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Electronic Spectra of Perylene Crystals

Jiro Tanaka, Tohru Kishi, and Masashi Tanaka
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa, Nagoya 464

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The electronic absorption and emission spectra of α and β forms of perylene have been investigated. The low-temperature spectra have been studied with the (001) plane, and a detailed vibrational analysis is presented. The reflection measurements with the (001) plane and the (110) or (1$\bar{1}$0) plane are carried out, and the Kramers-Kronig transformation is carried out in order to obtain the absorption coefficient. The results present reasonable evidence for the existence of the intermolcecular CT transition in the 27000 cm^{-1} region. The emission spectra at 4.2 K present several novel features of the mechanism of a monomer-like emission of the α-crystal.

Since the absorption and fluorescence of perylene have been investigated on two crystalline forms of perylene,[1] many papers have apperared on this and related problems.[2-6] Detailed spectroscopic investigations of this system will still be of great value, because they will provide a unique chance to examine the conditions of the excimer formation in molecular crystals.[7] The intermolecular CT band between the same entity in a neat crystal is still a problem of dispute[8]; however, the CT band of 9,10-dichloroanthracene[9] has recently been confirmed by the electroreflectance experiment of Abbi and Hanson.[10]

In the present paper, we will report a further spectroscopic investigation of perylene crystals by using somewhat elaborate methods. First, the low-temperature absorption spectra at 1.6 K and 4.2 K of the α and β forms of perylene are measured by the transmission method, using a medium spectrograph. Then, the crystalline reflection spectra are recorded and the Kramers-Krnoig transformation is used to calculate the absorption spectra. By the latter method the spectra along a different crystalline direction which has not been measured in the previous paper can be obtained, and further discussions of the CT state and of hypochromism are presented. The emission spectra at 4.2 K are also photographed, and the Stokes shifts of fluorescence are discussed in connection with the crystal structure and intermolecular interactions.

Experimental

The perylene used was a product of Theodor Schuchardt of W. Germany. It was recrystallized, and then further purification was carried out by means of column chromatography. The α crystal for the transmission measurement was obtained by a sublimation method, and it was not difficult to obtain crystals about 5 mm×5 mm with a thickness of less than 1 μ. The thin crystal of the β form was rather difficult to obtain, but it could be grown from a solution of 90% benzene and 10% toluene. For the transmission measurement the crystal was polished with benzene until it showed retardation of about 300 mμ of a yellow colour. The crystals for the absorption measurement at a low temperature were mounted between thin quartz disks and then covered with a black mask with a pin-hole. The light penetrated through the pin-hole, with a diameter of less than 1 mm, and the pin-hole was placed on the uniformly thick part of the crystal. The crystals were placed in the holder in the direction in which the polarization effect of the grating spectrograph was not serious. The holder was then placed in the double quartz Dewar vessel and immersed in liquid helium.

The set-up of apparatus for absorption and emission measurements is shown in Fig. 1. The spectrograph used was a Shimadzu GE-100 apparatus, with a Bausch-Lomb grating of dispersion of 8.3 Å/mm. The light source for the absorption measurement was a tungsten lamp containing iodine of 100 W. A high-pressure mercury lamp of 250 W combined with a Toshiba DV-1 filter was used for the excitation of fluorescence. The fluorescence was either photographed by means of the spectrograph or was photo-electrically recorded by means of a Carl-Zeiss spectrofluorometer. For the measurement at 1.6 K, the helium Dewar was pumped out and the temperature was measured by means of the vapour pressure of helium.

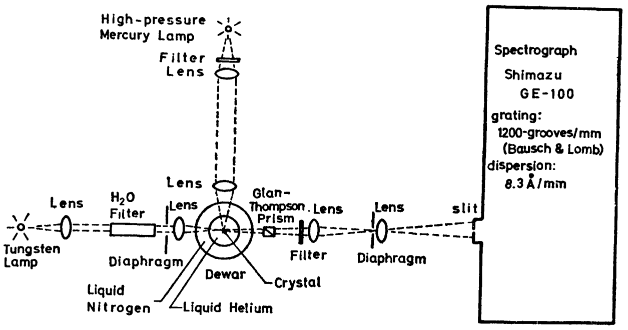


Fig. 1. The optical system for spectral measurement.

The reflection spectra are recorded with (001) and (110) or (1$\bar{1}$0) planes of α and β forms by means of a system which will be described in a separate paper.[11] Although the transmission measurements are confined along the a- and b-axes of α and β crystals, the reflection data are obtained with the other direction, perpendicular to the ab plane.

Results and Discussion

Low-temperature Absorption Spectra of α-Perylene. The low-temperature absorption spectra of the α-crystal at 1.6 K show clear vibrational structures in the beginning of the band series. The absorption band along the b-axis shows a particularly close resemblance to that of the solution (Fig. 2), while the band shape and intensities are greatly changed along the a-axis (Fig. 3). The 0–0 band origins are certainly confirmed along the a- and b-axes, and the Davydov splitting is determined as 820 cm^{-1}. The band systems are assigned with reference to the solution band system as is shown in Table 1. The band width is much broader along the a-axis, and the width of the 0–0 band at 1.6 K was 300 cm^{-1} for the a-axis and 190 cm^{-1} for the b-axis. The width in the *n*-hexane solution was smaller than 10 cm^{-1}, which may be a typical pattern

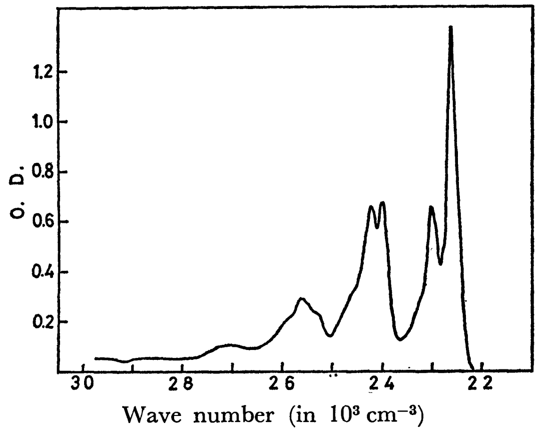


Fig. 2. Absorption bands of perylene in EPA solution at 77 K.

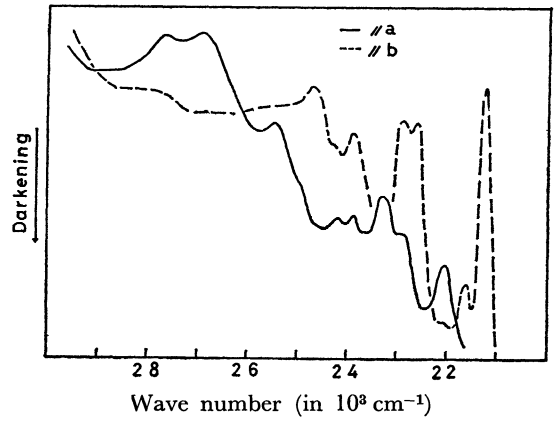


Fig. 3. Polarized absorption spectra of α crystal at 1.6 K.

of the Shpolskii effect.[12] At higher vibrational levels the band widths are much broader for the a- and b-axes; this may be induced by the effect of other types of transitions near-by or overlapping.

Above 26000 cm^{-1} the band becomes very broad and it may be supposed that the band in this region is composed of transitions of a different character rather than of vibrational progressions of a unique electronic origin. The intermolecular CT transition, which has been suspected because of its weak intensity, is found in this spectra in the 26500—29000 cm^{-1} region. There have been several discussions of the presence of the CT band, because only a weak and broad band was found at room temperature in an earlier paper.[1] One of the criticisms of the CT mechanism is based on the calculation of the vibronic structure of the coupled dimer,[2,4] but the broad character of the band at very low temperatures can not be reasonably explained by this mechanism because each vibronic band is clearly resolved in the 21000—25000 cm^{-1} region. Therefore, the overlapping of the intermolecular CT band and the vibrational progressions of the first $^1B_{2u}$-type transition seem the most reasonable explanations of the anomalous

Table 1. Absorption bands of perylene at 21000—29000 cm^{-1} region

Solution		α-Form						
(cm^{-1})	$\Delta\nu$	a-axis	$\Delta\nu$	b-axis	$\Delta\nu$	~c-axis	$\Delta\nu$	$\Delta\nu_{ab}$
22630	(0)	22050	(0)	21230	(0)	21800	(0)	820
22960	(+330)			21640	(+410)			
23340	(+710)							
23960	(+1330)	22950	(+900)	22620	(+1390)			330
24240	(+1610)	23320	(+1270)	22850	(+1620)	23200	(+1400)	470
25250	(+2620)	23910	(+1860)	23840	(+2590)	23600	(+1800)	70
25600	(+2970)	24210	(+2160)	24260	(+3030)			
25900	(+3270)							
27100	(+4470)	25500	(+3450)	24740	(+3510)	24800	(+3000)	
		26900	(+4850)					
		27700	(+5650)					

Solution		β-Form						
(cm^{-1})	$\Delta\nu$	a-axis		b-axis		~c-axis		$\Delta\nu_{ab}$
22630	(0)	21640	(0)	20810	(0)	21500	(0)	830
22960	(+330)	22070	(+430)	21180	(+370)			
23340	(+710)			21650	(+840)			
		22440	(-+800)	22160	(+1350)			280
23960	(+1330)	23120	(+1480)	22360	(+1550)	23000	(+1500)	760
24240	(+1610)			22730	(+2690)			
				22970	(+2160)			
		23700	(+2060)	23500	(+2690)			
25250	(+2620)	23950	(+2310)	23750	(+2940)			
25600	(+2970)			24100	(+3290)			
25900	(+3270)					24500	(+3000)	
27100	(+4470)			25500	(+4690)	26200	(+4700)	

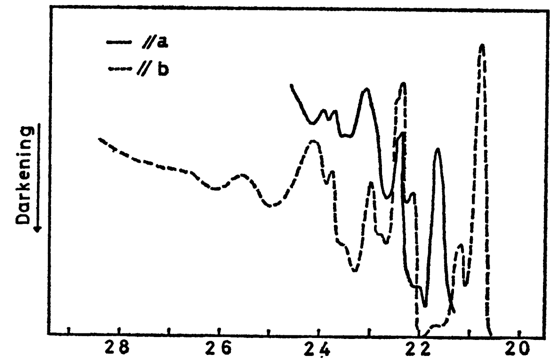


Fig. 4. Polarized absorption spectra of β crystal at 1.6 K.

band shape.

Low-temperature Absorption Spectra of β-Perylene. The spectra photographed at 1.6 K with the (001) plane are shown in Fig. 4. The 0–0 band origin and the details of the vibrational structures were clearly resolved. The Davydov splitting is 830 cm^{-1}, of nearly the same magnitude as the α crystal. In an earlier paper[1] a much larger value was assigned for this splitting, but it should be corrected because the 0–0 band origin has now been clearly confirmed.

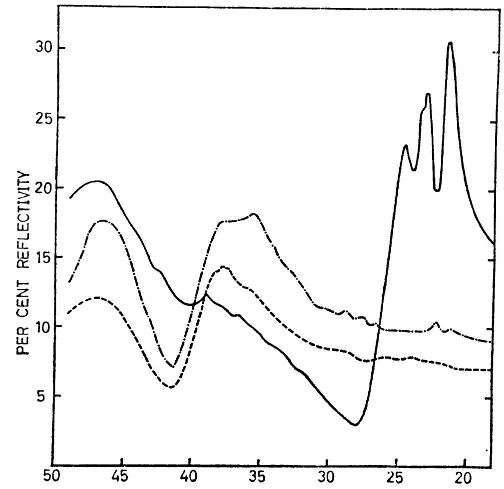
The vibrational progressions of the b-axis spectra are nicely correlated with the solution spectra, since the band shape is nearly regular. On the other hand, the band shape is rather anomalous along the a-axis, and the band width for the a-axis is broader than for the b-axis. For instance, the half-width of the 0–0 band is 290 cm^{-1} for the a-axis and 180 cm^{-1} for the b-axis. The pattern of vibrational progression along the a-axis is also modified from the solution band. There are several reasons for this change; one is the change in Franck-Condon factors from the free molecule to the molecule in the crystal, which means that the vibrational mode in the excited state involves a significant anisotropy. Another possible effect may be due to the CT transition or band-to-band transition along the direction of the stacking of the molecule. Although the intensities of these transitions may be quite small, they may be influential upon the a-axis band in causing hypochromism or broadening. In this respect, several weak humps around the 28000—31000 cm^{-1} region may be suspected as CT bands, because these bands were enhanced under high pressures.[13]

Two more characteristics of the low-temperature spectra of the α and β crystals are that the Davydov splitting for higher vibrational progressions are rather small, while the band splitting is not proportional to the intensity of each vibronic band. The assignment of band splitting with higher levels was rather difficult; it appears thereby that the intramolecular vibrational coupling is much stronger than the excitonic interaction between adjacent molecules in the crystalline lattice. At any rate, the weak coupling scheme must be used to analyse the perylene crystalline spectra rather than the intermediate or strong coupling, because the band splittings were found at all vibronic levels.

Reflection Spectra of α and β Perylene. The reflection measurement has several advantages over the transmission method; for instance, the thick crystal can be used to determine the polarization direction with more than two crystalline faces, and the intensity of a very strong band can be determined rather accurately.

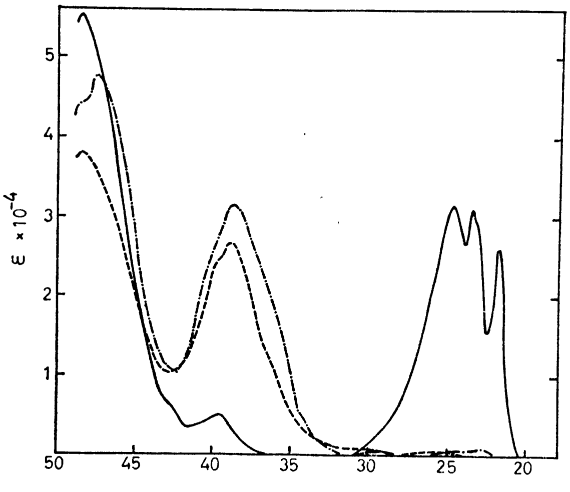
The reflectivities of the α and β forms are shown in Figs. 5 and 6. The Kramers-Kronig transform of the reflectivity gave the absorption spectra shown in Figs. 7 and 8. The spectra are taken with the (001) and ($\bar{1}$10) planes of the α crystal and with the (001) and (110) planes of the β crystal. Although the direction perpendicular to the (001) plane is not exactly coincident with the c-axis, it is in nearly the same direction. The spectra show several interesting properties which have not been recognized in earlier transmission measurements on the (001) plane.

The first absorption region of the α crystal, at 20000—28000 cm^{-1}, can be recorded for all three directions.



Wave number (in 10^3 cm^{-1})

Fig. 5. Reflectivity of α crystal at room temperature.
---- a-axis, —·— b-axis, —— c-axis.



Wave number (in 10^3 cm^{-1})

Fig. 6. Absorption spectra of α crystal obtained from Kramers-Kronig transformation.
---- a-axis, —·— b-axis, —— c-axis.

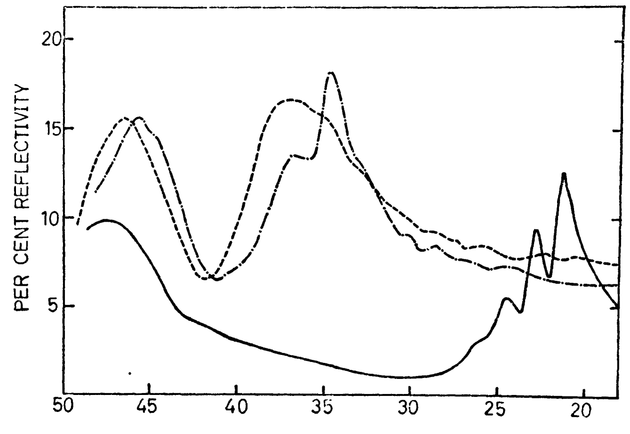


Fig. 7. Reflectivity of β crystal at room temperature.
---- a-axis, —·— b-axis, —— c-axis.

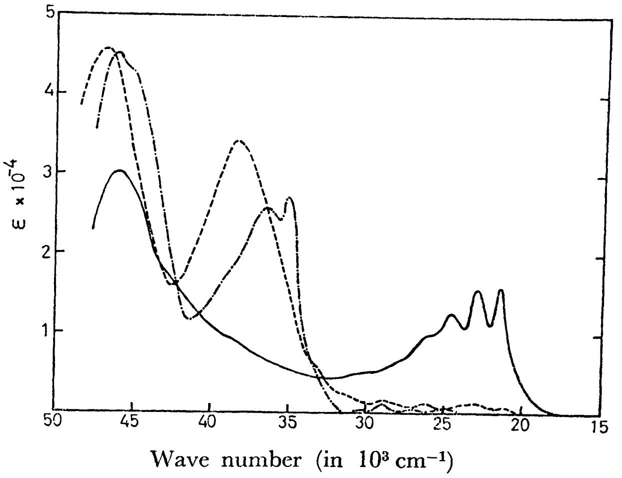


Fig. 8. Absorption spectra of β crystal at room temperature.
---- a-axis, —·— b-axis, —— c-axis.

It is quite interesting that the spectrum along the c-axis is nearly in agreement with the powder state spectra in KBr disk measured by Offen and Beardslee;[13]) this result is reasonable since the intensity is strongest along this axis. The absorption curves obtained by reflection for the $^1B_2$ and the CT bands of the a- and b-axes were not accurate enough as compared with the transmission results. The c-axis spectrum of the β-crystals shows vibrational progressions which resemble those of the solution spectra; this may imply that the whole band in this region is of a unique character. On the other hand, the c-axis band of the α crystal is in marked contrast; there the vibrational progressions higher than 23500 cm^{-1} are greatly changed from their regular shape.

Theoretically, the energy levels of a molecular crystal should conform to the group theoretical splitting, and the levels must be the same for the a- and c-axes bands in a monoclinic crystal. Therefore, the band positions should be coincident for the a- and c-axes if the same electronic transition is involved. Actually, this prediction is almost in accord with the first several vibronic levels when we compare the band positions of the a-axis obtained by the transmission method with the c-axis band based on the reflection data. Moreover, the band shape of the c-axis spectrum is in accord with neither the a-axis spectrum nor the theoretical curve of Witkowskii *et al.*[4])

On the other hand, a similar change in band shape has been observed in the case of the mixing of the CT state with the molecular exciton state. The CT transition may cause such an anomaly; for instance, the c-axis band of 9,10-dichloroanthracene is changed from the regular band shape in solution. In this crystal, the CT transition with the out-of-plane polarization has been found along the particular crystalline direction (a-axis);[9]) the presence of such a CT state influences the shape of the in-plane transitions along the c-axis. Therefore, the marked change in the α perylene spectra along the c-axis in this range may be regarded as another token of this type of mixing, indicating the existence of the CT transition in the 26000—28000 cm^{-1} region of the a-axis. The enhancement of the 25000 cm^{-1} band of α perylene under high pressure has been reasonably explained by the CT mechanism.[13])

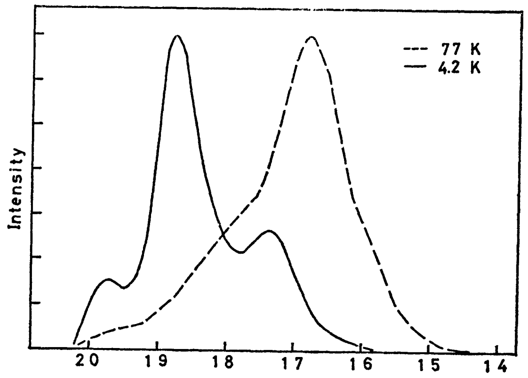
Direct evidence for the existence of the CT state with the (001)-plane reflection spectra was rather difficult to obtain because of the weak intensity of the bands along the a-axis. In spite of this difficulty, though, several weak bands were observed with the a- and b-axes of the α and β-form crystals in this region. It may be said that the detection of a weak CT transition is rather difficult by the reflection method unless the crystal structure is mostly favoured; a negative result with dibenzoselenophene[14]) may be understood by this reasoning.

The second absorption region at 33000—42000 cm^{-1} is due to the short-axis polarized transition of the $^1B_{3u}$ type, and the absorption shape is different for the α and β crystals. The absorption spectra transformed from the reflection data for the α form gave a pattern similar to that of the transmission result, but the β form spectrum was somewhat different from the earlier transmission result. Along the a-axis band of the β crystal, a vibrational progression resembling that of the solution was observed. A Davydov splitting of the same sign and magnitude as the calculated value given in the previous paper was found with the β crystal.

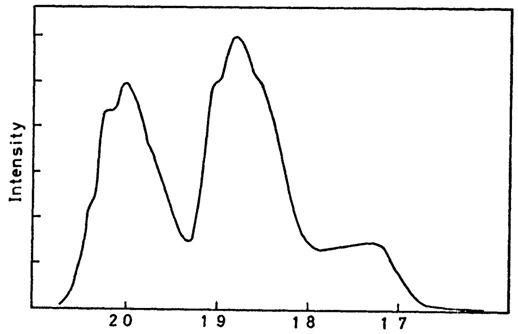
The higher energy transition in the 44000—53000 cm^{-1} region in a solution is confirmed to be composed of several long- and short-axes polarized bands. This was also found by Fuke, Kaya, and Nagakura[15]) independently.

In the light of the present results, it is quite interesting that the dimer spectra in a rigid solution found by Ferguson[3]) showed a band shape similar to that of the a-axis band of the α crystal. Since the average of intensities with three crystalline axes is more or less the same as that of the solution spectrum, it appears that the dimer or its aggregates in a rigid solution may have a much more symmetrical or specific structure than in crystals, because the hypochromism and the anomaly of the band shape is rather pronounced.

Fluorescence Spectra of α and β Perylene. At 4.2 K the excimer fluorescence of the α form does not appear; instead, a monomer-like emission is observed. In an earlier investigation the effect of the re-absorption of the crystalline surface on the shape of the fluorescence



Wave number (in 10^3 cm^{-1})
Fig. 9. Emission spectra of α crystal at 4.2 K.



Wave number (in 10^3 cm^{-1})
Fig. 10. Emission spectra of β crystal at 4.2 K.

was not properly taken into account;[5] therefore, a detailed band analysis is undertaken in this study. The fluorescence spectra of α and β perylene are illustrated in Figs. 9 and 10, where the results at 4.2 K are presented. No essential difference in spectra were found at 1.6 K and 4.2 K. The spectra are recorded on a Carl-Zeiss fluorometer.

In the photograph of β emission at 1.6 K, very sharp lines are observed, and the 0–0 band origin is assigned at 20517 cm^{-1}. The vibrational progressions are tabulated in Table 2, together with the values found in a solution. The Stokes shift in a solution is only 30 cm^{-1}, while the corresponding value for the β crystal is 293 cm^{-1}.

The α-form emission at 77 K shows the peak of the excimer band at 16850 cm^{-1}, but weak components at 19000—20000 cm^{-1} are also observed. Inoue *et al.*[6] showed, by time-resolving spectroscopy, that these results are due to a monomer-like emission.

The photographs at 4.2 K and 1.6 K show only broad emission bands, situated at 19800, 18750, and 17400 cm^{-1}. The band origin was not clearly ascertained since no fine structure could be detected at the beginning of the first band. The Stokes shift was estimated as about 1000—1400 cm^{-1}, significantly larger than that of the β crystal.

It has been suggested in an earlier paper[1] that the intermolecular approach of two molecules in the excited state is essential for the excimer formation. This point seems to be substantiated by the following investigations. At 4.2 K in the α crystal, the excimer emission is absent, but there still remains a significant red shift of the emission band. The shift is certainly larger than the monomer emission band of the β crystal. This may imply that the levels in the α crystal are split by the excitonic interaction at the distance of the ground-state configuration or that the shift of the level is accompanied by a slight distortion of the structure. The lower energy level will be forbidden in a strict D_{2h} symmetry, but the band is actually observed to the red of the 0–0 absorption band; this may suggest a deformation of the paired molecule from the parallel arrangement. In other words, the intermolecular interaction is much larger for the α-form than for the β-form even at 4.2 K.

TABLE 2. SHARP EMISSION LINES OF β-PERYLENE CRYSTAL

β-Crystal (cm^{-1})	$\Delta\nu$	n-Hexane solution[12] $\Delta\nu$
20517	(0)	0
20496	(−21)	
20473	(−44)	
20408	(−109)	
20333	(−184)	
20182	(−335)	−357
20145	(−372)	
19389	(−1128)	−1104
19314	(−1203)	
19283	(−1234)	
19212	(−1305)	−1298
19144	(−1373)	−1375
18939	(−1577)	−1578

The emission spectrum of the perylene dimer[3] in a rigid solution is reported to have a maximum at 18280 cm^{-1}, and the band shape at 20 K is composed of the excimer type and a monomer-like band of the α crystal. The crystalline bands are 500 cm^{-1} higher in energy than that found for the dimer. This finding suggests that the excitonic and charge-resonance interaction will be easier for the dimer in a rigid solution than in crystals.

In the earlier paper the monomer-like emission of the α-form at 4.2 K was simply called a monomer band, and it was considered it was nearly the same in character as the β-form emission band. As a matter of fact, the level is significantly shifted; therefore, the previous interpretation of this level must be revised so as to involve a different character rather than the Franck-Condon excitonic state.

Recently Inoue *et al.*[6] claimed that the excimer formation from the Franck-Condon excited state competes with the process of the relaxation to a monomer-like emission level. The discrimination of the monomer-like emissive level of the α crystal from the Franck-Condon excited level will be important for any further analysis of the excimer process.

The red shift of the excimer emission of the α-form at 77 K may be estimated to be as large as 9000 cm^{-1} if we take the origin of the CT band at 26000 cm^{-1}. Therefore, such a large shift can be explained only when the distortion of molecules in the excited state is allowed to move to a closer distance than in a crystal at 4.2 K[1,16] where the interaction of the charge-resonance state with the excitonic state will be very much larger than for the above-mentioned deformed configuration.

Concluding Remarks. The existence of the CT state in neat molecular crystals is a problem of interest, and evidence of such a state obtained by an accurate spectral study has been presented for perylene crystals. The polymorphism of the crystal has been shown to be of great help for such an investigation. Although the reflection method in crystalline spectroscopy is very powerful, its limitation for weak transitions has been presented. The combination of reflection with the transmission method will give the most reliable results in determining the polarization character. The investigation of the CT state in neat molecular crystals will still be a challenging problem, and the critical condition for observing such a band must be sought in further studies.

Although the geometry of the excimer state is still not known, it has been found that the shape and position of the emission band are greatly dependent on the relative orientation of molecules in the crystal. Further investigation will elucidate the structure of the excimer state in a crystal or in a fluid solution.

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