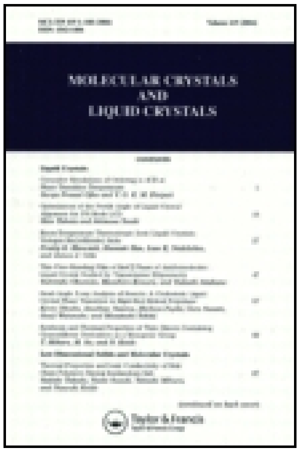

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Interaction between Pyrene and Perylene in Solid State

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Abstract—The emission spectra of solid solutions of pyrene and perylene in benzene and of mixed crystals of pyrene and perylene were investigated. The dependence of these spectra on the concentration of pyrene and perylene, on temperature and on the excitation wavelength was determined. The results for solid solutions showed clearly that there is an interaction between pyrene excimer and perylene which gives rise to a new emission spectrum. These results also helped us to interpret the emission spectra of mixed crystals of pyrene and perylene.

Introduction

The mixed crystals of pyrene and perylene have received much attention in recent years.[1–5] The fluorescence of perylene in a crystalline solution in pyrene is shifted to the red when compared with the emission of similar concentrations of perylene in liquid solution and is shifted to the blue relative to the emission of perylene dimeric crystals (α perylene). On the basis of this experimental evidence and an estimate of the location of the (perylene$^+$-pyrene$^-$) charge transfer state, Hochstrasser[1] suggested that this anomalous emission originates from an excited-state mixed perylene-pyrene dimer which is considerably stabilized by charge transfer interaction. A different interpretation was given by Tanaka.[2] He noted that the emission band of the mixed crystal at 5100 Å resembles rather closely the emission spectrum of a perylene crystal of monomeric structure (β perylene). He concluded that the " anomalous " emission is mainly due to the particular arrangement of the perylene molecules in the pyrene crystal, and is not the result of any specific interaction between perylene and the host crystal. On the other hand Kawaoka and Kearns[5] claim that the " anomalous " emission spectrum of the perylene–pyrene crystal is primarily, but not entirely, due to reabsorption of the monomeric perylene emission, rather than to the formation of perylene–pyrene or perylene–perylene excited dimers. However, from their investigation of the emission and absorption properties of perylene when dissolved in different solvents, they concluded that there is also an excited state interaction between perylene and pyrene. The present work was undertaken in order to decide whether the " anomalous " emission band of perylene in pyrene is that of the perylene molecules only (due to the position at which they are situated in these crystals) or whether this band is the result of mixed excimers of pyrene and perylene. In the latter case the elucidation of the detailed nature of this interaction was aimed at. For this purpose the luminescence of the system perylene–pyrene was investigated for frozen solutions of these solutes in benzene as well as for their mixed crystals. The interpretation of the results made use of a recently found property of pyrene, namely that the excitation spectrum of pyrene monomer differs markedly from that of the excimer.[6] This then permitted us to decide whether the alleged interaction between perylene and the pyrene host crystal involves the monomer or excimer state of pyrene.

A. Luminescence of frozen solutions of perylene and pyrene in benzene

EXPERIMENTAL

Mixed solutions of various concentrations of perylene and pyrene were prepared. The luminescence of the frozen solutions was investigated with regard to intensity and spectral distribution. This was done for varying conditions of concentration, excitation wavelength, temperature and annealing. The techniques of preparation and measurement are identical with those employed elsewhere.[6]

RESULTS

Perylene monomer

(*a*) *Influence of added pyrene.* Figure 1 shows the emission spectra of a frozen solution of $2{,}5.10^{-5}$ mole/liter of perylene in benzene at 90 °K. The wavelength of the exciting radiation was 410 mμ (at which wavelength pyrene is totally transparent). The different curves of the figure correspond to different concentrations of added pyrene. In this figure as in all the following figures of this article only the shapes but not the intensities of the spectra shown in one figure are to be compared. It is seen that with increasing concentration of pyrene the intensity of the emission in the wavelength region around 500 mμ increases relative to the emission at shorter wavelengths. We found that frozen solutions of perylene to which pyrene has been added can be excited at wavelengths which are not absorbed either by perylene or by pyrene at the given concentrations. Excitation at this long wave-

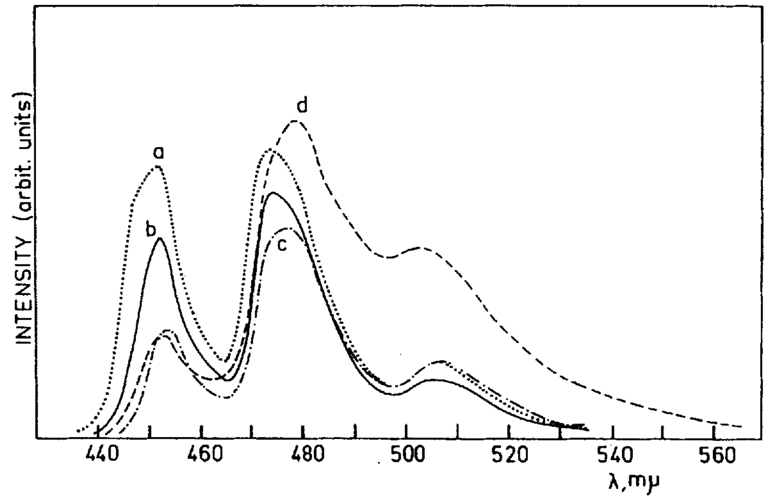

Figure 1. Emission spectra of $2{,}5.10^{-5}$ mole/lit perylene in benzene at 90 °K at various concentrations of pyrene (mole/lit). a: 0; b: 10^{-5}; c: 5.10^{-4}; d: 10^{-3}. The wavelength of the exciting radiation is 410 mμ.

length (e.g. at 462 mμ) yields a new emission spectrum (extending from about 480 to 560 mμ), which is shown in Fig. 2 (curve a). (This effect is enhanced by increasing the concentration of pyrene). This spectrum should be compared with the spectra which are obtained by excitation at 360 mμ (for which pyrene excimers are efficiently formed), at 340 mμ (for which the formation of pyrene excimers is less efficient) and at 410 mμ (which is strongly absorbed by pure perylene). These spectra are shown in curves (b), (c) and (d) of Fig. 2 for a solid solution of 2,5 × 10^{-5} mole/liter perylene and 10^{-3} mole/liter pyrene in benzene at 90 °K.

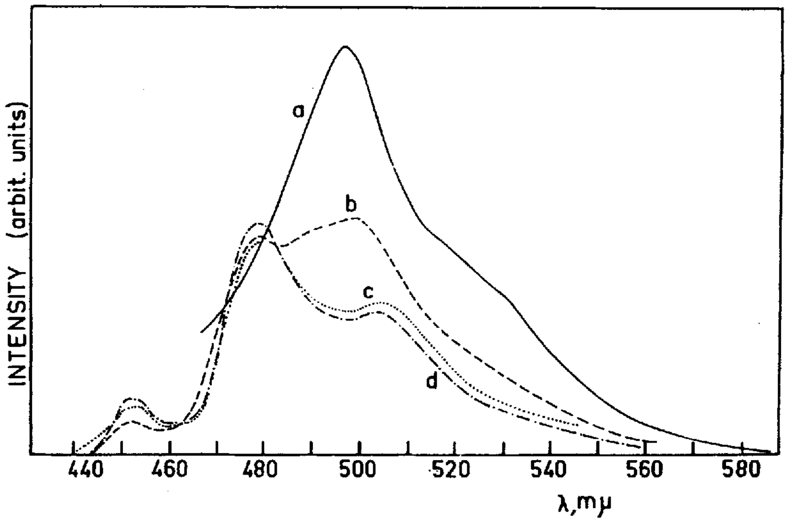

Figure 2. Emission spectra of 2,5.10^{-5} mole/lit perylene and 10^{-3} mole/lit pyrene in benzene at 90 °K at various excitation wavelengths: a: excitation wavelength 462 mμ; b: excitation wavelength 360 mμ; c: excitation wavelength 340 mμ; d: excitation wavelength 410 mμ.

The spectrum shown in Fig. 2 (curve a) should be compared also with that shown in Fig. 1 (curve a) for pure perylene at the same conditions. The remarkable difference between these two spectra is noted. The other spectra, shown by curves (b), (c) and (d) of Fig. 2 may be considered to represent different mixtures of these two basic types. We also note that in the region of excitation which gives rise to efficient formation of excimers (360 mμ) the relative weight of the new emission band is greater than for excitation at shorter wavelengths for which excimers are less efficiently produced.

In order to investigate further whether the monomer of pyrene or its excimer are primarily involved in the appearance of this new " combination " emission of perylene and pyrene we determined the excitation spectrum of this band by recording its intensity at 500 mμ as a function of excitation wavelength (Fig. 3 curve (a)). Curve b shows the same function for the 472 mμ peak of perylene (an identical curve is obtained for the 450 mμ peak of perylene). The most noteworthy feature of this figure is the appearance of an excitation peak at 376 mμ for the new emission band. This peak is absent in the excitation spectrum of

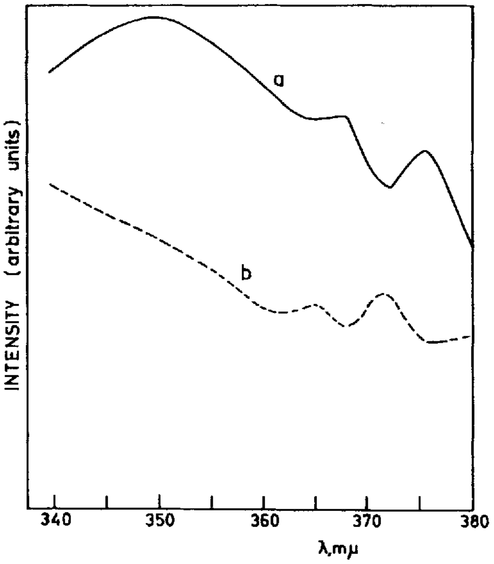

Figure 3. Dependence on excitation wavelength of fluorescence intensity of 2,5.10^{-5} mole/lit perylene and 10^{-3} mole/lit pyrene in benzene at 90°K. a: 500 mμ; b: 472 mμ.

the perylene band. This latter spectrum shows a peak at 372 mμ. It has been shown elsewhere that these two peaks correspond to peaks in the excitation spectra of pyrene excimer and pyrene monomer, respectively. This is evidence that the interactions between perylene and pyrene which result in the emission of the new luminescence band involve predominantly the excimer state of pyrene.

(*b*) *Annealing and temperature variations.* Annealing enhances the new emission band. This effect is seen in Fig. 4. Curve (a) shows the emission spectrum of frozen solution of 2.5×10^{-5} mole/liter perylene and 5×10^{-4} mole/liter pyrene at 90 °K when excited by radiation at 360 mμ before annealing; curve b shows the emission spectrum after annealing. Annealing also changes the shape of the new emission band. This is best seen when this band is exclusively excited by radiation of wavelength 462 mμ. The emission spectrum which is then obtained is shown in curve (c) of Fig. 4. The effect of annealing on the shape of this band is best seen by comparing this curve with curve (a) of Fig. 2.

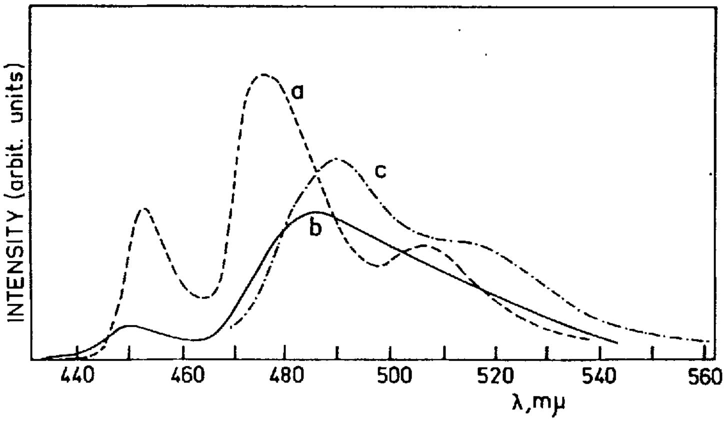

Figure 4. Emission spectra of $2{,}5.10^{-5}$ mole/lit perylene and 5.10^{-4} mole/lit pyrene in benzene. a: The emission before annealing; excitation wavelength 360 mμ; b: The emission after annealing; excitation wavelength 360 mμ; c: The emission after annealing; excitation wavelength 462 mμ.

Curve (b) in Fig. 4 can be interpreted as a superposition of curves (a) and (c) with proper weighting factors.

Preliminary measurements showed that the relative intensity of the new emission band increases when the temperature is raised from 90 °K to 200 °K.

Perylene dimer

Figure 5 (curve (a)) shows the emission band which is observed for frozen solutions of pure perylene at higher concentrations.

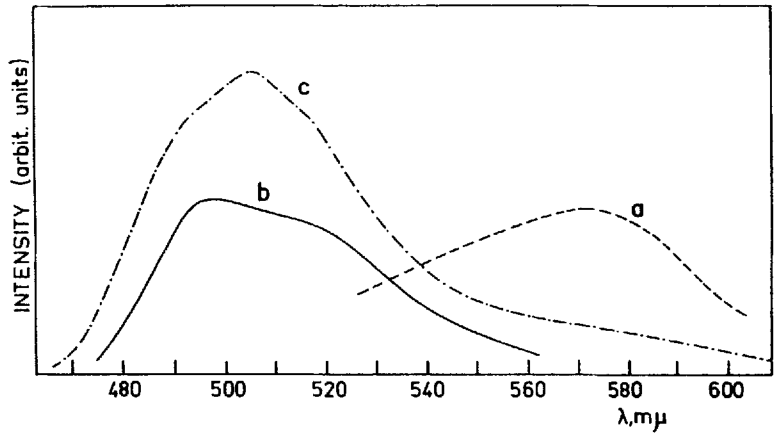

Figure 5. Emission spectrum of $2{,}5.10^{-4}$ mole/lit perylene in benzene at 90°K at various concentrations of pyrene (mole/lit) and at various excitation wavelengths: a: 0–462 mμ; b: 10^{-3}–462 mμ; c: 10^{-3}–410 mμ.

This emission, which is not observed for low concentrations and has been ascribed to the formation of perylene dimers[7] can be excited at wavelengths which are longer than the absorption limit of monomeric perylene (say 462 mμ); the monomer fluorescence is then not observed. Addition of pyrene (at 10^{-3} mole/liter) and excitation under similar conditions changes the dimer spectrum drastically (Fig. 5, curve (b)). From Fig. 5 it is then concluded that the dimeric emission is efficiently quenched in the presence of pyrene. Excitation of the mixed system at wavelength 410 mμ yields the emission spectrum shown in curve (c) of Fig. 5.

This spectrum remains practically unchanged when the excitation wavelength is changed to 360 mμ or to 340 mμ. The strong influence of excitation wavelength which has been found for low concentrations of perylene is thus absent for higher concentrations.

Discussion

The appearance of the new emission band between 480–560 mμ upon addition of pyrene to the perylene solutions and the fact that this band is excited at wavelengths for which perylene as well as pyrene themselves are transparent, leads to the conclusion that this band is due to an interaction product of perylene and pyrene as has been indeed suggested by Hochstrasser. The mechanisms involved in this interaction are still not fully understood. If charge transfer processes were to contribute significantly to the interaction, the new absorption region could be interpreted in terms of a charge transfer spectrum. This new absorption region corresponds apparently to the observations by Kawaoka and Kearns of the absorption of perylene in a crystalline solution in pyrene. Their interpretation, however, that this shift is due to the refractive index of the medium does not seem to hold in our system. If the appearance of the new emission band were due to an interaction which involves only the excited state with no noticeable implications for the absorption of the system it would be difficult to understand why this emission should be predominantly excited at the new absorption region and not at other wavelengths. The question as to why excitation in this region should be so much more efficient in producing this new emission spectrum remains as yet unsolved. We most tentatively propose the existence of a very loosely bound ground state trimer consisting of two pyrene molecules and one perylene molecule which are responsible for the new absorption and emission bands.

On grounds of the excitation spectrum of the new band (emission at 500 mμ) it has already been pointed out that the interaction between pyrene and perylene which is responsible for this emission involves primarily the pyrene in the excimer state. One could possibly argue that this combination band lies in a region which strongly overlaps the emission spectrum of pyrene excimer and that a major contribution to this band may simply be due to the fluorescence of pyrene excimer; hence the excimeric excitation spectrum. Against this argument stands the fact that the excitation spectrum for the normal perylene band at 472 mμ (which coincides with an intense part of the pyrene excimer spectrum) is purely monomeric. This shows that the *regular* spectrum of perylene is excited by energy transfer from pyrene *monomer*. Moreover this result shows that pyrene excimer is strongly quenched by its interaction with perylene. In addition it is seen that changing conditions of temperature and annealing which enhance the formation of pyrene excimers also enhance the intensity of the new emission band.

Summarizing the results it is seen that the new species which presumably is composed of two pyrene molecules and one perylene molecule each retaining its basic excitation spectrum can be excited either via excitation of pyrene (with successive formation of pyrene excimer), or by excitation into the perylene absorption band (where pyrene is transparent), as well as by excitation in the new absorption region for which each of the individual constituents is transparent.

The strong quenching of the perylene dimer band with peak at 570 mμ (which appears at high concentration of perylene) and the simultaneous increase of the pyrene–perylene band upon addition of pyrene, shows that the interaction between pyrene and perylene competes strongly with the formation of perylene dimers. The fact that the excitation spectrum of this band is still close to that of pyrene excimer leads to the conclusion that for solutions which contain pyrene and perylene, both at high concentrations, a double mixed excimer (or excimer–dimer) is formed which is composed of two pyrene and two perylene molecules.

B. Luminescence of mixed crystals of pyrene and perylene

EXPERIMENTAL

Pyrene was zone refined. Perylene was used without further purification after its purity had been established by absorption and emission measurements. The mixed crystals were grown by sublimation in an atmosphere of argon. The set up for the measurement of the luminescence was identical with that described in an earlier publication.[6] With this method the fluorescence was measured after it transversed the crystal. In one case the front surface luminescence was also measured, using a correspondingly modified arrangement.

RESULTS

(a) *Influence of concentration of perylene*

Kawaoka and Kearns[5] showed that the emission and absorption spectra of perylene in pyrene are shifted to the red relative to the spectra in liquid solution of perylene. The changes in the emission spectrum, however, were attributed mainly to effects of self-absorption at variance with the conclusion of Hochstrasser[1] who related these spectral changes to the formation of mixed dimers of pyrene and perylene. In order to clarify the nature of these effects and to find out whether reabsorption is their major cause the " front surface fluorescence " was measured for crystals containing perylene at various concentrations. For near-normal incidence of the exciting radiation, effects of self-absorption should be independent of concentration.[8] Figure 6 (a), (b) and (c) show the emission obtained from pyrene crystals for concentrations of 10^{-2}; 10^{-3} and 10^{-4} mole/mole of perylene at 300 °K. The wavelength of the exciting radiation was 435 mμ, for which pyrene is transparent. Since self-absorption cannot account for the changes of the spectra with concentration, the results thus represent a non-trivial effect of concentration. Excitation of the crystal with radiation which is strongly (and primarily) absorbed by pyrene (e.g. 313 mμ) yielded very similar spectra with the addition of a shoulder at 450 mμ which represents the residue of the fluorescence of crystalline pyrene. (The greater part of excitation energy has been transferred to perylene). In the following we will attempt to give an argument for the assumption that peaks B and C in curves (c) and (a) represent two different processes. From the figure it is, however, already seen that the process which gives rise to the

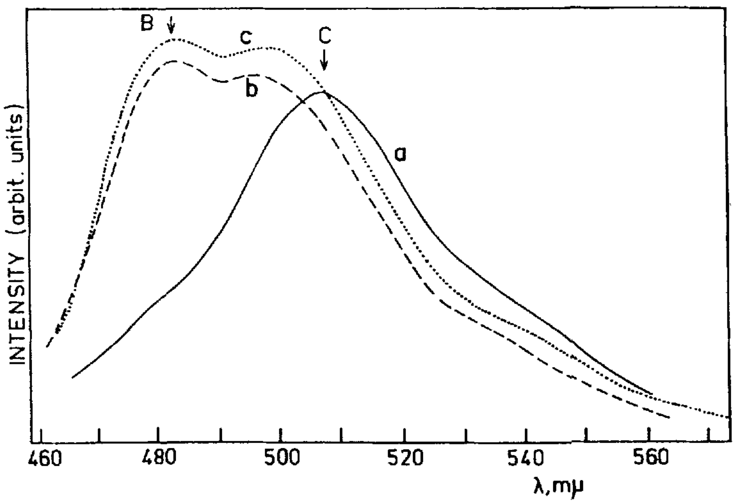

Figure 6. Emission spectra of various concentrations of perylene mole/mole in pyrene crystals at 300 K, obtained by "front surface" illumination. a: 10^{-2}; b: 10^{-3}; c: 10^{-4}. Exciting wavelength 435 mμ.

shorter wavelength peak (*B*) decreases with increasing concentration of perylene, while the process which is responsible for the long wavelength peak (*C*) persists.

Curves (a), (b) and (c) in Fig. 7 show the emission spectra for the same concentrations when the fluorescence passed through the thin crystal. Comparison of Fig. 6 and 7 shows that for thin crystals there is no essential difference between the spectra, obtained by the two methods, hence again self-absorption is not the reason for the changes in the spectral distribution with changing concentration. Having established this fact we performed the following experiments for reasons of convenience by measuring the transmitted fluorescence only.

(*b*) *Effect of temperature*

The emission spectra change considerably with changing temperature. This is seen by comparing the spectra shown in Fig. 7 which have been obtained at 300 °K with those of Fig. 8

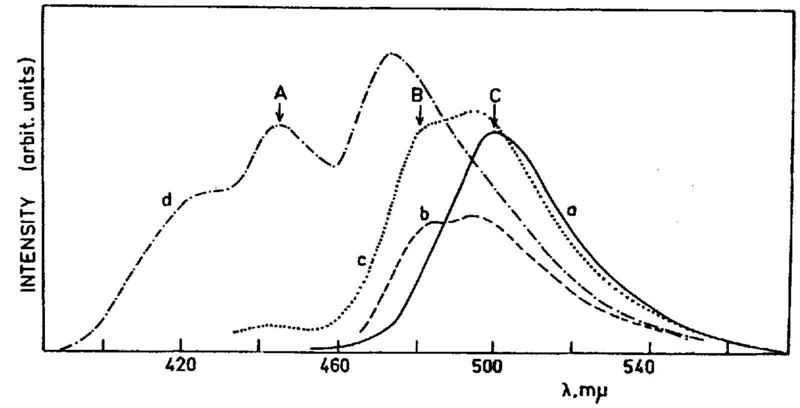

Figure 7. Transmitted emission spectra of various concentrations of perylene mole/mole in pyrene crystals at 300°K. a: 10^{-2}; b: 10^{-3}; c: 10^{-4}; d: 10^{-5}.

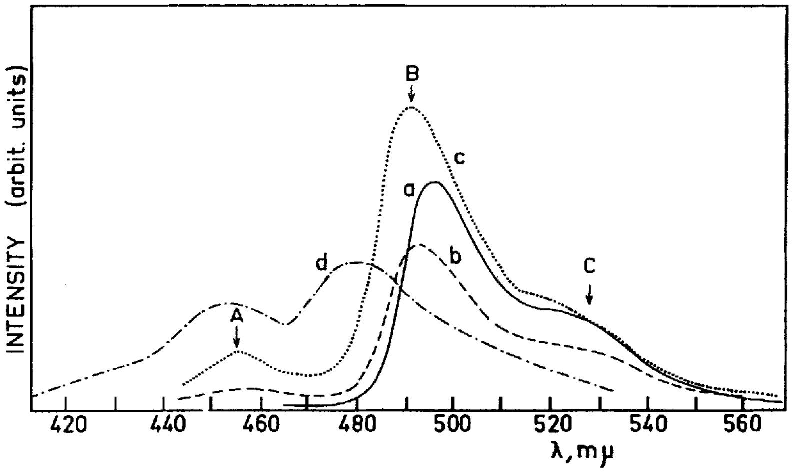

Figure 8. Emission spectra of various concentrations of perylene mole/mole in pyrene crystal at 90°K. a: 10^{-2}; b: 10^{-3}; c: 10^{-4}; d: 10^{-5}.

which were obtained at 90 °K. Similar results have been obtained by Ishii and Matsui.[4] The effect of changing spectral distribution with changing temperature is a gradual one and is more pronounced at higher concentrations. Further inspection of Figs. 7 and 8 discloses a red shift of all three emission peaks. (Compare peaks *A*, *B* and *C* in both figures). It is further seen that decreasing the temperature yields a similar effect to decreasing the concentration at higher temperature.

To conclude this section we point out that peak *A* is not observed when perylene is directly excited by radiation for which pyrene is transparent (e.g. 435 mμ). Also in this case (90 °K, excitation wavelength 435 mμ) the ratio of the intensity of peak *C* to that of peak *B* (at 90 °K) is greater than for excitation at wavelengths which are absorbed by pyrene. No influence of excitation wavelength is observed at 300 °K.

DISCUSSION

The results lead to the following conclusions as to the region of the three peaks which appear in the spectra of the mixed crystals under the various conditions of concentration, temperature and excitation wavelength:

(1) Peak *A* (445 mμ–453 mμ, depending on temperature) belongs to the emission of pyrene only, modified by the absorption band of the mixed complex. This follows from the absence of this peak when the excitation wavelength is beyond the pyrene absorption limit.

(2) Peak *B* (483 mμ–490 mμ, depending on temperature) represents the emission of the mixed excimer of pyrene and perylene. This follows from the coincidence of this peak with the peak of the mixed dimer emission in frozen solutions of pyrene and perylene.

(3) Peak *C* (503 mμ–530 mμ, depending on temperature) represents the emission of an interaction product of two or more perylene molecules. This follows from the strong dependence of the ratio *B*/*C* on perylene concentration. This does not exclude the possible influence of the pyrene

environment on this product. The particular crystalline arrangement of pyrene seems, however, to be unimportant for the creation of this product, since an identical peak is observed for the amorphous solution of perylene in pyrene (obtained from melting and cooling of the mixed crystal).

From the temperature dependence of the spectra (peak *C* decreases with cooling, while peak *B* increases) we conclude that the interaction between perylene molecules competes with the interaction between perylene and pyrene which leads to the formation of the mixed dimer.

From the influence of the excitation wavelength on the emission spectrum at low temperature we conclude that under these conditions the interaction between perylene molecules is more efficient when perylene is excited directly than for excitation via energy transfer from pyrene.

These results do of course not exclude the occurrence of effects of self-absorption on the observed spectra. In fact such effects were observed throughout this work for higher concentrations of perylene. Self-absorption, however, is by no means the mechanism which determines the major features of the emission spectra of this system.

Summary

Comparison of the spectra of frozen solutions and of mixed crystals of perylene and pyrene shows that the three different bands which appear in the spectra of the mixed crystals may be attributed to *three different processes*. They *do not* represent the vibrationally structured emission of perylene which is modified by self-absorption in the case of higher concentrations, as assumed by Kawaoka and Kearns,[5] and Ishii and Matsui.[4] We assume that the processes involve the interaction between one molecule of perylene and two molecules of pyrene at low concentration of perylene, and interactions between two perylene molecules (probably through intermediacy of pyrene molecules) at high concentrations of perylene.

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