A Study of the Charge-Transfer Complexes. II. The Complexes of Pyromellitic Dianhydride with Polycyclic Aromatic Compounds*

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Many interesting properties of the solid complexes formed between pyromellitic dianhydride and polymethylbenzenes were reported in the preceding paper of this series.(1) In fact, pyromellitic dianhydride is characterized by the special ease with which it forms solid complexes with many aromatic compounds. Relatively few papers have, however, been published on the spectroscopic study of such charge-transfer complexes in the solid state.(2) In studying the complexes in solution, it has been quite common to consider the variation in the absorption maximum of the charge-transfer band as changing the donor molecule for a given acceptor. The results of such experiments are generally used to estimate the electron affinity of the acceptor molecule.(3) Dewar and Lepley showed that essentially the same technique can be fruitfully applied to the case of solid complexes.(4) The same type of experimental results will be presented here on charge-transfer complexes with pyromellitic dianhydride employed as the common acceptor. Polycyclic aromatic compounds were used as donors in order to cover a wide range of ionization potential for the donor molecule. Some other aromatic compounds were also used in the experiment in order to observe the donor dependence of the charge-transfer band in more detail. It may be adequate to mention here that the KBr disk method or something similar has been the most popular technique for measuring the absorption spectra of solid complexes.(2,4,5) In the present experiment, use was made of the diffuse reflectance method, which had been proven to be quite successful in studying solid molecular complexes.(6)

Experimental

Materials.—Naphthalene and anthracene were purchased from the Wako Pure Chemical Industry Co., while chrysene, pyrene and phenanthrene were provided by the Tokyo Kasei Organic Chemicals Co. All of these compounds were purified by repeated recrystallization from various solvents, such as ethanol, acetic acid and toluene. The m. p.'s and ultraviolet spectra agreed well with those reported in the literature. *trans*-Stilbene was synthesized from benzaldehyde through benzoin.(7) α-Methylnaphthalene was made by catalytic dehydrogenation following the dehydration of 1-methyltetralol.(8) Anisole was purchased from the Wako Pure Chemical Co. *para*-Methylanisole and *p*-dimethoxybenzene were synthesized by the usual method from the corresponding sodium phenolate and dimethylsulfate. All the liquid samples were found pure by gas chromatography and were identified by means of the infrared and NMR spectra. Reagent-grade ethylacetate was washed with a saturated aqueous sodium carbonate solution and then dried over calcium chloride. Further purification was made by repeated fractional distillation in the presence of phosphorus pentoxide. Pyromellitic dianhydride was obtained by dehydrating pyromellitic acid, as supplied by the Tokyo Kasei Organic Chemicals Co., in boiling acetic anhydride; it was then recrystallized from purified ethylacetate before use (m. p. 299.8—300.0°C).(1)

Spectroscopic Measurements.—Solutions of the complexes were prepared by dissolving pyromellitic

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1) Y. Nakayama, Y. Ichikawa and T. Matsuo, This Bulletin, **38**, 1674 (1965).

2) J. W. Eastman, G. M. Androes and M. Calvin, *J. Chem. Phys.*, **36**, 1197 (1962).

3) G. Briegleb, *Angew. Chem.*, **76**, 326 (1964).

4) M. J. S. Dewar and A. R. Lepley, *J. Am. Chem. Soc.*, **83**, 4560 (1961).

5) R. Foster and T. J. Thomson *Trans. Faraday Soc.*, **59**, 296 (1962).

6) G. Kortüm and W. Braun, *Z. Phys. Chem.*, *N. F.*, **18**, 242 (1958).

dianhydride (10^{-2} mol./l.) and the donor compounds into ethylacetate. The donor concentration varied from 10^{-2} to 10^{-1} mol./l., depending on the stability and on the solubility of the complex. The spectra were measured in 1 cm. cells in the visible range on a Hitachi model EPS-2U recording spectrophotometer. Solid molecular complexes were prepared by the method described in the previous paper.1) The complex was dispersed in talcum powder, and it relative diffuse reflectance was measured with a Hitachi model EPU-2A photoelectric spectrophotometer equipped with an integrating sphere.1)

Results and Discussion

Examples of the appearance of the charge-transfer absorption band of the complex in an ethyl acetate solution are shown in Fig. 1 for the cases of α-methylnaphthalene and anthracene. The spectra were measured using ethyl acetate as the reference; the absorptions due to the components are not substracted from the data. The absorption of pyromellitic dianhydride (abbreviated as PMDA hereafter) itself, however, is small enough to be neglected in the visible region.1) The bands indicated by the arrows in Fig. 1 may, then, be easily identified as the charge-transfer absorption, as they are clearly separated from the bands mainly due to the donor absorption on the higher frequency side. There are cases, however, where the charge-transfer band appears as just a weak shoulder superimposed on the tail of a strong absorption on the higher frequency side. Such overlapping bands were resolved graphically, as is illustrated in Fig. 2 for the case of a PMDA-stilbene complex. The absorption maxima obtained by these methods for various donors are summarized in Table I, together with the errors involved in the resolution.

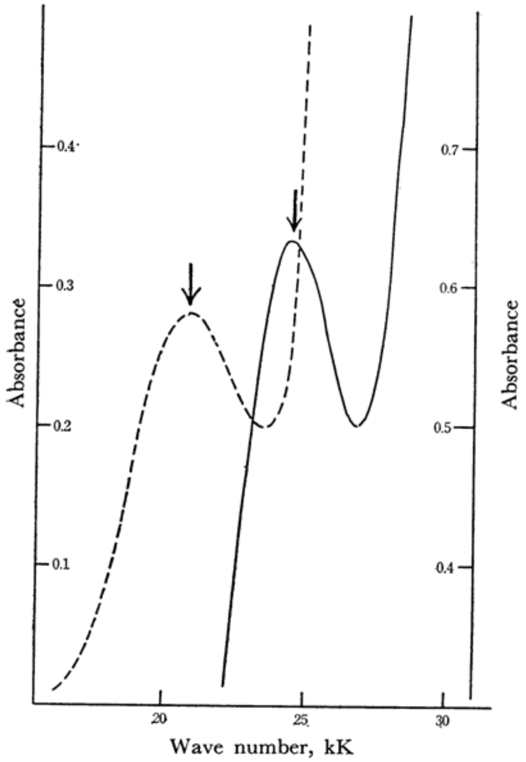

Fig. 1. The appearances of charge-transfer absorption bands of PMDA complexes with α-methylnaphthalene (solid line) and anthracene (broken line) in ethyl acetate. The left scale is used for anthracene, and the right scale for α-methylnaphthalene.
The following concentrations were used in the experiments:
α-Methylnaphthalene; 6.67×10^{-2} mol./l.
Anthracene ; 2.0×10^{-2} mol./l.
PMDA ; 1.0×10^{-2} mol./l.

By definition, the Kubelka-Munk remission function, $f(R)$, is the ratio of the absorption to the scattering coefficients, k/S, of the powdered sample;

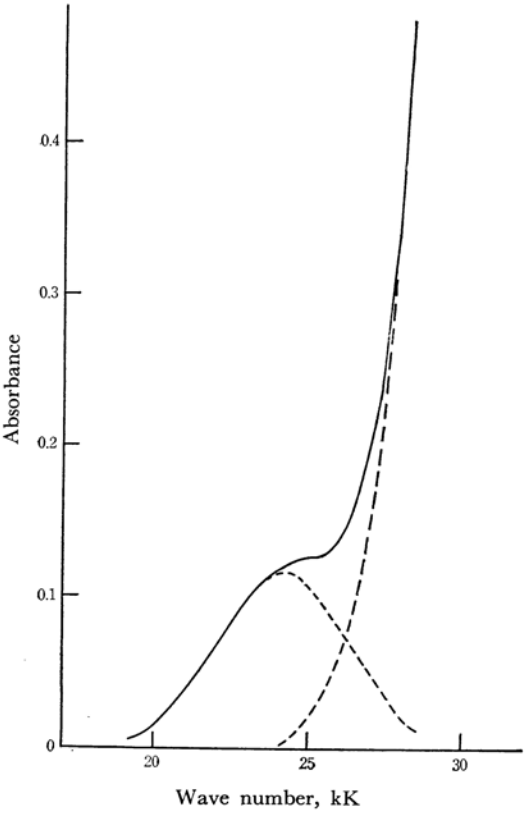

Fig. 2. Resolution of the charge-transfer absorption illustrated by the case of *trans*-stilbene-PMDA complex. The observed absorption curve (solid line) consists of two components shown by the dotted lines.
PMDA; 1.15×10^{-2} mol./l.,
trans-Stilbene; 1.38×10^{-1} mol./l.

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[7] R. L. Shriner and A. Berger, "Organic Synthesis," Coll. Vol. III, 786 (1955).

[8] The author is indebted to Mr. Shinji Isatake for preparing the authentic sample of α-methylnaphthalene by this method.

TABLE I. THE CHARGE-TRANSFER ABSORPTION BANDS OF PMDA COMPLEXES WITH VARIOUS DONORS AND THE ENERGY LEVELS OF THE HIGHEST OCCUPIED MO OF THE DONOR MOLECULES

Donor	m	$\tilde{\nu}_{CT}$ in EtOAc kK	$\tilde{\nu}_{CT}$ in solid kK
Anthracene	0.414	20.9 ± 0.1	19.6 ± 0.1
Pyrene	0.445	21.3 ± 0.1	20.1 ± 0.1
trans-Stilbene	0.504	24.2 ± 0.3	22.0 ± 0.1
Chrysene	0.520	23.1 ± 0.3	22.5 ± 0.2
p-Dimethoxybenzene	(0.520)	23.5 ± 0.2	
α-Methylnaphthalene	(0.565)	24.6 ± 0.1	
p-Methylanisole	(0.591)	25.0 ± 0.3	
Phenanthrene	0.605	25.0 ± 0.3	24.8 ± 0.3
Naphthalene	0.618	25.8 ± 0.1	24.7 ± 0.1
Anisole	(0.690)	27.1 ± 0.5	

The m values in parentheses are estimated from the charge-transfer bands of chloranil complexes with the same donor as explained in the text.

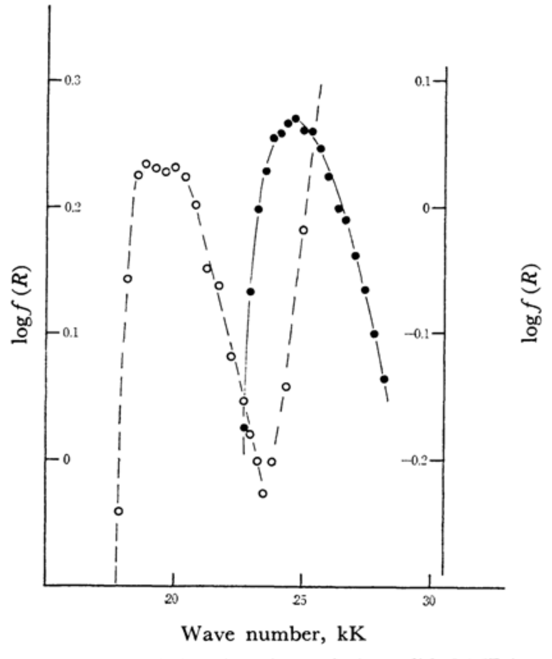

Fig. 3. Remission functions of the solid PMDA complexes with naphthalene (filled circle) and anthracene (open circle).
The right scale is for the case of naphthalene only.
Naphthalene-PMDA complex (45 mg.) in talcum powder (389 mg.)
Anthracene-PMDA complex (34 mg.) in talcum powder (402 mg.).

it is expressed in terms of the measured diffuse reflectance, R, by the following equation:[9]

$$f(R)=\frac{k}{S}=\frac{(R-1)^2}{2S} \tag{1}$$

Assuming that the scattering coefficient, S, is independent of the wavelength, $f(R)$ is taken to reproduce the absorption band in the region under investigation. This treatment is not entirely valid from the theoretical point of view. Experimental observation has, however, shown that the remission function is good enough to estimate the absorption maxima of molecular complexes in the solid state.[1,6] In addition, no violent treatment is applied to the molecular complexes in preparing the sample for diffuse reflectance measurement, in contrast to the KBr disk method. The remission functions of PMDA complexes with anthracene and naphthalene are shown in Fig. 3. The absorption maxima thus obtained for the solid complexes are given in the fourth column of Table I. The frequency of the charge-transfer absorption band is correlated with the electron affinity of an acceptor, E_A, and the ionization potential of the donor, I_P, by the following well-known equation:

$$h\nu_{CT}=I_p-E_A+\Delta \tag{2}$$

where Δ stands for a correction mainly due to the Coulombic interaction in the complex. The ionization potentials of polycyclic aromatic compounds are known to be linearly dependent on the energy level of the highest-occupied MO's, as calculated by the Hückel MO method.[10] Thus the following equation may be expected to hold:

$$h\nu_{CT}=am-E_A+\Delta \tag{3}$$

where the energy of the highest occupied MO is expressed as:

$$E=\alpha+m\beta \tag{4}$$

If the correction factor, Δ, is assumed to be the same for a series of complexes with a common acceptor, Eq. 3 may be rewritten as:

$$h\nu_{CT}=am+b \tag{5}$$

The relationship expressed by Eq. 5 has been verified to hold in various series of complexes.[4,11] An attempt will be made here to treat the data of PMDA complexes given in Table I by the same method. The energies of the highest-occupied MO's in β units are given in the second column of Table I. The values for ordinary polycyclic aromatic compounds are those calculated with the Hückel MO. The values for the substituted compounds were estimated by using the relationship $\tilde{\nu}_{CT}$ and m for the chloranil complexes of polycyclic aromatic hydrocarbons reported by Kuboyama.[11g] The method of estimation is illustrated in Fig. 4.

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[9] G. Schreyer, *Z. Phys. Chem.*, *N. F.*, **12**, 359 (1957) and the references quoted therein.

[10] A. Streitwieser, Jr., "Molecular Orbital Theory," Wiley & Sons, Inc., New York (1961), p. 192.

[11] a) M. J. S. Dewar and H. Rogers, *J. Am. Chem. Soc.*, **84**, 395 (1962); b) A. R. Lepley, ibid., **84**, 3577 (1962); c) A. Kuboyama, *J. Chem. Soc. Japan*, *Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 375 (1962).

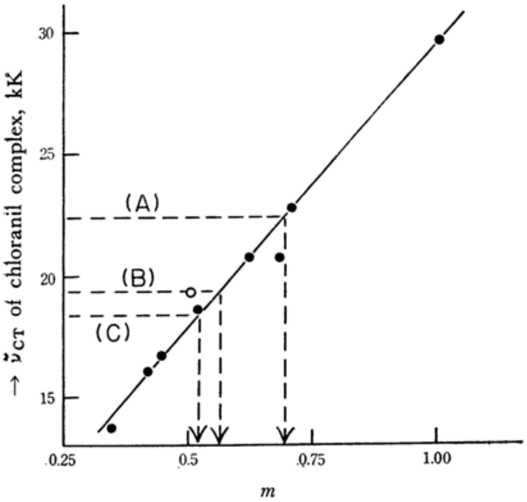

Fig. 4. Estimation of the energy level of the highest occupied MO. The experimental points and the solid line are as reported by Kuboyama.[11c)]
(A) Anisole, (B) α-Methylnaphthalene and (C) p-Dimethoxybenzene.
The open circle represents the data of chloranil - *trans*-stilbene complex.

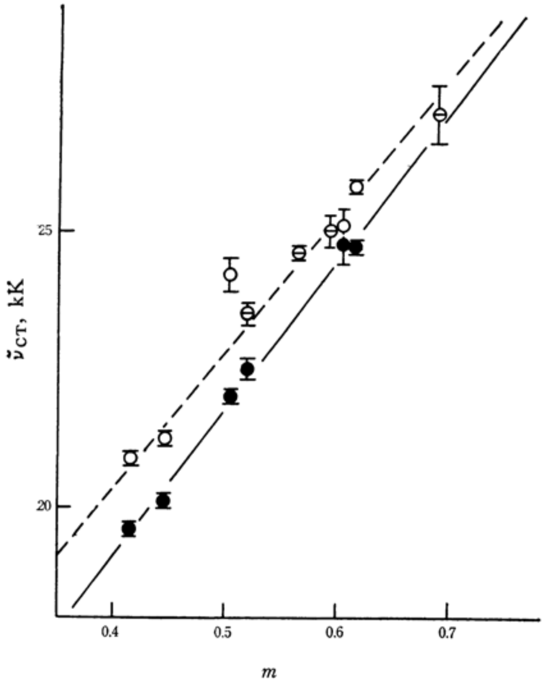

Fig. 5. Correlation of $\tilde{\nu}_{CT}$ and m in the cases of the PMDA complexes with aromatic compounds.
● Solid complex,
○ Complex in solution (m as calculated by Hückel MO)
⊖ Complex in solution (m as estimated from Fig. 4)

The data in Table I are used in Fig. 5 to illustrate the close correlation between $\tilde{\nu}_{CT}$ and m for the PMDA complexes of aromatic compounds, both solution and in the solid state. The charge-transfer band shows a bathochromic shift going from the solution to the solid state. The extent of the shift varies depending on the particular donor in question. The overall linear relationships observed between $\tilde{\nu}_{CT}$ and m in both phases, however, are almost parallel each other.

The PMDA complex of *trans*-stilbene presents an anomalous example. In contrast to the fact that the experimental point for the solid complex rests exactly on the line, the corresponding $\tilde{\nu}_{CT}$ in the solution is located at much higher frequency than might be expected from the m value. A similar situation is also met in the chloranil complex of stilbene, as is shown in Fig. 4. A part of the reason for this anomalous behavior may be that the m value is calculated by means of the Hückel MO. The calculation is made by assuming that all the α's and β's are the same in the conjugate system. It is obvious from the structure that the assumption would hold to a lesser extent in the case of *trans*-stilbene than in the cases of ordinary polycyclic aromatic hydrocarbons. In addition, the suggestion may be made that *trans*-stilbene can be slightly twisted around its essential single bond in a solution. As a result, the conjugation in the molecule is reduced and the energy level of the highest-occupied MO is lower than expected. In the solid state, a coplanar structure would be restored for *trans*-stilbene to enable it to form a strong molecular complex with PMDA. Other donor molecules attached to a conjugate group through an essential single bond seem to show behavior more or less similar to that of *trans*-stibene.

The linear relationships between $\tilde{\nu}_{CT}$ and m observed above (excluding the point for the *trans*-stilbene complex in a solution) are expressed by the following equations:

in a solution,

$$\tilde{\nu}_{CT}=24.6\,m+10.5 \qquad \text{(in kK)}, \qquad (6)$$

and in the solid state,

$$\tilde{\nu}_{CT}=26.5\,m+\ 8.5 \qquad \text{(in kK)}. \qquad (7)$$

By comparing Eqs. 6 and 7 with Eq. 5 and by also remembering that

$$b=-E_A+\Delta, \qquad (8)$$

one may estimate that the electron affinity of PMDA in ethyl acetate is lower than that in the solid state by 0.25 eV. The value can not be taken too seriously because an assumption is made here that the correction factor, Δ, is the same for both phases. It should be remembered at this point that all of the molecules and the complexs under consideration are solvated at both their ground and excited states. Due to this solvation effect, the equilibrium and the Franck-Condon states concerning the charge-transfer absorption will not be the same in various media. Consequently, it is quite unlikely that the correction factor, Δ, is the same for an ethyl acetate solution and solid state. The parallel relation observed between Eqs. 6 and 7 indicates, however, that the difference in Δ value between the complexes in the two phases is almost constant in this series and nearly independent of the donor property. Thus, it appears that the electron affinity of PMDA in the solid state is higher than that in ethyl acetate by the before-mentioned amounts. As is clear from the above discussion, 0.25 eV. is the upper limit of the value of the change in the electron affinity of PMDA since the solvent effects on the donor and complex are also included in that number. No attempt will be made here to estimate the latter effects because too many unknown factors are involved for a successful reasoning to be carried out. A similar zero-order treatment suggests that PMDA in ethyl acetate behaves as an electron acceptor weaker by 0.53 eV. than chloranil in carbon tetrachloride.(11c) The difference in the electron affinity of these compounds has previously been given by Briegleb as 0.52 eV.(3) The agreement between these two results is surprisingly close in spite of the possible difference in the media.

Summary

The frequency of the charge-transfer absorption of the PMDA complex has been found to be linearly dependent on the energy level of the highest-occupied MO of the aromatic donor as estimated by the Hückel MO method. The behavior of the complex in the solid state is almost parallel to that in a solution. On the basis of these linear relationships, it has been suggested that PMDA in ethyl acetate behaves as if it is an electron acceptor weaker than that in a solid complex and chloranil in carbon tetrachloride by about 0.2 eV. and 0.53 eV. respectively in the zero order approximation.

Another suggestion has been made that *trans*-stilbene may be slightly twisted around its essential single bond in a solution but not in the solid complex.

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