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Electronic Absorption and Emission Spectra of 9, 10-Dichloroanthracene and 9, 10-Dibromoanthracene Crystals

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The electronic absorption spectra of three crystalline modifications of anthracene derivatives have been measured; they are the α and β form of 9, 10-dichloroanthracene and 9, 10-dibromoanthracene. The assignment has been presented for each absorption band. The charge transfer absorption which is regarded to the transition between two stacked molecules has been observed in the α-form of 9, 10-dichloroanthracene; also a Rydberg type transition which has an out of plane polarization is found in this crystal starting at 290 mμ. It is unusually broad and is regarded as a band to band transition. The emission band has been measured at different temperature; it is found that excimer type emission is most prominent in the β-form of 9, 10-dichloroanthracene, in which intermolecular approach in the excited state will occur with less difficulty. A criterion for strong, medium, and weak interactions in the excited state is presented by comparing the shift, and the shape of the emission band with the intermolecular vibrational spacing. These results show that the charge transfer interaction and excimer formation are greatly dependent on the relative orientation of molecules, the π-electron overlap, and the difficulty of intermolecular approach in the excited state, particularly with its correlation to the steric repulsion of the bulky substituent groups.

Recently a number of investigations have been published on the problem of excimer and the charge transfer state of aromatic hydrocarbon crystals. The absorption spectra of anthracene crystals have been studied by many people,[1-3] but spectroscopic evidence of the charge transfer state has not been obtained as yet. On the other hand, recent experiments on the photoconductivity of anthracene crystal by Castro and Hornig,[4] Geacintov and Pope,[5] and by Chaiken and Kearns[6] have shown that a band to band transition may exist in pure anthracene crystal in the 280 mμ region. As regards the excimer of anthracene derivatives, Chandross and Ferguson[7] have succeeded in observing excimer emission and absorption spectra at lower temperature in solution. Kuwano and Kondo[8] have found a new crystalline form of 9, 10-dichloroanthracene, and have discussed the anomalous emission characteristics of the new form. Trotter[9,10] has already analysed the crystal structure of the other form of 9, 10-dichloroanthracene, and 9, 10-dibromoanthracene. The comparison of absorption and emission spectra of different types of crystals will clarify the mechanism of excimer formation in the crystalline state, the charge transfer absorption, and the band to band transition of anthracene type crystals.

Experimental

9, 10-dichloroanthracene was synthesized by the method of Ware and Borchert.[11] Actually, the reactants were purified before starting the synthesis and after reaction the product was purified by repeated recrystallization from hexane and several passages of column chromatography. 9, 10-Dibromoanthracene was a product of the Tokyo Kasei Co., and was recrystallized for five to six times from hexane solution. The crystal for emission measurement was grown from hexane solution and the new crystal form of 9, 10-dichloroanthracene was made by heating the crystal in a sealed glass tube at 180°C for twenty hours. This temperature is reported to be the transition point from the α to the β-form. The crystals for the absorption measurement were made by three different methods: first, by the usual

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[*1] Present address: Governmental Industrial Research Institute, Tosu, Saga.

1) D. P. Craig and J. R. Walsh, *J. Chem. Soc.*, **1958**, 1613.

2) M. S. Brodin and S. V. Marisova, *Opt. Spect.*, **10**, 242 (1961).

3) R. S. Berry, J. Jortner, J. C. Mackie, E. S. Pysh and S. A. Rice, *J. Chem. Phys.*, **42**, 1535 (1965).

4) G. Castro and J. F. Hornig, *ibid.*, **42**, 1459 (1965).

5) N. Geacintov and M. Pope, *ibid.*, **45**, 3884 (1966).

6) F. Chaiken and D. R. Kearns, *ibid.*, **45**, 3966 (1966).

7) E. A. Chandross and J. Ferguson, *ibid.*, **45**, 3546 (1966).

8) H. Kuwano and M. Kondo, This Bulletin, **39**, 2779 (1966).

9) J. Trotter, *Acta Cryst.*, **12**, 54 (1956).

10) J. Trotter, *ibid.*, **11**, 803 (1958).

11) C. Ware and E. E. Borchert, *J. Org. Chem.*, **26** 2263 (1961).

recrystallization method, second, by dropping a solution onto a quartz plate and growing the crystals on the plate and, third, by sublimation in a small beaker onto cotton wool. All crystals were examined with a polarization microscope in order to find the orientation, and the crystalline axis of some crystals was confirmed by taking X-ray photographs.

The absorption of the crystals was measured using an ultraviolet microspectrophotometer, consisting of a Carl Zeiss monochromator and light detection system, an Olympus microscope with Ultrafluar lenses of Carl Zeiss, and a Rochon type polarizer made of quartz. This instrument is capable of measuring crystals as small in area as $10\ \mu \times 10\ \mu$; the wavelength region is from 220 mμ to 2.0 μ. The emission spectra were observed using a Carl Zeiss spectrophotometer PMQ II combined with a mercury excitation lamp and suitable filters, and were also photographed using a Shimadzu Spectrograph GE-100 with Kodak 103a-F plates. The polarization of emission spectra was measured using a specially designed microscope of the Olympus Optical Co.

Results and Discussion

1. Absorption Spectra of Crystals. *a) α-Form of 9, 10-Dichloroanthracene.* The electronic absorption and fluorescence spectra of 9, 10-dichloroanthracene (hereafter called DCA) in hexane solution are shown in Fig. 1. They resemble that of anthracene, and the lower excited state at 27000 cm^{-1} is regarded as the $^1B_{3u}$ (^1L_a) excited state, with the polarization being along the short-axis, and the second excited state at 34900 cm^{-1} is assigned to the $^1B_{2u}$ (^1B_b) excited state, the polarization being along the long axis. The crystalline structure analysis made by Trotter[9] on the α-form of DCA showed that the molecules are nearly parallel to the bc plane (Fig. 3).

The crystals grown from solution and by sublimation show a habit of developing the ac plane. The a-axis is nearly perpendicular to the plane of the benzene ring, therefore, it does not involve the component of the π-π transition. If we take the isolated-molecule approximation (oriented-gas model) in the crystal then molecular π-π

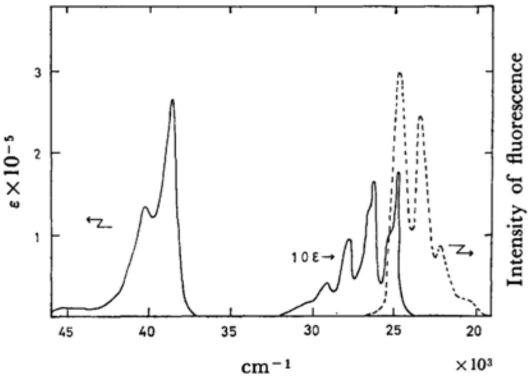

Fig. 1. Absorption and fluorescence spectra of 9, 10-dichloroanthracene in hexane solution.

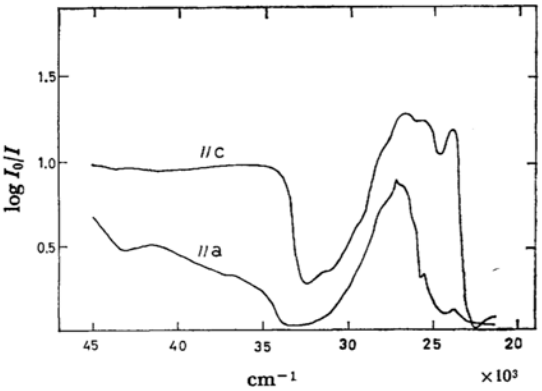

Fig. 2. Crystalline absorption spectra of α-form of 9, 10-dichloroanthracene.

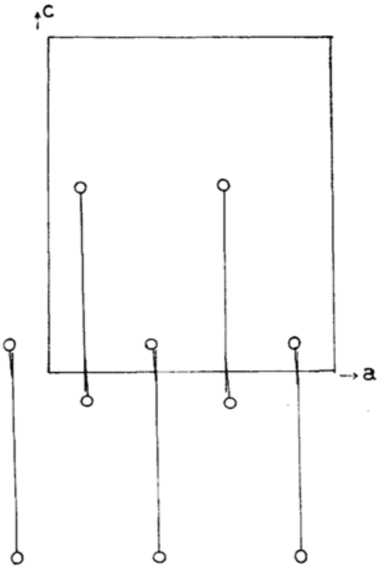

Fig. 3(a).

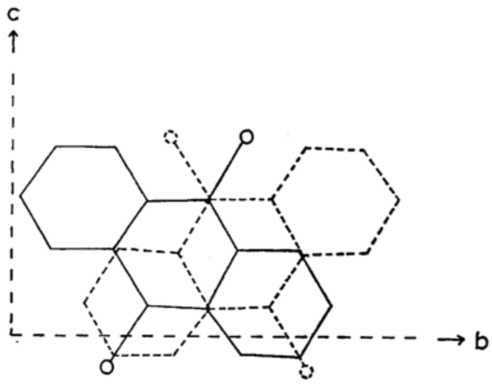

Fig. 3(b).

Fig. 3. Projection of 9, 10-dichloroanthracene molecules onto ac and bc plane in α-form crystal (a) ac-projection (b) bc-projection.

transition to both the $^1B_{3u}$ and $^1B_{2u}$ excited states may occur only along the c axis in the ac plane. The crystalline spectrum is shown in Fig. 2.

The first absorption band at 23800 cm^{-1} is in good agreement with this prediction, since the first 0–0 transition is much stronger along the c axis than the a axis, and the second peak at 25500 cm^{-1} is also stronger along the c axis. The third peak around 26600 –27000 cm^{-1} shows a significant deviation from this character, therefore this band should be regarded as being mixed with a band different origin than that of the first and second peaks. The measured plane is an ac plane of a monoclinic crystal, therefore the possibility of Davydov type band splitting can be eliminated since there is no difference in the crystalline selection rule between the a-axis and the c-axis. The most reasonable explanation for the appearance of the out of plane absorption band in this region can be based on a charge transfer mechanism between the molecules in the crystal. The direction of the transition moment for the charge transfer absorption band should be along the line connecting the center of the donor and acceptor molecules. Therefore in the region around 26000—28000 cm^{-1}, there might be two bands with different polarization character which are overlapping each other. The first is the in-plane band, which is the third vibrational progression of the transition to the $^1B_{3u}$ state, and the second is the charge transfer transition, which has a polarization vertical to the plane of the benzene rings in this crystal. Rice and his coworkers[12] have estimated the charge transfer level for the anthracene crystal to be 3.5±0.5 eV, while the present result shows that it is 3.36 eV in this crystal.

The next absorption band around the 34000 to 40000 cm^{-1} region also shows peculiar characteristics. The absorption band along the c-axis might be the transition to the $^1B_{2u}$ state, the polarization being along the long axis of the molecule, but the structure is blurred. The a-axis component shows again an exceptional out-of-plane polarization, therefore it should be regarded as a Rydberg type transition of $2p\pi$ to 3s or to higher Rydberg states in an isolated molecule. However, the 3s and 4s or higher s orbitals have larger radii than the $2p\pi$ orbital, therefore the Rydberg levels of 3s or *ns* will form broader energy bands in the crystal. The ionization continuum level may be lowered in the crystal, thereby causing mixing of the ns band with the continuum level. The position of this band starts at 34000 cm^{-1}, which is in good agreement with the energy threshold for the anthracene[4-6] band to band transition. The band shape of this transition shows a gradual increase up to the higher energy region; this characteristic is certainly different from the usual band shape of molecular transitions. Anyway, the so-called band to band transition found by photoelectric conductivity measurement should be regarded as due to the $2p\pi$ band - *ns* Rydberg band transition.

The c-axis polarized absorption band shows unusually smooth features, although the absorption peak of the $^1B_{2u}$ molecular excited state transition should be located in this region. A drastic change in the molecular $^1B_{2u}$ excited state might be resulted through the interaction of the $2p\pi$ excited state with the Rydberg *ns* and continuum states.

The developed plane of the α-form of DCA crystal presents a fortunate case for observing a charge transfer absorption and the band to band transition of a 2p→*ns* type. It is confirmed that a charge transfer absorption takes place even between the same molecules, one acting as a donor and the other as an acceptor. It should also be emphasized that spectroscopic evidence of the Rydberg and continuum states is obtained for the present crystal in which the molecules are stacked parallel to each other, but which are actually in a skewed sandwich configuration in an infinitely linear array. The intensity of the charge transfer absorption band is extraordinarily enhanced in the present crystal, which may mean that the charge transfer transition is borrowing intensity from the continuum level of the band to band transition.

b) β-Form of 9, 10-Dichloroanthracene. By sublimation both the α-form and the β-form of DCA crystal could be obtained; it was possible to distinguish between the two forms with a polarization microscope. The crystalline absorption of the β- form of DCA is presented in Fig. 4, in which spectra are shown for light polarized along the c- and the a-axis. The crystalline structure analysis of the β- form is now being carried out by Kuwano and Kondo,[13] and we present their preliminary results in Fig. 5.

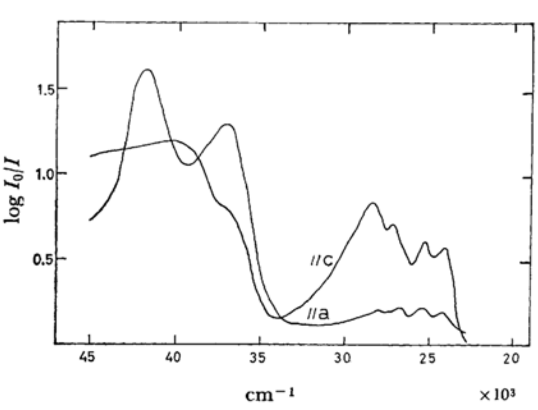

Fig. 4. Crystallin absorption spectra of β-form of 9, 10-dichloroanthracene crystal.

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[12] S. A. Rice, Private communication.

[13] H. Kuwano and M. Kondo, private communication.

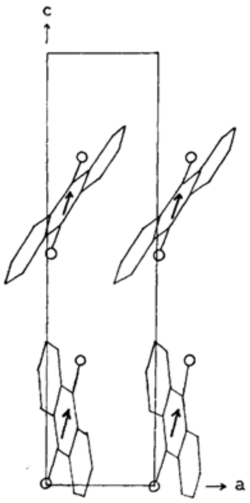

Fig. 5. Projection of 9, 10-dichloroanthracene molecules onto ac plane in β-form crystal, where arrows means the direction of the short-axis polarized transition.

The first absorption band at 23800 cm^{-1} is assigned to the short axis polarized band of $^1B_{3u}$ character.

The molecular exciton state function for a triclinic crystal including two molecules in a unit cell is written as

$$\left.\begin{aligned}\Psi_+ &= \frac{1}{\sqrt{2N}}\left(\sum_{i=1}^{N}\phi_{1i}' + \sum_{j=1}^{N}\phi_{2j}'\right)\\ \Psi_- &= \frac{1}{\sqrt{2N}}\left(\sum_{i=1}^{N}\phi_{1i}' - \sum_{j=1}^{N}\phi_{2j}'\right)\end{aligned}\right\} \qquad (1)$$

in which ϕ_{1i}' means that the molecule in the 1st site of the ith cell is excited and all other molecules are in the ground state. In the present case the (+) state of the $^1B_{3u}$ excited state has an additional contribution from the transition moments of both molecules, while in the (−) state two transition moments nearly cancel each other, with a slight residual moment along the c-axis.*2 The polarization ratio calculated for the (+) $^1B_{3u}$ excited state by using the assumption of the oriented-gas model is 12.6, while the observed value is 7.6.

The band splitting for each vibronic band is: the first peak is split by about 300 cm^{-1}, the c-axis is lower in energy, the splitting of the second peak is about 150 cm^{-1}. Around the third peak we found rather curious band shapes, and the c-axis band is much more separated from the 2nd peak and the splitting $(\nu_a-\nu_c)$ is -550 cm^{-1}. The splitting of the fourth peak is -450 cm^{-1}.

The next transition in the 37000—42000 cm^{-1} region is related to the $^1B_{2u}$ molecular excited state.

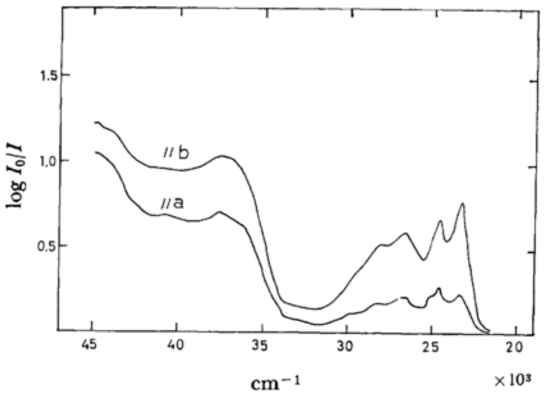

Fig. 6. Crystalline absorption spectra of 9, 10-dibromoanthracene crystal.

The two peaks along the c-axis polarized band are separated by about 4800 cm^{-1}, and this might be correlated with the (+) and (−) states of Eq. (1) of the $^1B_{2u}$ molecular excited state.

The intensity ratio for (+) and (−) states is calculated to be 4 : 1, but the observed bands are overlapped, and it is difficult to separate into components and to discuss the intensity ratio for each transition. By combining those two transitions, the c-axis polarized band should have a much larger intensity than the a-axis polarized band, but it is actually smaller and broader. Following the result presented for the α-form of DCA, this could be the band to band transition in this region. It is expected that the mixing of the Rydberg or ionized continuum states with the molecular excited state will lead to such a complicated pattern of spectra.

c) 9, 10-Dibromoanthracene. The crystalline absorption spectra of DBA are shown in Fig. 6, which is measured with the ab plane by the light polarized along the a- and b-axes. The projection of molecules onto the ab plane is shown in Fig. 7 following the result of Trotter.[10] The exciton state of the triclinic crystal is given by Eq. (1), and the band splitting and polarization ratio can be discussed in terms of these exciton state functions.

The first absorption band around the 32400 cm^{-1} region is regarded as the transition to the $^1B_{3u}$ excited state, but the vibrational progression is slightly distorted as compared with the solution spectra. By careful examination of the a- axis spectra, it is found that a little hump exists at 25300 cm^{-1} in the a-axis polarized spectrum. This small shoulder might be assigned to a transition of the charge transfer type between molecules in the same crystallographic position. The reason for the small intensity of this band might be due to the weak electron overlap between the molecules. The vibrational progressions of the apparent 0-0, 0–1 and 0–2 transitions are different from that in solution; this discrepancy may be attributed

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*2 Here the (+) state means in-phase combination of two transition moments shown in Fig. 5.

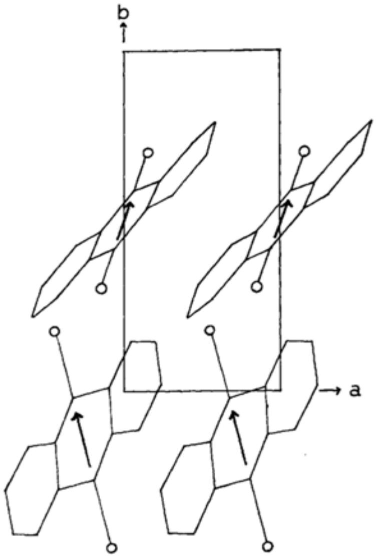

Fig. 7. Projection of 9, 10-dibromoanthracene molecules onto the ab plane, where arrows means the direction of the short-axis polarized transition.

to the interaction between the vibronic state and the charge transfer state.

The polarization ratio of the first 0–0 band (I_b/I_a) is 3.2, while the value calculated on the basis of the oriented gas model is 12.1. These values are not in good agreement, but this sort of discrepancy can be explained as due to crystal field mixing with higher excited states.

The second absorption band around the 37000 cm^{-1} region does not show any appreciable splitting. When we take the excition state function as given by Eq. (1) (see Fig. 7), transitions to the (+) state should occur both along the a- and b-axes, but transitions to the (−) state may cancel and will therefore not be seen in the crystal absorption.

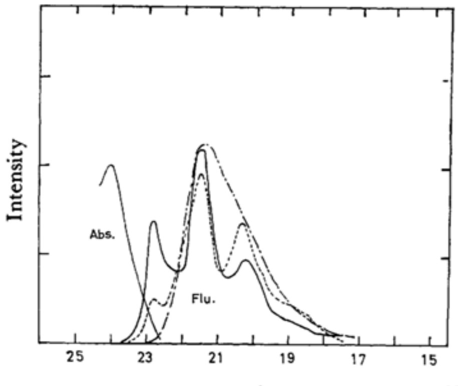

Fig. 8. Temperature dependence of crystalline flourescence spectrum of α-form of 9, 10-dichloroanthracene.
—— 4.2°K ······ 77°K ·—· 330°K

The polarization ratio (I_a/I_b) observed is 1.5 while the calculated value is 0.9. The third absorption band increases in intensity with increasing energy in the 45000 cm^{-1} region, and it may be related to the higher molecular excited states and the continuum state. Also a contribution from the band to band transition may occur in this region.

2. Fluorescence Spectra of Crystals. *a) α-Form of 9, 10-Dichloroanthracene.* The fluorescence spectra of the α-form of DCA is shown in Fig. 8 for different temperatures, the measurement being made with a Carl Zeiss monochromator with a slit width of less than 0.1 mm. The absorption edge at 300°K is also shown in order to illustrate the effect of reabsorption by the crystal. The absorption starts at 22500 cm^{-1} at 300°K, while emission begins at 23700 cm^{-1} at 4.2°K. The origin of the emission band is overlapped with the absorption at 300°K, therefore the effect of reabsorption will change the shape of the emission band at 300°K. At lower temperatures the absorption band edge moves to the shorter wavelength region, and therefore the first 0–0 emission band in the crystal can be clearly recognized. The fluorescence spectra of DCA thus far reported[7,14] are all different from the present result, and it may be that these spectra have been reported for crystals not as pure as the present one. The fluorescence spectra show a resolved vibrational progressions of about 1400 cm^{-1} at 4.2°K, while the solution value for emission is 1400 cm^{-1}.

The shift of the first 0–0 band from absorption to emission is about 860 cm^{-1} and it is almost certain that excimer formation does not take place in this crystal as judged from the shift and the shape of the emission band. This situation is illustrated in Fig. 9 together with cases of stronger interaction in the excited state. In this figure, the electronic energy level is correlated with the intermolecular distance R. The horizontal levels drawn in the potential curve denote the energy of the intramolecular vibrational mode, not the intermolecular vibration. The three potential

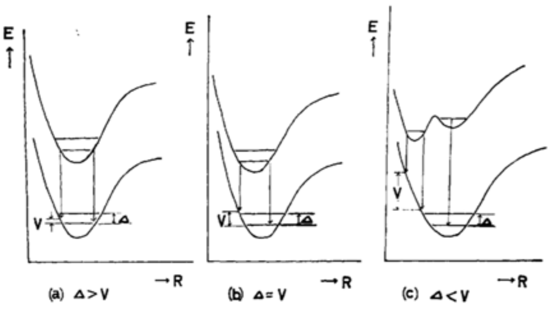

Fig. 9. Potential energy diagram of the excited and ground state of the dimer pair.

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[14] E. Bock, J. Ferguson and W. G. Schneider, *Can. J. Chem.*, **36**, 507 (1958).

curves illustrate the weak, medium and strong types of excited state interaction. It is thought that excimer formation will occur after excitation by the exciton and the charge transfer type interaction at a closer intermolecular distance than in the ground state. In this case the movement of molecules is considered to occur so as to avoid the steric repulsion between the bulky substituent groups. The magnitude of the stabilization will be dependent on the intermolecular distance and electron overlap between molecules.[15]

However, the energy of the emission band of the excimer is also dependent on the potential energy curve of the repulsive ground state, and this might be the reason why the excimer emission is always broad and structureless. In Fig. 9 the V-value shows the uncertainty in the ground state potential energy, and we assume that this value represents the width of the ground state potential energy. Therefore we will take this value as the uncertainty in the energy under the condition that emission is occurring at the bottom of the excited state potential curve. From this criterion, the α-form of DCA has a V-value smaller than the intramolecular vibrational spacing, Δ, implying that the center of the excited state potential function moves slightly to smaller intermolecular distances in the excited state.

This behavior may be explained on the basis of the steric repulsion between the two chlorine atoms, which have larger van der Waals radii than the carbon atoms. The present crystal has an unfavorable configuration to form the excimer, since intermolecular appoach in the excited state will be hindered by the overcrowding of the chlorine atoms.

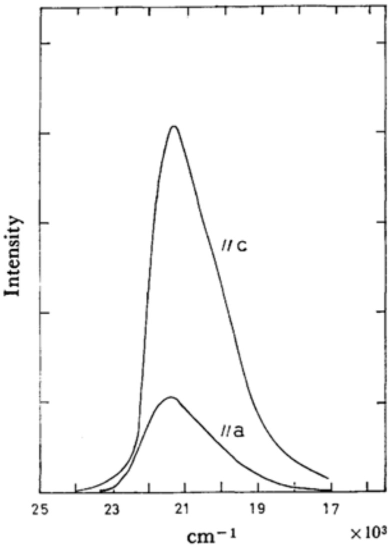

Fig. 10. Polarization of the fluorescence spectrum of α-form of 9, 10-dichloroanthracene.

Further evidence for molecular characteristics in the emission of α-form type crystal is that the polarization ratio of the emission along the c-axis is much stronger than along the a-axis (*cf.* Fig. 10). The ratio is 4 : 1 ($I_c : I_a$), which is less than in the case of absorption (12 : 1), but still the high dichroic ratio indicates the molecular character of the $^1B_{3u}$ excited state in the emission.

b) β-Form of 9, 10-Dichloroanthracene. The emission spectra of the β-form of DCA at several different temperatures are shown in Fig. 11, and it is found that drastic change in emission spectra occurs with the change of temperature. A broad emission band is observed at 19280 cm^{-1} at 300°K, which is 4700 cm^{-1} below the first crystalline absorption peak. This broad band moves to lower frequency at 77°K, the peak being at 18600 cm^{-1}, which is 5400 cm^{-1} below the crystal absorption. At liquid helium temperature the peak shifts to 18200 cm^{-1}, and in addition to this broad band, a monomer band with two or three vibrational bands has been observed starting at 22940 cm^{-1}. The appearance of two kinds of emissions, one, that of the excimer, and the other, that of the monomer, can be explained by assuming a hump in the potential energy curve in the excited state.*[3] A similar situation has been recognized in the case of perylene excimer emission.[16] This mechanism will be explained by the energy diagram in

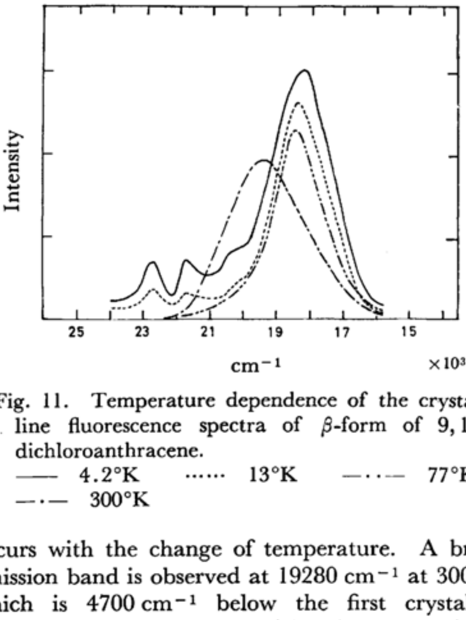

Fig. 11. Temperature dependence of the crystalline fluorescence spectra of β-form of 9, 10-dichloroanthracene.
—— 4.2°K …… 13°K —‥— 77°K
—·— 300°K

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[15] J. N. Murrell and J. Tanaka, *Mol. Phys.*, **7**, 363 (1964).

*[3] The possibility of a phase transition from the β-form to the α-form at lower temperature is excluded since the change in the fluorescence spectra is reversibly observed with change of the temperature, in spite of the fact that a modification of the crystalline form was not observed. If the phase transition were taking place at lower temperature a significant change in the optical properties of the crystal should be detectable with a polarization microscope.

[16] J. Tanaka, This Bulletin, **36**, 1237 (1963).

Fig. 9 (c) where the excited molecule will move to a shorter intermolecular distance to form the excimer, but the movement of the molecule will be hindered at lower temperatures due to the existence of the little hump in the potential curve and eventually will emit monomer type emission. The broader band character of the longer wavelength emission can be explained by assuming a V-value which is larger than the vibrational spacing. The relatively large temperature dependence of the longer wavelength band at higher temperature is typical of excimer emission. It is interesting that the so-called 6000 cm^{-1} rule17) is nearly satisfied in the present crystal, the value at 4.2°K being 5800 cm^{-1}.

c) 9, 10-Dibromoanthracene. The fluorescence spectra of DBA have been measured at several different temperatures, and are shown in Fig. 12. They show relatively little temperature dependence, but the emission band as a whole shifts to lower frequency as compared with the α-form of DCA. The shift measured at the first 0-0 transition is 2150 cm^{-1}, which is larger than the α-form of DCA, but far less than the β-form of DCA. The potential energy levels based on these numbers are pictured in Fig. 9 (b), and it is estimated that the V-value is nearly the same order of magnitude as the Δ-value of the vibrational spacing. It is also interesting that the 0–0 emission band is clearly seen at 77°K rather than at 4.2K; this indicates that the equilibrium configuration of the excited state is shifted from the center of the ground state configuration, resulting in a small Franck-Condon overlap factor for the 0-0 transition at 4.2°K. Comparison with the cases of the α- and β-forms of DCA shows that both the shift of the emission band and the V-value are intermediate in the DBA crystal. The polarization ratio of the emission band measured along the b- and a-axes is 1.7, while that of the absorption is 3.2 (*cf.* Fig. 13). The decrease in the dichroic ratio means that the charge transfer contribution to the emission component is increased in the DBA crystal.

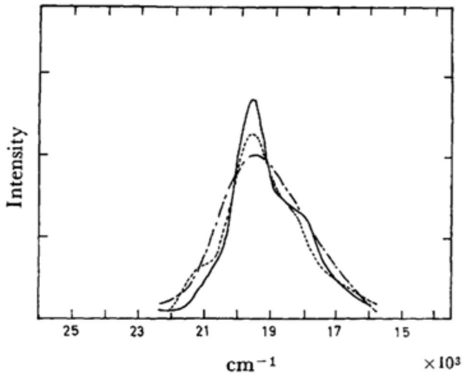

Fig. 12. Temperature dependence of the crystalline flourescence spectrum of 9, 10-dibromoanthracene.
—— 4.2°K ...... 77°K —·— 300°K

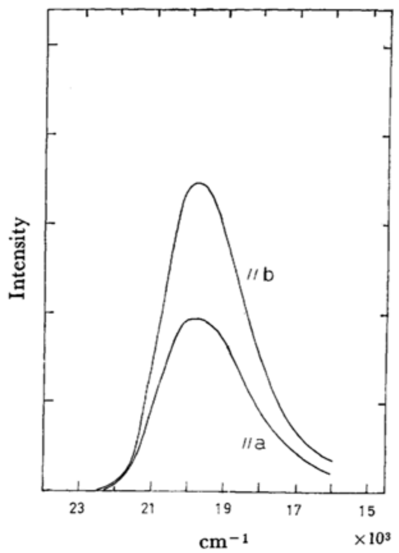

Fig. 13. Polarization of the fluorescence spectrum of 9, 10-dibromoanthracene.

The results obtained for the three different crystals indicate that excimer formation is most favorable when intermolecular approach in the excited state is not hindered by bulky substituent groups. The larger shift for β-DCA compared with DBA indicates that the π-electron overlap is more efficient for β-DCA than for DBA even in a similar crystallographic relationship, since the van der Waals radii are smaller for chlorine atoms than for bromine.

Conclusion

The electronic interaction of molecules in a crystal is primarily governed by the relative orientation and the interatomic distances between molecules. The charge transfer absorption band could be observed for the α-DCA crystal where the inter-molecular electron overlap in the ground state configuration is apparently larger than for other crystals. The excimer type emission is found most prominently in the β-DCA, and DBA crystals, where the molecules are stacked nearly parallel to each other but at relatively large distances. This configuration is most favorable for excimer formation, since the bulky substituent groups are located in such a way that the molecular movement to the shorter intermolecular distance in the excited state may be least hindered. The intermolecular electron overlap is essential for excimer formation, therefore it can be naturally concluded that the molecules will move to as short an intermolecular distance as possible in the excited state.

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17) J. B. Birks, M. O. Lumb and I. H. Munro, *Proc. Roy. Soc., (London)*, **A280**, 289 (1964).

For the ground state configuration the intermolecular separation is larger for the β-DCA and DBA crystals than for the α-DCA crystal, therefore it is most probable that the excimer force should operate to bring the molecules into a closer position in the excitd state. The nature of the excimer force has not been fully discussed in the present text. It is conventionally divided into two parts: the exciton type and charge transfer type interactions will be most important; the former will be dominant at longer distances, and the latter is significant in the region of strong electron overlap. At the real excimer equilibrium distance, both forces will be strongly mixed and will be balanced by the potential of the exchange repulsion. The van der Waals radius of each atom in the ground state will be determined by this latter type of exchange repulsion between closed-shell atomic systems. For the excited state, however, an open-shell electron configuration will allow the molecules to approach each other, since the exchange repulsion between open-shell excited configuration and ground configuration will be smaller than that with closed shell ground electron configurations. It will mean that the van der Waals radius may be smaller for the excited state than the ground state configuration.

Finally, it should be emphasized again that the band to band transition of $2p\pi$ to ns type is found for the α-DCA crystal in the 34000 cm^{-1} region. This finding should throw some light on the mechanism of photoconductivity in organic crystals.

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