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Excimer Fluorescence of 1,2-Di(9-anthryl)ethane, 1,3-Di(9-anthryl)propane, and 9,9′-Bianthryl at High Pressures

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Fluorescence spectra of 1,2-di(9-anthryl)ethane (**1**), 1,3-di(9-anthryl)propane (**2**), and 9,9′-bianthryl (**3**) have been studied at high pressures up to 50 kbar both in crystalline state and in PMMA matrix. In the case of **1** and **2** in crystalline state, the excimer emissions appear reversibly at high pressures accompanied by the reversible red shifts. While in PMMA the fluorescence spectra assigned as locally excited state are observed, whose peak shifts are quite analogous to that of anthracene in the same matrix. As for **3**, a new band also appears at high pressure which is similar to the intramolecular charge-transfer band. Possible interpretations of the pressure effects are discussed.

Since the first discovery by Förster and Kasper[1] concerning the complexes between excited and ground state aromatic hydrocarbons which were named "excimer," numerous aromatic hydrocarbons have been found to exhibit excimer fluorescence and the results have been summarized in some reviews.[2] Their prominent feature is the broad and structureless fluorescence band which is shifted 4000—6000 cm^{-1} to lower frequencies relative to the normal molecular fluorescence. This fluorescence has been observed both in fluid solutions and in solid state at atmospheric pressure, if the structure allows a close overlap of molecular planes.

Recently the presence of the so-called "second excimer"[3] with a smaller overlap between the two anthracene moieties as compared with the sandwich arrangement has been suggested for 1,2-di(9-anthryl)ethane in solution by Hayashi *et al.*[4] Dianthrylalkanes, where a pair of anthracene molecules are linked with methylene groups, have a possibility of the formation of intramolecular excimers.

The primary effect of pressure is to decrease interatomic distances and to increase overlap between adjacent electronic orbitals. Thus, the excimer formation in the solid state is expected to be highly pressure dependent if the crystal structures or molecular conformations are appropriate to allow a sandwich conformation. In the crystals such as anthracene, which has not a dimer structure, the excimer formation has been reported by the application of high pressure,[5] although the crystals with dimer structure such as perylene, pyrene, and 9-methylanthracene are known to exhibit excimer fluorescence at atmospheric pressure.

In this paper we report our studies of the pressure dependence of the excimer formation in 1,2-di(9-anthryl)ethane (**1**), 1,3-di(9-anthryl)propane (**2**), and 9,9′-bianthryl (**3**) [*i.e.*, (anthracene)–$(CH_2)_n$–(anthracene) for n=2, 3, and 0, respectively] up to 50 kbar both in the crystalline state and in the plastic media. Previously we published a preliminary results of **1**.[6] This paper presents the results of a more complete analysis where some points are corrected. In addition, since the high pressure cell, the emission apparatus, and the operation employed for this work have not been previously described, some details are also given here.

Experimental

Materials. The samples of **1**, **2**, and **3** used in this studies were prepared according to the literature procedure.[7—9] **1** was recrystallized from toluene and purified further by sublimation under vacuum. **2** and **3** were purified by successive recrystallizations from benzene and acetic anhydride, respectively. No impurity was detectable in TLC analysis, elementary analysis, and spectroscopic analysis of the purified samples.

The measurements were carried out for the crystals diffused in the NaCl crystal which was used as pressure transmitting medium, and for the poly(methyl methacrylate) (PMMA) film. Methyl methacrylate monomer was purified by the ordinary method[10] and thermally polymerized in bulk. The PMMA was purified by reprecipitations from benzene solution with methanol as precipitant. The compound and the PMMA were dissolved in dichloromethane at a concentration of less than 1%, forming approximately 0.07 mm thick films after evaporating the solvent under nitrogen atmosphere and at reduced pressure. The salt pellet is usually 0.5 mm thick. Two half cylinders of NaCl single crystal are cut to fit the sample hole of the high pressure cell and the pellet or film is inserted in between.

High Pressure Cell. The high pressure cell used for emission measurements is similar to Drickamer's type 1 cell[11] except for some modifications. It has two windows at 90° and uses NaCl as a pressure transmitting fluid, as well as NaCl windows. The outer steel jacket is SNCM hardened to HRC: 45—50. The inner cell is made from maraging steel YAG 300 hardened to HRC: 60. The carboloy pistons are jacketed with SNCM.

The pressure calibration was based on the shift of the R_1 fluorescence line of ruby at 694.2 nm as determined at the NBS (0.75 cm^{-1}/kbar)†. This cell can be used up to 50 kbar with no trouble in pistons as well as in windows.

Emission Apparatus. A block diagram of the emission spectrometer apparatus is shown in Fig. 1. The 27300 cm^{-1} band of a Hanovia 200 W Hg–Xe arc lamp is used as the excitation light source, which is mounted in an LH 150 lamp housing of Schoeffel LPS 271 power supply. The exciting light is dispersed through an ISA Jobin-Yvon H20 monochromator. Quartz lenses focus the excitation light into the high pressure cell. The emitted light is observed by the front surface illumination at 90° to the excitation light. Quartz lenses then collect the emitted light from the sample and focus it onto the entrance slit of the emission monochromator, an ISA Jobin-Yvon HRS 600 mm monochromator with a 1200 grooves/mm grating. For detection

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† 1 bar=10^5 Pa.

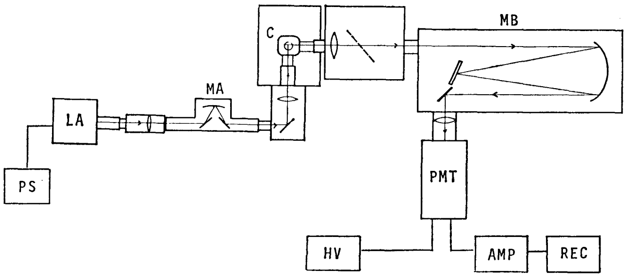


Fig. 1. Schematic diagram of apparatus for measuring the pressure effect on fluorescence.
C: High pressure cell, LA: excitation lamp, MA: excitation monochromator, MB: emission monochromator, PMT: cooled photomultiplier, PS: power supply, HV: high voltage power supply, AMP: amplifier, REC: recorder.

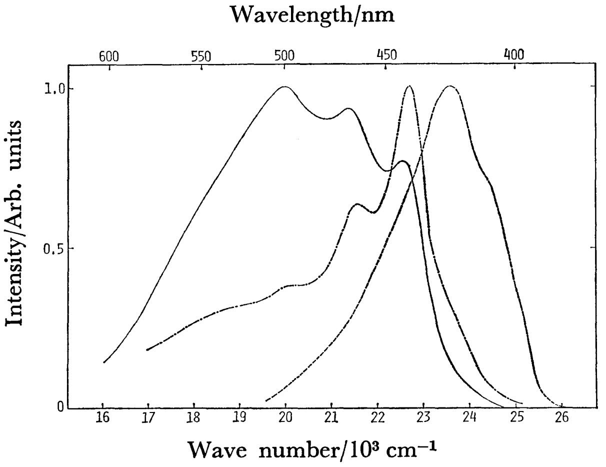


Fig. 2(a). Fluorescence spectra of **1** in different matrices at atmospheric pressure.
——: Crystals in NaCl pellet, —·—·: crystals, — — — —: in PMMA matrix. (They are normalized at the wavenumber corresponding to the maximum intensity.)

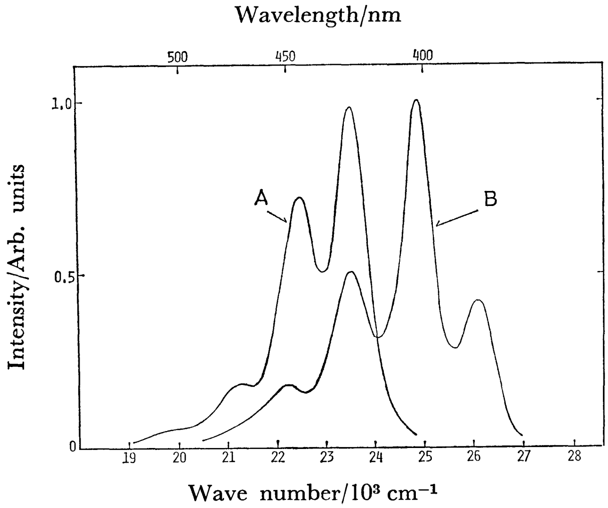


Fig. 2(b). Fluorescence spectra of anthracene.
A: Crystals in NaCl pellet, B: in PMMA

of the emitted light, the photomultiplier tube used is a Hamamatsu R562 which is operated at a cathode voltage of −1000 V by Fluke 415B, and cooled to −70 °C by a Hamamatsu C659 cooling apparatus. The amplified signal is displayed on a recorder.

The spectrometer can also be employed to measure excitation spectra, where the broad spectrum of a Hanovia 150 W Xe arc lamp and the wavelength drive of the excitation monochromator are required. The spectral corrections were made by quinine sulfate in 0.05 M H_2SO_4 (1 M= 1 mol dm^{-3}) as a reference standard.

Results

Fluorescence Spectra of ***1.*** Figure 2(a) summarizes the fluorescence spectra of **1** in different matrices at atmospheric pressure, which are normalized at each peak maximum. The spectrum of the crystal exhibits the normal fluorescence, which corresponds to that from ^1L_a state of anthracene. By forming into NaCl pellet with the compression of less than 7 kbar, this band decreases and a new broad structureless band appears at the energy of about 20000 cm^{-1}, although it is relatively weak in intensity. The corresponding change is not observed in the fluorescence excitation spectra. The new band decreases by the thermal annealing and reverts to the original crystalline spectra for 2 h at 100 °C. Thermal annealing removes the irreversible effects.

In PMMA, on the other hand, the main band at around 24000—25000 cm^{-1} are also assigned as the locally excited band, although the vibrational structure disappears. As a reference standard the fluorescence spectra of anthracene at atmospheric pressure in both matrices are shown in Fig. 2(b), where the concentration is about twice of that in **1**. The loss of vibrational structures in **1** may come from some intramolecular interactions accompanied by the substitution at the 9 position of anthracene since the transition moment of ^1L_a state is along the short molecular axis of anthracene. But it has appeared in **2** with larger separation between the two anthracene parts.

Figures 3 and 4 illustrate the effect of pressure on the fluorescence spectra of **1** in crystalline state and in PMMA matrix, respectively. They are normalized at their peak maxima. In crystals the new broad band grows in intensity at the expence of the normal emission with increasing pressure. These effects are reversible with pressure. The intensity of the normal emission returns to the spectrum obtained before compression, which indicates that no photochemical process is occuring at high pressures.

In PMMA, the band at 20000 cm^{-1} is not observed, but a new shoulder at 22000—23000 cm^{-1} appears as the pressure is applied. It is also reversible with pressure. The fluorescence excitation spectra do not show any new bands at high pressures and the behavior on the spectra are also reversible with pressure.

Fluorescence Spectra of ***2.*** Figure 5 shows the fluorescence spectra of the crystal at various pressures. A broad structuresless band is observed even at atmospheric pressure as a dominant band. The normal fluorescence appears as a small shoulder which disappears with increasing pressure.

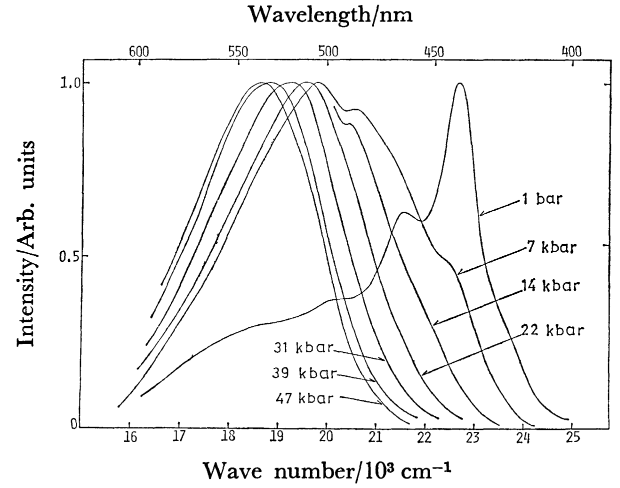


Fig. 3. Fluorescence spectra of **1** in crystals at various pressures.

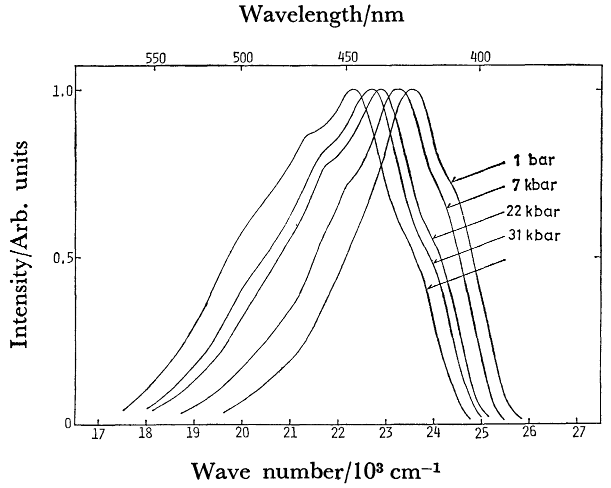


Fig. 4. Fluorescence spectra of **1** in PMMA matrix at various pressures.

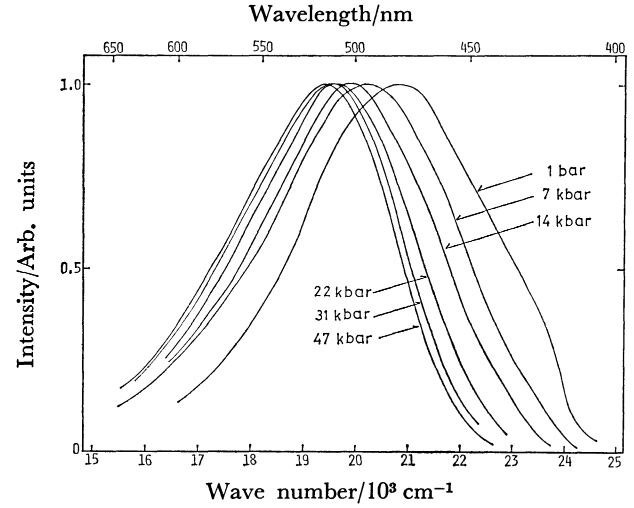


Fig. 5. Fluorescence spectra of **2** in crystals at various pressures.

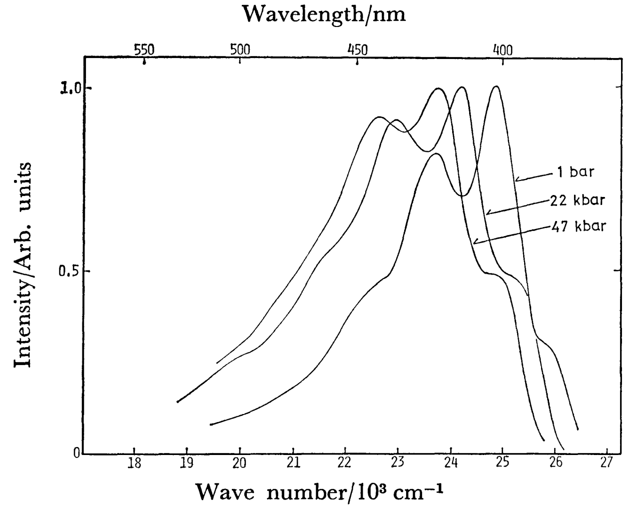


Fig. 6. Fluorescence spectra of **2** in PMMA matrix at various pressures.

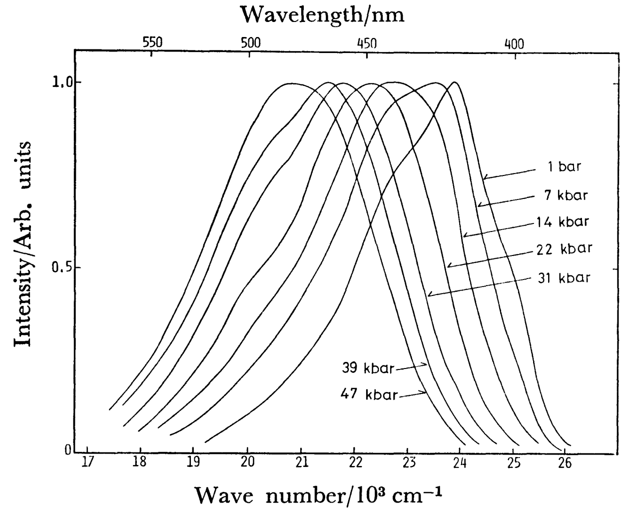


Fig. 7. Fluorescence spectra of **3** in crystals at various pressures.

Figure 6 shows the fluorescence spectra of **2** in PMMA. The spectrum at atmospheric pressure agrees with that in methanol–ethanol reported by Kobayashi *et al.*[13)], except that there exists a shoulder at around 22000 cm^{-1}. It corresponds to that of anthracene monomer. In all cases the fluorescence excitation spectra shows no corresponding change with pressure except for the peak shift.

*Fluorescence Spectra of **3**.* Figure 7 illustrates the fluorescence spectra of the crystal at various pressures. The spectrum of **3** at atmospheric pressure exhibits a broad emission at 22200 cm^{-1}. As the pressure is applied, this band decreases relatively with accompanying a red shift and a new band appears at around 20000 cm^{-1} at a pressure of 14 kbar. At the higher pressure the intensity of this peak increases and shifts toward red.

The effect of pressure in PMMA matrix are shown in Fig. 8. The spectrum at atmospheric pressure agrees with that in MCH–IP (1:3) reported by Schneider *et al.*[14)] As the pressure is applied, it seems that the broad band of the lower energy grows up relatively, and at the pressure higher than about 14 kbar only

Table 1. Emission peak maximum of **1**, **2**, **3**, and anthracene

Pressure	Peak maximum/10^3 cm^{-1}							
	1		**2**		**3**		Anthracene	
	Crystal	In PMMA	Crystal	In PMMA	Crystal	In PMMA	Crystal	In PMMA
1 bar	—	23.5	20.9	24.8	22.2	23.8	—	24.9
7 kbar	19.8	23.3	20.3	24.7	21.7	23.5	21.0	24.6
14	19.8	23.2	20.0	24.4	21.1	22.7	20.1	24.4
22	19.5	22.9	19.7	24.2	20.0	22.3	19.8	24.1
31	19.2	22.7	19.7	23.9	19.4	21.7	19.3	23.9
39	18.8	22.5	19.6	23.8	18.7	21.3	18.5	23.7
47	18.6	22.3	19.5	23.7	18.1	20.7	17.8	23.6

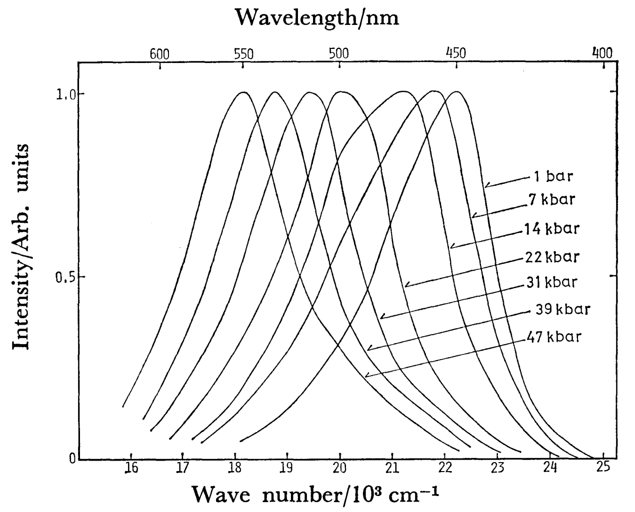


Fig. 8. Fluorescence spectra of **3** in PMMA matrix at various pressures.

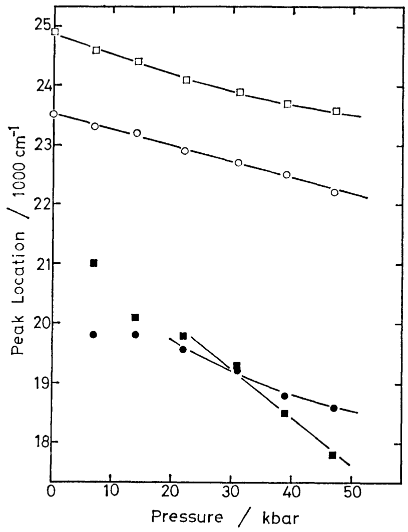


Fig. 9. Peak shift of **1** and anthracene.
○: **1** in PMMA, ●: **1** in crystals, □: anthracene in PMMA, ■: anthracene in crystals.

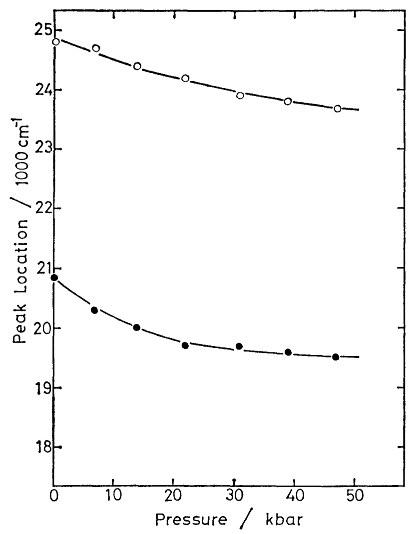


Fig. 10. Peak shift of **2** in crystals (●) and in PMMA (○).

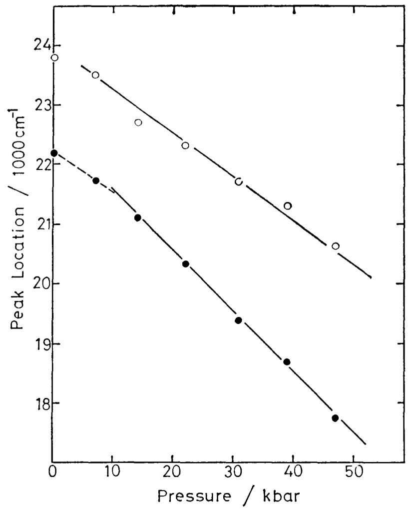


Fig. 11. Peak shift of **3** in crystals (●) and in PMMA (○).

this peak remains. In both cases no change is observed in the fluorescence excitation spectra. These effects are completely reversible with pressure.

Spectral Shifts with Pressure. As expected, there is a red shifts with pressure in all the fluorescence bands. The effects of pressure on the peak locations of **1**, **2**, and **3** both in crystalline state and in PMMA matrices are given in Table 1 and Figs. 9—11. Maxima were carefully read from the corrected curves. The peak shift of anthracene that is measured also in this work for the sake of comparison is included in Table 1 and in Fig. 9. The amounts of the peak shift of **1** and **2** in PMMA with pressure agree with that of anthracene in the same matrix. The result confirms that the emissions in PMMA for these compounds are originated from the locally excited state in anthracene parts and that these are not the excimer like band with special interactions between the two anthracene chromophores. On the other hand, the excimer emission exhibits a larger shift as compared with that of the locally excited state in PMMA. The lower pressure region of **1** in crystal is the band for the locally excited state.

Careful examination of the results of **3** in crystal indicates that there might be two types of pressure sensitivity. So long as seeing in the peak shift, no nonlinear behavior with pressure is detected in PMMA matrix.

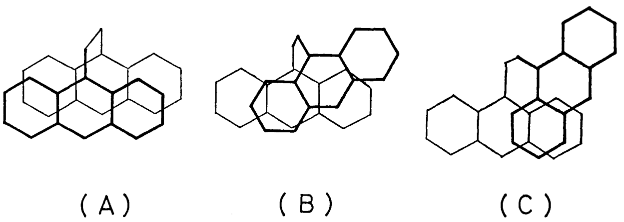
Discussion

The application of high pressure to crystals may create structural defects which are supposed to be crystallographic imperfections with excimer structure and act as a trap to capture singlet excitons. The effect of the creation of such defects is to be observed as irreversible pressure effects.⁵⁾ The irreversible behavior for **1** in the formation of sample pellet is likely to be originated from this effect. Thus, all the completely reversible pressure effects at the pressure higher than the residual pressure indicate the intrinsic effects on the excimer conformations. The residual pressure is less than 7 kbar.

The fluorescence spectra of **1** exhibits the vibrational structure from anthracene chromophores at atmospheric pressure. It looks like the type A crystals as classified by Stevens,15) which fluoresce only normal emissions such as anthracene, naphthalene, and phenanthrene. For the crystal of **1** in NaCl matrix resembling to anthracene, the new broad band which appears at a lower energy region than the normal fluorescence by about 3000 cm^{-1} as the pressure is applied can be assigned as the excimer existing only in the excited state, since no change is observed in the excitation spectra except for the peak shift.

Ferguson *et al.*16,17) developed an ingenious technique for producing the excimers of **1**. They prepared in single crystals of photocycloadduct of **1** by photocleavage so that a complete parallel conformation for **1** are kept by the constraint in the rigid matrix. By this method they observed three types of excimer emissions for **1**. Based on its energy value, our high-pressure induced excimer emission for **1** with a maximum at 19800 cm^{-1} at 14 kbar seems to correspond to the species B excimer by Ferguson *et al.*16) with a maximum at 19600 cm^{-1} at 6 K. They proposed to its molecular conformation a partially overlapped sandwich structure with parallel molecular planes. Thus, if the high-pressure induced excimer is intramolecular, it will be the type of species B. If it is intermolecular, it is not a type of completely overlapped sandwich type excimer. The fact that the corresponding band is not observed in PMMA and the analogous behavior to anthracene suggest that this excimer is formed intermolecularly. However, the shoulder appeared in PMMA matrix at around 21000 cm^{-1} under pressure may indicate a formation of intramolecular one, whose peak maximum is close to that observed by Hayashi *et al.*4) in solution.

The excimer fluorescence observed for **2** in crystals resembles that of type B crystals in which the molecules are arranged pair-wise. The fact that such type B structure is easily achieved suggests that this excimer is formed intramolecularly. This explanation is also based on the results that in PMMA matrix there exists a shoulder band besides the main band of the locally excited state as seen in Fig. 6, and that the relative intensity increases at lower energy region, and this behavior does not change with concentration. Its band maximum lies in the higher wave number as compared with 9-methylanthracene which has a pair-wise structure in the crystal. The amount of the peak shift, however, is similar to that of 9-methylanthracene. This may indicate that the excimer formed has not a complete sandwich arrangement, but has a structure with different mutual orientations such as the species B or C by Ferguson *et al.*, and also the type II by Hayashi *et al.* that have been reported for **1**. The proposed molecular conformations of the excimers for **1** by Ferguson *et al.* are visually shown as follows;



where (A) is the species A with a complete overlapped sandwich structure, while (B) and (C) are the species B and C, respectively with a smaller overlapped structure. The structure (B) corresponds to type II by Hayashi *et al.*

The excimer peak shifts of **1** and **2** under pressure saturate at the higher pressure region in comparison with that of anthracene. In the case of **2**, it shows only a little change with pressure at higher than 30 kbar, as seen in Fig. 10. While in anthracene it shows a linear pressure dependence of -73 ± 7 cm^{-1}/kbar, which agrees with the reported result⁵⁾ within the error limits of the experiments. The difference in peak shifts among these compounds reflects that the more bulky molecule is the more difficult in the molecular motion to stabilize the excimer conformation.

As for **3**, it is impossible to achieve the intramolecular sandwich arrangement. The interesting properties have been reported by Schneider *et al.*14) that the interaction between the two chromophores shows characteristics of the charge-transfer interactions in the excited state under the influence of solvent perturbations, which accompanies a small conformational change. The fluorescence in polar solvent shows a broad featureless band which is caused by the intramolecular charge transfer resulted from the conformational change in the excited state.

The band maximum of the fluorescence spectra of **3** in crystals at atmospheric pressure is 22200 cm^{-1} as seen in Fig. 7. This cannot be assigned to the charge-transfer band, but to the locally excited fluorescence band from anthracene moiety. In some solvents the corresponding band has been observed at atmospheric pressure, and it has been confirmed that π-electron systems of two anthracene chromophores are scarecely interact with each other, not only by the measurements of absorption and fluorescence spectra,$^{14)}$ but also by the measurements of polarizability,$^{18)}$ dipole moment,$^{18)}$ half reduction potential,$^{19)}$ molecular refraction,$^{20)}$ and conbustion energy.$^{21)}$ Hexane is one of such solvents in which only the locally excited fluorescence band appears. The measurement of pressure effects in hexane up to 6 kbar showed *ca.* $-50\ \mathrm{cm}^{-1}/\mathrm{kbar}$,$^{22)}$ which is analogous to that observed in PMMA matrix and in the lower pressure region in the crystal.

On the other hand, the new band observed at the higher pressure than about 15 kbar in crystal can be assigned as the charge-transfer band. It has a peak shift of $-77\pm13\ \mathrm{cm}^{-1}/\mathrm{kbar}$. Such a larger peak shift corresponds to that in polar solvents as methanol in which only the charge-transfer band is observed.$^{22)}$ The high sensitivity with pressure indicates the characteristics of the charge-transfer state. The charge-transfer state shows also a high sensitivity with the solvent polarity change. Thus, the increase in pressure has the same effect as the increase in solvent polarity.

It has been calculated by Schneider *et al.*$^{23)}$ that the twisted angle between the two anthracene chromophores in **3** is 90° in the ground state, while in the excited state it changes by $\pm12°$. The results of the pressure-induced new band and its larger red shift with pressure are considered to be correlated with the analogous intramolecular conformational change at high pressures. Namely, the change of the twisted angle is to be achieved with increasing pressure, and as the result, the charge transfer state is more stabilized. Further details of the research will be reported in a subsequent paper.

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