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ABSORPTION SPECTRA OF ORIENTED AND AMORPHOUS NAPHTHACENE AND PENTACENE FILMS

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The absorption spectra of the oriented and amorphous naphthacene and pentacene films were measured at room temperature. The electronic state and the reactivity for both states were discussed.

We have already reported that the orientation of the polycyclic aromatic molecules in an evaporated film varied as a function of substrate temperature.1),2) Further, recently, the absorption spectra of the amorphous evaporated films of several aromatic compounds have been measured and discussed comparing with the crystal-state spectra by Maruyama and Iwasaki.3) It is well known that the Davydov splitting of 0-0 band of the naphthacene single crystal is about 575 cm^{-1}. The splitting of this band can be describable even for a randomly oriented microcrystalline film with the use of unpolarized light.4) On the other hand, in the spectra of the amorphous state, the Davydov splitting is not found. These hydrocarbons, naphthacene and pentacene, are somewhat unstable against the light and the heat treatment in the atmosphere.

In this report, we present some findings on the absorption spectra of the oriented and also the amorphous naphthacene and pentacene films and will discuss the electronic state and the reactivity for both states.

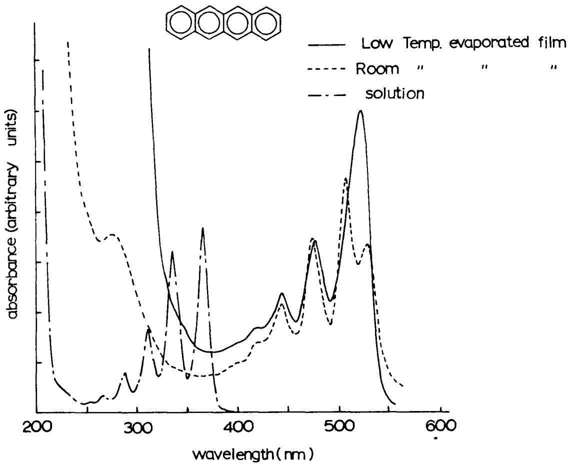

Fig. 1 Absorption spectra of naphthacene

Naphthacene and pentacene were purified by repeated sublimation. Their amorphous films were prepared on glass or quartz plate, which were cooled down to near 170 K, by an evaporation at 10^{-4} Torr. The absorption spectra of the organic films were measured at room temperature. The X-ray diffraction lines corresponding to (001) planes were observed for the oriented films, but no diffraction lines appeared for the amorphous films. Fig. 1 shows the optical absorption spectra of naphthacene films —— oriented and amorphous ——and also the spectrum in toluene solution. In the figure, two peaks at 503 and 520 nm in the oriented film spectrum are originated from the Davydov splitting of 0-0 band.* In the case of amorphous film, on the other hand, the Davydov splitting is not found and the spectrum is similar to that of corresponding free molecules in the solution. However, as illustrated in Fig. 1, the relative intensity of each vibronic bands is different from that of the solution spectrum: The intensity of 0-0 band in amorphous state spectrum is anomalously large. These findings agree with recent work of Maruyama and Iwasaki.3)

The difference between the absorption spectra of the oriented and amorphous pentacene films is illustrated in Fig. 2. The spectral band appeared at 662 nm in the amorphous state splitted into two peaks, 630 and 668 nm in the oriented state. Though the origin of this splitting in visible region has not been studied yet, it seems to arise from the Davydov splitting of 0-0 band. The marked difference of pressure induced red shift, approximately -130 cm^{-1}/kbar for 668 nm, and -50 cm^{-1}/kbar for 630 nm band, indicates that these bands are the components of the Davydov splitting. The detail of the pressure effect on the absorption spectra of the pentacene films will be reported elsewhere.6)

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* Through the various experiments on the absorption spectra of aromatic hydrocarbons under pressure, the assigment of these two peaks is confirmed by the fact that the rates of pressure induced red shift of these two bands are very different.5)

Fig. 3a and 3b exhibit the time dependence of the absorption spectra of the oriented and the amorphous naphthacene films at room temperature in an atmospheric pressure. The time response shows that the amorphous state in the visible region changes remarkably with time: The intensity of bands at 445, 475, 520 nm decreased day by day, and further, a new band appeared near 380 nm. On the contrary, in the visible region the spectra of oriented film showed almost no change with time. The similar behaviour was also observed in pentacene films.

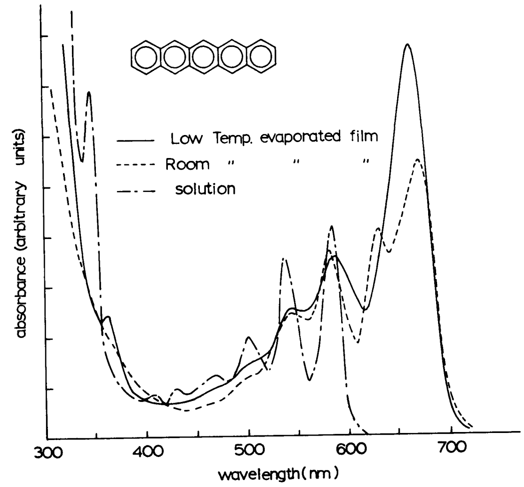
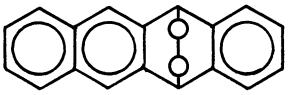


Fig. 2 Absorption spectra of pentacene

It is known that the polyacenes are easily oxidized photochemically in the polar solvent and changed to the peroxide illustrated as follows:



The visible bands in the absorption spectra of pentacene disappeared at very high pressure, up to 600 kbar; this is due to the change of conjugated system on the

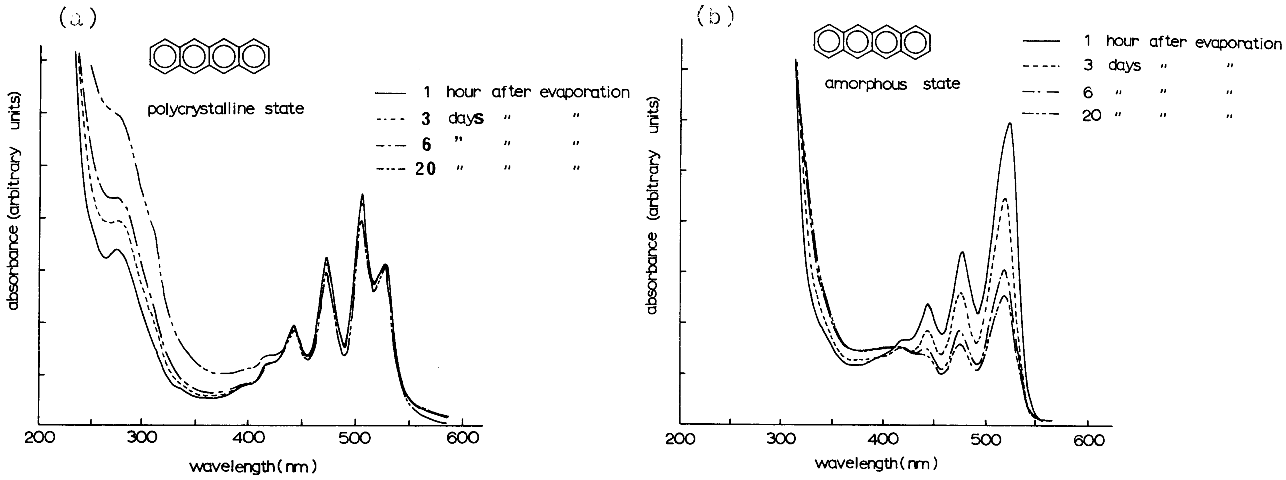


Fig. 3a, 3b Time dependence of the absorption spectra of oriented (a) and amorphous (b) naphthacene basis of the pressure induced solid phase reaction.[7)]

Judging from these facts, the variation of absorption spectra with time for the evaporated films arise from the solid phase reaction. As shown in Fig. 3, it should be noted that the reactivity of amorphous state is much stronger than that of oriented state.

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