

Intramolecular Electronic Interaction in Etheral Bichromophoric EDA Systems in Supersonic Free Jet

Norikazu Tsujiya, Kiyoe Kitaura, Yae Kumamoto, and Michiya Itoh*

Department of Physical and Chemical Biodynamics, Graduate School, and Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920, Japan

Received: March 29, 1996; In Final Form: September 10, 1996[⊗]

Excited-state charge transfer interaction was studied in bichromophoric electron donor–acceptor (EDA) systems, 1- and 9-(*p*-*N,N*-(dimethylamino)phenylethyloxy)anthracenes (1- and 9-An-O(CH₂)₂-DMA) and 1- and 9-(*p*-*N,N*-(dimethylamino)benzyloxy)methylanthracenes (1- and 9-An-CH₂OCH₂-DMA), in supersonic expansion. Intramolecular exciplex fluorescence, depending on excess vibrational energy, was observed in jet-cooled 9-An-O(CH₂)₂-DMA. In 1-An-O-(CH₂)₂-DMA, the existence of two isomeric conformers was observed in fluorescence excitation spectra. The UV fluorescence excitation spectrum shows well-resolved vibrational structures, while the visible fluorescence excitation spectrum exhibits considerably broad and 4.5 nm blue-shifted vibrational structures from the UV excitation spectrum. The latter visible excitation spectrum is attributable to intramolecular van der Waals interaction between EDA moieties followed by the exciplex formation. Another conformer exhibits no significant exciplex fluorescence. The other etheral compounds, 1- and 9-An-CH₂OCH₂-DMA, exhibit neither exciplex nor charge-transfer complex fluorescence in supersonic expansion but show exciplex fluorescence in solution.

Introduction

Jet-cooled intramolecular exciplex formation has been reported in some bichromophoric electron donor–acceptor (EDA) systems since pioneering works by Zewail and his co-workers.^{1,2} These intramolecular exciplexes are mostly limited to the bichromophoric EDA systems with trimethylene except in only a few cases.³ We reported several papers concerning with the jet-cooled exciplex and excimer formations from van der Waals (vdW) complexes.^{4,5} Similar jet-cooled exciplex formations of vdW complexes were reported by other research groups.^{6–8} Furthermore, we reported the intramolecular exciplex in the bichromophoric EDA system.^{9–12} In these inter- and intramolecular exciplex formations, the excess vibrational energy dependence for the exciplex formation is one of the most interesting features in supersonic jet spectroscopy. Recently, we have reported that multiconformations are involved in 1-(1- and 9-anthryl)-3-(*m*-*N,N*-(dimethylamino)phenyl)propanes (abbreviated to 1- and 9-An-*m*-DMA) by hole-burning spectroscopy.¹¹ Furthermore, the vibrational energy thresholds for the exciplex formations have been demonstrated to depend on the ground-state conformations of these compounds.

On the other hand, the photochemistry in solutions, such as that involved with the excimer/exciplex¹³ and biradical formations^{14,15} by a hydrogen atom transfer, have been investigated in several bichromophoric systems with some etheral chains, for instance –O(CH₂)_{*n*}O– and –CH₂OCH₂–. Since the synthesis of the etheral bichromophoric chain compounds is much easier than that of alkyl chain compounds, the etheral bichromophoric compounds were used sometimes for studies of the intramolecular electronic interactions. In these etheral chain compounds, no significant difference from trimethylene was observed in some cases of the photochemical behavior. However, some new spectroscopic features in the etheral bichromophoric EDA systems different from those of the trimethylene chain are expected in supersonic expansion.

This paper presents studies on the excited-state charge-transfer interaction in etheral bichromophoric EDA systems, 1- and

9-(*p*-*N,N*-(dimethylamino)phenylethyloxy)anthracene (1- and 9-An-O(CH₂)₂-DMA) and 1- and 9-(*p*-*N,N*-(dimethylamino)benzyloxy)methylanthracene (1- and 9-An-CH₂OCH₂-DMA), in supersonic expansion. Intramolecular exciplex formation, depending on excess vibrational energy, was observed in jet-cooled 9-An-O(CH₂)₂-DMA, which is very similar to the bichromophoric EDA systems with trimethylene. In 1-An-O-(CH₂)₂-DMA, the existence of two isomeric forms was identified by fluorescence excitation spectra. The visible fluorescence excitation spectra of this compound show considerably broad and blue-shifted vibrational structures, while the UV fluorescence excitation spectra show well-resolved vibrational structures. The excitation of the former band shows exciplex fluorescence, which may be attributable to the excited-state transformation of the van der Waals interaction between EDA moieties in the ground state. The latter well-resolved UV fluorescence excitation spectra suggest no exciplex fluorescence. The other type of bichromophoric compounds, 1- and 9-An-CH₂OCH₂-DMA, exhibit neither exciplex nor charge-transfer complex fluorescence in supersonic expansion. The different spectroscopic features between An-O(CH₂)₂-DMA and An-CH₂OCH₂-DMA were discussed in terms of fluorescence quenching of the anthryl moieties by the etheral oxygen atom of An-CH₂OCH₂– and the intramolecular vibrational energy redistribution in these compounds.

Experimental Section

Materials. Etheral compound 1-An-O(CH₂)₂-DMA was synthesized from 1-hydroxyanthracenes and *p*-(*N,N*-dimethylamino)phenethyl tosylate. 1-Hydroxyanthracene was prepared from 1-aminoanthracene (Nakarai Tesque) and sodium hydroxysulfite by refluxing for 24 h in ethanol/water (1:2). *p*-(*N,N*-Dimethylamino)phenethyl tosylate was synthesized from *p*-(*N,N*-dimethylamino)phenethyl alcohol (Aldrich) and *p*-toluenesulfonyl chloride in pyridine at <0 °C. 9-An-O(CH₂)₂-DMA was synthesized from 9-anthrone/NaOH and *p*-(*N,N*-dimethylamino)phenethyl tosylate. 1- and 9-An-CH₂OCH₂-DMA were synthesized from 1- and 9-anthryl methanol and *p*-(*N,N*-dimethyl-

[⊗] Abstract published in *Advance ACS Abstracts*, December 15, 1996.

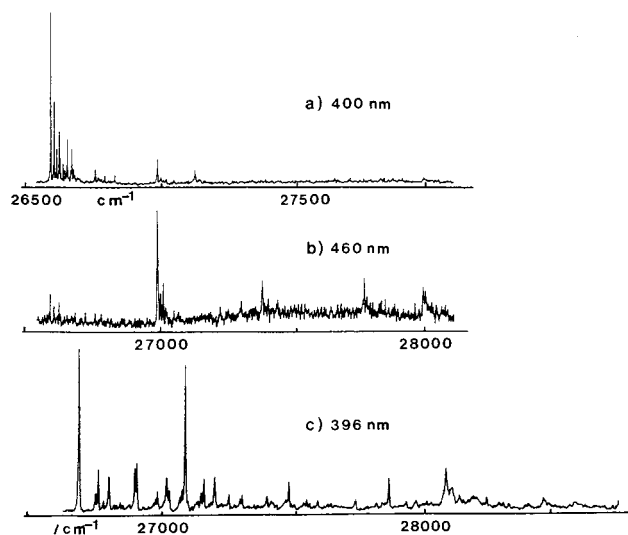


Figure 1. Fluorescence excitation spectra monitored at (a) 400 and (b) 460 nm of jet-cooled 9-An-O(CH₂)₂-DMA. (c) An UV fluorescence excitation spectrum (400 nm) of 9-An-OCH₂CH₃ in similar supersonic expansion.

lamino)benzyl bromide. These compounds were purified by column chromatography (silica gel/dichloromethane/hexane) and repeated recrystallization and further vacuum sublimation before use. Structures and purities were confirmed by elementary analysis and NMR (270 and 500 MHz) and mass spectroscopies. 1-An-O(CH₂)₂-DMA: mp 138–139 °C. Mass (*m/z*) 341 (M⁺). Calcd for C₂₄H₂₃NO: C, 84.42; H, 6.79; N, 4.10. Found: C, 84.13; H, 6.72; N, 4.09. 9-An-O(CH₂)₂-DMA: mp 81–82 °C. Mass (*m/z*) 341 (M⁺). Found: C, 84.23; H, 6.70; N, 4.12. 1-An-CH₂OCH₂-DMA: mp 126–127 °C. Mass (*m/z*) 341 (M⁺). Found: C, 84.32; H, 6.79; N, 4.00. 9-An-CH₂OCH₂-DMA: mp 124–127 °C. Mass (*m/z*) 341 (M⁺). Found: C, 84.40; H, 6.74; N, 4.15.

General Procedures. The experimental setup and procedures of fluorescence spectroscopy of the pulsed supersonic free jet were identical to those described in the previous papers.^{10,11} The 10 Hz pulsed supersonic free jet backed by He (two to three atms) was excited at 10–12 mm downstream of a nozzle by an excimer-laser-pumped dye laser (Lambda Physik Compex 102/FL 3002). The setup and procedures of the laser-induced fluorescence spectra and decay were almost the same as described previously.^{11,12} The spectra were detected through a grating monochromator (Nikon G-250) by a photomultiplier (Hamamatsu R1246). The spectral resolutions for the fluorescence excitation and for the dispersed fluorescence were approximately 5 and 3 nm, respectively. The output signal was processed by a boxcar integrator (SRS 250) and a personal computer system. Fluorescence decay was determined by a digital oscilloscope (Tektronix TDS 520) and processed by a computer-simulated convolution.

Results

Fluorescence Spectroscopy of Jet-Cooled 9-An-O(CH₂)₂-DMA. The UV fluorescence excitation spectrum of jet-cooled 9-An-O(CH₂)₂-DMA exhibits considerably resolved vibrational structures starting with an origin band at 376.71 nm (26 545 cm⁻¹), as shown in Figure 1. The vibrational structures with low-frequency vibrations of 10–11 and 29–30 cm⁻¹ were observed in the origin band region. The former 10–11 cm⁻¹ progressions are very similar to those of the UV fluorescence excitation spectrum of 9-An-DMA extensively studied previously,^{1,2,10,16} though the spectrum of this ethereal compound

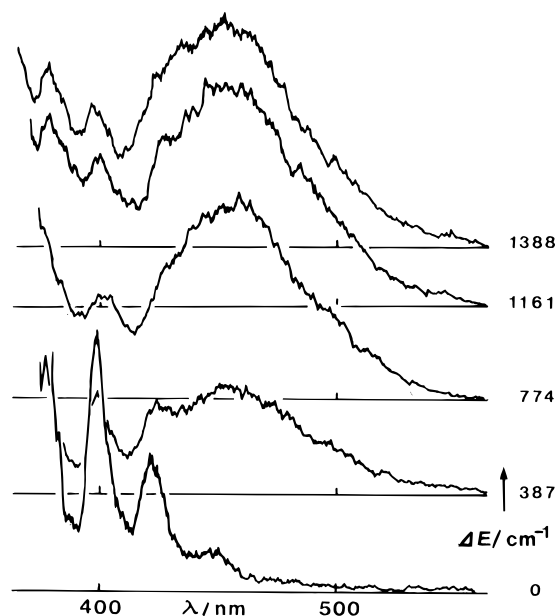


Figure 2. Excess vibrational energy dependence of the dispersed fluorescence spectra of 9-An-O(CH₂)₂-DMA.

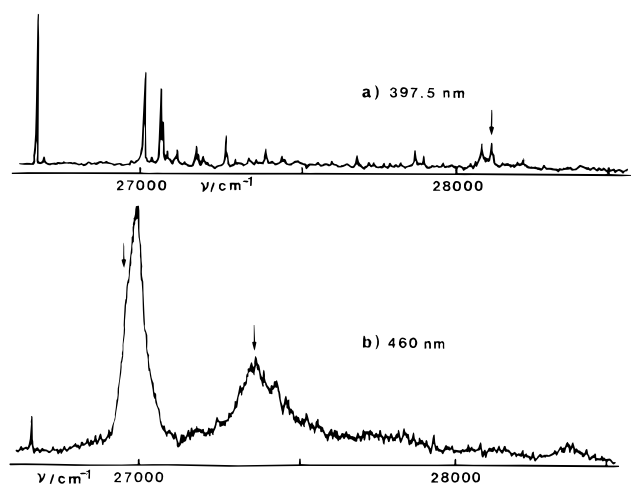
shows approximately a 1.9 nm red shift from that of the latter. The low-frequency vibrations in 9-An-DMA were ascribed to vibronic coupling of anthryl with methylene hydrogen atoms of the center of trimethylene by Zewail and his co-workers, as mentioned above. Figure 1 also shows the fluorescence excitation spectrum of 9-An-OCH₂CH₃. The spectrum exhibits an approximately 2.2 nm blue shift from that of 9-An-O(CH₂)₂-DMA and lacks low-frequency vibration of 10–11 cm⁻¹ and 29–30 cm⁻¹ progressions. Therefore, the chain conformation of 9-An-O(CH₂)₂-DMA seems considerably different from that of 9-An-OCH₂CH₃. The UV fluorescence excitation spectra of the former show a remarkable decrease in intensity with increasing in vibrational energy, while the visible (460 nm) fluorescence excitation spectra increase in intensity in the vibronic band region with excess energy of >400 cm⁻¹, as shown in Figure 1. These fluorescence excitation spectra suggest that this compound exhibits the intramolecular exciplex fluorescence by the excitation of vibronic bands at approximately 400 cm⁻¹ higher than the origin band. Figure 2 shows the dispersed fluorescence spectra of this compound in a supersonic expansion, which are remarkably dependent on the excess vibrational energy. The dispersed fluorescence spectra demonstrate that the jet-cooled exciplex in this ethereal compound seems to be generated in the excess vibrational energy threshold (ΔE) lower than those in 9-An-DMA (900 cm⁻¹) and 1-An-DMA (500 cm⁻¹) with trimethylenes.^{1,2}

Fluorescence decay times of the anthryl moiety of 9-An-O(CH₂)₂-DMA were determined to be 16.4 ns in the origin band excitation (376.72 nm) and 5 ns at 371.31 nm. Furthermore, those were less than 1–2 ns in the excitations of higher vibronic band regions. The anthryl fluorescence decay time (16.4 ns) of the origin of this compound is similar to that (19.1 ns at the origin) of a compound without the DMA moiety, 9-An-OCH₂-CH₃. However, the decrease of decay times in the former was more significant than that of the latter with increasing excess vibrational energy. The exciplex fluorescence decay times remarkably decrease with increasing excess vibrational energy from 85 ns (at 371.31 nm, $\Delta E = 387$ cm⁻¹) to 17 ns (at 358.0 nm, $\Delta E = 1388$ cm⁻¹), though the exciplex decay times of 9-An-DMA with trimethylene were almost independent of excess vibrational energy.¹⁰ These spectroscopic and decay features of the ethereal compounds may be attributable to the

TABLE 1: Anthryl Fluorescence Decay Times in the Origin Band Excitations of Etheral Bichromophoric EDA Systems in Comparison with Those of Similar Trimethylene Systems^{10,16}

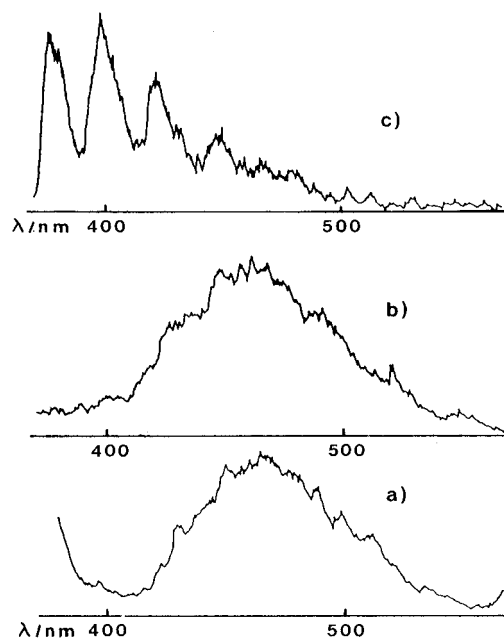
compound	origin band nm (cm ⁻¹)	decay time ns
9-An-CH ₂ OCH ₂ -DMA	370.29 (27 005)	9.6
9-An-CH ₂ OCH ₃	370.39 (26 983)	8.3
9-An-(CH ₂) ₃ -DMA (t)	374.77 (26 683)	19
(g)	(26 600–28 400)	9
1-An-CH ₂ OCH ₂ -DMA	363.72 (27 493)	7.4
9-An-O(CH ₂) ₂ -DMA	376.71 (26 545)	19.1
9-An-OCH ₂ CH ₃	374.52 (26 701)	16.4
1-An-O(CH ₂) ₂ -DMA	374.74 (26 685) ^a	14.0
	370.44 (26 995) ^b	<2
1-An-(CH ₂) ₃ -DMA (t)	368.70 (27 122)	20
(g)	(27 050–27 100)	

^a An origin band of sharp vibrational structures exhibiting no significant exciplex fluorescence. ^b An origin band of intramolecular vdW state exhibiting exciplex fluorescence.

**Figure 3.** Fluorescence excitation spectra monitored at (a) 397.5 and (b) 460 nm of 1-An-O(CH₂)₂-DMA in supersonic expansion.

intramolecular interaction between anthryl and oxygen atom, as will be mentioned later. These fluorescence decay times are summarized in Table 1.

Fluorescence Spectroscopy of Jet-Cooled 1-An-O(CH₂)₂-DMA. Figure 3 shows fluorescence excitation spectra of 1-An-O(CH₂)₂-DMA in a supersonic expansion. The origin band at 374.74 nm (26 685 cm⁻¹) of the UV fluorescence excitation spectrum exhibits a remarkable red shift from that of the corresponding bichromophoric compound 1-An-DMA with trimethylene (368.70 nm, 27 122 cm⁻¹). However, no significant low-frequency vibration was observed in the origin band region of this etheral compound. The vibrational structures of the UV fluorescence excitation spectrum are very similar to that of anthracene (an origin, 27 695 cm⁻¹) except for a large red shift from the latter. The visible (460 nm) fluorescence excitation spectrum of 1-An-O(CH₂)₂-DMA shows very broad congested bands, which are blue-shifted approximately 4.3 nm from the sharp origin and the respective vibronic bands of the UV fluorescence excitation spectrum, as shown in Figure 3. It is noteworthy that no sharp vibronic bands were observed in addition to the broad bands in the visible fluorescence excitation spectra. The fact suggests that the excitation of the sharp vibronic bands exhibits no exciplex fluorescence, while the broad band excitations reveal the visible fluorescence, probably the exciplex fluorescence. Dispersed fluorescence spectra obtained by the typical sharp and broad band excitations are shown in Figure 4. Castella, Tramer, and PiuZZi⁷ reported the existence of two isomeric forms in the jet-cooled intermolecular

**Figure 4.** Dispersed fluorescence spectra excited at (a) 370.70 nm (26 976 cm⁻¹), (b) 359.40 nm (27 824 cm⁻¹), and (c) 355.10 nm (281 612 cm⁻¹). The excitation bands are indicated by arrows in Figure 3.

system of anthracene and *N,N*-dimethylaniline (DMA). The fluorescence excitation spectrum looks like a superposition of a broad and diffuse band system and the closely spaced narrow band system. The origin bands of the former and latter band systems were red-shifted approximately 403 and 525 cm⁻¹ from that of anthracene, respectively. Furthermore, they reported that the narrow band excitations exhibit vibrationally resolved fluorescence of the complex, while the broad band excitation does the exciplex fluorescence at 420–480 nm.⁷ On the other hand, Kizu and Itoh⁹ reported the jet-cooled exciplex fluorescence from the van der Waals (vdW) complex between 9,10-dicyanoanthracene and naphthalene. This jet-cooled system showed a rather broad fluorescence excitation spectrum whose intensity was dependent on the vapor pressure of naphthalene. In the 1-An-O(CH₂)₂-DMA system, the shape and relative intensity of the broad bands shown in Figure 3b were independent of vapor pressure of the sample variable with nozzle temperature. Therefore, these broad bands may be attributable to the intramolecular interaction between bichromophoric EDA moieties of 1-An-O(CH₂)₂-DMA. Furthermore, taking account the existence of two isomeric forms involved in the jet-cooled intermolecular anthracene/DMA system,⁷ the vibrationally resolved structures in the UV fluorescence excitation spectrum and the broad congested bands in the visible one (Figure 3) were tentatively ascribed to open and closed forms of the etheral chain system, respectively. If there is a strong charge-transfer interaction between EDA moieties in the ground state of the closed form, the visible fluorescence excitation spectrum may be very broad bands without vibrational structures. Therefore, the considerably congested vibrational structures in the visible fluorescence excitation spectrum shown in Figure 3b suggests a weak van der Waals interaction between EDA moieties in the closed form of this etheral chain compound.

Anthryl fluorescence decay times were obtained to be 14.0 ns in the sharp origin band excitation and considerably decreased in the excess vibrational energy region (for instance 9.3 ns at $\Delta E = 1396$ cm⁻¹). However, the excess energy dependence of the anthryl decay time of this compound was not so remarkable as that of 9-An-O(CH₂)₂-DMA, which means there is no significant exciplex formation in this open form as

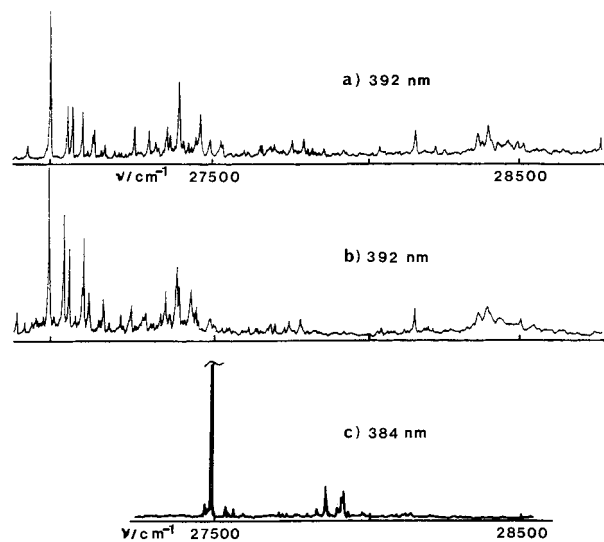


Figure 5. Fluorescence excitation spectra of (a) 9-An-CH₂OCH₂-DMA and (b) 9-An-CH₂OCH₃ in supersonic expansion. (c) A fluorescence excitation spectrum of 1-An-CH₂OCH₂-DMA. Fluorescence was detected at 392 nm in (a) and (b) and at 384 nm in (c).

mentioned above. On the other hand, the UV fluorescence decay times were less than 2 ns in excitations of the broad vdW bands of the closed form even in the origin band region. The facts suggest that the visible fluorescence, probably exciplex, may be generated by the excited-state transformation of the intramolecular vdW state (the closed form) of this compound. These fluorescence spectral and decay features are consistent with the assignments that the sharp and broad bands shown in Figure 3 were attributable to the open and closed forms, respectively. However, the actual structures of these ethereal chain conformations and the possibility of the exciplex formation from the open form in the higher vibronic band region are not obvious at the present stage.

Fluorescence Spectroscopy of Jet-Cooled 1- and 9-An-CH₂OCH₂-DMA. Figure 5 shows UV fluorescence excitation spectra of 1- and 9-An-CH₂OCH₂-DMA monitored at 392 nm and that of a model compound, 9-An-CH₂OCH₃ (392 nm), in a supersonic expansion. The fluorescence excitation spectra detected at 440 nm of two former compounds exhibit almost identical vibrational structures and relative intensities with their respective UV fluorescence excitation spectra. Figure 6 shows typical dispersed fluorescence spectra of 9-An-CH₂OCH₂-DMA in excitations of an origin and several vibronic bands. These fluorescence excitation and dispersed fluorescence spectra indicate that no exciplex fluorescence was detected in these jet-cooled compounds, though these compounds exhibit exciplex fluorescence in polar and nonpolar solutions. A typical exciplex fluorescence spectrum of 9-An-CH₂OCH₂-DMA in a deaerated 3-methylpentane solution is shown in Figure 6b.

As shown in Figure 5, the excitation spectra of 9-An-CH₂OCH₂-DMA and 9-An-CH₂OCH₃ exhibit almost identical vibrational structures, and their origins are very much red-shifted (490–510 cm⁻¹) from that of 1-An-CH₂OCH₂-DMA. The comparison of excitation spectra between the 9-An-CH₂OCH₂-DMA and 9-An-CH₂OCH₃ indicates no significant intramolecular interaction between anthryl and DMA moieties in the former. The facts may be confirmed from the excess vibrational energy dependence of the anthryl fluorescence decay times, as will be mentioned later. Fluorescence decay times (decay rate constants) of these ethereal compounds were measured in the excitations of the origin and major vibronic bands. Figure 7 illustrates the excess energy dependence of fluorescence decay rate constants of the ethereal compounds in comparison with

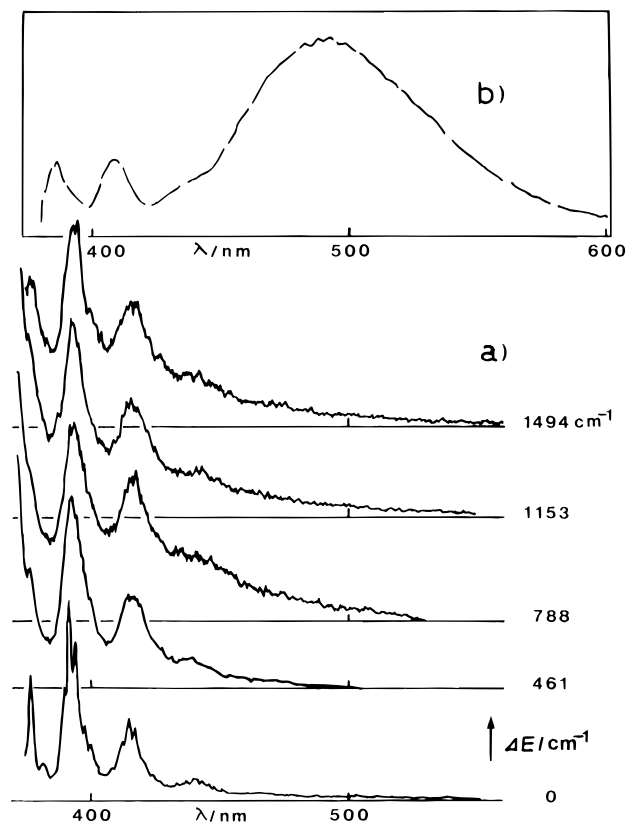


Figure 6. (a) Excess vibrational energy ($\Delta E/\text{cm}^{-1}$) dependence of dispersed fluorescence spectra of 9-An-CH₂OCH₂-DMA in supersonic jet. (b) Fluorescence spectrum of this compound in a deaerated 3-methylpentane solution (excitation wavelength, 365 nm) at room temperature.

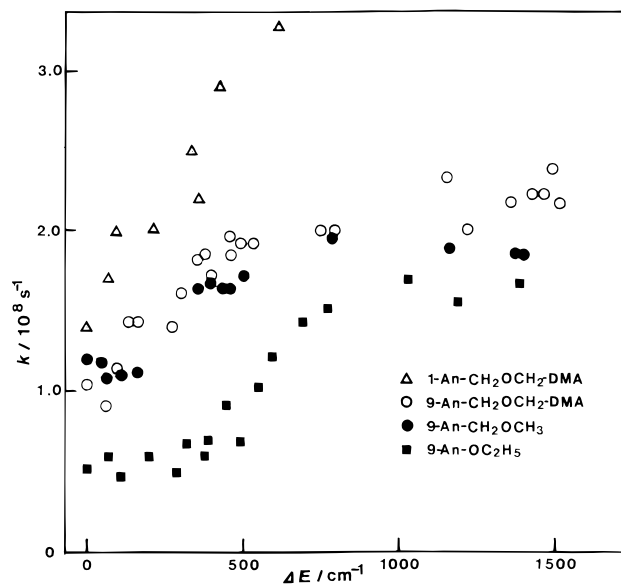


Figure 7. Plots of decay rate constants of anthryl fluorescence vs excess vibrational energies (ΔE) of four jet-cooled compounds indicated in figure. Errors of decay rate constants are approximately <10%. Those of 9-An-OCH₂CH₃. The fluorescence decay rate constants of 9-An-CH₂OCH₂-DMA and 9-An-CH₂OCH₃ show very similar excess energy dependence throughout $\Delta E = 0\text{--}1400$ cm⁻¹. In 1-An-CH₂OCH₂-DMA, the UV fluorescence excitation spectrum exhibits a considerable blue shift from those of the former as mentioned above. Furthermore, anthryl decay rate constants remarkably increase with increasing excess vibrational energy. The fact suggests a considerable fluorescence quenching of the 1-anthryl group in the higher vibronic

band region, though no significant exciplex fluorescence was observed, as mentioned above. However, it is not obvious why 1-anthryl fluorescence is more quenched than 9-anthryl in these ethereal chain molecules at the present stage.

Discussion

Hopkins *et al.*¹⁷ reported the rotational isomers of *trans* and *gauche* conformations in jet-cooled propylbenzene. The rate constant of the intramolecular vibrational energy redistribution (IVR) was suggested to be much smaller in the *gauche* conformer (*g*) than the *trans* one (*t*) in propylbenzene.¹⁸ At a low He backing pressure of the supersonic expansion, the similar *gauche* and *trans* conformers were reported in the trimethylene bichromophoric compounds, 1-(1- and 9-anthryl)-3-phenylpropanes (1- and 9-An-Ph) and also in 1- and 9-An-DMA. The *gauche* conformers of 1- and 9-An-DMA were reported to exhibit no significant exciplex fluorescence. The fluorescence decay times of the origin bands of the *gauche* conformer of 9-An-Ph and 9-An-DMA were approximately 9 ns, while those of the *trans* were 19–20 ns. The smaller decay times of the *gauche* were ascribed to a considerable fluorescence quenching of the anthryl moiety in the origin band region. These features of the *gauche* conformers in 1- and 9-An-DMA were ascribed to the smaller IVR rate constant than those of the *trans* ones. In the *gauche* form, the anthryl vibrational energy transfer to the trimethylene leading to the favorable conformation in the exciplex was suggested to be prevented. The smaller possibility of IVR in this conformer of the trimethylene was reported to be responsible for no significant exciplex formation in the *gauche* conformer of 1- and 9-An-DMA in the previous paper.^{10,16}

In jet-cooled 1- and 9-An-CH₂OCH₂-DMA, anthryl fluorescence decay times of the origin band region are 7.4 and 9.6 ns, respectively, as mentioned in the last section (Table 1). These decay times are considerably shorter than those of 9-An-OCH₂-CH₃ (16.4 ns) and 9-An-O(CH₂)₂-DMA (19.1 ns). The short decay times of the anthryl in 1- and 9-An-CH₂OCH₂-DMA seem to suggest a weak intramolecular interaction between an ethereal oxygen atom of -CH₂OCH₂- and the anthryl moiety. It is likely that the intramolecular interaction between the ethereal oxygen and the anthryl moiety is attributable to a weak charge-transfer character induced by the nonbonding electrons on the oxygen atom to the anthryl in these compounds. This intramolecular interaction leads to a rigid chain conformation of these -CH₂OCH₂- bichromophoric compounds. Preliminary results of AM-1 semiempirical calculations of the ethereal chain conformation suggest that the rigid conformation is similar to the *gauche* conformation of the trimethylene.¹⁹ By analogy to the spectral and IVR features in the methylene *gauche* conformer in 1- and 9-An-DMA, the smaller possibility of anthryl vibrational energy transfer to the rigid ethereal chains, leading to the favorable chain transformation for the exciplex, seems to be responsible for no exciplex formation and small anthryl decay times in 1- and 9-An-CH₂OCH₂-DMA (7.4 and 9.6 ns at the origin), as mentioned above.

As mentioned in the last section, the exciplex fluorescence decay time in 9-AnO(CH₂)₂-DMA was observed in the excess vibrational energy of >400 cm⁻¹. The anthryl decay time of 19.1 ns in the origin band region remarkably decreased with increasing excess vibrational energy, whose decrement of the decay times in the higher vibronic region may be attributable to the increase of rate constants of the exciplex formation as well as to the nonradiative process. Taking into account the anthryl decay time of the origin region, the intramolecular interaction between the oxygen atom of -O(CH₂)₂- and the

anthryl moiety does not seem so significant in the low vibrational energy region of this compound. These spectral features are almost similar to those of 9-An-DMA. In 1-An-O(CH₂)₂-DMA, however, two isomeric forms are involved, as mentioned in the last section. One of them exhibits rather diffuse fluorescence excitation spectra and exciplex fluorescence by the excited-state transformation of the intramolecularly interacting state, which was ascribed to the van der Waals interaction between two moieties. The vdW state may be tentatively ascribed to the intramolecularly closed form. Another isomer shows no significant exciplex fluorescence in the excess energy region of <1300 cm⁻¹. In the higher vibronic band regions, no significant difference between two isomeric forms can be distinguished for the exciplex formation. Taking account of the 14–15 ns of anthryl decay time of the origin band in this isomer, there seems to be only small intramolecular interaction between the two moieties, which may be a possible open form.

Acknowledgment. This work was supported by a Grant-in-Aid on Priority-Area-Research "Photoreaction Dynamics" (No. 06239103) from the Ministry of Education, Science, Sports, and Culture of Japan. The authors are indebted to Dr. T. Shinoda, Faculty of Pharmaceutical Sciences, Toyama Medical and Pharmaceutical University, for his kind AM1 calculations of geometrical optimization of molecules.

References and Notes

- (1) Felker, P. M.; Syage, J. A.; Lambert, W. R.; Zewail, A. M. *Chem. Phys. Lett.* **1982**, *92*, 1.
- (2) Syage, J. A.; Felker, P. M.; Zewail, A. M. *J. Chem. Phys.* **1984**, *81*, 2233.
- (3) (a) Wegewijs, G.; Hermant, R. M.; Verhoven, J. W.; Kunst, A. G. M.; Rettschnick, R. P. H. *Chem. Phys. Lett.* **1987**, *140*, 567. (b) Shou, H.; Alfano, J. C.; van Dantzig, N. A.; Levy, D. H. *J. Chem. Phys.* **1991**, *95*, 711. (c) van Dantzig, N. A.; Shou, H.; Alfano, J. C.; Yang, N. C.; Levy, D. H. *J. Chem. Phys.* **1994**, *100*, 7068.
- (4) (a) Saigusa, H.; Itoh, M. *Chem. Phys. Lett.* **1984**, *106*, 391; *J. Chem. Phys.* **1984**, *81*, 5682. (b) Saigusa, H.; Itoh, M.; Baba, H.; Hanazaki, I. *J. Chem. Phys.* **1987**, *86*, 2529. (c) Itoh, M.; Morita, Y. *J. Phys. Chem.* **1988**, *92*, 5693, and references cited therein.
- (5) Itoh, M.; Sasaki, M. *J. Phys. Chem.* **1990**, *94*, 6544.
- (6) Castella, M.; Prochorow, M.; Tramer, A. *J. Chem. Phys.* **1984**, *81*, 2511.
- (7) Castella, M.; Tramer, A.; Piuze, F. *Chem. Phys. Lett.* **1986**, *129*, 112.
- (8) Anner, O.; Haas, Y. *J. Am. Chem. Soc.* **1988**, *110*, 1416, and references cited therein.
- (9) Kizu, N.; Itoh, M. *J. Phys. Chem.* **1990**, *96*, 5796.
- (10) Kizu, N.; Itoh, M. *J. Am. Chem. Soc.* **1993**, *115*, 4799.
- (11) (a) Kurono, M.; Takasu, R.; Itoh, M. *J. Phys. Chem.* **1994**, *98*, 5925. (b) Kurono, M.; Takasu, R.; Itoh, M. *J. Phys. Chem.* **1995**, *99*, 9668.
- (12) Kurono, M.; Itoh, M. *J. Phys. Chem.* **1995**, *99*, 17113.
- (13) (a) Wang, Y. C.; Morawetz, H. *J. Am. Chem. Soc.* **1976**, *98*, 3611. (b) Mugnier, J.; Valeur, B.; Gratton, E. *Chem. Phys. Lett.* **1985**, *119*, 217.
- (14) Tanimoto, Y.; Kita, A.; Itoh, M.; Okazaki, M.; Nakagaki, R.; Nagakura, S. *Chem. Phys. Lett.* **1990**, *165*, 184.
- (15) (a) Tanimoto, Y.; Okada, N.; Takamatsu, S.; Itoh, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1342. (b) Tanimoto, Y.; Nagano, M.; Fujiwara, Y.; Kohtani, S.; Itoh, M. *J. Photochem. Photobiol. A* **1993**, *74*, 153.
- (16) Takasu, R.; Kizu, N.; Itoh, M.; Shinoda, H. *J. Chem. Phys.* **1994**, *101*, 7364.
- (17) (a) Hopkins, J. B.; Powers, D. E.; Mukamel, S.; Smalley, K. E. *J. Chem. Phys.* **1980**, *72*, 5049. (b) Hopkins, J. B.; Powers, D. E.; Mukamel, S.; Smalley, R. E. *J. Chem. Phys.* **1980**, *77*, 5049.
- (18) Syage, J. A.; Felker, P. M.; Semmes, D. H.; Zewail, A. H. *J. Chem. Phys.* **1985**, *82*, 2896.
- (19) Private communication from Dr. H. Shinoda, Toyama Medical and Pharmaceutical University, which will be submitted elsewhere. The AM-1 calculations were carried out by the same method as reported in ref 16.