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The Influence of Molecular Conformation on the Electronic Relaxation Processes. Complex Formation in the Ground State and Triple Fluorescences of 6-Acetoxyspiro[aceanthyrylene-2(1*H*),9′(10′*H*)-anthracene]-10′-one

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The absorption spectra of 6-acetoxyspiro[aceanthyrylene-2(1*H*),9′(10′*H*)-anthracene]-10′-one(**2**) in cyclohexane, dichloromethane, and chloroform have been observed. The absorption spectra have been also observed as a function of concentration of chlorinated methanes in mixtures with cyclohexane. It was revealed that **2** forms a ground state complex with chlorinated methanes. The equilibrium constants for the ground-state complex formation with dichloromethane and chloroform were determined to be 0.14 and 0.17 $\text{mol}^{-1}\,\text{dm}^3$, respectively. The fluorescence and fluorescence excitation spectra of **2** have been obtained as a function of excitation wavelengths and emission wavelengths in cyclohexane and chlorinated methanes. The spiro compound emits structured fluorescence(FM) in cyclohexane. On the other hand, three types of fluorescence bands (FM, FC, and FE) were observed in chlorinated methanes. The FC and FE bands are both structureless and their peak wavenumbers are 20800 and 18700 cm^{-1}. The quenching of fluorescence quantum yield and lifetime were treated by Stern–Volmer kinetics considering the complex formation in both the ground and the excited states of the system. Based on the experimental findings, the origins of FM, FC, and FE bands are explained by the complex formation between **2** and chlorinated methanes in the ground state and exciplex formation in the excited state.

The emission spectra of molecules which have somewhat specific molecular geometry in the ground and excited states are interesting problem from the stand point of the relation between the electronic structure and the geometrical specificity of the molecules. In previous papers the authors presented the influence of molecular conformation on the electronic relaxation processes of biphenyl[1] and *m*-terphenyl[2] which have conformational flexibility. Becker and Sandross[3] found dual fluorescences for 1′2′-dihydrospiro[anthracene-9(10*H*),3′-[3*H*]benz[*de*]anthracene]-10-one(**1**, Diagram 1) in various solvents. **1** has a six-membered ring containing a spiro carbon atom and has two possible conformations. The anthracene ring is not perpendicular to the anthrone ring in **1**. Photoexcitation of the anthracene chromophore in **1** in chloroform and other solvents gives rise to two types of fluorescences. One is an anthracene-like fluorescence and its assigned to the anthracene moiety. The other fluorescence is a structureless emission (σ_{max}=18700 cm^{-1}). They attributed this fluorescence band to radiative deactivation of an excited intramolecular charge-transfer complex between the electron-donating anthracene moiety and the electron-withdrawing anthrone moiety.

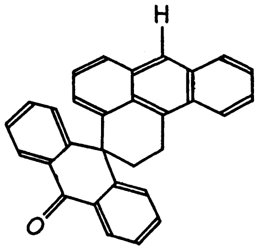

Diagram 1. 1′,2′-Dihydrospiro[anthracene-9(10*H*), 3′-[3*H*]benz[*de*]anthracene]-10-one.

In this paper, the absorption, fluorescence, and fluorescence excitation spectra of 6-acetoxyspiro[aceanthyrylene-2(1*H*), 9′(10′*H*)-anthracene]-10′-one(**2**, Diagram 2) in cyclohexane, dichloromethane, chloroform, and cyclohexane–chlorinated methane mixtures are reported. In contrast to the case of **1**, **2** has a five-membered ring containing a spiro carbon atom and has a rigid geometry. The anthracene position is connected to the anthrone ring though the five-membered ring. The two rings are precisely perpendicular.

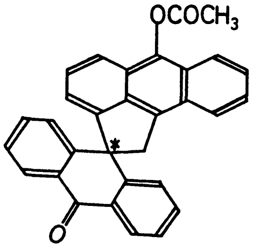

Diagram 2. 6-Acetoxyspiro[aceanthyrylene-2(1*H*), 9′(10′*H*)-anthracene]-10′-one.

The fluorescence spectrum of **2** has an anthracene-like structure in cyclohexane. In the mixtures of cyclohexane and chlorinated methanes shows a remarkable excitation-wavenumber dependence. In chlorinated-methanes, however, two broad fluorescence

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bands are observed and anthracene-like fluorescence spectrum is strongly quenched in the solvents. This remarkable fluorescence change of **2** suggests that **2** may specifically interact with chlorinated methanes in an energetically favourable conformation.

Fluorescence quenching is discussed based on the data of quantum yield and lifetime. It is shown that **2** forms a ground state complex with chlorinated methanes and emits three types of fluorescence. Fluorescence quenching by added chlorinated methanes is interpreted by Stern–Volmer kinetics. The origins of the triple fluorescences are explained by the complex formation between **2** and chlorinated methanes in the ground and excited states.

Experimental

2 was synthesized according to the method given in the literature.[4] Cyclohexane and dichloromethane (Wako Pure Chemical Industries Inc., Luminasol grade), chloroform (Wako, Spectrosol grade), ethanol (Wako, S. G. S. grade), and sulfuric acid (Wako, S grade) were used without further purification. The absorption and emission spectra were observed at room temperature using a Hitachi 220 recording spectrophotometer and a Hitachi MPF-2A fluorescence spectrophotometer. The data were transferred to an NEC PC-8001 microcomputer for processing. The fluorescence quantum yields were determined with reference to those of anthracene in cyclohexane,[5] 9,10-diphenylanthracene in ethanol,[6] and quinine sulfate in sulfuric acid.[7] Fluorescence lifetimes were determined with a single-photon fluorescence lifetime instrument arranged in this laboratory. The fluorescence lifetimes obtained by the instrument were found to agree well with the widely accepted literature values.[8] The sample solutions were prepared just prior to measurements and stored in the dark. The solutions were degassed when necessary.

Results and Discussion

Absorption Spectra and Complex Formation in the Ground State. The absorption spectra of **2** in cyclohexane and dichloromethane are shown in Fig. 1. Although the spectrum in dichloromethane shifts to the red compared with that in cyclohexane, the spectral difference between these spectra is small, except that a very weak absorption band appears between 23500 and 21500 cm^{-1} in chlorinated methanes (see next).

The absorption spectrum at high concentration of **2** in chloroform is shown in Fig. 2. It is seen from Fig. 2 that a very weak and broad band exists around 22700 cm^{-1}. This frequency region coincides with a new fluorescence excitation band for FC emission (see below). Almost the same spectral feature was obtained in **2** and dichloromethane system.

The spectrum observed in chloroform is similar to that observed in dichloromethane. These spectral features were unchanged after a week. The band with fine structure which appears between 23800 and 31200 cm^{-1} and the intense band which appears between 35700 and 43500 cm^{-1} closely resemble the ^1L_a and ^1B_b transitions of anthracene. The band which appears between 31200 and 35700 cm^{-1} can be assigned to the local transition of the anthrone chromophore in **2**. Therefore the whole absorption spectrum of **2** is composed of the absorption spectrum of the anthracene chromophore and that of the anthrone chromophore except for an band in the lowest frequency region that appears in chlorinated methanes. Note that the strong ^1L_a transition due to the anthracene chromophore obscures the weak n-π^* transition of anthrone around 25000 cm^{-1}.[9]

To make clear the origin of the very weak absorption band which appears in chlorinated methanes, the absorption spectra of **2** in cyclohexane-dichloromethane and cyclohexane-chloroform mixed solvents are shown in Figs. 3 and 4 respectively as a function of the

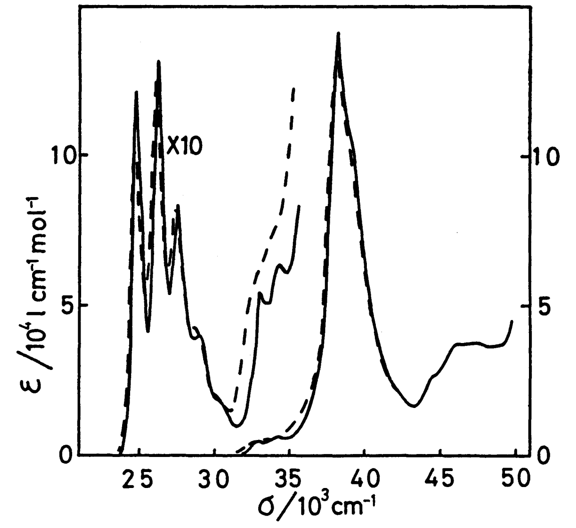

Fig. 1. The absorption spectra of **2** in cyclohexane (——) and dichloromethane (----). The spectrum observed in chloroform is almost the same as that observed in dichloromethane.

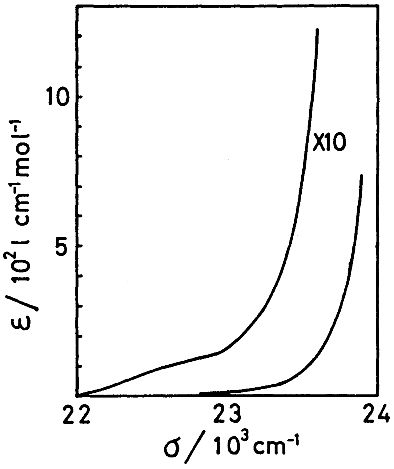

Fig. 2. The absorption spectrum of **2** in dichloromethane at higher concentration.

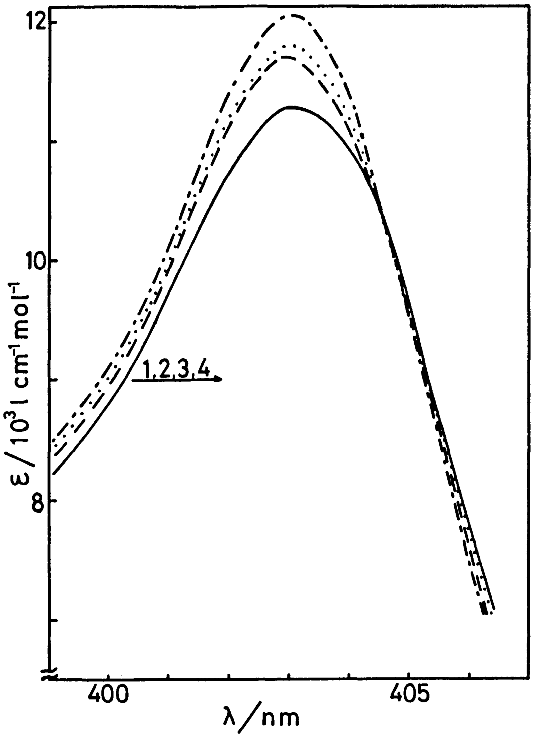

Fig. 3. The absorption spectra of **2** in cyclohexane–dichloromethane mixed solvent. Concentrations for dichloromethane are 1: 0, 2: 0.20, 3: 0.31, 4: 1.01 mol dm^{-3}.

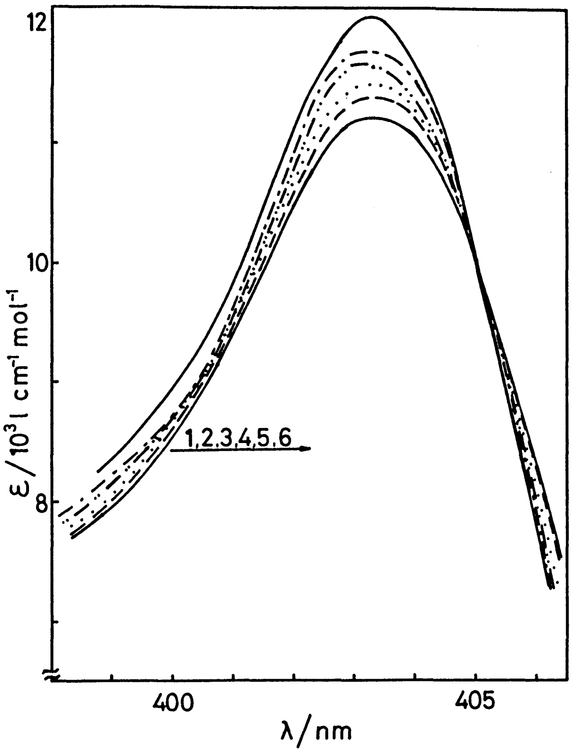

Fig. 4. The absorption spectra of **2** in cyclohexane–chloroform mixed solvent. Concentrations for chloroform are 1: 0, 2: 0.10, 3: 0.20, 4: 0.40, 5: 0.70, 6: 1.0 mol dm^{-3}.

concentration of chlorinated methanes. As the concentration of dichloromethane increases, the peak intensity of vibrational bands decreases (Fig. 3). An isosbestic point appears in the spectra. These observations indicate that an equilibrium between two species occurs in the ground state of this system. A similar spectral feature is also seen in the cyclohexane-chloroform mixed solvents (Fig. 4). The spectral feature was unchanged after a week unless the solutions were stored in the light. Therefore it is safely concluded that a complex is formed between chlorinated methanes and **2** in its ground state. The equilibrium constant of the ground state complex, K_C, can be determined by the usual procedure.[10] The K_C values were 0.14 and 0.17 mol dm^{-3} for the ground state complex between **2** and dichloromethane and between **2** and chloroform, respectively.

It is noted that the K_C value in **2** and chloroform system is larger than that in **2** and dichloromethane system. This difference between two K_C values may be attributable to the difference of the numbers of chlorine atoms in dichloromethane and chloroform.

The formation of ground-state complexes between aromatic molecules and halomethanes has been established for anthracene.[11,12] In the ground-state complexes of anthracene, halomethanes are located on the plane of anthracene ring. Ware and Lewis showed that there are higher complexes of carbon tetrachloride with anthracene and this higher complexes are responsible for the origin of wavelength effects in the fluorescence quenching of anthracene.[12]

There are two possible configurations for a complex between **2** and chlorinated methanes. One is the configuration in which chlorinated methanes are located on the anthracene ring, similar to complexes between anthracene and halomethanes. The other is the configuration in which chlorinated methanes are connected to the C=O group of **2** through hydrogen bonding between **2** and chlorinated methanes. Baba and Takemura found that anthrone forms a ground-state complex with triethylamine.[13] They also reported that a very weak n–π* absorption band appears in the red edge side of a stronger absorption band due to the formation of a complex between anthrone and triethylamine in the ground state. This situation is similar to what we observe for **2** and chlorinated methanes. Therefore it is safely concluded that chlorinated methanes are either connected to the C=O group of **2** through a hydrogen bond or are located on the plane of **2** in the ground state.

This very weak absorption band is not obvious in cyclohexane solution. Taking into account the discussion in the previous section, one possible interpretation for the appearance of the band is an n–π* band in anthrone, normally around 25000 cm^{-1}, shifted to the red due to a ground-state complex formation between **2** and chlorinated methanes. Another possible interpretation of this band is that the n–π* band shifts to the red due to the distortion of the anthrone ring system in **2**.

Fluorescence and Fluorescence Excitation Spectra. The fluorescence and fluorescence excitation spectra of **2** in cyclohexane are given in Fig. 5. Although it is not shown in Fig. 5, there are no excitation-wavenumber and no emission-wavenumber dependent changes in the fluorescence emission or fluorescence excitation spectra of **2** in cyclohexane. The fluorescence spectrum of **2** has an anthracene-like structure and the fluorescence excitation spectrum of **2** also has an anthracene-like structure. Hereafter the anthracene-like structured band is referred to as FM fluorescence band, meaning "molecular fluorescence." It is noted that the FM band is a similar emission band observed in cyclohexane for **1**.[3)]

Figure 6 shows the excitation-wavenumber dependence of fluorescence spectra of **2** in dichloromethane. When **2** is excited at 33330 and 25000 cm^{-1}, it exhibits an anthracene-like fluorescence band on the higher wavenumber side and a broad band on the lower wavenumber side (σ_{max}=18700 cm^{-1}). On the other hand, when **2** is excited at 23800 cm^{-1}, it has only one broad and structureless fluorescence band (σ_{max}=20800 cm^{-1}). Similar characteristics are seen in the excitation-wavenumber dependence of fluorescence spectra of **2** in chloroform (Fig. 7). Hereafter the broad bands which show peaks at 20800 and 18700 cm^{-1} are referred to as FC and FE fluorescence bands, respectively. They will be assigned below to "complex fluorescence" and "exciplex fluorescence." It is noted that the FE band has seen in some solvents for **1** but the FE band was not seen in the fluorescence spectra of **1**.[3)]

Figure 8 shows the observation-wavenumber dependence of the fluorescence spectra of **2** compound in dichloromethane. When the spectrum is observed at a wavenumber of 22730 cm^{-1}, which corresponds to a peak of the FM band, the spectrum is similar to the fluorescence excitation spectrum observed in cyclohexane. With decreasing the observation wavenumber below 22730 cm^{-1}, a shoulder appears on the red side of the anthracene-like band. When the spectrum is observed at 20830 cm^{-1}, which corresponds to the peak of the FC band, a new excitation band appears around 22700 cm^{-1}. A mirror symmetry relation is found

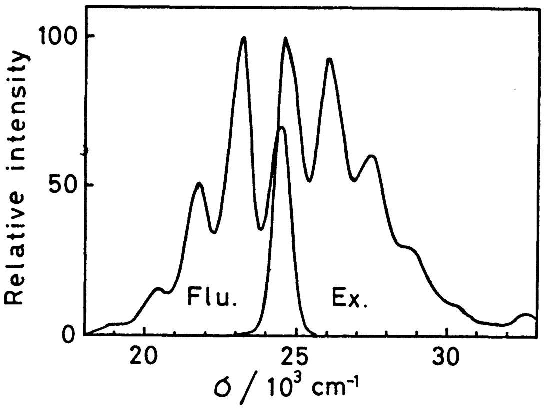

Fig. 5. The fluorescence and fluorescence excitation spectra of **2** in cyclohexane.

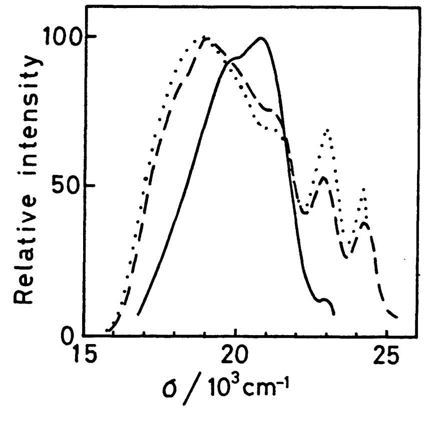

Fig. 6. The fluorescence spectra of **2** in dichloromethane. Excitation wavenumbers are as follows, 1(----): 33300, 2(······): 25000, 3(——): 23800 cm^{-1}.

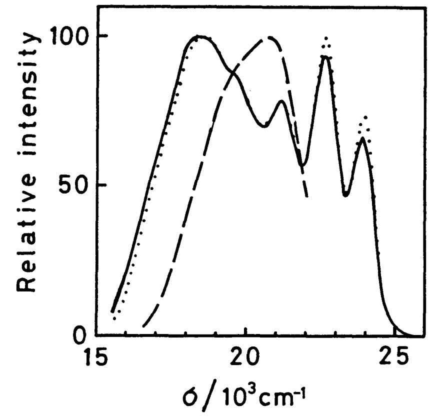

Fig. 7. The fluorescence spectra of **2** in chloroform. Excitation wavenumbers are as follows, 1(——): 31250, 2(······): 27780, 3(----): 23810 cm^{-1}.

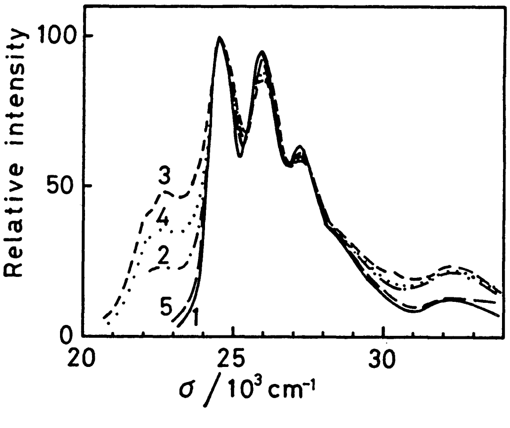

Fig. 8. The fluorescence excitation spectra of **2** in dichloromethane. Emission wavenumbers are as follows, 1(——): 22730, 2(-·-·-): 21740, 3(----): 20330, 4(······): 20000, 5(——): 17860 cm^{-1}.

between this broad band and the FC band. When the spectrum is observed at around 18000 cm^{-1}, which corresponds to the peak of the FE band, the spectrum is similar to the fluorescence excitation spectrum observed in cyclohexane.

The observation-wavenumber dependence of fluorescence excitation spectra of the compound in chloroform is given in Fig. 9. It is seen from Fig. 9 that the spectral features in chloroform are almost the same as in dichloromethane, but the spectral characteristics in chloroform are not so obvious as in dichloromethane.

These results indicate that the FM and FE bands originate from the same ground-state species which show the anthracene-like fluorescence excitation spectra. On the other hand, the FC band originates from a ground state species which shows a broad fluorescence excitation spectrum around 22700 cm^{-1} in chlorinated methanes.

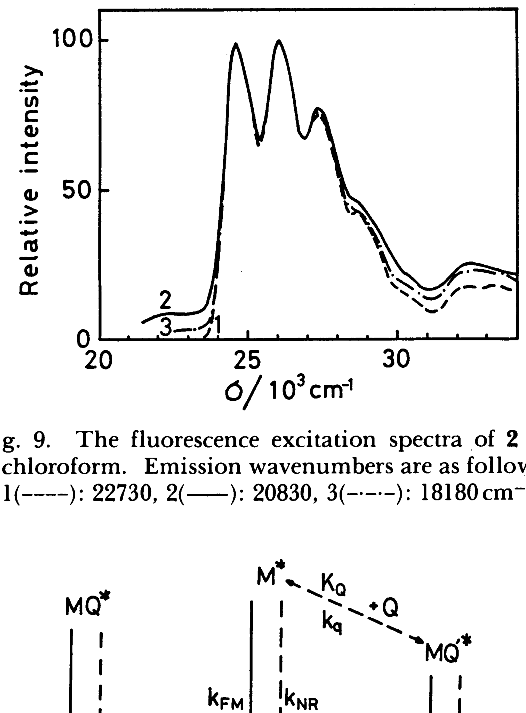

Fig. 9. The fluorescence excitation spectra of **2** in chloroform. Emission wavenumbers are as follows, 1(----): 22730, 2(——): 20830, 3(–·–·–): 18180 cm^{-1}.

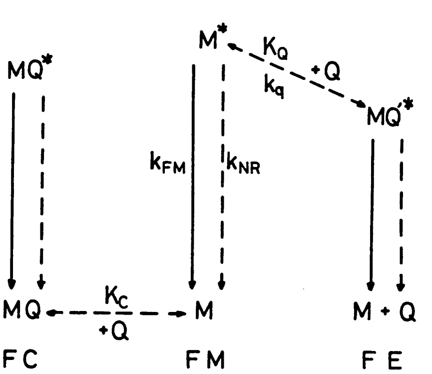

Fig. 10. Reaction scheme of **2**. M is **2**, Q is chlorinated methanes, MQ is a ground-state complex between **2** and chlorinated methanes, M* and MQ* are an excited-state species of M and MQ, MQ′* is an exciplex between M* and chlorinated methanes, K_C is equilibrium constant of complex formation in the ground state. K_Q is defined in the text and k's are rate constants. When the initial concentration of quencher, [C], is enough larger than that of **2**, then we can put [Q]=[C].

The data in Figs. 1 to 9 indicate the origins of the fluorescence bands, FM, FC, and FE may be summarized as follows: The FM band can be assigned to a fluorescence of the anthracene chromophore from the excited **2**. The FC band originates from excitation of a complex which is formed between **2** and chlorinated methanes in the ground state. The FE band is an emission from an exciplex which is formed between excited **2** and chlorinated methanes.

Kinetic Consideration. The reaction scheme for the interaction of **2** with chlorinated methanes discussed in the above section is illustrated in Fig. 10. If initial concentration of quencher, initial concentration of **2**, equilibrium concentration of **2**, equilibrium concentration of quencher, and equilibrium concentration of the complex are denoted by [C], [B], [M], [Q], and [MQ], respectively, then

$$[\mathrm{B}] = [\mathrm{M}] + [\mathrm{MQ}], \tag{1}$$

$$[\mathrm{C}] = [\mathrm{Q}] + [\mathrm{MQ}]. \tag{2}$$

Equilibrium constant of complex formation among M, Q, and MQ is

$$K_{\mathrm{C}} = \frac{[\mathrm{MQ}]}{[\mathrm{M}][\mathrm{Q}]} \tag{3}$$

Therefore [MQ] is represented as

$$[\mathrm{MQ}] = K_{\mathrm{C}} \times [\mathrm{M}] \times [\mathrm{Q}]. \tag{4}$$

The fraction of the incident light intensity absorbed by M is given by[5)]

$$\alpha = \frac{\varepsilon_{\mathrm{M}}[\mathrm{M}]}{\varepsilon_{\mathrm{M}}[\mathrm{M}] + \varepsilon_{\mathrm{MQ}}[\mathrm{MQ}]} \tag{5}$$

$$= \frac{1}{1 + a \times K_{\mathrm{C}} \times [\mathrm{Q}]}, \tag{6}$$

where ε_{M} and $\varepsilon_{\mathrm{MQ}}$ represent the molar absorption coefficients for M and MQ and a is equal to $\varepsilon_{\mathrm{MQ}}/\varepsilon_{\mathrm{M}}$.

The fluorescence intensity of the FM band in the absence of quenchers is written as

$$F_0 = \frac{k_{\mathrm{FM}}}{k_{\mathrm{FM}} + k_{\mathrm{NR}}} \times [\mathrm{M}^*]_{[\mathrm{Q}]=0} \tag{7}$$

where $[\mathrm{M}^*]_{[\mathrm{Q}]=0}$ indicates excited concentration of **2** at equilibrium concentration ([Q]) of chlorinated methanes is equal to 0. When [Q] is not equal to 0, the fluorescence intensity of **2** can be written as

$$F_{\mathrm{Q}} = \frac{k_{\mathrm{FM}}}{k_{\mathrm{FM}} + k_{\mathrm{NR}} + k_{\mathrm{q}}[\mathrm{Q}]} \times [\mathrm{M}^*]_{[\mathrm{Q}]}, \tag{8}$$

where $[\mathrm{M}^*]_{[\mathrm{Q}]}$ represents excited concentration of **2** where equilibrium concentration of chlorinated methanes is [Q]. $[\mathrm{M}^*]_{[\mathrm{Q}]}$ can be rewritten as

$$[\mathrm{M}^*]_{[\mathrm{Q}]} = [\mathrm{M}^*]_{[\mathrm{Q}]=0} \times \alpha. \tag{9}$$

Then Stern-Volmer equations for the ratio of the fluorescence intensity (RQY) and for the ratio of the fluorescence lifetime (RTF) for the FM band can be rewritten as

$$\mathrm{RQY} = \frac{F_0}{F_\mathrm{Q}} = \frac{k_\mathrm{FM} + k_\mathrm{NR} + k_\mathrm{q}[\mathrm{Q}]}{k_\mathrm{FM} + k_\mathrm{NR}} \times \frac{[\mathrm{M}^*]_{[\mathrm{Q}]=0}}{[\mathrm{M}^*]_{[\mathrm{Q}]}}$$

$$= (1 + a \times K_\mathrm{C} \times [\mathrm{Q}]) \times (1 + K_\mathrm{Q} \times [\mathrm{Q}]), \quad (10)$$

$$\mathrm{RTF} = \frac{k_\mathrm{FM} + k_\mathrm{NR} + k_\mathrm{q}[\mathrm{Q}]}{k_\mathrm{FM} + k_\mathrm{NR}}$$

$$= 1 + K_\mathrm{Q} \times [\mathrm{Q}], \quad (11)$$

where

$$K_\mathrm{Q} = \frac{k_\mathrm{q}}{k_\mathrm{FM} + k_\mathrm{NR}}$$

Under the condition that the initial concentration of quencher, [C], is much larger than that of **2**, [B], Eqs. 10 and 11 can be written as

$$\mathrm{RQY} = (1 + a \times K_\mathrm{C} \times [\mathrm{C}]) \times (1 + K_\mathrm{Q} \times [\mathrm{C}]) \quad (10a)$$

$$\mathrm{RTF} = 1 + K_\mathrm{Q} \times [\mathrm{C}]. \quad (11a)$$

Figure 11 plots the RQY for the FM band of **2** as a function of [C], a concentration of dichloromethane or chloroform, in cyclohexane–dichloromethane or cyclohexane–chloroform mixed solvents. It is seen from Fig. 11 that the plots are nonlinear. This nonlinearity is attributed to the decrease of concentration of free **2** at higher concentration of chlorinated methanes due to the formation of the ground-state complex between **2** and chlorinated methanes. The nonlinearity is also attributed to exciplex formation between the excited **2** and chlorinated methanes. The experimental curves are well represented by Eq. 10a. The Stern–Volmer constant for deexcitation processes, K_Q, can be determined by Eq. 10a. The K_Q values of 0.20 and 0.09 $\mathrm{mol^{-1}\,dm^3}$ were obtained for the deexcitation processes between the excited compound and chloroform and between the compound and dichloromethane, respectively.

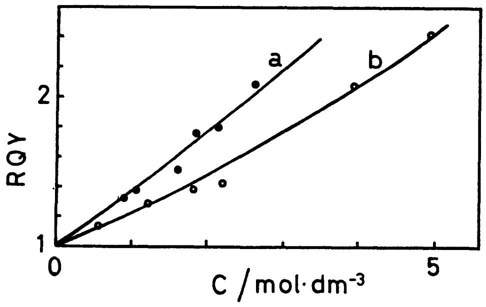

Fig. 11. Stern–Volmer plots of fluorescence quantum yield of **2** in cyclohexane–dichloromethane(a) and cyclohexane–chloroform(b). Since the excitation wavelength corresponds to an isosbestic point, a=1 in Eq. 10a. The solutions are not degassed.

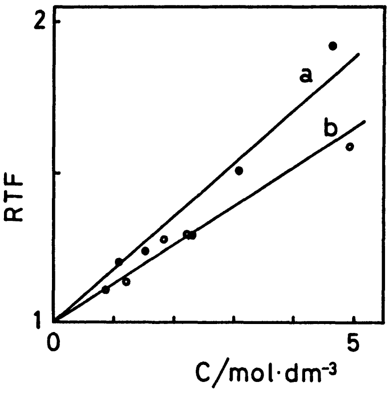

Fig. 12. Stern–Volmer plots of fluorescence lifetime of **2** in cyclohexane–dichloromethane(a) and cyclohexane–chloroform(b). The solutions are not degassed.

Figure 12 plots the RTF of **2** as a function of [C] in cyclohexane–dichloromethane and cyclohexane–chloroform mixed solvents. Figure 12 shows that the plots are linear within the experimental error and experimental results are well represented by Eq. 11a. The K_Q values obtained from the RTF plots are 0.18 and 0.12 $\mathrm{mol^{-1}\,dm^3}$ for chloroform and dichloromethane system, respectively.

The K_Q values obtained from the quenching of fluorescence quantum yields agree well with those obtained from the decrease in fluorescence lifetimes. These results confirm that the FM band originates from an excited **2**, the FC band originates from a complex formed in the ground state, and the FE band originates from an exciplex between excited **2** and chlorinated methanes.

Comparison of 2 with 1.[3] **1** and **2** are similar compounds. **1** emits only the FM and FE bands. Becker and Sandross has assigned the FM band to a fluorescence of the anthracene chromophore and the FE band to an exciplex fluorescence which originates from a solvent-assisted intramolecular charge-transfer interaction between the ground-state anthrone and excited-state anthracene. On the other hand, **2** emits the FM, FC, and FE fluorescences.

This difference may be attributable to the difference of molecular geometries between **1** and **2**. The geometry of **1** and that of **2** are similar but not identical. **1** has the six-membered ring containing a spiro carbon atom and has two possible conformations. Furthermore, the twisted angle between anthracene and anthrone rings are not perpendicular. **2**, however, has the five-membered ring containing a spiro carbon atom and has a rigid conformation. The anthracene ring is precisely perpendicular to the anthrone ring in **2**.

The assignment about the origin of the FM band by Becker and Sandross agrees with our conclusion. On the origin of the FE band, our conclusion is not in conflict with Becker and Sandross since the formation of an intermolecular complex may be responsible for an excited-intramolecular charge-transfer complex. Although it is difficult at present to presume what type geometry is acceptable for the exciplex geometry, there are possible geometries for the exciplex between **2** and chlorinated methanes. One is a similar conformation to the ground-state complex between anthracene and halogenated methanes where halogenated methanes are located on the plane of anthracene ring.10) The other is a conformation where halogenated methanes are located surrounding the anthrone ring. In this case anthrone ring has geometrical distortion due to the connection through the five-membered ring with the anthracene ring. The electronic structure of the exciplex would resemble that of a σ–π complex suggested by Becker and Sandross for **1**.3) The study of the more detailed kinetic consideration including similar compounds as **1** and **2** will be the object of further work.

The authors are much indebted to Professor Takeshi Takemura of Hokkaido University for his helpful suggestion about the possible structures of the ground-state complex between **2** and chlorinated methanes.

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