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Fluorescence Spectra of Anthracene Liquid

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Synopsis. An excimer-like fluorescence band at 470 nm was observed for anthracene liquid. A distinct shoulder at 414 nm was recognized in the absorption spectrum of anthracene liquid. These results suggest the existence of dimeric aggregates in this liquid.

Optical properties of pure organic liquids have been studied in only a very few cases compared with corresponding solids, gases or solutions. Experimental and theoretical difficulties may partly be responsible for this fact. Only benzene and substituted benzenes have been rather extensively studied on the absorption or fluorescence spectra of the liquids.[1)]

On the other hand, optical properties of amorphous organic films, which may be regarded as a somewhat frozen-liquid in structure, have recently been studied by several workers, and many interesting characteristics have been revealed.[2)] Most prominent features of such amorphous solids are broadening of bands and/or disappearance of Davydov splitting in the absorption spectra[3)] and appearance of strong excimer-like emission in the fluorescence spectra.[4,5)] The existence of excimer-like fluorescence which is absent in the crystals means that there are significant numbers of dimeric molecular aggregates in these amorphous solids which are more strongly interacting with each other than in the corresponding crystalline solids. The concentration of the dimeric molecular pairs has been tentatively estimated to be 10^{-3} mol/mol or more in an amorphous anthracene film.[5)] However, considering the facts that the red-shift and/or the enhancement of long wavelength tail of the lowest absorption band are usually observed in such amorphous films,[6)] the dimeric molecular pairs might occur in higher concentrations in a more disordered state, such as a liquid state. In fact, an amorphous anthracene film is colored slightly yellow, although its crystallized film by annealing is colorless in spite of the larger grain size in the latter.

A colorless anthracene crystal turns to yellow liquid on melting in an inactive gas atmosphere, and returns to colorless again on solidifying. This coloration on melting has usually been ascribed to a vibrational hot-band effect[7)] or an impurity effect. However, if sufficient numbers of dimeric molecular pairs are prevailing in the liquid, they may contribute to make the color of the liquid yellow, and thus excimer-like emissions could be observed for the liquid anthracene. This point is our main motivation for the present work. Ferguson *et al.* observed the excimer emission from sandwich dimers of anthracene by the photolysis of photodimers of anthracene, and he also proposed the existence of 55° dimers of anthracene.[8)] Excimer fluorescence of anthracene has also been observed in amorphous films, in a deformed crystal under high pressure[9)] and also in a saturated $CHCl_3$ solution.[10)] Pyrene and naphthalene excimer emissions in the liquid state has been reported by Birks.[11)] In this note, we report the fluorescence spectra of liquid anthracene and discuss the possibility of the exsistence of the dimeric molecular aggregates as the structural units in such an organic liquid.

Experimental

Anthracene used was purified by recrystallization, sublimation and zone melting. A single crystal was grown with the Bridgman method in a quartz tube sealed off with 0.5 atm He gas and directly used for optical measurements. A larger diameter quartz tube wound by a wire heater was coaxially set with the sample tube for melting. Optical spectra were measured by a conventional technique for stationary fluorescence detection. Light from a 500 W xenon lamp was fed to a monochromator (Bosch-Lomb 1200 G/mm), of which output, 300 nm light, was used for excitation. Fluorescence was detected with a HT VR376 photomultiplier tube through a TEC G-250CT monochromator. Front surface excitation and viewing geometry was mainly used except for the case of meniscus viewing. Other geometries were carefully tested to check the reabsorption effect.

Results and Discussion

Fluorescence intensity of an anthracene crystal gradually decreased with increasing temperature and the total intensity became very low when it was melted. The reducing ratios were different from band to band. Especially, 470 nm band of the crystal most slowly decreased its intensity. A typical fluorescence spectrum of a single crystal at 300 K is shown in Fig. 1(b).

When a crystal in a quartz tube was melted and irradiated by 300 nm exciting light, bluish green fluorescence was emitted from the meniscus which was about 10 mm apart from the irradiated point in the liquid, and it was carried there by total-internal-reflection effects. Its spectrum at 493 K is shown as curve I in Fig. 1(a). The most intense emission in this spectrum is the band around 470 nm which is corresponding to the excimerlike band in the emission spectrum of an amorphous anthracene solid.[4,5)] Intensities of monomer emission bands were rather weak in this spectrum because of reabsorption effect. The bulk of the liquid faintly fluoresced in nearly the same color as in the meniscus, but the spectral distribution of the intensity was rather different. Monomer emission bands were rather intensified in the fluorescence spectrum just from the excited region as shown by curve II in Fig. 1. The 386 nm (25906 cm^{-1}) band in this spectrum may be assigned to the 0-0 fluorescence band which corresponds to the 396 nm (25252 cm^{-1}) 0-0 absorption band in the crystalline

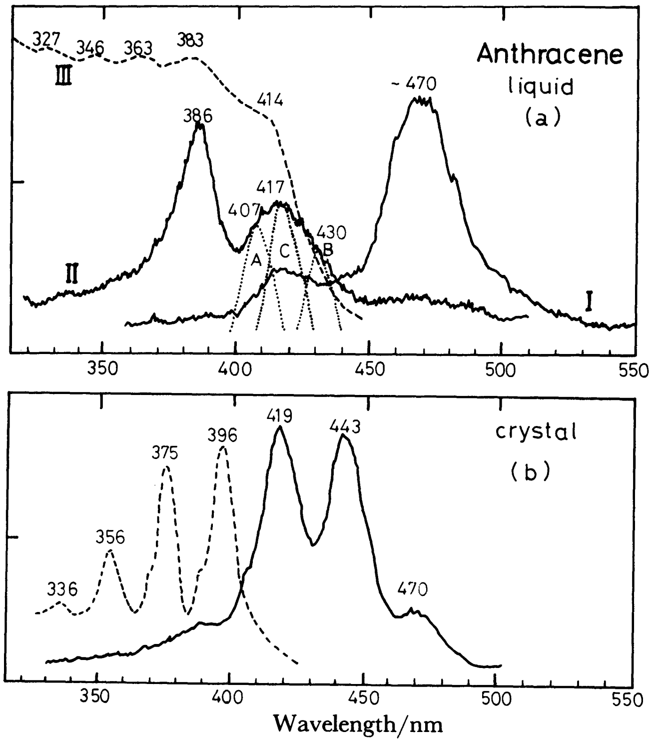

Fig. 1. (a) Fluorescence (full lines I and II) and absorption (in absorbance; dashed line III) spectra of anthracene liquid. Dotted lines show the resolved bands (see the text). (b) Fluorescence (full line) and absorption (in absorbance; dashed line) spectra of anthracne crystal. The absorption sepctrum is of a thin film deposited *in vacuo*.[6]

state. The second band around 417 nm is rather so broad that it could be resolved into three components. A possible procedure for resolving of this band was as follows; assuming the similar vibrational progression in the liquid state as in the crystalline state, the first and second vibronic band peaks could be 407 nm (24570 cm^{-1}) (A) and 430 nm (23256 cm^{-1}) (B) referring to the 386 nm (25907 cm^{-1}) 0-0 band. The halfwidths of these bands were also assumed to be proportional to that of the 386 nm band and the subtraction of these two bands from the observed broad band resulted in the band (C) around 417 nm, as shown in Fig. 1(a).

In order to pursue the origin of the 417 nm band and also to confirm the assignment mentioned above, we tried to observe an absorption spectrum of liquid anthracene, using a ≈50 μm thick Pyrex glass cell. This absorption spectrum is shown in Fig. 1(a) together with the fluorescence spectra for convenience of comparison with each other. The 383, 363, 346, and 327 nm absorption bands are recognized to be monomeric vibronic bands. However, the remarkable extra absorption shoulder at 414 nm may be assigned to the dimeric molecular aggregates origin, since it is separated by much larger energy, 1955 cm^{-1}, than the monomer vibrational progression (1450 cm^{-1}) mentioned above. Although the monomer–monomer interactions in a sandwich type geometry in the ground state are usually considered to be repulsive, some configurations might be favourable for attractive interactions because of the reported cluster formation in some molecular beams.[12] Thus, the 417 nm fluorescence band could be assigned to the dimer emission which comes directly from the 414 nm absorption. Then, the 470 nm fluorescence band in the liquid state may be an excimer band which is emitted from the more strongly interacting excimeric molecules in the excited state.

In conclusion, all these observed facts suggest that the existence of fair amounts of dimeric molecular aggregates in the liquid anthracene and these units may also be responsible for the yellow coloration of the liquid, since it has the 414 nm absorption band which is never regarded as a hot band. Further confirmation by the use of time-resolved spectroscopy will appear elsewhere soon.

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