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(19) R. H. Baker, L. S. Minckler and A. S. Hussey, *J. Am. Chem. Soc.*, **81**, 2379 (1959).

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Molecular Complexes of Pyromellitic Dianhydride¹

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The ability of pyromellitic dianhydride to form molecular complexes is demonstrated for a large number of compounds. Both solid and solution complexes are formed, although the former have more rigorous steric requirements than the latter. Using binary mixtures of the C₈-aromatic hydrocarbons, competitive experiments were performed to determine relative stabilities of their solid complexes. The phenomenon of solid complex formation limits is discussed. Quantitative data, thermodynamic and spectral, are given for the solution complexes of a family of substituted benzenes. These data are compared with other series of complexes and several correlations are drawn. The free energies of formation indicate that pyromellitic dianhydride is among the strongest acceptor molecules known in complex formation.

Introduction

The first molecular complexes, aromatic hydrocarbons with picric acid, were discovered in 1858,² and a large number of similar complexes have been discovered since.^{3,4} Only a single reference⁵ is known to complexes with pyromellitic dianhydride (abbreviated PMDA, the anhydride of 1,2,4,5-benzenetetracarboxylic acid). That work described PMDA complexes with four compounds: tetralin, anisole, veratrol and hydroquinone dimethyl ether. PMDA, in fact, complexes with a wide variety of aromatic hydrocarbons, heteroaromatic compounds, and even some non-aromatic materials. These complexes are of the charge transfer type⁶ in which PMDA serves as the electron acceptor or π -acid and a large number of organic materials can serve as the electron donor or π -base.

Discussion

PMDA is sparingly soluble in most organic liquids. However, when solid PMDA is mixed with a suitable electron donor, the solid increases in volume strikingly, changes color from white to yellow, orange or red, and becomes warm. If the solid is collected, it is observed that it has gained more weight than is expected by simple mechanical wetting of the crystals. However, most of the solid complexes are not stable in the absence of excess hydrocarbon. These are the qualitative observations accompanying complexing of PMDA with many compounds. The complex formation can be verified by ultraviolet absorption spectra of the colored solutions. These complexes, both the solids and the solutions, have a 1:1 ratio of the donor and acceptor molecules. This was determined for the solids by weight gain and for the

solutions by studying the effect of dilution on the extinction coefficient.

Information obtained on the formation and stability of solid complexes, on the qualitative aspects of solution complexes, and on thermodynamic and spectral data of solution complexes will be discussed in turn.

Solid Complexes.—The formation of solid complexes appears to have important steric as well as electronic demands. Benzene and all the methyl-substituted benzenes up to durene were shown to form solid complexes. On the other hand, none of the following materials form solid complexes at room temperature: ethylbenzene, cumene, *t*-butylbenzene, *o*- and *p*-ethyltoluene, and a mixture of diisopropylbenzenes. The fact that compounds containing these electron-donating substituents do not undergo solid complex formation must mean that the steric requirements are severe. It is possible that the solid complexes are graphite-like with the aromatic compounds in the space between planes. Calculations of closest approach to form such a sandwich structure show that ethyl-substituted compounds should be much less stable than methyl substituted.⁷ Both chlorobenzene and *o*-dichlorobenzene fail to form solid complexes, but apparently for electronic reasons since chloro groups are about the same size as methyls. It is interesting to note that at 0° *o*-ethyltoluene, chlorobenzene and *o*-dichlorobenzene form weak complexes.

The relative stabilities of several complexes were determined by competitive experiments. In these experiments a pair of aromatic compounds was mixed with an insufficient amount of PMDA. The mother liquor was separated from the solid complex and examined to determine the new ratio of the aromatic pair. Assuming that the compound suffering the greater depletion formed the more stable complex, in one series the following order was found: durene > *o*-xylene > pseudocumene > mesitylene.

(1) Presented, in part, to the Division of Petroleum Chemistry, American Chemical Society, Boston, Mass., April, 1959.

(2) J. v. Fritsche, *J. prakt. Chem.*, **73** [1], 282 (1858).

(3) P. Pfeiffer, "Organische Molekülverbindungen," 2nd edition, Ferdinand Enke, Stuttgart, Germany, 1927.

(4) L. J. Andrews, *Chem. Revs.*, **54**, 713 (1954).

(5) R. Seka and H. Sedlatschek, *Monatsh.*, **47**, 516 (1926).

(6) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952).

(7) R. E. Merrifield and W. D. Phillips, *ibid.*, **80**, 2778 (1958).

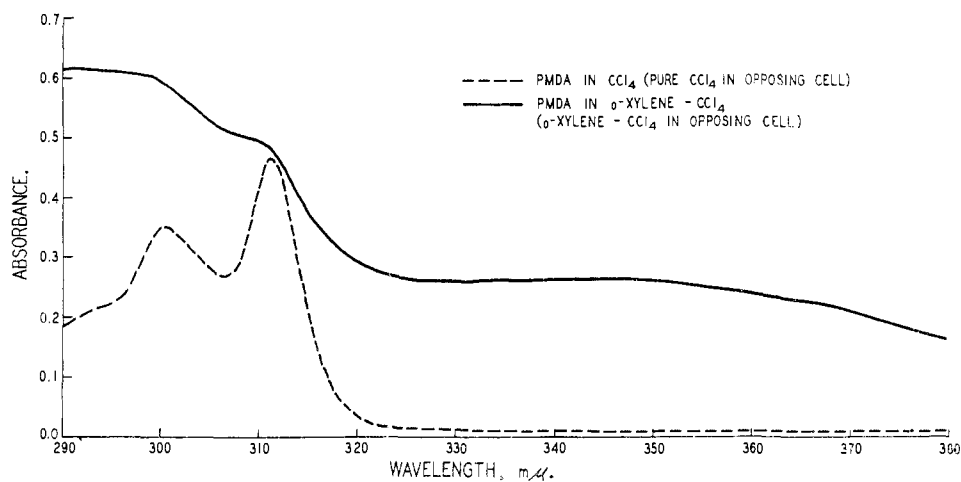


Fig. 1.—Typical spectra of complexed and uncomplexed PMDA.

More extensive competitive studies were made on the solid complex formation with the C_8 -aromatic hydrocarbons. Experiments were run on all of the six possible pairs from these four compounds. In all cases but one, complexing behavior changes below a certain limit of concentration of the stronger complexing hydrocarbon. The limit was determined in a series of experiments with successive dilutions of the stronger complexor (Table I). At

TABLE I
CONCENTRATION LIMITS FOR SOLID COMPLEXING FOR
 C_8 AROMATICS (25°)

Pair of components	Concentration of first component at limit, wt. %	Behavior at limit
<i>o</i> -Xylene-ethylbenzene	17	Complexing stops at 17% <i>o</i> -xylene
<i>m</i> -Xylene-ethylbenzene	ca. 80	Complexing stops at about 80% <i>m</i> -xylene
<i>p</i> -Xylene-ethylbenzene	33	Complexing stops at 33% <i>p</i> -xylene
<i>o</i> -Xylene- <i>p</i> -xylene	34	Complexing continues at limit ratio
<i>p</i> -Xylene- <i>m</i> -xylene	49	Complexing continues at limit ratio
<i>o</i> -Xylene- <i>m</i> -xylene	<10	

the point of the limit, further addition of PMDA will not change the concentration of the two hydrocarbons. For example, when a mixture containing 35% of *o*-xylene and 65% ethylbenzene is treated with sufficient PMDA, the filtrate contains 17% of *o*-xylene. Further treatment with PMDA fails to form a complex or to change the composition of the filtrate. This is due to the fact that the free energy of *o*-xylene in solution below 17% is too low to have the complex in equilibrium with it. The same phenomenon accounts for the lack of drying of gases by dehydrating agents when the water vapor pressure of the gas is below a given limit.

If we compare the limits obtained for the three xylene-ethylbenzene pairs, we can say qualitatively that the order of solid complex stability is: *o*-xylene > *p*-xylene > *m*-xylene >>> ethylbenzene. More quantitative data on equilibrium constants in a later section agree with this order.

The complexing behavior of the xylene pairs is different from the xylene-ethylbenzene pairs. While the latter cease complexing at the limit, the former continue to complex. This probably means that the two xylenes are complexing independently at a ratio that represents their relative complexing abilities. Fortunately, for two of the pairs the free energy limit is not reached at the constant ratio describing the relative stabilities. These pairs, *o*-xylene-*p*-xylene and *p*-xylene-*m*-xylene, continue to complex at the unchanging ratio. No limit was found down to 10% *o*-xylene in the *o*-xylene-*m*-xylene pair. A limit probably exists, but complex formation is very slow at low *o*-xylene concentrations so the limit was not determined.

The ability to complex is reduced with increasing temperature. This was shown for the three pairs involving the xylenes and ethylbenzene. In each case the higher the temperature, the higher the limit; *i.e.*, the less stable the complex. For example, the *o*-xylene-ethylbenzene limit changes from 6% *o*-xylene at -29° to 24% at 40°.

The rate of formation of solid complexes are difficult to measure accurately, but some qualitative observations were made. Pure *o*- or *p*-xylene complexes in less than one-half hour at room temperature. *m*-Xylene or mixtures, however, are much slower. Lower temperatures slow the rate of complexing. The *p*-xylene-ethylbenzene mixture at -29° continues to complex for at least four days.

Solution Complexes.—Complexes in solution usually absorb light in the visible region, but a more sensitive measure involves ultraviolet spectra. A typical ultraviolet absorption spectrum (Fig. 1) shows that the absorption peak of the complex is easily detected. Using this method, a series of pure compounds was mixed with PMDA to determine if solution complexes are formed. Table II lists these materials and their complex absorption maxima where appropriate.

It appears that the formation of PMDA complexes in solution is determined largely by electronic factors. Size cannot be too serious a consideration, for benzene with substituents from methyl to *t*-butyl all form complexes. Of those tried, all aromatic compounds with electron-donating substituents formed complexes. Even certain ambivalent

TABLE II
COMPLEXES OF PMDA WITH EXCESS PURE SUBSTRATE
AT 26°

Substrate	λ_{\max} , m μ	Complex	PMDA	Remarks
C ₆ H ₆ S	Thiophene	340	..	
C ₅ H ₅ N	Pyridine	No apparent complex
C ₆ H ₅ Cl	Chlorobenzene	340	311	
C ₆ H ₆	Benzene	330	311	
C ₆ H ₅ O	Phenol	Yellow solid complex; no solution complex
C ₆ H ₇ N	Aniline	^a	..	Red ^b
C ₇ H ₅ N	Benzonitrile	..	317	No apparent complex
C ₇ H ₅ O	Benzaldehyde	No apparent complex
C ₇ H ₈	Toluene	346	311	
C ₇ H ₉ O	Anisole	385	311	
C ₇ H ₇ N	N-Methylaniline	^a	..	Red ^b
C ₈ H ₈	Styrene	384	..	
C ₈ H ₉ O	Acetophenone	No apparent complex
C ₈ H ₁₀	Ethylbenzene	346	311	
C ₈ H ₁₀	<i>o</i> -Xylene	342	311	
C ₈ H ₁₀	<i>m</i> -Xylene	344	311	
C ₈ H ₁₀	<i>p</i> -Xylene	354	311	
C ₈ H ₁₁ N	N,N-Dimethylaniline	^a	..	Dark red solution
C ₉ H ₁₂	Isopropylbenzene	344	300	
C ₁₀ H ₈	Naphthalene	407	..	
C ₁₀ H ₁₂ O	Anethole	^a	..	Blood red solution
C ₁₀ H ₁₄	<i>t</i> -Butylbenzene	348	300	
CCl ₄	Carbon tetrachloride	..	315	No apparent complex
C ₃ H ₃ N	Acrylonitrile	..	300	No apparent complex
C ₄ H ₅ O ₂	Vinyl acetate	..	312	No apparent complex
C ₅ H ₈	Isoprene	347	308	
C ₅ H ₁₀	1-Pentene	..	311	No apparent complex

^a Absorption of the substrate interferes with absorption maximum of complex. ^b Initial complex disappears as amine reacts with PMDA.

substituents do not prevent complex formation; *i.e.*, chlorobenzene and styrene form complexes. On the other hand, electron-withdrawing substituents prevent complex formation at least at 26°; *i.e.*, acetophenone, benzaldehyde and benzonitrile do not complex. In addition, naphthalene complexes very well and thiophene complexes, but pyridine does not. Isoprene, a moderate electron donor, is the only one of the non-aromatic compounds tried which formed a complex in solution.

Thermodynamic and Spectral Data for an Aromatic Family of Complexes.—Having found that PMDA complexes with a variety of aromatic compounds, the question remained as to whether PMDA was typical of complexing agents such as picric acid. In order to check this, the complex equilibrium constants for a series of substituted benzenes were determined. One of the more common tools used to determine complex formation involves measurement of absorption spectra of solutions of complexes. Benesi and Hildebrand (B-H), in a classic paper,⁸ elucidated a simple approach to determining equilibrium constants and extinction coefficients for complex formation. Recently, however, much discussion has appeared in the literature on the interpretation of the absorption spectra of complexes.^{4,9-13} For this reason, it

(8) H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

(9) S. P. McGlynn, *Chem. Revs.*, **58**, 1113 (1958).

(10) N. S. Bayliss and C. J. Brackenridge, *J. Am. Chem. Soc.*, **77**, 3959 (1955).

(11) L. E. Orgel and R. S. Mulliken, *ibid.*, **79**, 4839 (1957).

(12) J. N. Murrell, *ibid.*, **81**, 5037 (1959).

(13) N. J. Rose and R. S. Drago, *ibid.*, **81**, 6138 (1959).

is necessary to examine the various arguments in order to determine the value of spectra in explaining complex formation.

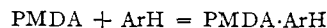
This type of complex which is believed to involve actual partial exchange of electrons is probably better described as a charge-transfer complex⁸ than a π -complex. Charge-transfer in a simple 1:1 or 2:1 complex does not explain all the spectral data, however. At least some of the absorption is due to electronic excitation caused by close contact of the donor and acceptor molecules even if the contact is temporary. The effect has been called a "physical perturbation"¹⁰ but more recently by Orgel and Mulliken it is called contact pair absorption.¹¹ This is an important phenomenon because absorption due to contact pairs may exceed absorption due to classical complexes in certain cases.¹²

It is believed, however, that the equilibrium constants as determined by the B-H method are real thermodynamic quantities, but that the equilibria studied include all types of complex formation from classical to contact.⁹

The meaning of the extinction coefficient remains debatable. In no cases reported have the extinction coefficients increased regularly with increasing complex stability as would be expected.¹² Within some of the more stable complex series the extinction coefficients tend to increase with increasing stability. The best of these, chloranil,¹² tetracyanoethylene (TCNE)⁷ and PMDA, show imperfect correlations of this nature. Most others fail, and some even show decreasing extinction coefficients with increasing complex stability.⁸

A recent paper¹³ has suggested a more rigorous mathematical modification of the B-H approach. This rigorous treatment reduces to the B-H treatment in the work under discussion here since calculations show that the added terms in the detailed approach are negligible for this system. In light of the above information, the B-H approach was used as a simple, but meaningful, method for determining equilibrium constants for a family of complexes.

The B-H equation results from the algebraic addition of Beer's law for absorption due to complex formation and the equilibrium expression for the equation

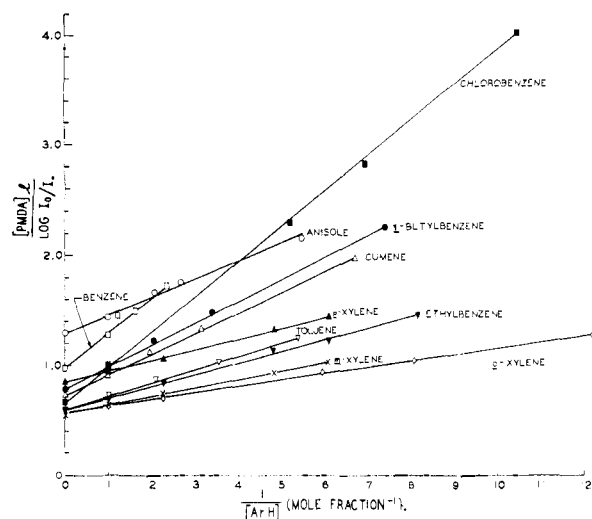


The final equation including assumptions is

$$[\text{PMDA}] l / \log I_0/I = (1/K \epsilon_0) 1/[\text{ArH}] + 1/\epsilon_0$$

where [PMDA] is the concentration of PMDA in m./l., l = length of absorption cell in cm., $\log I_0/I$ absorbance at λ_{\max} for the complex, K is the equilibrium constant (dimensionless because of mole fraction for aromatic concentration), ϵ_0 is the extinction coefficient in l./m. cm., [ArH] is the concentration of the aromatic compound expressed as a mole fraction. The data obtained by plotting the measured left-hand term *vs.* $1/[\text{ArH}]$ are shown in Fig. 2 for the entire series. The values of K and ϵ_0 calculated from the slopes and intercepts are given in Table III.

The evidence is clear from the plots that we are dealing only with 1:1 complexes. The equilibrium

Fig. 2.—Determination of K and ϵ .

constants for PMDA are slightly larger than those for TCNE⁷ for any given substituted benzene. If the small temperature difference and solvent differences between the TCNE work (22°, CH₂Cl₂) and this work (25°, CCl₄) can be ignored, this means that PMDA is among the strongest complexers known for aromatic hydrocarbons and their derivatives. (A number of compounds related to PMDA are poor complexers; see Experimental.)

TABLE III
EQUILIBRIUM AND SPECTRAL DATA FOR PMDA AND AROMATICS AT 26° (CCl₄ DILUENT)

Compound	K_{eq}	$-\Delta F^0$, cal.	λ_{max} , m μ	ϵ_{max} , c.m. ⁻¹	Total PMDA soluble in pure compound, m.l. ⁻¹ × 10 ³	Ionization potentials, kcal.
Benzene	3.05	660	330	1030	0.559	21.3 ^a
Toluene	5.03	960	346	1670	2.86	20.3 ^a
<i>o</i> -Xylene	10.3	1390	342	1710	1.34	19.1 ^b
<i>m</i> -Xylene	7.60	1220	344	1750	10.68	19.8 ^a
<i>p</i> -Xylene	8.25	1260	354	1210	4.44	19.5 ^a
Ethylbenzene	5.68	1030	346	1670	4.08	20.2 ^b
Isopropylbenzene	3.86	800	344	1380	1.20	20.2 ^a
<i>t</i> -Butylbenzene	4.00	820	348	1260	1.15	19.6 ^a
Anisole	7.75	1220	385	775	13.7	8.20 ^c
Chlorobenzene	2.08	440	340	1490	7.32	9.07 ^a
Carbon tetrachloride	0	..	311	1300	0.275	..

^a K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957). ^b See ref. 17.

The data in Table III do not show any simple correlations between λ_{max} and K . Even ϵ_{max} does not correlate too well with K , but it is more in line than ϵ_{max} 's for most series of complexes.¹² Sometimes ϵ_{max} shows a linear relationship to λ_{max} ,¹⁴ but this is not true for PMDA complexes. A correlation can often be drawn between the free energy of formation (ΔF^0) of the complex and the ionization potential of the donor molecule^{7,14} because both

(14) H. McConnell, J. S. Ham and J. R. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

phenomena require the donor molecule to reach a similar ionic or excited state. Actually, a good straight line can be drawn in a plot of ΔF^0 and ionization potential for the first six compounds in Table III. The other members of the series do not fit at all. This is similar to the experience with TCNE and remains to be explained. Attempts to correlate ionization potentials with $\bar{\nu}_{max}$ have even less success in the PMDA series than other series.^{7,14} It should be noted that PMDA complex stabilities show no correlation with Hammett's σ^- or σ^+ values.

The column giving solubility data for PMDA in the various aromatic compounds show that the solubility approach³ to determining complex equilibrium constants fails completely in this series.

Table IV compares the relative stability constants for a common series of complexes of PMDA, picric acid¹⁵ and TCNE. With exception of the weakest complexes, the relative stabilities for the three sets show a remarkable consistency in the

TABLE IV
RELATIVE STABILITIES FOR THREE SETS OF AROMATIC COMPLEXES (*p*-XYLENE = 1.00)

Compound	PMDA ^a	PA ^b	TCNE ^c
Benzene	0.37	0.70	0.26
Toluene	0.61	0.84	.48
<i>o</i> -Xylene	1.25	1.03	.91
<i>m</i> -Xylene	0.92	0.98	.79
<i>p</i> -Xylene	1.00	1.00	1.00
Ethylbenzene	0.69	0.74	..
Cumene	.47	.59	..
<i>t</i> -Butylbenzene	.48	.51	..
Anisole	.94	..	0.58
Chlorobenzene	.25	..	0.10

^a Data from this paper at 26°; solvent, CCl₄; actual *p*-xylene K = 8.25. ^b Picric acid data from ref. 15 at 18° solvent, CHCl₃; actual *p*-xylene K = 0.61 l./m. ^c Tetracyanoethylene data from ref. 7 at 22°; solvent, CH₂Cl₂; actual *p*-xylene K = 7.64.

effect of substituents. It is of interest to note that a series of substituted naphthalene complexes with picric acid exhibits a similar pattern with respect to substituents.¹⁶ The pattern exhibited in all these series^{3,7,15-17} shows that electron-donating groups on the donor molecule enhance the stability of the complex. As methyl substituents are added the complex stability increases to a maximum at hexamethylbenzene. The size of the donating group plays a role too; ethylbenzene, cumene and *t*-butylbenzene all have equilibrium constants which indicate that bulky substituents have a destabilizing effect. Anisole with a bulky but powerful electron-donating substituent has a lower equilibrium constant than would be expected from electron release data. Methyl groups appear to be at an optimum with respect to size and electron-donating ability. Larger groups regardless of their donating abilities are less effective.

The most interesting discrepancy between this and earlier work occurs in a comparison of the xy-

(15) H. D. Anderson and D. L. Hamnick, *J. Chem. Soc.*, 1089 (1950).

(16) P. D. Gardner, R. L. Braudon, N. J. Nix and I. Y. Chang, *J. Am. Chem. Soc.*, **81**, 3413 (1959).

(17) W. C. Price, *Chem. Revs.*, **41**, 257 (1947).

lene isomers. In the PMDA series the *o*-xylene complex is considerably more stable than the other xylene complexes. This enhanced stability is difficult to explain, for *p*-xylene might be predicted to give the most stable complex with PMDA because of possible "lock and key" fit. The observed stability may be related to the fact that *o*-xylene has the largest dipole moment of the three.

Up to now the best acceptor molecules in charge-transfer complexes have had cyano or nitro groups. The current work shows that the anhydride group belongs in the same category. Unfortunately, data are not available to make a meaningful comparison of the relative efficacy of these substituents. The most effective substituents for the acceptor molecule have in common the fact that they are in the same plane as the aromatic or olefinic nucleus. Other good electron-withdrawing groups which can in part lie outside of this plane have not been reported to be favorable substituents; *i.e.*, carbalkoxy alkyl carbonyl, sulfonic acid, etc.

Experimental

Purification of Materials.—The PMDA used was commercial material available from du Pont which was purified by recrystallizing it twice from methyl ethyl ketone. The recrystallized PMDA had the theoretical neutral equivalent.

All of the aromatic compounds used were reagent grade. In addition, for the quantitative runs, each one was distilled from PMDA below 50° at reduced pressure in order to remove traces of water or extraneous impurities which might complex with PMDA. The carbon tetrachloride used as a diluent was treated in the same way.

Solid Complex Formation.—The usual method of complex formation involved mixing PMDA with an excess of the aromatic compound. The mixture was then filtered and the liquid portion analyzed. In a typical experiment 10 g. (0.046 mole) of PMDA was mixed with 20 ml. (17.3 g., 0.163 mole) of a 50:50 mixture of *p*-xylene and ethylbenzene at 25°. The mixture was left overnight and then filtered; the yellow solid weighed 18.5 g. and the filtrate 7.5 g. Mechanical losses amounted to 1.3 g., probably by evaporation during filtration. Because of the close boiling points of *p*-xylene and ethylbenzene, the effect of the evaporation loss upon the ratio of the two is negligible.

All PMDA, free or as part of the sparingly soluble complex, was removed from the filtrate by extraction with 5% sodium hydroxide solution. The hydrocarbon was washed with water and dried with magnesium sulfate and analyzed by ultraviolet absorption. The analysis showed 33% *p*-xylene and 63% ethylbenzene. In order to have this composition, 4.38 g. (0.0402 mole) of *p*-xylene had to be removed by complexing. This would correspond to an 87% yield in forming a 1:1 complex between *p*-xylene and PMDA. The wet cake was 8.5 g. heavier than the original PMDA

so the additional 4.1 g. would be in the form of filtrate, merely wetting the cake. This latter observation was confirmed by experiments with ethylbenzene which does not form a solid complex but does wet the cake.

The composition of the complex was determined by analysis of the distillate obtained by heating the complex under vacuum. In a typical experiment at 20 mm. pressure, rapid evolution of the hydrocarbon starts at 60°, is half complete at 80°, and 90% complete at 135° and continues slowly to about 200°. The first distillate usually has the composition close to that of the filtrate. The latter distillation cuts approach 95% purity of the complexed aromatic compound.

Analysis of the xylene mixtures was carried out, in general, by standard ultraviolet procedure. In cases involving *p*-xylene, freezing points were also used and compositions were determined from phase diagrams. In all cases the two methods checked.

Qualitative Spectra.—The determination of the absorption peaks of various compounds was made by adding an excess of recrystallized PMDA to the pure compound. The supernatant liquid was examined spectrophotometrically after standing overnight.

Typical Quantitative Spectral Run.—A saturated solution of PMDA in the aromatic compound under examination was prepared by heating an excess of PMDA in the aromatic compound and allowing the material to stand for several days at room temperature. Aliquots of the saturated solution were taken and the solubility of PMDA was determined by titration with standard base. Dilutions for spectral runs were made using the saturated solutions with additional amounts of the complexing aromatic compound and carbon tetrachloride as desired.

The spectra were determined in 1-cm. cells in a Cary recording spectrophotometer, model 14. The temperature of the solutions during the measurements was 26.0 ± 0.5°. Small temperature variations made no difference in the absorption spectra. Additional measurements from 22 to 28° showed negligible effect on the absorption spectra.

Several checks were made to determine whether equilibrium was obtained before the measurement was made. It was shown that identical spectra are observed whether the measurement was made 1 minute after mixing the solutions or 3 days after.

In order to check whether carbon tetrachloride had any tendency to complex with PMDA, some absorption spectra were run with mixtures of carbon tetrachloride and chloroform. The extinction coefficient for PMDA is essentially invariant in solutions ranging from 100% carbon tetrachloride to 50% carbon tetrachloride and 50% chloroform.

PMDA Substitutes.—A number of compounds related to PMDA were also tested to see if they formed solid complexes at room temperature. To check these, a 70:30 mixture of *p*-xylene-ethylbenzene was used as standard. As the test for complexing, the ratio of the solvent mixture was checked to see if a change occurred. The compounds analyzed included pyromellitic acid, dimethyl pyromellitate, tetramethyl pyromellitate, pyromellitimide, pyromellityl chloride and bithiopyromellitic dianhydride. Only pyromellityl chloride showed any signs of complexing, and it was much weaker than PMDA.