies (cm^{-1}) from the origin band energy level (27 122 cm^{-1}).

exhibits an approximately single exponential decay curve. The decay times decrease remarkably from 19 to <2 ns with an increase in the excess vibrational energy of excitation ($E = 0$ to 1400 cm^{-1}), while the exciplex fluorescence decays are almost independent of the excess energy (>600 cm^{-1}). The facts indicate that the intramolecular exciplex formation takes place through intramolecular collision between the S_1 state of the anthryl moiety in the higher vibrational energy levels (>600 cm^{-1}) and the ground state (dimethylamino)phenyl group, since the possibility of intermolecular exciplex formation between the EDA moieties of different molecules may be removed because of the very low vapor pressure of this compound.

The UV fluorescence excitation spectrum shown in Figure 1a is remarkably dependent on the He backing pressure of less than 760 Torr. Very broad and congested bands appeared in the regions red-shifted approximately 50-cm^{-1} from the origin and each vibronic bands. Figure 3 shows the fluorescence excitation spectra of the origin band region at different He backing pressures. Taking into account structure and intensity, these congested bands do not seem attributable to hot bands of these spectra but rather to the other isomeric conformation of this compound in the jet-cooled condition. Figure 4a shows the visible fluorescence excitation spectra of this compound in the vibronic band region at the low He backing pressure of 750 Torr. The spectra were somewhat similar to the visible fluorescence excitation spectra observed at higher He backing pressure (> ~760 Torr) shown in Figure 1. However, the UV fluorescence excitation spectra (Figure 4b) in the higher energy region (>28 000 cm^{-1}) exhibit very dispersed bands ~50 cm^{-1} red-shifted from each vibronic band observed at the higher He backing pressure (Figure 1b). Therefore, the facts suggest that the excitations of the ~50-cm^{-1} red-shifted bands, which were ascribed to the different ground state isomeric form of this compound, show no significant visible fluorescence but only UV fluorescence. The dispersed fluorescence spectra in the excitations of ~50-cm^{-1} red-shifted bands really exhibit UV fluorescence. Further, decay times of these UV fluorescence spectra are almost independent (10.5–9.5 ns) of excitation energy in contrast with those of UV fluorescence in the excitations of the original vibronic bands mentioned above. If the very broad red-shifted (~50 cm^{-1}) bands appearing at low He backing pressure are really attributable to a different ground state isomeric conformer, no significant exciplex formation occurs in the different conformer at least up to an excess vibrational energy level of 2000 cm^{-1}. If the broad red-shifted bands observed in low He backing pressure (600–700 Torr) are attributable to a type of hot bands, the excitation of red-shifted bands corresponding to vibronic bands (ΔE > 600 cm^{-1}) should exhibit the exciplex fluorescence. This occurs because the excitation of the hot band leads to the same vibronic state as does the excitation of the original vibronic band. Therefore, the red-shifted bands are ascribed to the different ground state isomeric conformer of this compound. The structures of both the usual and the different conformers and their different features of intramolecular exciplex formation will be discussed in the next section.

The intramolecular EDA system of 1-An-DEA, which has the (diethylamino)phenyl moiety instead of (dimethylamino)phenyl present in 1-An-DMA, exhibits considerably different excess vibrational energy dependence in the intramolecular exciplex formation. Figure 5 shows the UV fluorescence excitation spectra of 1-An-DEA in the supersonic expansion of around 2 atm He backing pressure. The spectrum exhibits very similar vibrational structures starting from an origin band at 27 081 cm^{-1} (369.26 nm) to those of 1-An-DMA. However, the UV excitation spectrum of this compound does not decrease in intensity as remarkably as that of 1-An-DMA in the higher vibronic band region. In the visible fluorescence excitation spectra of this compound, no appreciable excitation spectrum was observed in the low vibrational energy region, while very broad congested bands were observed only in the vibrational energy region higher than 28 800 cm^{-1} (ΔE > 1800 cm^{-1}). Dispersed fluorescence spectra were obtained in the excitations of several vibronic bands. Figure 6 illustrates these spectra normalized in the intensity of UV fluorescence. The spectra really demonstrate the excess vibrational energy dependence of the intramolecular exciplex formation in 1-An-DEA, which reveals a striking difference in the excess vibrational energy from that of 1-An-DMA (see Figure 2). In order to estimate the energy threshold for the exciplex formation in comparison with several EDA systems reported here, the ratios of the relative quantum yields for exciplex and anthryl-type fluorescence against excess vibrational energy were plotted in Figure 7. The plots indicate a remarkably different energy threshold for exciplex in 1-An-DEA (1400 cm^{-1}) than that for 1-An-DMA (~500 cm^{-1}). These data provide us with important kinetic features of the exciplex formation in the several intramolecular EDA systems studied. The results will be discussed in the next section.

In the UV fluorescence excitation spectrum of a supersonic free jet of 1-An-DEA at low He backing pressure, very dispersed bands appeared in the energy region red-shifted 50–100 cm^{-1} from the origin and vibronic bands, whose spectral features are very similar to those of 1-An-DMA at the low backing pressure mentioned above. The dispersed fluorescence spectra and decay times in excitations of the red-shifted bands indicate no significant exciplex fluorescence up to the excess vibrational energy region of 2000 cm^{-1}. Since fluorescence decay times (17.5 ns) in the red-shifted-band excitations are distinguishable from those of the origin and vibronic band excitations in the original vibrational structures (14 ns) at low He pressure, this red-shifted-band series also may be attributable to the different conformer from the originally proposed open form in the jet-cooled condition, as mentioned above.

Fluorescence Spectroscopy of Jet-Cooled 1-(9-Anthryl)-3-(4-dimethyl- and diethylamino)phenyl)propanes. As mentioned in the introductory section, Syage et al.[1,2] reported extensive studies of the supersonic jet spectroscopy of 9-An-DMA. We will compare the fluorescence spectroscopy of jet-cooled 9-An-DMA with that of 9-An-DEA. The UV and visible fluorescence excitation spectra of 9-An-DMA (0_0^0; 26 683 cm^{-1}) in supersonic expansion are shown in Figure 8. A decrease in intensity of the UV fluorescence excitation spectra and an increase in intensity of the visible spectra were observed in the vibrational energy region higher than 27 600 cm^{-1} (ΔE > 1000 cm^{-1}), demonstrating the excess energy dependence of the exciplex formation in this compound. The dispersed fluorescence spectra were observed in the excitations of origin and major vibronic bands. The relative quantum yields for exciplex and anthryl-type fluorescence vs excess

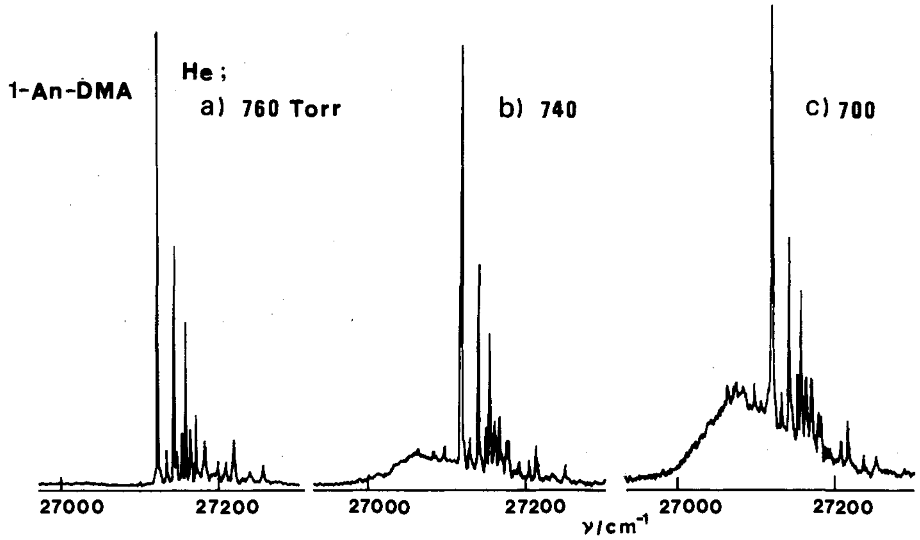


Figure 3. The UV fluorescence excitation spectra at the origin band region of jet-cooled 1-An-DMA at several He backing pressures.

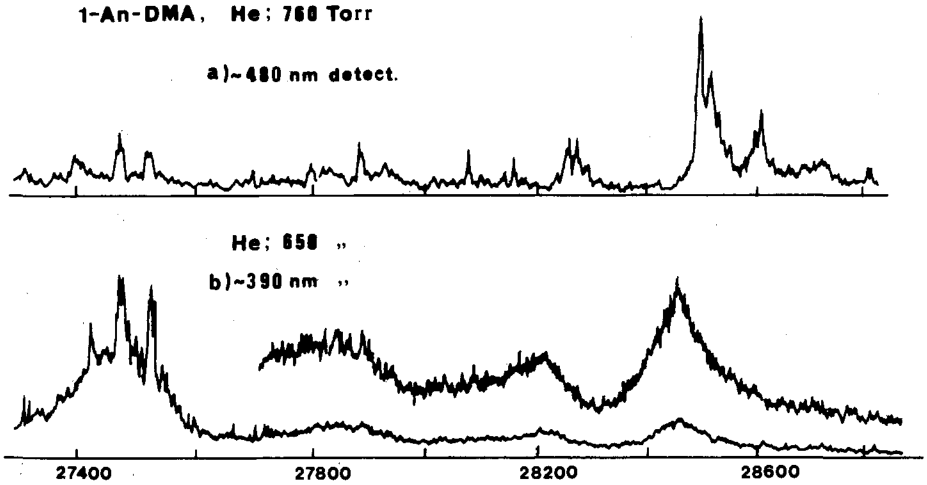


Figure 4. Fluorescence excitation spectra at the vibronic band region of jet-cooled 1-An-DMA. (a) The spectrum was determined at a He backing pressure of 760 Torr and detected at 480 nm. (b) The spectra were determined at a He backing pressure of 650 Torr and detected at 390 nm.

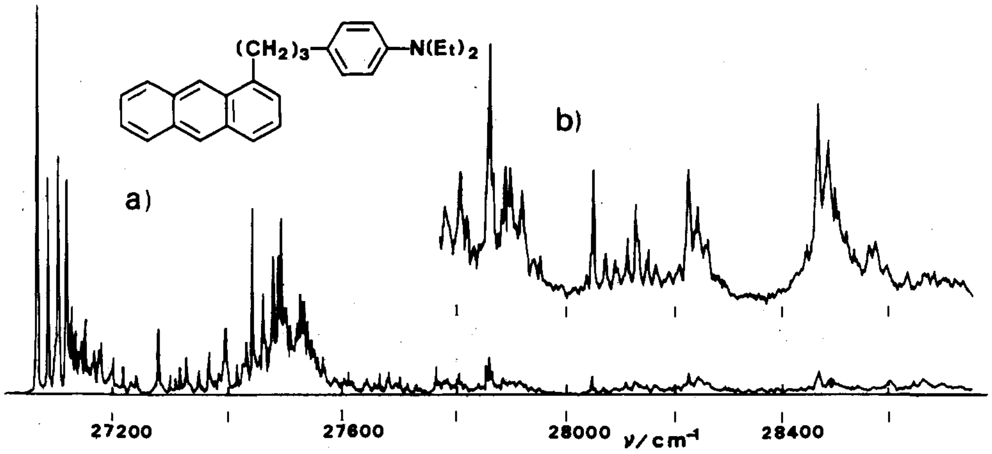


Figure 5. Fluorescence excitation spectra of jet-cooled 1-An-DEA. (a) The spectrum was detected at 390 nm and (b) remained essentially the same as in (a) except expanded in intensity and including several small peaks due to a different signal-to-noise ratio.

vibrational energy illustrated in Figure 7 are almost completely consistent with those reported in the literature.[2] The energy threshold for the exciplex formation was also estimated to be ca. 900 cm^{-1} (2.59 kcal/mol). Further, the time-resolved fluorescence and decay times of the anthryl-type fluorescence indicate the intramolecular collisional dynamics of the exciplex formation depending on the vibrational energy level.

The isomeric intramolecular EDA system of 9-An-DEA was investigated in the supersonic expansion, and the UV and visible fluorescence excitation spectra are shown in Figure 9. The vibrational structures of fluorescence excitation spectra of 9-An-DEA (0_0^0; 26 623 cm^{-1}) are very similar to those of 9-An-DMA (26 683 cm^{-1}) except for being red-shifted by approximately 0.9 nm. The excitation energy dependence of dispersed fluorescence

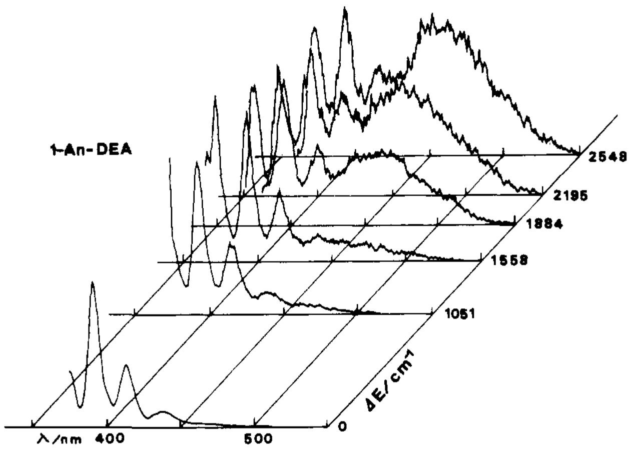


Figure 6. Excess vibrational energy dependence of the dispersed fluorescence spectra of jet-cooled 1-An-DEA. The spectra were normalized in intensity at the 390–400-nm band, and ΔE are excess vibrational energies from the origin band at 27 081 cm^{-1} (369.26 nm).

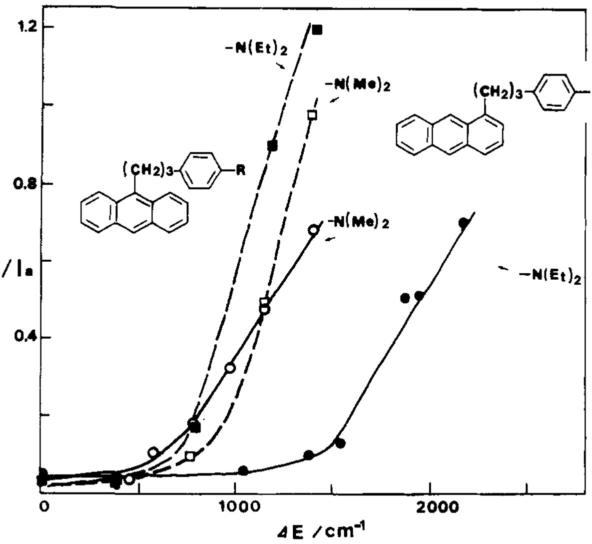


Figure 7. The ratio of relative fluorescence quantum yield for exciplex and anthryl-like fluorescence. The exciplex (I_e) and anthryl-like fluorescence (I_a) were monitored at 470 nm and at a maximum of 390–400 nm, respectively.

spectra is shown in Figure 10. The fluorescence behavior and exciplex formation in 9-An-DEA are essentially identical with those in 9-An-DMA. However, a slightly smaller energy threshold for the exciplex formation was determined to be ca. 700 cm^{-1} (ca. 2.0 kcal/mol) compared with that of 9-An-DMA (900 cm^{-1}, 2.59 kcal/mol) from plots of the relative fluorescence quantum yields shown in Figure 7. The different energy threshold of the exciplex formation between these compounds, and also that between 1-An-DMA and 1-An-DEA, will be discussed in terms of ionization potential (i_p) of the (dialkylamino)phenyl moiety and of steric factors for the intramolecular exciplex formation in the next section.

We have proposed the existence of two types of ground state conformers in 1-An-DMA and 1-An-DEA, which were observed in the fluorescence excitation spectra at a low He backing pressure of expansion, as mentioned above. These are reactive and nonreactive conformers for the intramolecular exciplex formation. When the backing pressure of supersonic expansion of 9-An-DMA and 9-An-DEA was reduced, broad and dispersed bands were observed red-shifted around 50 cm^{-1} from their origin and respective vibronic bands. The comparison of UV fluorescence spectra of 9-An-DMA in high and low backing pressure is shown in Figure 11. The newly observed red-shifted bands in the origin band region exhibit very low frequency vibration of 8–9 cm^{-1} in addition to 11 cm^{-1} vibration which is seen in the origin band region. Figure 12 shows the UV and visible fluorescence excitation spectra of 9-An-DMA at low backing pressure in the vibronic band region (27600–28400 cm^{-1}). The visible fluorescence excitation spectrum (Figure 13b) is essentially identical with that at high backing pressure (Figure 8), and the strong bands indicate the vibronic bands leading to the exciplex formation. However, the appreciably strong UV fluorescence excitation spectra were observed in the higher energy region approximately 50 cm^{-1} from respective vibronic bands. The dispersed fluorescence spectra and decay times were determined in the excitations of these red-shifted bands. The spectra exhibit no exciplex fluorescence, as illustrated in Figure 14. Further, the decay times of anthryl-type fluorescence in the excitation of the red-shifted band were not dependent very much on the excess vibrational energy (14–9 ns), which is in contrast with the remarkable dependence of decay times (19 to <1 ns) in the excitations of the original vibrational progression, as mentioned above. Therefore, the red-shifted band series observed at the low He backing pressure is ascribed to the different isomeric ground state conformer, which is nonreactive for the exciplex formation up to approximately 2000 cm^{-1}. Similar fluorescent behaviors of reactive and nonreactive isomeric conformations were also observed in the 9-An-DEA system. The reason why these isomeric conformers exhibit completely different kinetic features will be discussed in terms of the structure of trimethylene and IVR of the anthryl moiety.

Discussion

Ground State Conformations. As mentioned in the last section, the involvement of reactive and nonreactive conformers for the intramolecular exciplex formation was clearly demonstrated in several intramolecular EDA systems including 9-An-DMA. The reactive and nonreactive conformers were tentatively ascribed to the *t* and *g* conformations, respectively. Therefore, we have investigated isomeric conformers in jet-cooled 1-(9-anthryl)-3-phenylpropane (9-An-Benz) as a model compound of bichromophoric EDA systems reported here.

Fluorescence excitation spectra of 9-An-Benz show well-resolved vibrational structures starting from an origin band at 371.91 nm (26 744 cm^{-1}) in a supersonic free jet at 1 atm of He backing pressure (~1520 Torr). However, when the backing pressure decreased to 740–750 Torr, the broad congested bands appeared approximately 50–60 cm^{-1} red-shifted from the origin and each vibronic bands. The spectral features of fluorescence excitation spectra of jet-cooled 9-An-Benz are very similar to those of anthryl and (dialkylamino)phenyl bichromophoric systems reported here. The original vibrational structures and the newly observed congested ones were tentatively ascribed to *t* and *g* isomeric torsional conformers around the C_1–C_2 bonding in the trimethylene chain, respectively. The dispersed SVL fluorescence spectra of the *t* conformer become considerably congested in the excess vibrational energy region higher than 1000 cm^{-1}, while the spectra of the *g* conformer are almost independent of excess vibrational energy up to 2000 cm^{-1}.[14] The facts suggest that line broadening due to IVR may take place faster in the *t* than the *g* conformer. Hopkins *et al.*[8] demonstrated that the IVR process of the *g* conformation is slower than that of *t* for the same chain length, since the torsional motion so important for the IVR process is strongly hindered in the *g* conformer.

On the other hand, fluorescence decays following SVL excitations of *t* and *g* conformations of 9-An-Benz were measured as a function of excess vibrational energy. Decay curves exhibit approximately single exponential decays. The origin level decay time of the *t* conformer (19 ns) is similar to those of 9-hexylanthracene (18 ns) and 1-An-DMA (*t*, 20 ns). The *t* form decay time decreases remarkably with an increase in excess vibrational

---

[14] Details will be reported elsewhere.

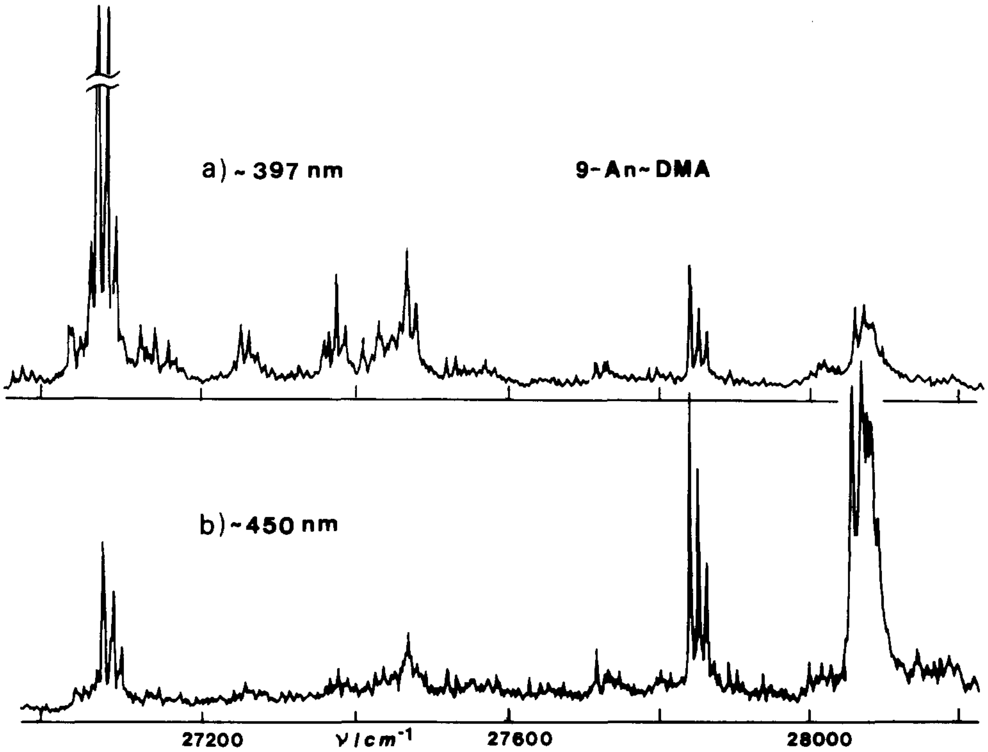


Figure 8. Fluorescence excitation spectra (vibronic band region > 27 000 cm^{-1}) of 9-An-DMA in supersonic expansion of He backing pressure of 1520 Torr. The spectra are detected (a) at 397 and (c) 450 nm.

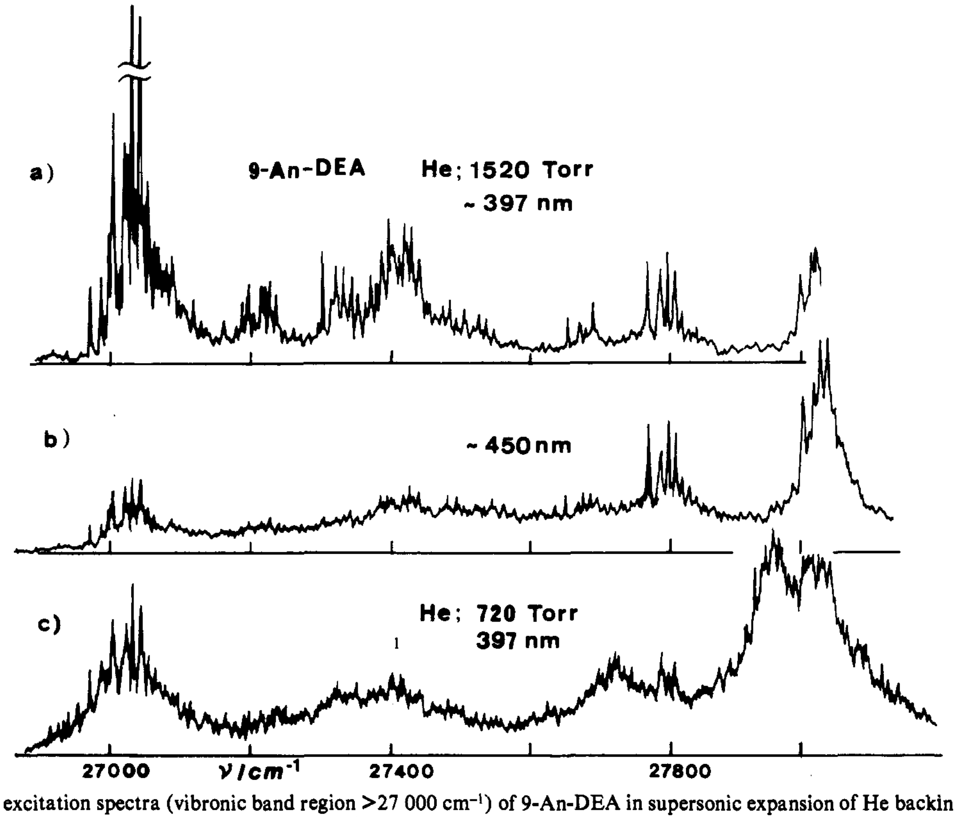


Figure 9. Fluorescence excitation spectra (vibronic band region >27 000 cm^{-1}) of 9-An-DEA in supersonic expansion of He backing pressures of 1520 and 720 Torr. The spectra were detected (a) at 397 nm (He pressure, 1520 Torr), (b) at 450 nm (1520 Torr), and (c) at 397 nm (720 Torr).

energy (7 ns at $\Delta E = 2000$ cm^{-1}). In the *g* conformer, the decay time (12 ns) of the origin band is considerably different from those of the *t* conformer of this compound and other alkyl anthracenes. The smaller decay time in the *g* conformer probably can be attributed to a consequence of intramolecular interaction between anthryl and the partially covered alkyl chain. However, the decay time of the *g* conformer is almost independent of excess vibrational energy (12–11 ns at $\Delta E = 0$–2000 cm^{-1}). The torsional motion around the C_1–C_2 bond of the trimethylene chain seems crucial to IVR by a steric hindrance in the folded *g* conformation, as mentioned above. Therefore, as pointed out by Hopkins *et al.* in the *t* and *g* conformers of alkylbenzenes, the IVR rate constant is smaller in the *g* than the *t* conformer in the higher vibronic band region.

In jet-cooled 1- and 9-An-DMA mentioned in the last section, the broad congested bands approximately 50 cm^{-1} red-shifted

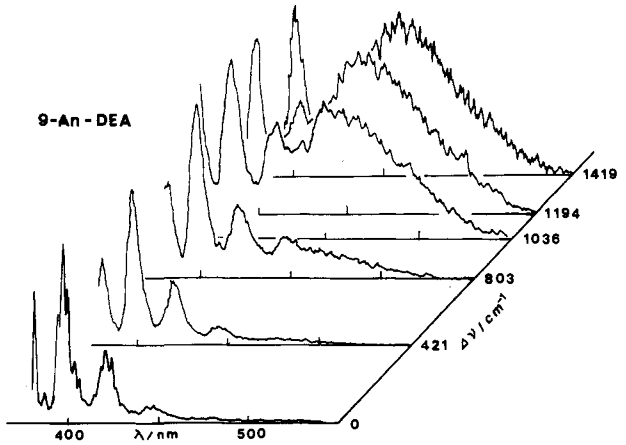


Figure 10. Excess vibrational energy dependence of dispersed fluorescence spectra of 9-An-DEA in supersonic expansion (He, 1520 Torr). The spectra were normalized in intensity at a maximum of 390–400 nm, and E are excess energies from the origin band at 26 623 cm^{-1} (375.62 nm).

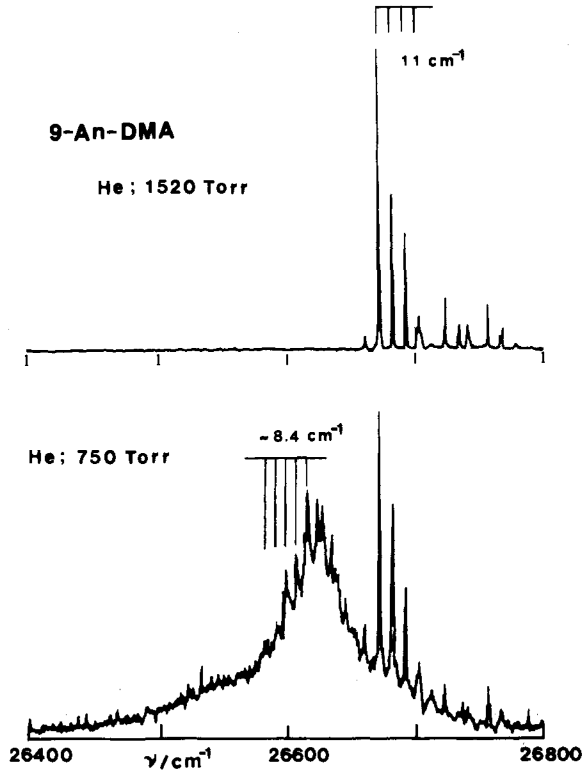


Figure 11. Fluorescence excitation spectra of jet-cooled 9-An-DMA in the origin band region at He backing pressures of 1520 and 750 Torr.

from origin and each vibronic band increased in intensity with decreasing He backing pressure, and their intensity ratios to that of the original reactive (t) conformer are very dependent on the He backing pressure. If thermodynamic cooling of molecules occurs some extent during the course of the expansion, a distribution of the t and g conformations seems to equilibrate considerably in the cooling condition. Taking into account the appearance of the nonreactive (g) conformer in a low He backing pressure, the g conformer may be endothermic in a Boltzmann distribution compared with the t conformation. However, an experimental estimation of the thermal energy between two conformations seems rather difficult at the present stage, though similar estimations of thermal energy of torsional conformations have been reported.[9-12] This is because an estimation of temperature in the cooled condition is not reliable.[15,16]

The t conformations of all bichromophoric EDA systems composed of anthryl and (dialkylamino)phenyl moieties reported here exhibit an approximately 11-cm^{-1} vibrational progression in the origin band region in the high He backing pressure of expansion, though the relative intensity ratio of vibrational structures is somewhat different for each structure. In An-$(CH_2)_3$-DMA, the t and g conformations are considered in An-C_1-C_2, and t and g conformations are also considered in C_2-C_3-DMA. Therefore, the tt, tg, gt, and gg may be considered as the major conformations of An-DMA. However, taking account of the steric factor of bulky aromatics of anthryl and DMA (and also DEA) moieties, the gg conformation may be removed from the possible ground state conformations of An-$(CH_2)_3$-X (X = DMA/DEA). Then, the major conformations may be tt, tg, and gt in the bichromophoric chain systems reported here, and the reactive conformers mentioned above seem tentatively ascribed to the tt and/or tg conformer. Therefore, the possible assignment for the 11-cm^{-1} mode observed in all of the bichromophoric EDA systems may be the torsional mode of the anthryl to C_1 bonding, as mentioned for 9-An-DMA in the literature.[2,12]

The fluorescence excitation spectra of the nonreactive g conformer exhibit low-frequency vibration of 8–9 cm^{-1} in addition to the 11-cm^{-1} progressions which were seen in the origin band regions of all of these compounds. As mentioned above, Hopkins *et al.* proposed the g conformer in addition to the t conformer for alkylbenzenes of chain length greater than two. A new distinct spectrum was observed arising from a folded conformation of the alkyl chain. In the folded g conformation, the torsional motion around the C_1–C_2 bond in the chain is severely restricted by steric interaction with the phenyl ring. Hopkins et al. demonstrated that the rate of intramolecular vibrational redistribution (IVR) in the $6b_0^1$ excited state is at least a factor of 5 slower in the folded g conformation than in the t conformation of n-butylbenzene and n-pentylbenzene. The fact suggests that the torsional vibrations of C_1–C_2 and/or C_2–C_3 bonding in An-$(CH_2)_3$-DMA (and -DEA) reported here may be crucial to the rate of IVR leading to the excess vibrational energy dependences of the exciplex formation. The slower rate of IVR in the folded g conformation seems responsible for the major cause of nonreactivity of the intramolecular exciplex formation. Further, it is likely that the low-frequency vibration of 8–9 cm^{-1} and congestion in the excitation spectra are attributable to the torsional motion of C_2–C_3 bonding in the folded g conformation.

Excess Vibrational Energy Dependence of Exciplex Formation. The excess vibrational energy dependence of the ratio of relative quantum yield of the exciplex and anthryl-type fluorescence (Figure 7) is remarkably dependent on the 1- and 9-positions of the anthryl moiety substituted by trimethylene and also on alkyl groups in the (dialkylamino)phenyl moiety. The energy thresholds of the intramolecular exciplex formation were estimated from the plots of Figure 7. As mentioned in the introductory section, Zewail and his co-workers[1,2] suggested that the energy threshold (900 cm^{-1}, 2.6 kcal/mol) of the intramolecular exciplex formation in jet-cooled 9-An-DMA is attributable to the rotational barrier of chain dynamics of trimethylene. The energy threshold (ΔE) of the exciplex formation for 9-An-DEA ($\sim$700 cm^{-1}) is smaller than that for 9-An-DMA (900 cm^{-1}). Since the activation energy of the exciplex formation may be considerably dependent on the stabilization energy of the exciplex state, the smaller ionization potential (I_p) of the (diethylamino)phenyl moiety (7.20 eV) than the (dimethylamino)phenyl group (7.45 eV) seems responsible for the smaller ΔE in 9-An-DEA. However, the difference in I_p (0.25 eV) values is much greater than that of ΔE. Therefore, it is likely that the steric hindrance of the bulky diethylamino group in the CT interaction compensates for the effect of the large difference of I_p in the exciplex formation between 9-An-DEA

---

(15) Levy, H. D. *Annu. Rev. Phys. Chem.* **1980**, *31*, 197 and references therein.

(16) Smalley, R. E.; Wharton, L.; Levy, H. D. *Acc. Chem. Res.* **1977**, *10*, 139.

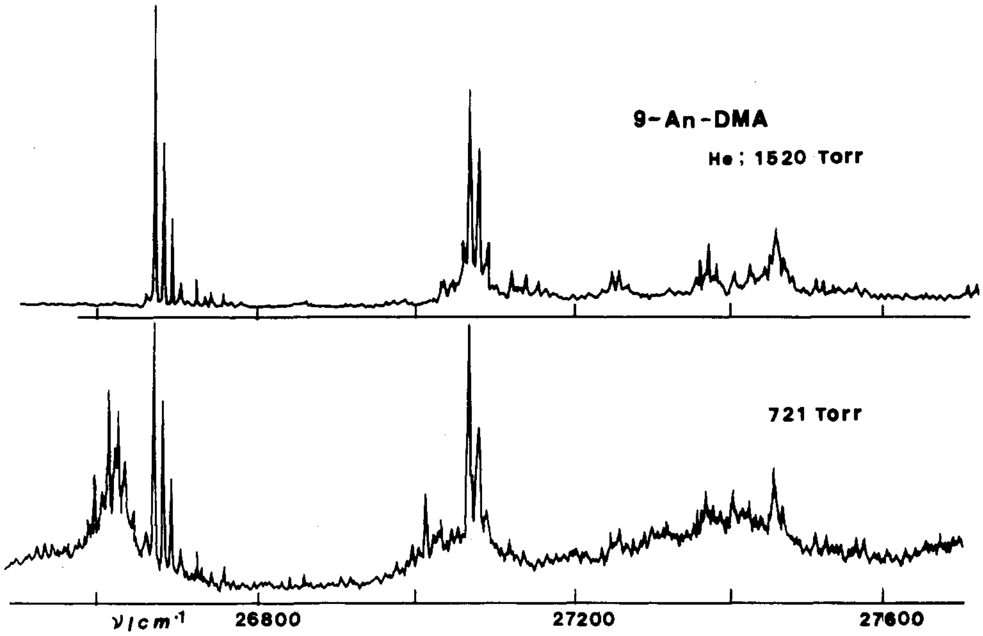


Figure 12. Fluorescence excitation spectra (26600–27600 cm^{-1}) of 9-An-DMA, monitored at 380–410 nm in the supersonic expansion of two different He backing pressures: (a) at 1520 and (b) 721 Torr.

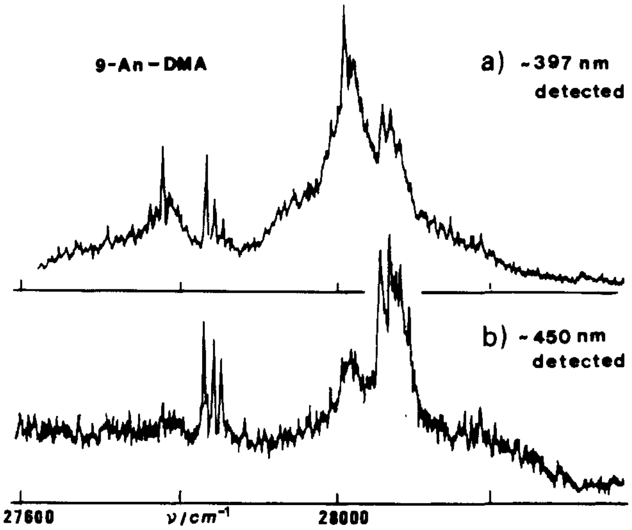


Figure 13. Fluorescence excitation spectra (27600–28200 cm^{-1}) of jet-cooled 9-An-DMA at a He pressure of 721 Torr. (a) The spectrum was monitored at 397 and (b) at 450 nm.

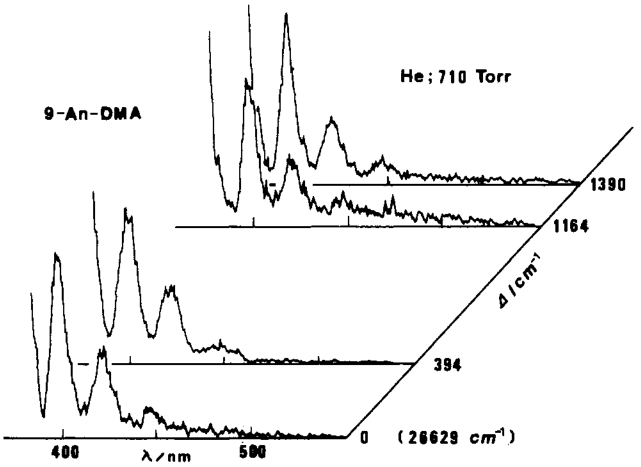


Figure 14. Dispersed fluorescence spectra of jet-cooled 9-An-DMA in excitations of newly observed bands due to the *gauche* conformer (He pressure, 721 Torr). The spectra were normalized in intensity at a maximum of 390–400 nm, and E is the excess vibrational energy from a peak of the newly observed band (26629 cm^{-1}) of the origin band region.

and 9-An-DMA. Details of the steric hindrance for the exciplex formation will be mentioned later.

As shown in Figure 7, it is noteworthy that ΔE of 1-An-DEA ($\sim$1400 cm^{-1}) is much greater than that of 1-An-DMA ($\sim$500 cm^{-1}). This is completely the reverse of the expected order from I_p of (diethyl- and dimethylamino)phenyl moieties. On the other hand, the maximum or appreciable overlap of two π-electron systems between electron donor and acceptor moieties is required for the exciplex formation even in the intramolecular bichromophoric EDA system. For the maximum overlap of two π-electron systems in the exciplex state, two long molecular axes of anthryl and (dialkylamino)phenyl moieties may lean considerably from the perpendicular to the parallel conformation. Therefore, the conformational transformation may take place from the open conformer to the closed exciplex state. Here, the open conformer means probably the *t* torsional conformation concerning the C_1–C_2 bonding of the trimethylene chain, since the *g* conformation is nonreactive for the exciplex formation, as mentioned above. Taking into account the maximum overlap of π-electron systems and the steric factor of the trimethylene chain, the geometry of the intramolecular exciplex was assumed for both 1- and 9-anthryl and (dialkylamino)phenyl systems, as illustrated in Figure 15. In the 9-An-DMA and 9-AN-DEA systems, dialkylamino groups as the electron donor center may be just on the edge of the 9-anthryl moiety (C_3–C_4 or C_5–C_6), but the dialkyl group may be on the outside of the aromatic ring. Then, the steric hindrance of each of the (dimethylamino)phenyl and (diethylamino)phenyl groups does not seem seriously different for the intramolecular exciplex formation. As a result, the variation of the energy threshold for the exciplex formation between 9-An-DMA ($\sim$900 cm^{-1}) and 9-An-DEA ($\sim$700 cm^{-1}) is not serious, though the steric hindrance due to the bulky (diethylamino)phenyl group seems to compensate for the electronic effect due to the larger I_p of this electron donor compared with that of the (dimethylamino)phenyl group, as mentioned above. In 1-An-DME and 1-An-DEA systems, however, the (dialkylamino)phenyl group may be nearly at the center of one of the anthryl benzene rings. The distance between electron donor and acceptor moieties may be greater in 1-An-DEA than in

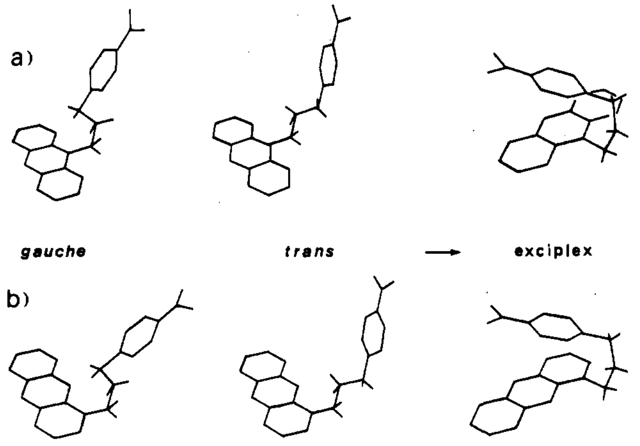


Figure 15. Schematic illustration of *t* and *g* conformations (open form) of 1- and 9-An-DMA and of tentatively assumed structures of the intramolecular exciplex.

1-DMA, which probably leads to a decrease of stabilization energy of the CT exciplex state in the former. The remarkable difference of the energy threshold between 1-An-DMA (~500 cm^{-1}) and 1-An-DEA (~1400 cm^{-1}) for the exciplex formation may be attributable to the variation of the CT stabilization energy by the steric factor. Contrary to the 1-An-DMA and 1-An-DEA systems, the steric factor for the exciplex formation in 9-An-DMA and 9-An-DEA may be somewhat overwhelmed by the electronic factor due to the ionization potential of the donor (DMA and DEA), as mentioned already. As for the steric hindrance of the dialkylamino group to the exciplex formation, the exciplex formation was examined in 1-(1- and 9-anthryl)-3-(*p*-(1-piperidyl)phenyl)propane in the supersonic expansion.[14] The UV fluorescence excitation spectra of these bichromphoric EDA systems exhibit considerably well-resolved vibrational structures. However, neither indication of the intramolecular exciplex formation nor quenching of the anthryl-like fluorescence decay time was observed, at least up to an excess vibrational energy of 2500 cm^{-1}. The facts further indicate the important role of the steric factor in the intramolecular exciplex formation.

Conclusion

Intramolecular exciplex formation and excess vibrational energy dependence in the jet-cooled gas phase were observed in the bichromophoric EDA systems of several 1-(4-(dialkylamino)-phenyl)-3-(1- and 9-anthryl)propanes. The significant aspect of this study is the finding that *t* and *g* torsional conformers concerning the C_1–C_2 bonding of trimethylene are involved in the ground states of these bichromophoric EDA systems. The *t* conformer exhibits the intramolecular exciplex formation depending on the energy threshold of the S_1 vibrational energy level, while no significant exciplex formation was observed in the *g* conformer. These remarkable different features of the exciplex formation were ascribed to a consequence of the extent of IVR in the S_1 vibrational energy level of these *t* and *g* conformations. In the *t* conformers of several bichromophoric EDA systems, the threshold of excess vibrational energy for the exciplex formation was obtained to be very much dependent not only on the electronic and steric factors of the electron donor but also on the alkyl-substituted position of the anthryl moiety.