A Study of the Charge-Transfer Complexes. I. The Interaction of Pyromellitic Dianhydride with Polymethylbenzenes*

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The formation of molecular complexes between pyromellitic dianhydride and aromatic compounds, such as anisole, tetralin etc., was first reported by Seka and Sedlatschek as early as 1926.[1] In spite of the remarkable advances made thereafter in the investigation of charge-transfer complexes, however, no further paper had been published on the phenomena until Heaton and others recognized pyromellitic dianhydride as a strong electron acceptor.[2] Heaton and his co-workers studied the complexes by the spectroscopic method and concluded that pyromellitic dianhydride was one of the strongest electron acceptors which had yet been found. Recently, Briegleb reported on the electron affinity of pyromellitic dianhydride, among other compounds, as estimated from the charge-transfer band.[3] Nothing else is known about the charge-transfer complexes of pyromellitic dianhydride, which is in contrast with the abundance of information about the behavior of such other acceptors as halogens, quinones, and nitro compounds. A little further investigation is reported, in this paper, into the complex formation of pyromellitic dianhydride (abbreviated as PMDA hereafter) with polymethylbenzenes, both in a solution and in the solid phase. Polymethylbenzenes were chosen as the donor to be studied for the following reasons.

1) The basicity or the ionization potential of each molecule is well known.[4]

2) The frame work of the π-electron system can be taken as a simple hexagon throughout the system.

3) The introduction of the methyl group into the benzene nucleus results in only a small perturbation in the π-electron system to be treated theoretically.

4) The charge-transfer complexes between polymethylbenzenes and iodine or chloranil have been studied fairly well in the past.[4b),5,6]

Consequently, the discussion of the experimental results becomes much easier than in the case of other aromatic donors, which have many complicated unknown factors. This experiment was designed with some emphasis on the investigation of the nature of the solid molecular complexes.

Experimental

o- and *p*-Xylenes were purified by repeated distillations and recrystallizations from commercial products until the purity in the gas chromatograph exceeded 98%. Tetralin was purchased from the Wako Pure Chemical Company, Ltd.; it was purified and proved to be free from naphthalene. Indan was synthesized by the reduction of indanone which had been prepared from cinnamic acid through 3-phenylpropionic acid.[7] Mesitylene was synthesized from acetone[8] and was determined to be pure by

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[1] R. Seka and H. Sedlatschek, *Monatsh. Chem.*, **47**, 516 (1962).

[2] L. L. Ferstandig, W. G. Toland and C. D. Heaton, *J. Am. Chem. Soc.*, **83**, 1151 (1961).

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

[4] a) Cf. R. L. Flurry, Jr., and P. G. Lykos, *J. Am. Chem. Soc.*, **85**, 1033 (1963), and the references therein for the basicity; b) Cf. R. E. Merrifield and W. D. Phillips, ibid., **80**, 2778 (1958) for the ionization potential.

[5] L. J. Andrews and R. M. Keefer, ibid., **74**, 4500 (1952).

[6] N. Smith, Ph. D. Thesis, University of Chicago, Illinois, cf. J. N. Murrell, *J. Am. Chem. Soc.*, **81**, 5037 (1959).

[7] S. Gabriel and J. Zimmerman, *Ber.*, **13**, 1680 (1880).

[8] R. Adams and R. W. Hufferd, "Organic Syntheses," Coll. Vol. I, 341 (1958).

CH analysis, infrared spectra and gas chromatography. Durene, penta- and hexamethylbenzenes were prepared by succesive Friedel-Crafts reactions and were purified by several fractional distillations and recrystallizations from either methanol or a methanol-benzene mixture. Infrared spectra and CH analysis were used to identify the prepared methylbenzenes, whose melting points are as follows: durene (80.8—81.0°C), pentamethylbenzene (52.7—53.2°C), and hexamethylbenzene (168.0—168.3°C).

Pyromellitic dianhydride was prepared by the dehydration of pyromellitic acid, a reagent-grade product of Tokyo Kasei Kogyo Co., Ltd., through refluxing in acetic anhydride for several hours. The product was then recrystallized from purified ethylacetate and proved to be free from any trace of the original acid. (Found: C, 55.05: H, 0.93%: m. p. 299.8—300.0°C). The melting points are the values as observed on a Kofler micro hot-stage and are uncorrected.

Solid molecular complexes were prepared by adding pyromellitic dianhydride either to a donor or to an ethyl acetate solution of the donor at an elevated temperature and then cooling the solution to room temperature. The formation of charge-transfer molecular complex could easily be noticed by the precipitation of crystals with a characteristic shape and color. Extra care was taken here to avoid the coprecipitation of the uncomplexed pyromellitic dianhydride. The degree of heating and the relative ratio of the donor to the pyromellitic dianhydride in the best conditions varied from case to case.

The ultraviolet and visible spectra were measured by a conventional method using an EPS-2U model Hitachi recording spectrophotometer.

The solid complexes were ground on an agate mortar and were dispersed evenly in approximately ten times as much talcum powder (as determined by weight). The sample was packed in a cylindrical cell and was mounted on the wall of the integrating sphere of the reflectance attachment of an EPU-2A model Hitachi photoelectric spectrophotometer. The reflectance of the sample was determined against a standard sample of talcum powder under the same geometrical conditions.

The X-ray diffraction data of the powdered solid samples were obtained by the use of a Norelco X-ray spectrophotometer.

Results and Discussion

Complexes in Solution.—After many attempts, ethyl acetate was found to be the best solvent for the complexes of PMDA with a wide variety of aromatic compounds. The newly-appeared absorption bands due to the complex formation of mesitylene, durene, penta- and hexamethylbenzenes with PMDA in ethylacetate are shown in Fig. 1. There is no appreciable absorption due to the donor in the longer-wavelength region beyond 330 mμ (Fig. 2). The absorption of PMDA is practically negligible in the visible range under these experimental conditions (Fig. 2). An unmistakable charge-transfer absorption band is observed for each complex of hexa- and pentamethylbenzenes with PMDA. The peak still appears as a shoulder in the case of durene, but it is not at all obvious in the case of the mesitylene complex.

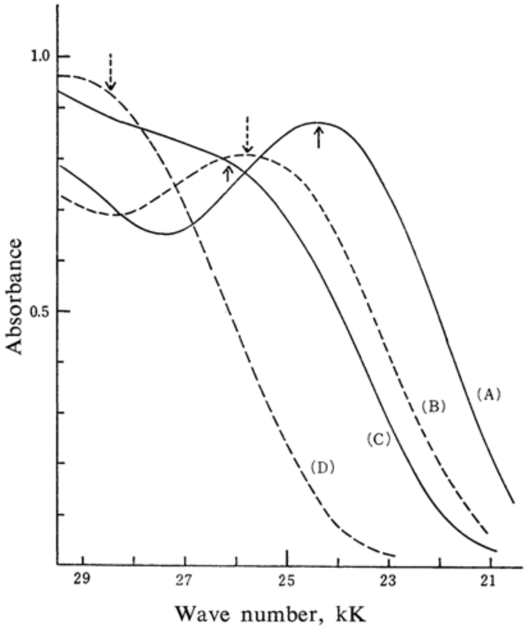

Fig. 1. The charge-transfer absorption bands of PMDA-polymethylbenzene complexes in ethyl acetate (18±1°C).

(A) Hexamethylbenzene (4.0×10^{-2} mol./l.)-PMDA
(B) Pentamethylbezene (7.3×10^{-2} mol./l.)-PMDA
(C) Durene (1.5×10^{-1} mol./l.)-PMDA
(D) Mesitylene (2.4×10^{-1} mol./l.)-PMDA
The concentration of PMDA is 1.0×10^{-2} mol./l.

Since the charge-transfer absorptions in general are expected to be sensitive to the solvent polarity, the charge transfer bands of the well-known chloranil complexes with polxmethylbenzenes or pyrene were studied in several solvents; the results are summarized in Table I. It may be seen from this table that the charge-transfer band shows a hypsochromic shift as the solvent polarity increases. In addition, the apparent peak height decreases considerably if the donor-acceptor pair is present in a polar medium. The frequency of the charge-transfer band ν is correlated with the electron affinity (E_A) of the acceptor and the ionization potential (I_D) of the donor by Eq. 1:

$$h\nu = I_D - E_A + \Delta \tag{1}$$

where Δ is a correction term mainly due to

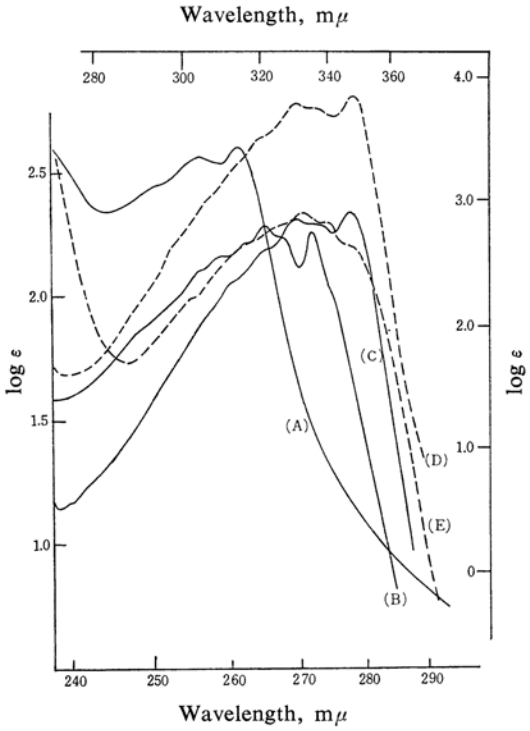

Fig. 2. Absorption spectra of PMDA and polymethylbenzenes used in the experiments. The upper and the right scales are to be used for PMDA only.
(A) PMDA (B) Mesitylene (C) Durene (D) Pentamethylbenzene (E) Hexamethylbenzene

TABLE I. THE CHARGE-TRANSFER ABSORPTION BANDS OF CHLORANIL COMPLEXES IN VARIOUS SOLVENTS*1

Donor	Solvent CCl$_4$	Butyl ether*2	Ethyl acetate
Mesitylene	23.5±0.1	24.4	24.2±0.1
Durene	20.5±0.1	21.3	21.9±0.1
Pentamethylbenzene	20.3±0.1	20.8	21.4±0.1
Hexamethylbenzene	19.2±0.1	19.8	20.1±0.1
Pyrene	16.5±0.1	—	17.5±0.1

*1 The values are expressed in kilo-kaysers (kK).

*2 Quoted from the Ref. 6.

the Coulombic interaction of D$^+$ and A$^-$.[9] Thus, the hypsochromic shifts observed above may be interpreted mainly as due to the decrease in the electron affinity of the acceptor level as a consequence of the solvation by the polar molecules. If the last term in Eq. 1 is approximately constant among the complexes with donors of a similar type, the band separation among the polymethylbenzene-chloranil complexes in ethyl acetate can be used to estimate the difference in the ionization potentials of the donors in the same solvent. Using these values and taking hexamethylbenzene as the standard, the location of the charge-transfer band of each polymethylbenzene-PMDA complex is calculated. The values are indicated by the arrows in Fig. 1. Then the newly-appeared absorptions of the polymethylbenzene-PMDA complex are resolved into two bands of a different nature. The first band is found at the frequency indicated by the arrow in Fig. 1; it is, of cause, believed to originate from the transfer of an electron from the highest-occupied donor orbital to the lowest unoccupied acceptor orbital. The band moves to the longer-wavelength region as the number of methyl groups increases. The second band, with a rather diffuse shape, is noticed clearly on the higher frequency side in the case of the hexamethylbenzene complex in Fig. 1. The first band becomes less distinct in comparison with the second band as the number of methyl groups decreases. In the case of the mesitylene complex, finally, the first band appears to be merged in the second band. The origin of this second band is not certain. Obviously, however, it is not the so-called "second charge-transfer band," which is defined as due to the electron transfer from the second highest occupied orbital of the donor to the lowest unoccupied orbital of the acceptor. It is more likely that the second band comes from the combination of many complexes with different geometries and electronic states, including the contact charge transfer.[10]

No matter where they come from, these newly-appeared absorption bands can be used to estimate the equilibrium constants of the charge-transfer complexes in the solution. It must be remembered, however, that the equilibrium constants thus obtained are contributed by charge-transfer complexes of various types.[11] The original Benesi-Hildebrand equation[12] for a one-to-one complex was modified into the follwing form:

$$\frac{1}{(\mathrm{ArH})}=\frac{[\mathrm{PMDA}]\times l}{\mathrm{ABS}}\times K\varepsilon-K \qquad (2)$$

where (ArH) is the concentration of methylbenzenes in mole fractions; [PMDA] is the concentration of PMDA in mol./l.; l stands

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[9] J. N. Murrell, *Quart. Revs.*, **16**, 191 (1962).

[10] R. S. Mulliken, *Rec. trav. chim. Pays-Bas*, **75**, 845 (1956).

[11] L. E. Orgel and R. S. Mulliken, *J. Am. Chem. Soc.*, **79**, 4839 (1957).

[12] H. A. Benesi and J. H. Hildebrand, ibid., **71**, 2703 (1949).

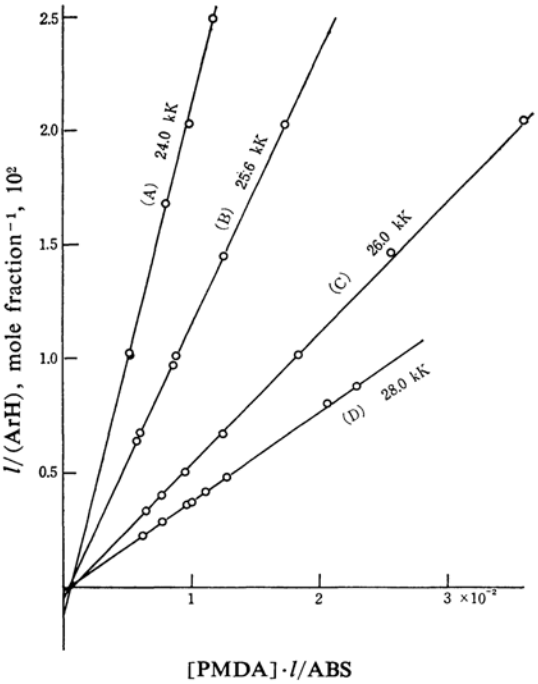

Fig. 3. Determintion of K and $K\varepsilon$. The concentration of each component is as follows.
(A) Hexamethylbenzene: 0.4×10^{-1}—1.0×10^{-1} mol./l.
(B) Pentamethylbenzene: 0.4×10^{-1}—1.6×10^{-1} mol./l.
(C) Durene: 0.5×10^{-1}—3.0×10^{-1} mol./l.
(D) Mesitylene: 1.2×10^{-1}—4.6×10^{-1} mol./l.
and PMDA: 0.1×10^{-1} mol./l. or less
The plots are made after converting the donor concentrations into mole fractions.

for the length of the absorption cell in cm.; K is the equilibrium constant (dimensionless quantity), and ABS and ε are the absorbance and the extinction coefficient (l./mol.) for the complex at a particular wavelength respectively.

Plotting 1/(ArH) vs. [PMDA]×l/ABS at a fixed wavelength yields the equilibrium constant and $K\varepsilon$ as the intercept and the slope of the straight line respectively. Examples are shown in Fig. 3, where the plots are made by using the data of four polymethylbenzene complexes at their absorption maxima. Rather low donor concentrations were used in these experiments because of the limited solubilities. The equilibrium constants of the complexes, however, hardly ever exceed ten, as may be found below. Therefore, a simple calculation shows that the concentrations of the complexed species are negligibly small in comparison with that of the added donor in the experiments. Thus the basic condition for the applicability of the Benesi-Hildebrand equation is fulfilled. The plotting of the experimental data as in Fig. 3 gives a straight line and verifies the correctness of the treatment. The equilibrium constants and $K\varepsilon$'s were evaluated by applying the method of least squares to the data at various frequencies of the absorption bands; an example is shown in Fig. 4. The arithmetic means of the values obtained over the absorption band of each complex are summarized in Table II. The equilibrium constants of the methylbenzene-chloranil complexes are also quoted from Smith's data⁶⁾ in the third column of Table II. The trends in both

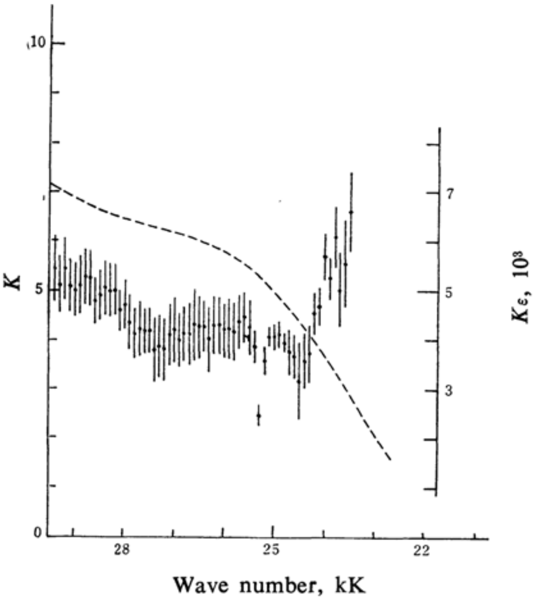

Fig. 4. The stability constant K as calculated by the modified Benesi-Hildebrand equation at various positions of the charge-transfer band of durene-PMDA complex in ethylacetate (18°C).
Molar fractions were used in the calculation as the units of donor concentration. The dotted line represents $K\varepsilon$ which is obtained from the slope of the modified Benesi-Hildebrand equation.

TABLE II. THE EQUILIBRIUM CONSTANTS OF POLYMETHYLBENZENE COMPLEXES WITH PMDA AND CHLORANIL*1

Donor	PMDA*2	Chloranil*3
Mesitylene	1.3±0.3	1.17
Durene	4.2±0.3	3.02
Pentamethylbenzene	5.7±0.3	5.32
Hexamethylbenzene	11.4±0.6	9.08

*1 The values are dimensionless since the donor concentrations were expressed in mole fractions (see the text).
*2 In ethylacetate solution, 18±1°C.
*3 In butylether.⁶⁾

series are in good agreement and indicate that the methyl groups have similar stabilizing effects on the charge-transfer complexes of both types, as was expected. No direct comparison was made of the present results with those reported by Heaton et al.,2) since the donors and the solvents used in the two experiments are quite different. It appears, however, that the equilibrium constants obtained in ethyl acetate are less than those measured in carbon tetrachloride. An attempt is now being made to investigate the solvent effect by employing donors whose equilibrium constants in complex formation can be determined in either solvent with a satisfactory accuracy.

Solid Complexes.—The relative diffuse reflectance, R, of a solid material is correlated with the absorption coefficient, k, by the following Kubelka-Munk remission function, $f(R)$:

$$f(R)=\frac{k}{S}=(R-1)^2/2R \tag{3}$$

where S denotes a scattering coefficient.13) Kortum and Braun successfully applied Eq. 3 in their studies of the pyrene- and anthracene-trinitrobenzene complexes.14)

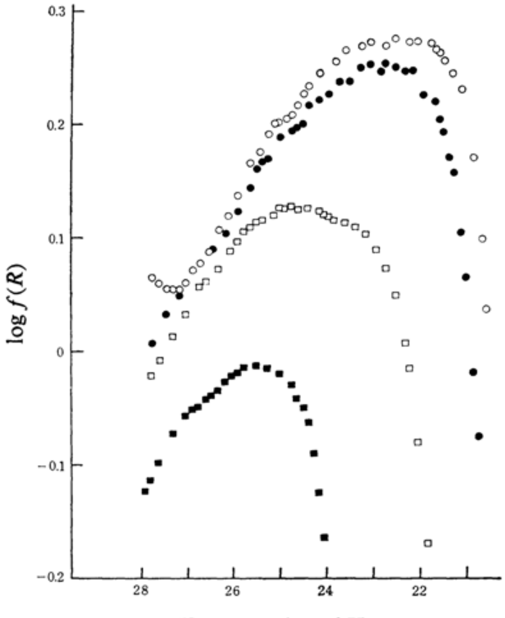

Fig. 5. The diffuse reflectance spectra of PMDA-polymethylbenzene complexes.
Filled square: Mesitylene complex (120 mg./400 mg. talc)
Filled circle: Durene complex (38 mg./400 mg. talc)
Open square: Pentamethylbenzene complex (33 mg./415 mg. talc)
Open circle: Hexamethylbenzene complex (44 mg./405 mg. talc)

The diffuse reflectances of PMDA-polymethylbenzene complexes obtained above were then used to calculate the $f(R)$ function; the results are shown in Fig. 5. When Fig. 5 is compared with Fig. 1, it may be noticed that the spectra of PMDA-polymethylbenzene complexes in the solid state show a regular red-shift from those in solution. The red-shift of the absorption of the durene-PMDA complex, however, is extraordinarily large, showing that the band is situated between those of penta- and hexamethylbenzene complexes. Apparently, the durene molecule takes a more favorable position with regard to the PMDA molecule in the charge-transfer complex than do other polymethylbenzenes. This odd behavior of durene in the solid state will be discussed, together with that of o-xylene, in the following section.

Heaton et al. noticed that the equilibrium constant of the o-xylene-PMDA complex exceeded those of meta and para isomers, and explained this as being due to the dipole moment of o-xylene.2) In solid states, the

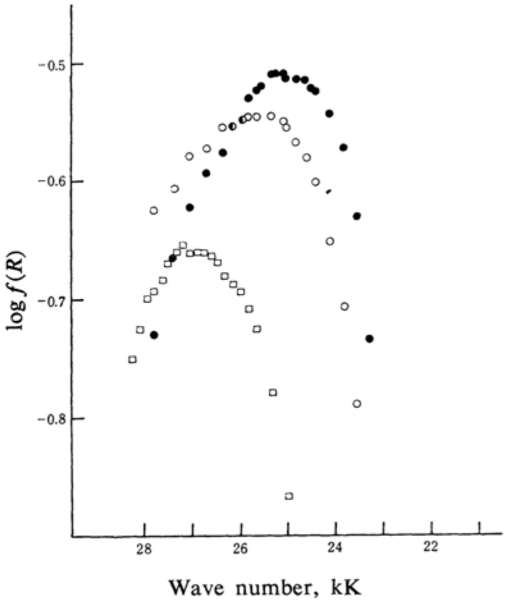

Fig. 6. The diffuse reflectance spectra of PMDA-xylene complexes.
Open circle: o-Xylene complex (53 mg./380 mg. talc)
Open square: m-Xylene complex (43 mg./380 mg. talc)
Filled circle: p-Xylene complex (45 mg./370 mg. talc)

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13) G. Schreyer, *Z. Phys. Chem., N. F.*, **18**, 123 (1958).

14) G. Kortum and W. Braun, ibid., **18**, 242 (1958).

TABLE III. THE MOLAR RATIOS OF PMDA COMPLEXES WITH POLYMETHYLBENZENES

Donor	Sample mg.	Loss mg.	Molar ratio Donor/PMDA	Condition
o-Xylene	81.5	40.0	1.98	80°C/20 mmHg
Tetralin	73.1	40.3	2.01	80°C/20 mmHg
Indan	83.3	43.2	1.99	80°C/20 mmHg
Toluene	62.3	18.5	1.00	70°C/50 mmHg
p-Xylene	68.0	22.2	1.00	80°C/20 mmHg
Mesitylene	104.8	37.0	0.99	70°C/50 mmHg
Durene	20.85	7.95	1.00	120°C/1 atm
Pentamethylbenzene	16.95	7.30	1.01	140°C/1 atm
Hexamethylbenzene	10.70	4.70	1.05	160°C/1 atm

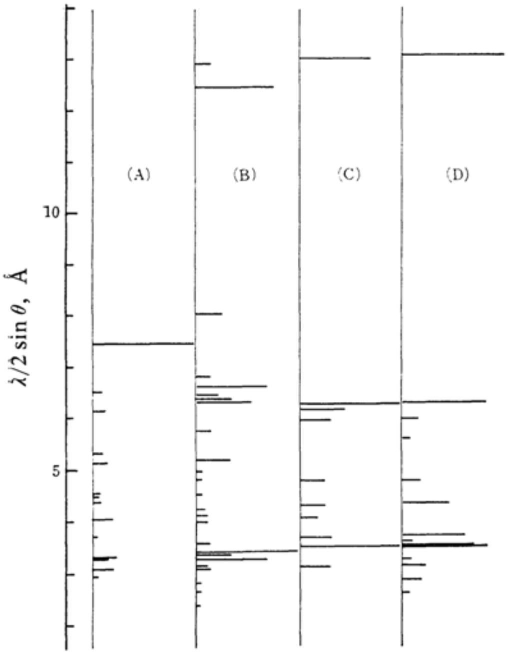


Fig. 7. X-Ray diffraction from the powered samples of the PMDA complexes with xylene isomers and the analogues. The relative intensity of diffraction at a Bragg angle θ is represented by the length of horizontal line.
(A) *p*-Xylene - PMDA (C) Indan-PMDA
(B) *o*-Xylene - PMDA (D) Tetralin-PMDA

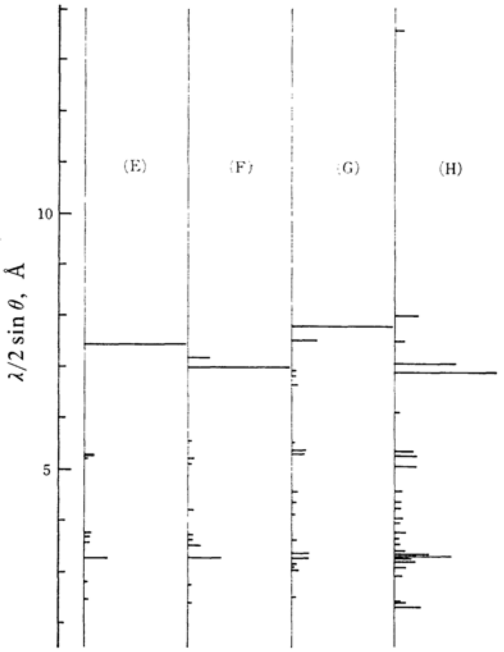


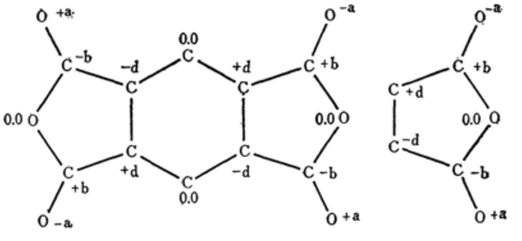
Fig. 8. X-Ray diffraction from the powered samples of the PMDA complexes with highly methylated benzenes.
(E) Hexamethylbenzene-PMDA
(F) Pentamethylbenzene-PMDA
(G) Durene-PMDA (H) Mesitylene-PMDA

absorptions of PMDA-xylene complexes are fairly sharp, as is indicated by $f(R)$ functions in Fig. 6, and simple, well defined structures may be expected for the molecular complexes. A comparison of the peak positions does not give any fruitful results in this case, since the solution spectra of the corresponding complexes are too broad to make a fine argument. The anomalous behavior of *o*-xylene becomes clear when the molar ratios of the donor to the acceptor in xylene-PMDA complexes are compared. The molar ratio was determined by heating the solid samples up to 80°C under reduced pressure and by then measuring the weight decrease due to the loss of the donor molecule. The results are summarized in Table III.

Included in the same table are complexes of tetralin and indan, which are taken as the analogues of *o*-xylene. These *o*-xylene analogues are seen to make definite two-to-one complexes with PMDA. All of the other polymethylbenzenes, dimethoxybenzene isomers, and polycyclic aromatic hydrocarbons, without exception, make one-to-one complexes. Therefore, the formation of two-to-one complexes with PMDA is a special characteristic of the *o*-xylene analogues which have two alkyl groups at adjacent positions on a benzene nucleus.

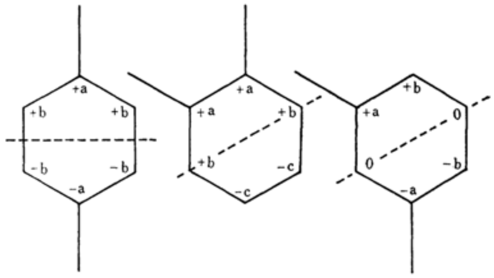
X-Ray diffraction from the powdered sample affords another method to differentiate between two-to-one and one-to-one complexes. As may be seen from Figs. 7 and 8, the two-to-one complexes show characteristic diffraction in the neighborhood of 13Å. Analogously strong peaks are observed around 7Å in the case of the one-to-one complexes. Not only the X-ray diffraction patterns but also the crystalline form of the complex changes vividly from monoclinic needles to leaflets as the molar ratio increases. Obviously, the arrangement of the molecules differs considerably for these two types of solid complexes. As is generally agreed, the smallest unit of a charge-transfer complex with π, π-interaction is a donor and acceptor pair, their molecular planes facing each other. Thus the structure of the one-to-one complex is considered to consist of the layers of the PMDA-donor pair in succession.

The presence and position of the second donor molecule in the two-to-one complex is more difficult to explain. In order to understand this problem more fully, the π-electron systems of PMDA and donor molecules were studied by the simple LCAO MO method. The coefficients of the atomic orbitals contributing to the lowest unoccupied molecular orbital of PMDA are shown in Fig. 9. On the basis of these figures, it is reasonable to consider PMDA as a bifunctional electron acceptor consisting of two molecules of maleic anhydride. The same LCAO MO calculation was made on polymethylbenzenes, assuming an inductive model for the methyl group. The energies and the coefficients of AO's for the



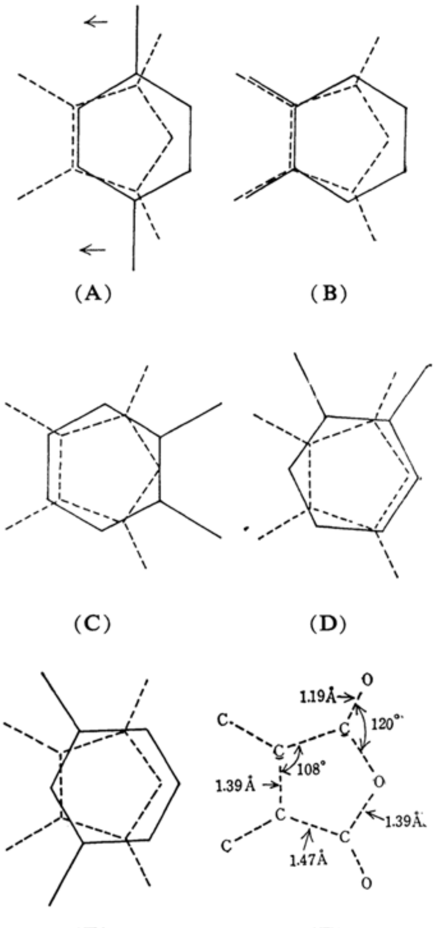
(A) (B)

Fig. 9. The coefficients of AO's in the lowest unoccupied molecular orbital of anhydride.
(A) PMDA: $a=0.317$, $b=0.283$, $d=0.263$
$E=\alpha+0.11\beta$
(B) Maleic anhydride: $a=0.449$, $b=0.401$, $d=0.372$
$E=\alpha+0.11\beta$
The parameters used in the calculation are as the following, $h_{\dot{O}}=1.0$, $h_{\ddot{O}}=2.0$, $k_{C=O}=1.0$, $k_{C-O}=0.8$ and an auxiliary inductive parameter as suggested by Streitwieser (A. Streitwieser, Jr., "Molecular Orbital Theory," John Wiley & Sons, Inc., New York (1961), p. 135).



(A) (B) (C)

Fig. 10. The symmetry properties of the highest occupied MO's of xylene isomers as calculated by the simple LCAO MO method.



(A) (B)

(C) (D)

(E) (F)

Fig. 11. Possible orientations of xylene isomers with respect to PMDA.
(A) *p*-Xylene (B), (C), (D) *o*-Xylene
(E) *m*-Xylene
The dotted lines indicate the right hand half of PMDA molecule. The dimensions as shown in (F) are assumed for PMDA on the basis of the reported X-ray data about maleic anhydride (R. E. Marsh, E. Ubell and H. E. Wilcox, *Acta Cryst.*, **15**, 35 (1962)).

occupied orbitals are listed in Table IV. The highest occupied MO's of xylene isomers are also shown in Fig. 10.

One of the most important conditions for a stable charge-transfer complex is a good overlapping between the acceptor orbital (the MO, as illustrated in Fig. 9(A) in this case) and the donor orbital (the highest occupied orbital of the donor in general). From this point of view, the symmetry properties of the above MO's may be seen to indicate that the anhydride group of PMDA would work as a better electron-accepting site to the donors under consideration than the central benzene ring in the same molecule. In addition to this electronic factor, the van der Waals repulsion should affect, to some extent, the relative orientation of the donor-acceptor pair. The highest occupied molecular orbital of *p*-xylene, for example, is ideal for " lock and

TABLE IV. THE OCCUPIED MOLECULAR ORBITALS OF METHYLBENZENES AS CALCULATED BY SIMPLE LCAO MO METHOD*,**

Toluene						
Energy	(1)	2	3	4	5	6
1.93	0.32	0.39	0.44	0.45	0.44	0.39
1.00	0.00	0.50	0.50	0.50	−0.50	−0.50
0.84	0.55	0.37	−0.24	−0.57	−0.24	0.37
p-Xylene						
Energy	(1)	2	3	(4)	5	6
1.85	0.37	0.43	0.43	0.37	0.43	0.43
1.00	0.00	0.50	0.50	0.00	−0.50	−0.50
0.69	0.54	0.32	−0.32	−0.54	−0.32	0.32
o-Xylene						
Energy	(1)	2	3	4	5	(6)
1.87	0.31	0.42	0.48	0.48	0.42	0.31
0.93	0.24	0.59	0.31	−0.31	−0.59	−0.24
0.73	0.54	0.12	−0.45	−0.45	0.12	0.54
m-Xylene						
Energy	1	(2)	3	4	5	(6)
1.86	0.37	0.35	0.44	0.48	0.44	0.35
0.91	0.66	0.30	−0.24	−0.52	−0.24	0.30
0.78	0.00	0.44	0.56	0.00	−0.56	−0.44
Mesitylene						
Energy	(1)	2	(3)	4	(5)	6
1.77	0.38	0.43	0.38	0.43	0.38	0.43
0.78	−0.50	−0.32	0.25	0.64	0.25	−0.32
0.78	0.00	0.56	0.44	0.00	−0.44	−0.56
Durene						
Energy	1	(2)	(3)	4	(5)	(6)
1.69	0.45	0.38	0.38	0.45	0.38	0.38
0.85	0.61	0.26	−0.26	−0.61	−0.26	0.26
0.50	0.00	0.50	0.50	0.00	−0.50	−0.50
Pentamethylbenzene						
Energy	1	(2)	(3)	(4)	(5)	(6)
1.61	0.52	0.42	0.36	0.34	0.36	0.42
0.67	−0.57	−0.19	0.35	0.60	0.35	−0.19
0.50	0.00	0.50	0.50	0.00	−0.50	−0.50
Hexamethylbenzene						
Energy	(1)	(2)	(3)	(3)	(5)	(6)
1.50	0.41	0.41	0.41	0.41	0.41	0.41
0.50	0.58	0.29	−0.29	−0.58	−0.29	0.29
0.50	0.00	0.50	0.50	0.00	−0.50	−0.50

* An inductive model was used for the methyl group ($h_C = -0.5$).

** The energy (in β units) is shown with respect to α. The integers stand for the numbering of carbon atoms. Parentheses are added if the atom is attached by a methyl group.

key" fitting[2] to the accepting orbital of the anhydride group, as is shown, in Fig. 11(A). The distance between the molecular planes is assumed to be 3.3Å, which is the value commonly found in the cases of chloranil- and trinitrobenzene complexes with aromatic hydrocarbons. Some van der Waals repulsion results from the methyl and carbonyl groups being in an exact superposition. This repulsion is relieved by shifting the donor molecule horizontally in the direction indicated by the arrows. The *o*-xylene analogues represent a case where the van der Waals repulsion between the substituents and PMDA strongly depends on their mutual orientation if the inter-planar distance is held at 3.3Å. In the orientation as is illustrated in Fig. 11(B), a considerable change in the van der Waals repulsion may be expected if the comparison is made between the complexes of *o*-xylene and tetralin or indan. Since all of these *o*-xylene analogues show similar complexing behavior, it is unlikely that a coordination of this type really exists. Furthermore, both models, B and C, may be eliminated by considering the symmetry properties of the MO's concerned. The model D is the only one left as a possible structure. Certainly it is not the best one as judged on the maximum overlap principle. The van der Waals repulsion mentioned above, however, is at a minimum in this configuration. Similar arguments predict model E as the most probable structure for the *m*-xylene - PMDA complex. This situation is rather satisfactory in view of both the electronic interaction and the intermolecular repulsion.

Coming back to the case of the two-to-one complex, the above theoretical considerations do not give any explanation of why it is found only in the *o*-xylene analogue. In any case, however, a donor molecule is taken to be located directly above one of the anhydride groups of PMDA. Therefore, there is not enough room left for another donor on the same side of PMDA. The second donor may come in freely from the back of PMDA, as is shown in Fig. 12. The formation of such a donor-acceptor-donor sandwich, if one exists, should be favored by a strong electron donor such as hexamethylbenzene or anthracene. Since this is not the actual case, however, such a system has very poor prospects to be the unit of the *o*-xylene analogue-PMDA complex in the solid state. As has been pointed out by Heaton et al.,[2] the existence of large dipolement is an important characteristic of the *o*-xylene and its analogue, differentiating them the isomers. The donor-acceptor pair in the charge-transfer complex is also polar by its own nature. Therefore, the truth may be that the second *o*-xylene (or its analogue) is paired off to the first donor-PMDA couple in such a way as to stabilize the whole system in the solid state. The role may be close to that played by the water of crystallization in ionic crystals. Of course, some charge-transfer-type interaction is to be expected between the second donor and the unoccupied anhydride group. Therefore, it may be predicted that the second donor will be found somewhere close to the vacant electron-accepting site of PMDA. The final answer must, however, await the results of the X-ray diffraction and spectroscopic studies of a single crystal of the complex.

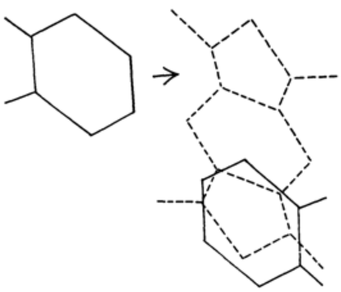


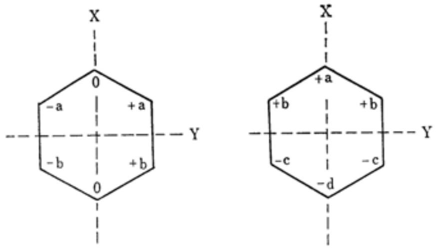
Fig. 12. One of the possible routes for the second donor to approach PMDA.

In the above discussion of the xylene complexes, the second-highest-occupied MO (abbreviated as SHO MO) of the donor is not taken into consideration. This treatment may be justified on the basis of the following facts:

(1) The SHO level of xylene is located between the highest occupied levels of toluene and benzene, as may be seen in Table IV.

(2) No solid complex is formed between benzene and PMDA, while the complex yielded from toluene is rather unstable.

The treatment, however, can not be applied to the highly methylated benzenes any more. In some of these donors, the energy of the SHO MO is too close to that of the highest occupied orbital to be neglected in the discussion. The difference between the highest-occupied and the SHO MO's is seen in their symmetry properties. The highest occupied MO's of mesitylene, durene, penta- and hexamethylbenzenes are shown schematically in Fig. 13(A). It should be noticed here that the coefficients are antisymmetric and symmetric with respect to the x and the y axes respectively. Exactly reverse situations are found for the coefficients in the corresponding SHO MO's (or the counterparts of the degenerate pairs in the cases of mesitylene and hexamethylbenzene), as Fig. 13(B) shows.



(A) (B)

Fig. 13. The symmetry properties of the highest and the second highest occupied molecular orbitals of the highly methylated benzenes.

The lowest unoccupied MO of PMDA, on the other hand, is antisymmetric with respect to the longitudinal axis of symmetry, as is shown in Fig. 9.

As far as the symmetry properties are concerned, therefore, the predicted orientation of the donor molecule with relation to PMDA is approximately ninety degrees apart, depending on the particular orbital used in the interaction. In other words, the electronic interaction between PMDA and the highest occupied MO is counteracted by that due to the SHO MO. The higher the energy level of the SHO MO, the stronger the interaction. If a strong counteraction is exerted, the actual orientation of the donor molecule becomes less favorable to the overlapping between the highest occupied MO and the acceptor orbital. Furthermore, the best orientation of the SHO MO's results in the worst situation for the van der Waals repulsion due to the methyl groups. As may clearly be seen in Table IV, the SHO MO of durene is located considerably lower than those of mesitylene, penta- and hexamethylbenzenes. Therefore, the anomalous peak position observed in the solid spectra of durene-PMDA complex may be explained as being due to the more effective overlapping between the highest occupied MO of the donor and the acceptor orbital than in the cases of other polymethylbenzenes.

The above theoretical prediction seems to explain the behavior of polymethylbenzene-PMDA complexes very well. The findings regarding simple LCAO MO method, however, should be applied to actual cases with great care. It is well known that the quantitative results obtained by the method differ considerably from the true values. Even a qualitative prediction is sometimes in error, as in the case of the iodine-benzene complex.[15] The situation is expected to be a little better for the $\pi-\pi^*$ charge-transfer complexes, where no other arrangement of the donor acceptor pair is conceivable except a sandwich type with their molecular planes facing each other. Many atomic orbitals in both the donor and the acceptor molecules are involved in the overlapping of the MO's. Consequently, a minor change in the relative orientation of the molecules causes an appreciable difference in the overlap integral between the donor and the acceptor orbitals. Therefore, the symmetry consideration of the problem would be more fruitful than it is in the cases of the other type of complexes. Nevertheless, it is advisable to evaluate the results of the simple LCAO MO method with some reservations. Further studies are required to solve the problem.

In summary, the study of PMDA-polymethylbenzene solid complexes reveals many characteristics which are not found in the complexes in solution. These phenomena may be explained as representing the finer differences in the donor properties, such as the polarity of the molecule, the symmetry of the orbitals concerned, and the van der Waals repulsion due to the substituents. The compact and well-defined arrangement of the donor-acceptor pair in the solid state is considered to be responsible for the appearance of these phenomena.

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