

AROMATIC MOLECULAR COMPLEXES OF THE ELECTRON DONOR-ACCEPTOR TYPE

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I. INTRODUCTION

At the time of publication of Pfeiffer's (235) classic review, *Organische Molekülverbindungen*, it was recognized that some aromatic hydrocarbons and certain of their substitution products could, in apparent violation of existing rules of chemical bonding, undergo additive combination with other organic compounds such as quinones, polynitroaromatics, and maleic anhydride and with inorganic compounds such as sulfur dioxide (205), silver perchlorate (146), and hydrogen bromide (20). In certain cases the resulting products were characterized as solids the compositions of which could be represented as simple molecular ratios, usually

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1:1, of the component parts. In other instances the interaction products were of sufficiently low stability so that their formation could be recognized only through the changes in color or other physical properties which resulted when the reactants were mixed in solution.

To explain the nature of the coördinate link between the components of this type of complex, Pfeiffer postulated the existence of secondary valence forces within aromatic nuclei which were susceptible to saturation through interaction with quinones and various other molecules. In recent years significant advances in the elucidation of the chemical and physical properties of aromatic addition complexes have led to a more precise description of these bonding forces. A large number of molecular complexes are now recognized which owe their existence to the capacity of aromatic molecules to function, by sharing their π electrons, as electron donors (213). In all such complexes the second component, by nature an electron acceptor, is additively combined with the aromatic nucleus by a process which must involve to some degree its acceptance of negative charge from that nucleus.

This review describes the developments since the appearance of Pfeiffer's book, both from an experimental and a theoretical point of view, which have led to the present conception of the structures and of the bonding forces between components of this type of aromatic complex.² Although considerable attention is given to the physical methods which have been used so successfully to demonstrate the existence and properties of the less stable complexes, no attempt is made here to present an exhaustive tabulation of the physical properties of the many complexes which are known. However, a summary is presented of the various types of electron acceptors which undergo coördination with aromatic substances. No detailed treatment of the chemistry of quinhydrone is presented except as it is pertinent to the general question of the structure of molecular complexes.

Certain types of associated substances which involve aromatic materials do not qualify for inclusion in this review as products of donor-acceptor interaction. In particular may be mentioned clathrate compounds such as $\text{Ni}(\text{CN})_2 \cdot \text{NH}_3 \cdot \text{C}_6\text{H}_6$ and those of hydroquinone with methanol, rare gases, and other small molecules and, in addition, another group of occlusion compounds of 4,4'-dinitrobiphenyl with 4,4'-substituted biphenyls. These substances, in which a crystal cage of one component surrounds the second component, have been adequately described in recent reviews (65, 249, 274).

II. EXPERIMENTAL PROCEDURES USED IN DEMONSTRATING COMPLEX FORMATION AND IN MEASURING THE STABILITY OF COMPLEXES

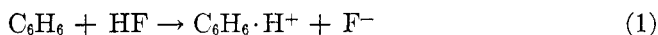
A large majority of the aromatic molecular complexes dissociate so readily into their components that they cannot be isolated as pure substances; hence the

² The terms *molecular complex*, *molecular compound*, and *molecular addition compound* are often used synonymously. The author prefers the first term for the description of aromatic addition products of the electron donor-acceptor type, since the word "compound" implies the formation of a much stronger bond than usually exists between the molecules of which these complexes are composed.

existence of many complexes has been recognized only through the investigation by physical methods of solutions or mixtures of their components. This section outlines the most important of these methods and describes their application in the determination of the composition of the unstable addition products and in the evaluation of equilibrium constants for their formation in solution.

A. Solubility measurements

Solubility studies often provide qualitative indication of the capacity of the aromatic nucleus to interact with reagents of the electron-acceptor type. As an example may be cited the fact that benzene is appreciably soluble in anhydrous liquid hydrogen fluoride (2.25 weight per cent at 0°C.), whereas the alkanes and cycloalkanes are virtually insoluble in this medium (172, 282). It seems likely that the solubility of benzene may be accounted for in terms of a transfer of protons from hydrogen fluoride molecules to aromatic nuclei (116).



Since, however, the relative solubilities of benzene, toluene, the xylenes, and anthracene in hydrogen fluoride are the reverse of the established order of these substances as electron donors, the solubility measurements must also reflect other factors than the proton affinity of the aromatic nucleus (49). Direct comparison of the relative solubilities of a series of benzene derivatives in a common acceptor-type solvent does not in general provide a reliable criterion of the relative strengths of the aromatic substances as donors unless the variations in the vapor pressures of the several solutes are taken into consideration (144). In interpreting the relative solubilities of several aromatic hydrocarbons in water Bohon and Claussen have first corrected the measured molar solubilities to the same vapor pressure (of the aromatic substance) (35). On this basis naphthalene and biphenyl are seven to ten times as soluble as are benzene and its simple alkyl derivatives. It has been suggested that some property of the ring itself is essential to the solubility process (perhaps the capacity for participation in hydrogen-bond formation with the oxygen of the water molecule).

Solubility procedures have also been developed (26) for determining the dissociation constants for complexes in solution. They have been employed in studying the interactions in chloroform of *s*-trinitrobenzene with various aromatic amines (197) and of picric acid with stilbene and related substances (13). In the latter of these investigations chloroform solutions of varying stilbene concentration were saturated with picric acid at 25°C., and the total picric acid content of the resulting solutions was determined. On the assumption that 1:1 complexes of stilbene and picric acid existed in these solutions in equilibrium with their components, the data were used to calculate dissociation constants K_d (as given by equation 2 in which (*S*), (*P*), and (*S*·*P*) represent, respectively, the molar

$$K_d = (S)(P)/(S \cdot P) \quad (2)$$

concentrations of free stilbene, free picric acid, and the complex). The term (*P*) was taken as equal to the solubility of picric acid in pure chloroform, and it was assumed in calculating K_d values that the concentration of the complex was

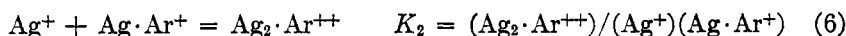
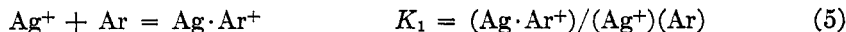
related to the total concentrations, both free and complexed, of picric acid, (P_T), and of stilbene, (S_T), by expressions 3 and 4.

$$(P_T) = (P) + (S \cdot P) \quad (3)$$

$$(S_T) = (S) + (S \cdot P) \quad (4)$$

The K_d values thus obtained for the picric acid complex of stilbene itself remained relatively constant (average 1.11) as the concentration of free stilbene in solution varied from 0.16 to 0.05 M , and equally good constants were obtained for the picric acid complexes of *p*-methyl- and *p*-chlorostilbenes and of ethyl cinnamate. Slightly higher values of K_d for the stilbene complex were obtained in an independent series of measurements based on colorimetric procedures. The K_d values derived from the solubility data may be of somewhat limited accuracy, since they were calculated on the assumption that the concentration of free picric acid in solution (P) is independent of the stilbene concentration. Yet α -methyl- and α -phenylstilbenes, which show only a weak affinity for picric acid in chloroform solution (as evidenced by the fact that their solutions are only a pale yellow in color as contrasted with the intense color of solutions of the stilbene complex), actually salt picric acid out of chloroform in proportion to their concentrations in solution. Bibenzyl, however, in moderate concentrations appears to have no effect on the solubility of picric acid in chloroform. It is therefore difficult to make an intelligent approximation of values of (P) as a function of stilbene concentration which can serve as a basis for correcting the reported K_d values.

In a related study the tendency for complex formation of aromatic hydrocarbons and their substitution products with silver ion has been investigated through solubility measurements (6, 7, 8). A series of saturated solutions of each aromatic substance in aqueous solutions which varied in silver nitrate concentration from 0 to 1.0 M , but which were fixed at unit ionic strength by the addition of potassium nitrate, were analyzed for total aromatic hydrocarbon content by a procedure which involved extraction of the saturated solution with hexane. The extract, which contained essentially all of the aromatic substance formerly contained in the silver nitrate solution, was analyzed for aromatic material by spectrophotometric procedures. The increase in solubility of the aromatics as a function of increasing silver-ion concentration of the aqueous solutions was larger than could be accounted for solely in terms of the formation of 1:1 complexes, $Ag \cdot Ar^+$. The data were interpreted on the assumption that both equilibria 5 and 6 were established.³



From the data taken for each compound a series of constants K were calculated from expression 7 by neglecting the term ($Ag_2 \cdot Ar^{++}$), which was not measured by the experimental procedures and which is very small. In this equation

³ Throughout this review the symbol Ar refers to the aromatic hydrocarbon and *not* to an aryl radical or group.

(Ar_c) and (Ar) refer respectively to complexed ($\text{Ag} \cdot \text{Ar}^+ + \text{Ag}_2 \cdot \text{Ar}^{++}$) and to free aromatic substance and (Ag_t^+) represents the total concentration of free and complexed silver ion.

$$K = (\text{Ar}_c)/[(\text{Ag}_t^+) - (\text{Ar}_c) - (\text{Ag}_2 \cdot \text{Ar}^{++})] (\text{Ar}) \quad (7)$$

The term (Ar) was evaluated by measurement of the solubility of the aromatic compound in 1 *N* potassium nitrate solution, and (Ar_c) was calculated by subtracting (Ar) from the measured solubility of the aromatic substance in the silver-ion solution.

Equation 7 may be rewritten in the form of equation 8. Thus if equilibria 5 and

$$K = K_1 + K_2(\text{Ag}^+) \quad (8)$$

6 uniquely explain the solubility data, a plot of *K* values against the corresponding silver-ion concentrations of the solutions should produce a straight line of intercept *K*₁ and slope *K*₂. The solubility data for a large number of substances in silver nitrate solution were treated successfully in this manner. In the case of benzene at 25°C. values of *K*₁ = 2.41 and *K*₂ = 0.21 were obtained.

Of the several assumptions made in treating the data by this procedure the only one to which serious objection might be raised is that the concentration of free aromatic substance in water solutions of fixed ionic strength is unaffected by the replacement of potassium ions in the solutions with silver ions (162). If, for example, silver ion, exclusive of complex formation, showed a salting-in effect for aromatic compounds, the observed *K*₂ values might have no real significance. However, to account for the results of a series of measurements of the solubility of toluene in 0 to 1 *M* silver perchlorate solutions of ionic strength 5 (adjusted with sodium perchlorate) it was again necessary to postulate the existence of $\text{Ag}_2 \cdot \text{Ar}^{++}$. In these solutions the salting effects resulting from the replacement of sodium ion by silver ion should be very small. There is also independent spectrophotometric evidence for the existence of $\text{Ag}_2 \cdot \text{Ar}^{++}$ in such solutions (162).

B. Distribution studies

Experiments of the distribution type have been used (202, 203) to compare the relative capacities of various hydrocarbons to function as electron donors⁴ in interacting with solutions of boron trifluoride in hydrogen fluoride. Solutions of two aromatic hydrocarbons in *n*-heptane were subjected to batchwise extraction at 20°C. with hydrogen fluoride containing 0.5 mole of boron trifluoride per mole of aromatic material in the system. From analyses of the *n*-heptane and hydrogen fluoride phases at equilibrium, single-stage separation factors, $\alpha(b/a)$,

$$\alpha(b/a) = \frac{N_b N'_b}{N_a N'_a} \quad (9)$$

⁴ The *relative electron-donor capacities* of aromatic substances are sometimes referred to as *relative basicities*. The use of the latter term in this connection may represent an unwise extension of the Lewis theory of acids and bases (196). However, it has proved convenient to adopt this shorter expression in discussing molecular complexes of the donor-acceptor type.

were calculated (b and a refer to the two aromatic substances and N_b and N_a represent their mole fractions in the extract phase and N'_b and N'_a those of the raffinate). The resultant $\alpha(b/a)$ values, which have been tabulated for a number of aromatic hydrocarbon systems in which p -xylene is the a component, are regarded as indicative of the relative capacities of the hydrocarbons to undergo reactions of the type



Thus $\alpha(b/a)$ values for hexamethylbenzene (which is generally regarded as a strongly basic hydrocarbon) and toluene are 44,500 and 0.01, respectively. This method is particularly revealing in the evaluation of relative basicities of aromatic substances, since the capacity of $\text{HF}-\text{BF}_3$ for coordination is very sensitive to changes in substituents on the aromatic nucleus. The extraction procedures on which these experiments are based show promise of becoming commercially important for the separation of isomeric mixtures of alkylbenzenes.

In similar experiments the partition coefficients of several hydrocarbons between n -heptane and hydrogen fluoride (containing no boron trifluoride) have been determined at 25°C. The resultant coefficients when corrected to the same vapor pressures of the aromatic substances are regarded as indicative of interactions of the type described in equation 1.

The equilibrium constants for the formation of picric acid complexes of aromatic hydrocarbons and their substitution products (and also of aniline and nitroaromatics) in chloroform solution have been measured by a method (209) which is based on a study of the distribution of picric acid between chloroform and water as influenced by the presence of varying amounts of aromatic substance in the chloroform phase. This procedure has recently been refined in connection with an investigation of picric acid-alkylbenzene interaction (4). In the presence of aromatic matter two effects serve, in opposition to each other, to alter the normal partition of picric acid between the two phases. The first effect, which corresponds to the formation of the picric acid-aromatic complex in the chloroform layer, causes an increase in the total concentration of picric acid in that layer from its normal value, P , to y_1 . The uncomplexed aromatic material has a salting-out effect for picric acid which tends to lower its concentration in the chloroform phase to y . The total molar concentration of picric acid in the chloroform phase at equilibrium is then given by the expression:

$$Y = y + y_1 - P \quad (11)$$

In the experimental procedure Y was determined by direct analysis of the chloroform phase. The term P was calculated from the picric acid content of the aqueous phase, using the known distribution coefficient of picric acid between chloroform and water. The molar concentration of aromatic substance in the chloroform phase, Z , was chosen so that it remained large as compared to $y_1 - P$.

To facilitate calculation of the equilibrium constant K (defined on the assumption

$$K = (y_1 - P)/P[Z - (y_1 - P)] \quad (12)$$

tion that a 1:1 picric acid–aromatic complex was formed), additional constants k and K_1 were defined.

$$k = (P - y)/yZ \quad (13)$$

$$K_1 = (Y - P)/PZ \quad (14)$$

These are, respectively, a constant for the depression of the solubility of picric acid in chloroform by the aromatic substance and an apparent solubility constant. It may readily be shown that as a close approximation

$$K = K_1 + k \quad (15)$$

By studying the effects of added hydrocarbons such as decalin, hexane, and cyclohexane (instead of the aromatic substance) on the distribution of picric acid between chloroform and water it was observed that the salting-out coefficient was proportional to the molecular volume of the hydrocarbon ($k = 0.0038 V$). Values of K_1 calculated from the experimental data were thus readily corrected to provide K values.

This treatment of the data does not take into account any self-association of picric acid in chloroform nor any interaction of picric acid with chloroform. The K values obtained are independent of the concentration of aromatic substance. For benzene at 20°C. values of K_1 , k , and K are respectively 0.090, 0.337, and 0.43. Limitations in the use of this procedure for studying certain types of donor–acceptor interactions have recently been pointed out (see footnote 8 in Section V, B).

Equilibrium constants for the formation of 1:1 and 1:2 complexes of aromatic amines with silver ion have been evaluated through studies of the effects of changing silver-ion concentration on the partition of the amines between cyclohexane and aqueous silver nitrate (103). The general method has been developed in connection with studies of the interaction of olefins and silver ion (129, 327). It is presumed that in the 1:1 complexes silver ion is coordinated with the amino nitrogen atom and that the second silver ion in the 1:2 complexes is coordinated at the aromatic nucleus. Similar methods have been employed in studying 1:1 complexes of cresol and silver ion (104).

C. Vapor pressure measurements

Qualitative indications of interactions of the donor–acceptor type may sometimes be obtained through measurements of the vapor pressures of multicomponent systems. The observation that the deviations of the vapor pressures (from those predicted by perfect solution laws) for solutions of phenol, the cresols, and cyclohexanol with benzene reached maxima for mixtures approximately 50 mole per cent in benzene was originally explained in terms of 1:1 complex formation (313, 314, 317, 318). Since, however, the deviations were positive in nature, it was decided that they must be ascribed to the dissociation in solution of associated forms of one of the components (312, 315, 316).

Scatchard, Wood, and Mochel have constructed vapor pressure–composition

diagrams for the system benzene-methanol at various temperatures (273). The data have been used to calculate the change of free energy, enthalpy, and entropy of mixing at 35°C. (in excess of those for ideal solutions). The first two of these terms are positive over the entire range of compositions. The first reaches a maximum at a methanol mole fraction of 0.5 and the second at a methanol mole fraction of 0.3. The last term is positive until the methanol mole fraction reaches 0.3 and then becomes negative. These results are interpreted in terms of interactions involving hydrogens of the methanol hydroxyl group and the electrons of the aromatic nucleus. In view of these results it seems likely that further work on the benzene-phenol system should be undertaken, since phenol is potentially a more favorable hydrogen-bonding agent than is methanol.

The observation that the partial pressure of hydrogen chloride over its solution in benzene shows negative deviations from Raoult's law although it obeys Henry's law is taken as an indication of solvent-solute interaction to form a complex, $C_6H_6 \cdot HCl$ (228). Attempts have been made to determine the extent of this interaction and those of other aromatic substances with hydrogen chloride through considerations based on the observed Henry's law constants (224, 226, 227). Although the conclusion that the halobenzenes are less basic with respect to hydrogen chloride than is benzene seems correct, the conclusion that nitrobenzene is a stronger base than benzene is in conflict with more recent opinion. It is probable that these vapor pressure measurements reflect other characteristics of the solution in addition to the extent to which complex formation occurs. Similar vapor pressure data have been recorded for the system hydrogen bromide-benzene (159, 225).

An interesting demonstration of the use of vapor pressure measurements in determining the relative capacities of various aromatic hydrocarbons to function as electron donors is found in the work of Brown and Brady (49). These investigators measured the vapor pressure of hydrogen chloride at $-78.51^\circ C$. over its dilute solutions in *n*-heptane or toluene containing small amounts of the aromatic hydrocarbons in question. The Henry's law constants, k , calculated from the resultant data (P_{HCl} and N_{HCl} in equation 16 represent, respectively, the measured vapor pressure and the mole fraction of hydrogen chloride in solution)

$$P_{HCl} = kN_{HCl} \quad (16)$$

diminished as the aromatic hydrocarbon content of the solution increased and were in general smaller for solutions of the more basic hydrocarbons. These constants were presumed to measure the relative stabilities of 1:1 complexes (see equation 17).



Dissociation constants, K_d , for these complexes

$$K_d = N_{Ar} \times P_{HCl} / N_{complex} \quad (18)$$

were evaluated for each hydrocarbon from data taken from a series of solutions of widely varying hydrogen chloride concentration. The term $N_{complex}$ was calcu-

lated from the difference in the known mole fraction of hydrogen chloride in solution and that of hydrogen chloride in the pure solvent (*n*-heptane or toluene) at the observed vapor pressure. The term N_{Ar} was taken as the difference between the mole fraction of total aromatic substance in solution and that of the complex. For 5, 2, and 1 per cent mesitylene solutions in *n*-heptane average K_d values determined by this procedure were 240, 270, and 220 mm., respectively.

This method is particularly satisfactory for the study of complex formation by hydrogen chloride, since the use of low temperatures eliminates the necessity for correcting the measured vapor pressure for the partial pressure of the hydrocarbon. The use of dilute solutions of the hydrocarbon minimizes the influence of secondary interactions on the vapor pressure of hydrogen chloride.

Similar experimental methods have been used in studying the relative stabilities of complexes of the $ArH+BF_4^-$ type (202, 203). From measurements of the vapor pressures of solutions of aromatic hydrocarbons and boron trifluoride in hydrogen fluoride at 0°C. data have been obtained which have been used, in a few cases, to calculate equilibrium constants for the complex formation. The $\alpha(b/a)$ values (equation 9) probably constitute a more realistic criterion of relative basicity of the hydrocarbons than do these equilibrium constants, the calculation of which from experimental data is based on the assumption that laws of dilute solution are obeyed.

The vapor pressures which are recorded in these experiments are, in themselves, of qualitative value in establishing the extent to which the various hydrocarbons interact to form hydrogen fluoride-boron trifluoride complexes. For example, the vapor pressures of solutions of boron trifluoride in hydrogen fluoride which contain mesitylene are abnormally low as compared to those of mesitylene-free solutions. Indeed, the anticipated increases in vapor pressure as the boron trifluoride content of the systems is increased do not occur until the mole ratio of boron trifluoride to mesitylene is almost unity. Apparently the equilibrium with respect to complex formation lies far to the right. In similar measurements of hydrogen fluoride-boron trifluoride solutions of *m*-xylene, abnormally low vapor pressures again have been recorded for solutions of low boron trifluoride content. However, significant increases in the vapor pressure of the solutions with increasing boron trifluoride concentration have been observed to occur considerably before the boron trifluoride:*m*-xylene mole ratios of the solutions reach unity. One may therefore conclude that the *m*-xylene complex is considerably less stable than that of mesitylene.

Vapor pressure measurements have also been used in the determination of the composition of aluminum chloride-hydrogen chloride complexes of toluene (52, 53). While toluene and aluminum chloride do not appear to react at -84.1°C., their mixtures slowly absorb hydrogen chloride to form green solutions. The process is reversible. From observations of the drop in vapor pressure which occurs in a closed system during this process of hydrogen chloride absorption it has been concluded that 1 mole of hydrogen chloride is absorbed for each mole of aluminum chloride which dissolves. When this experiment is performed at -45.4°C., a yellow solution is produced, and the vapor pressure drop corresponds

to the absorption of 1 mole of hydrogen chloride per 2 moles of dissolved aluminum chloride. Presumably the green and yellow colors of the solutions are characteristic respectively of the complexes $\text{CH}_3\text{C}_6\text{H}_5^+ \text{AlCl}_4^-$ and $\text{CH}_3\text{C}_6\text{H}_5^+ \text{Al}_2\text{Cl}_7^-$. Similar methods have been used recently in the investigation of complexes of the type $\text{ArH}^+ \text{AlBr}_4^-$ and $\text{ArH}^+ \text{Al}_2\text{Br}_7^-$ (54).

In contrast to the observation that toluene and aluminum chloride do not interact are the results of measurements of changes in vapor pressure with composition of the system benzene–aluminum bromide at 15°C ., which indicate the formation of a solid complex containing equimolar quantities of benzene and aluminum bromide (302). The decomposition pressure of the complex is 2 mm. at 15°C . The formula of the complex has been written $\text{Al}_2\text{Br}_6 \cdot 2\text{C}_6\text{H}_6$, since there is evidence from cryoscopic measurements that aluminum bromide is dimeric in benzene (297, 302). Eley and King believe that the solid complex should be distinguished from the solution complex, $\text{Al}_2\text{Br}_6 \cdot \text{C}_6\text{H}_6$, which has been detected by spectrophotometric study (82, 84). These authors attribute the existence of the solid complex to the formation of a high-energy lattice and prefer to write its formula as $\text{AlBr}_3 \cdot \text{C}_6\text{H}_6$. Aluminum chloride complexes of this type are presumed not to form because of the great stability of the ionic lattice of aluminum chloride itself. Brown and Wallace have questioned whether this distinction between solid- and liquid-phase aluminum bromide complexes is justified and have concluded from vapor pressure–composition studies that the solid complexes of benzene and toluene also have the formula $\text{Al}_2\text{Br}_6 \cdot \text{Ar}$ (54). The colors of mixtures of aluminum bromide with *m*-xylene or mesitylene and molecular weight determinations of solutions of mesitylene and aluminum bromide in cyclopentane suggest that these hydrocarbons form similar interaction products. Very recent evidence (50) from phase studies indicates that two solid complexes, $\text{AlBr}_3 \cdot \text{Ar}$ and $\text{Al}_2\text{Br}_6 \cdot \text{Ar}$, of *m*-xylene and mesitylene may exist.

D. Melting point–composition diagrams

The investigation of the influence of changes in composition on the melting or freezing points of two-component systems is an obviously valuable procedure for the detection of molecular complexes. Complex formation is associated with the existence of two or more eutectic mixtures, and maxima which appear in the melting point–composition diagrams correspond to the complex. In some cases the complexes are sufficiently unstable to display incongruent melting points.

This procedure for examining two-component systems for complex formation has been used extensively and has been found particularly useful for studying mixtures of metallic halides and aromatic substances. For example, the solid aluminum bromide–benzene complex (1:1 mole ratio) has been encountered in the preparation of solid–liquid phase diagrams (242, 243) as well as in studies of the vapor pressures of the two-component systems, and is found to have an incongruent melting point of 37°C . (82). Evidence for the existence of both 1:1 and 1:2 antimony trihalide complexes of aromatic substances has also been obtained through the preparation of melting point–composition diagrams (278, 285), but diagrams for binary mixtures of arsenic tribromide and aromatic substances give no indication of component interactions (254).

There are apparently many pitfalls in establishing the existence of complexes through thermal analysis of binary systems. Although Seyer and Peck (276) have reported that the system benzene-sulfur dioxide shows only one eutectic ($-79^{\circ}\text{C}.$) with no abnormalities in freezing-point behavior, Mazzetti and De Carli (205) have prepared a freezing point-composition diagram which shows the existence of three addition products, $\text{C}_6\text{H}_6 \cdot \text{SO}_2$ (m.p. $-15^{\circ}\text{C}.$), $\text{C}_6\text{H}_6 \cdot 2\text{SO}_2$ (m.p. $-40^{\circ}\text{C}.$), and $\text{C}_6\text{H}_6 \cdot 3\text{SO}_2$ (m.p. $-52^{\circ}\text{C}.$). Similar diagrams have been prepared for the systems toluene-sulfur dioxide, ethylbenzene-sulfur dioxide, and tetralin-sulfur dioxide (70, 71). Whereas Wyatt (330) was able to detect only $\text{C}_6\text{H}_6 \cdot \text{CCl}_4$ and $\text{C}_6\text{H}_6 \cdot 2\text{CCl}_4$ from studies of the freezing points of benzene-carbon tetrachloride mixtures, Kapustinskiĭ and Drakin (157) report a third addition product, $\text{C}_6\text{H}_6 \cdot 3\text{CCl}_4$, and there is disagreement between the two groups as to the melting points of the complexes. They agree, however, that interaction between benzene and chloroform cannot be detected by these methods.

Kofler (175) has pointed out that detection of molecular complexes through the preparation of solidification curves is subject to technical difficulties such as supercooling, secondary reaction of the components, and the occurrence of solidification blanks. He has employed an interesting method of examining two-component systems which in the hands of an experienced technician is a rapid and presumably reliable procedure. In this procedure, which is useful only for systems which melt above room temperature, a hot-stage microscope is used in the melting-point determinations (176, 177, 178, 179). One component in its molten state is allowed to cover approximately one-half the space between the object holder and cover glass. After the melt is solidified, the second component is added in a similar fashion to fill the remaining space. The lower melting of the two components is then held for a short time at a temperature about $1^{\circ}\text{C}.$ above its melting point and is then cooled. This treatment permits the formation of a strip of the molecular complex in the region of the boundary between the two components. The melting characteristics of the material on the object holder are then observed. Melting is first detected in the boundary regions which correspond in composition to the two eutectic mixtures of the molecular complex and the pure components. The melting point of the complex, which separates as a solid island between these two melts, can easily be recognized. It is claimed that the eutectic temperatures can be determined through the melting of as little as 1 per cent of the components. This method has been applied successfully to the examination of systems such as naphthalene-2,4-dinitrotoluene, phenanthrene-2,4-dinitrophenol, *s*-trinitrobenzene- β -naphthylamine, and others in which 1:1 complex formation occurs.

Sinomiya has attempted to estimate the relative stabilities of various aromatic donor-acceptor complexes through consideration of melting point-composition diagrams of mixtures of the components (284, 285). In congruent-type diagrams (two eutectics and a maximum corresponding to the complex) for the systems which form the most stable interaction products, the extent to which the melting-point curve flattens at the dystectic point is considered to be representative of the degree of dissociation of the complex in the fused state. The relative stabilities of complexes of various substituted nitrobenzenes with naphthylamines and

related substances and of antimony trichloride with alkylbenzenes have been compared on the basis of the relative magnitudes of values of τ , "the melting-point elevation," as defined in equation 19.

$$\tau = t_C - \frac{mt_A + nt_B}{m + n} \quad (19)$$

The terms t_A , t_B , and t_C represent the melting points of the two components and of the complex, respectively, and $m:n$ is the mole ratio of A and B in the complex. The constant τ represents the difference between the melting point of the complex and the weighted average of the melting points of its components. There is no apparent theoretical justification for the use of these "melting-point elevations" as quantitative measures of the relative stabilities of structurally related complexes. However qualitatively, at least, many of the recorded τ values conform to the same basicity series for aromatic substances as has been observed in other types of investigation. For example, Sinomiya concludes from his melting-point data that the stabilities of antimony trichloride-methylbenzene adducts increase as the number of ring methyl substituents increases.

E. Spectrophotometric measurements

Pronounced changes in absorption spectra are often observed to accompany the reaction of two substances to form molecular complexes. Indeed, the existence of many aromatic complexes was first recognized through the visible color effects produced by the interaction of the component molecules. For example, the red to brown color of solutions of iodine in aromatic solvents, as contrasted to the violet color of the halogen in inert solvents such as carbon tetrachloride, was ascribed to the formation of iodine solvates (174) before convincing proof of the interaction was provided. The intense color (orange to red) of the solid 1:1 complexes formed by certain weakly basic aromatic amines and picric acid served to distinguish these addition products structurally from the yellow salt-like amine picrate formed by the more strongly basic amines (131, 135).

The relative stabilities of complexes of a series of aromatic substances with a particular acceptor-type reagent have been assigned on the basis of the differences in color of the addition products. Thus the color of the adducts of *s*-trinitrobenzene with a series of diphenylpolyenes shifts from yellow in the case of stilbene to a dark brown with diphenyldecapentaene (188). The same effects are observed with other acceptor reagents such as quinone, which in the fused state forms a colorless melt with stilbene and a reddish brown one with diphenyloctatetraene. In general, increasing stability of a complex appears to be associated with visible absorption at increasingly longer wave lengths. The fact that hexamethylbenzene picrate is orange-yellow whereas benzene picrate is colorless (21) is therefore to be regarded as an indication of the enhancement of the electron-donor capacity of benzene through methyl substitution. On the basis of similar colorimetric evidence concerning quinhydrones and complexes of aromatic substances with polynitroaromatics it has been concluded (80) that the contributions of certain substituents in the quinoid or nitroid components to the stabilization or destabili-

zation of the complexes are just opposite to those observed when the same substituents appear in the benzenoid components.

In recent years, because of the availability of new and versatile instruments, spectrophotometers have been used extensively in the investigation of the less stable complexes which exist only in solution. Many of these unstable complexes display no visible absorption but rather have been recognized through the appearance of bands in the ultraviolet or infrared spectra of solutions of two components which are not characteristic of the parent compounds. Hunter and Northey (149) were perhaps the first investigators to report measurements outside the visible region in the detection of complex formation. They observed that the ultraviolet spectra of thin films of solutions of quinones in various simple benzene derivatives were shifted toward the visible as compared to the spectra of the fused quinones. The shifts were sufficiently large for solutions of dimethylaniline in certain of the quinones to suggest the marked occurrence of interaction between the components.

Spectrum measurements are often used to establish the molecular ratio of the components in complexes formed in solution. The formula $C_6H_6 \cdot WF_6$ was assigned (252) to the red complex produced in solutions containing tungsten hexafluoride and benzene on the basis of the observation that the optical densities of carbon tetrachloride solutions of these substances (520–570 $m\mu$ region) varied directly with the concentration of either reactant.

This procedure has been extended in several instances to provide an estimate of the relative stabilities in solution of structurally related complexes which display characteristic absorption spectra. An interesting application of the general method is to be found in the work of Michaelis and Granick (207), who studied the interactions in dilute solutions of quinones with certain phenolic compounds and their ethers and with hexamethylbenzene in different solvents. All of the solutions showed pronounced absorption maxima in the visible or near ultraviolet (λ_{max} , for chloranil and hexamethylbenzene in benzene occurred at 512 $m\mu$) in wave-length regions at which the components were either transparent or absorbent only to a minor degree. The optical densities of the solutions, which were generally measured at the complex absorption maximum against the solvent as a blank, varied directly with the concentrations of the two components. The optical density, d , is defined by equation 20, in which c represents the molar concentration of the complex, l is the width of the absorption cell in centimeters, and ϵ is the molar extinction coefficient of the complex.

$$d = \log \frac{I_0}{I} = \epsilon lc \quad (20)$$

The equilibrium constant for formation of the 1:1 complex,

$$K = c/(q - c)(b - c) \quad (21)$$

where q and b represent, respectively, the concentrations of both free and complexed quinoid and benzenoid components, could not be evaluated directly from the experimental data. However, since c in all cases was small compared to q and

b , values of $K\epsilon$ for each complex could be ascertained using equation 22 and the

$$d/qb = K\epsilon \quad (22)$$

optical densities (corrected for the absorption of the components) of solutions of q and b of 1 cm. width. On the assumption that ϵ values for all of the complexes which were investigated were closely similar, $K\epsilon$ values were taken as representative of the relative stabilities of the several complexes. This assumption can only be employed justifiably, even as an approximation, if the various complexes are very closely related structurally. Similar methods have been used in comparing the relative stabilities in solution of complexes of various aromatic substances with tetranitromethane (69, 125) and of *s*-trinitrobenzene with aromatic amines (115).

A more satisfactory procedure provides for the independent evaluation of both the equilibrium constant and the extinction coefficient of the complex. This can be accomplished spectrophotometrically only when an appreciable fraction of one of the components in solution exists in the form of the complex. The studies of Benesi and Hildebrand (28) on the ultraviolet spectrum of iodine in benzene and other aromatic solvents serve as an illustration of the general method. While others had attempted to study iodine-benzene interaction in terms of visible spectra of solutions (97) or ultraviolet spectra of mixtures of iodine and benzene vapor (63), these investigators discovered a high-intensity absorption peak in the ultraviolet region ($\lambda_{\text{max.}} = 290 \text{ m}\mu$) for solutions of iodine in benzene which was lacking in the spectrum of iodine in solvents such as carbon tetrachloride or *n*-heptane and which presumably was characteristic of a complex. As had been observed previously (110, 305), they found that the visible absorption maximum of iodine in its reddish solutions in benzene was only slightly displaced toward the ultraviolet from the absorption peak of iodine in its violet solutions ($\lambda_{\text{max.}} = 518 \text{ m}\mu$) in carbon tetrachloride.

The optical densities of a series of dilute solutions of iodine in various benzene-carbon tetrachloride solvent mixtures were measured at the ultraviolet absorption maximum against the corresponding solvent mixtures as blanks. Although an appreciable quantity of the iodine existed in these solutions in the form of a benzene adduct, the mole fraction or molar concentration of benzene in solution was always very high compared to that of the complex. It was shown, using the assumption that this complex was of the 1:1 type, that the measured optical densities (see equation 20) were related to the equilibrium constant for complex formation by equation 23, in which (I_2) and (Ar) represent total concentrations of the halogen and benzene in solution.

$$(I_2)l/d = (1/K\epsilon)[1/(Ar)] + 1/\epsilon \quad (23)$$

The validity of this interpretation was established by the fact that plots of experimentally determined values of I_2l/d versus the reciprocals of the corresponding mole fractions of benzene in the solvent gave straight lines. Values of ϵ and $K\epsilon$ were evaluated, respectively, from the slopes and intercepts of these lines.

This procedure for determining K values is subject to certain experimental and

theoretical limitations. First, the observed $1/\epsilon$ values are usually very small, and it is difficult to read them from the intercepts with accuracy. Secondly, no correction is provided for the contribution of free halogen (usually small) to the observed optical densities. However, if this contribution is appreciable, the observed optical densities can be corrected on the basis of approximate K values calculated without taking into account the absorption of free halogen. A more exact equation than equation 23 has been developed for application to spectrophotometric studies of other systems and includes this correction (166). The assumptions that K and ϵ values do not change with changing benzene-carbon tetrachloride ratios are probably not exactly correct. Actually the wave length of maximum absorption does shift slightly with changes in solvent composition for solutions of high benzene content, and presumably ϵ values are also affected. Cromwell and Scott (66) prefer to interpret the data on the assumption that ϵ (but not K) is invariant. In the interpretation of similar spectrophotometric data for other systems in which relatively dilute solutions of aromatic substances were used, these assumptions concerning the constancy of K and ϵ values are probably valid (11).

The ultraviolet spectrum of bromine in benzene and other aromatic solvents also shows a high-intensity absorption peak in the neighborhood of $290\text{ m}\mu$ (3) which is regarded as characteristic of a 1:1 complex (33, 160). Spectrophotometric methods similar to those employed in studying the iodine complexes have been used to evaluate equilibrium constants for the formation of a number of complexes of bromine and aromatic compounds. Solutions of iodine monochloride (11, 161), chlorine (9), sulfur dioxide (10), oxalyl chloride (272), maleic anhydride and quinones (12, 20), and of aluminum bromide (84) in aromatic solvents also display ultraviolet absorption which is characteristic of solvent-solute interaction products. The method of Benesi and Hildebrand has been used to evaluate equilibrium constants for the formation of many of these complexes. Modifications of this procedure have been employed in studying the stabilities of complexes of aromatic nitro compounds with aromatic hydrocarbons and amines (13, 47, 92, 111, 190, 197) in chloroform solution. Colorimetric studies showing the existence of 1:1 complexes of maleic anhydride and various styrenes in chloroform solution (22, 306) have recently been extended (96), using the Job (150) method of continuous variations (reviewed by Vosburgh and Cooper (303)) to show that in some cases 2:1 complexes may also be present in these solutions.

Recently it has been shown (86) that the coloration resulting on the uptake of oxygen by dimethylaniline solution occurs reversibly. Oxygenated solutions of other aromatics, including benzene, naphthalene, and several monosubstituted benzenes, show absorption maxima in the near ultraviolet, which disappear when the oxygen is removed. These absorption phenomena have been attributed to the formation of aromatic-oxygen complexes similar to those formed by the halogens and sulfur dioxide.

The observation that the products of interaction of electron-acceptor reagents with aromatic substances display characteristic visible or ultraviolet absorption bands is sufficiently general so that the absence of such bands in the spectrum of

a particular complex has been taken as an indication that the binding forces between the components are not of the donor-acceptor type. Such, for example, is the case for the complex $(\text{CH}_3)_4\text{Pt} \cdot 0.5\text{C}_6\text{H}_6$ (269). It is, however, erroneous to conclude on the basis of spectrum measurements of dilute solutions of solid complexes that the spectra of the adducts are the summation of those of the components (148), since in very dilute solutions the complexes may be essentially completely dissociated (153). It should further be noted that the postulation of internal complex formation as the explanation for the color of certain compounds (in particular the nitroanilines (73)) is not justified unless the influence of resonance stabilization on the spectra of those compounds is also considered.

The application of infrared spectroscopy to the study of aromatic donor-acceptor complexes has been particularly valuable in revealing interactions of a type in which the aromatic nucleus participates in an association akin to hydrogen bonding with reagents such as hydrogen chloride and methanol. In benzene and other aromatic solvents the fundamental absorption band of hydrogen chloride at 3.46μ is shifted to longer wave lengths (106, 107, 247, 324). Although such shifts are normally observed to parallel increases in the dipole moment of the solvent, the magnitude of the change in several of the aromatics is too large to be accounted for solely in these terms.

Similar shifts in various OD or OH absorption bands of CH_3OD or methanol in benzene or its substitution products have been observed (105, 152, 290). In the region of the third harmonic of the OH band (9600 \AA.) two maxima appear when more highly methylated benzenes are used as solvents, while only one maximum is encountered when benzene is the solvent (152). It is suggested that in these methylated benzenes two types of interaction products are formed, the bond strengths of which are considerably different in magnitude. The shifts in the 2689 cm.^{-1} (as measured in carbon tetrachloride solution) OD band of CH_3OD in various substituted benzenes parallel the increases in the heats of mixing of equimolar quantities of the same aromatic substances with chloroform (using *o*-dichlorobenzene as a reference standard) (290). It is inferred, because of the success of this correlation, that the observed interactions of the aromatic substances with chloroform as well as with CH_3OD may be ascribed in large part to hydrogen bonding.

Whiffen (323) has found that the width at half the maximum absorption of the infrared band of chloroform near 760 cm.^{-1} is much greater for solutions in benzene, nitromethane, methyl acetate, acetone, and dioxane than in saturated hydrocarbon solvents or in carbon disulfide. Professor Hildebrand (145) has suggested that this widening of the absorption band may possibly be regarded as representative of interactions (presumably of the hydrogen-bond type) occurring between the chloroform and solvent molecules.

Attempts to discover infrared absorption bands for 1:1 aromatic-halogen complexes have been unsuccessful. Although it has been reported (239) that solutions of iodine in mesitylene show such bands, measurements with solutions of highly purified mesitylene show that the absorption which occurs appears to be the summation of that of the components (114). However, there is some recent

evidence (99) that certain features of this spectrum may be attributed to a mesitylene-iodine complex. Absorption bands attributable to a complex are not observed over the region 2.5–25 μ for solutions of iodine in benzene (113). The complex of iodine with pyridine, however, shows strong absorption in the infrared. These facts are presumed to indicate that the aromatic-halogen interactions do not represent true complex formation but are instead only mild perturbations induced in the solute molecules by the surrounding cage of solvent molecules (113). It is probably unwise, however, to propose arguments against the existence of aromatic complexes on the basis of observations of the spectrum of the pyridine-iodine complex, since in the latter complex the halogen is undoubtedly preferentially coordinated at the nitrogen atom of the pyridine ring (331).

Interaction between mesitylene and metallic ions has also been postulated to account for certain infrared and visible absorption phenomena which are characteristic of their mixtures (155, 239). It now seems likely (27) that these spectrum changes are produced by interactions of an impurity in the mesitylene rather than by those involving the aromatic hydrocarbon itself.

Among other types of aromatic donor-acceptor interactions which may be recognized through infrared absorption studies are those of aniline with nitrobenzene (294), dimethylaniline with *s*-trinitrobenzene, and acenaphthene with *m*-dinitrobenzene (59). The spectra (700–3000 cm^{-1}) of the 3:1 occlusion compounds of *p,p'*-dinitrobiphenyl with biphenyl and *p*-hydroxybiphenyl, which owe their existence to the fact that they form a lower-energy crystal lattice than does *p,p'*-dinitrobiphenyl, are the summations of those of their components.

F. Other methods

The formation of complexes in multicomponent systems has been detected through the application of various other physical methods of measurement. The interaction products frequently are more polar than their constituents and may therefore be recognized through the determination of the dipole moments of the solutions in which they are formed. For example, solutions of hydrogen chloride in benzene show a higher dipole moment than does gaseous hydrogen chloride (87), and aluminum bromide and iodide display appreciable moments in benzene but not in carbon disulfide solution (218, 299, 300). Antimony trichloride also shows a high moment in benzene (319). The large moments recorded for tin and titanium tetrachloride complexes of benzonitrile, acetophenone, and benzaldehyde (298) probably reflect interactions in which the ring substituent rather than the aromatic nucleus shares electrons with the metallic halide.

The uncertainty as to whether or not solutions of iodine in benzene show dipole moments (68, 156, 210, 308, 325, 326) was finally resolved by the experiments of Fairbrother (88), who demonstrated that solutions of iodine in the "violet" solvent, cyclohexane, gave no measurable moment as contrasted to the appreciable moments recorded for the red to brown solutions of iodine in benzene, *p*-xylene, cyclohexene, dioxane, and diisobutylene. The moments for the aromatic solutions were ascribed to interaction products to the structures of which polar forms of the type ArI^+I^- contribute. It was also noted that the capacity of the

solvent to coördinate iodine is dependent not on the dielectric constant of the solvent (solutions of iodine in highly polar nitro compounds are violet) but rather on the ability of the solvent molecules to function as electron donors.

Similarly, Weiss (310) interpreted the observation that the addition products of *s*-trinitrobenzene and benzene or naphthalene (193) and of *p*-dinitrobenzene and benzene (44) have appreciable dipole moments as an indication that the complexes are significantly ionic in character. The fact that the total polarizations at radio frequencies of a number of crystalline addition products of aromatic hydrocarbons or amines with aromatic nitro compounds show both positive and negative deviations from the sums of the polarizations of the components has also been considered to reflect the partial ionic character of the complexes (186). Similar interpretations have been placed on the results of measurements of the total polarizations of benzene solutions of this type of complex (271).

Interactions of the solvent-solute type leading to aromatic donor-acceptor complex formation may often be detected through conductance measurements. The anthracene·H⁺F⁻ complex, for example, is presumed to account for the conductivity of solutions of anthracene in hydrogen fluoride (171). The highly ionic nature of the bromine-tetraarylethylene complexes has been also demonstrated by conductance studies (55).

Conductance measurements have been employed in several instances (108, 215, 246) to investigate the interaction of aromatic substances with metallic halides. Among the most interesting of these experiments were those of Wertyporoch and Adamus, who were concerned primarily with the nature of the intermediates in the Friedel-Crafts reaction (320). They observed that aluminum bromide solutions in benzene, toluene, and xylene were non-conducting. On addition of hydrogen chloride or bromide to these solutions a thick, strongly conducting oil was formed. In view of the recent work of Brown and Pearsall (52) it seems likely that this material was ArH⁺AlX₄⁻ or some closely related complex. In later work (328) it was found that the addition of benzene to solutions of aluminum bromide in ethyl bromide caused a marked increase in their conductivities, which reached maximum values after an interval of several hours. During this time the benzene was converted to hexaethylbenzene. Evidence was obtained from transference experiments which suggested that complexes of the structure Al(C₂H₅Br)_n[C₆(C₂H₅)₆]₄(AlBr₄)₃ were responsible for the conductivity of these solutions. Similar methods were used to demonstrate that the most reasonable formulation of the aluminum bromide-hydrogen bromide-*s*-triethylbenzene complex is [C₆H₃(C₂H₅)₃H⁺][Al₂Br₇⁻] (223).

Kilpatrick and Luborsky (169) recently have calculated equilibrium constants

$$K = (F^-)(ArH^+)/ (Ar)(HF) \quad (24)$$

at 20°C. from the equivalent conductances, Λ , of solutions of a number of polymethylbenzenes in anhydrous hydrogen fluoride. The degrees of association, α , of the hydrocarbons

$$\alpha = \Lambda/\Lambda' \quad (25)$$

required to determine K values have been calculated on the assumption that as a first approximation Λ' is equal to Λ_0 for hexamethylbenzene. This approximation

seems justified, since this hydrocarbon is complexed to a high degree. It has also been assumed that the mobilities of all cations, ArH^+ , formed from the various hydrocarbons are the same. This assumption seems reasonable, since the equivalent conductances of solutions to which a large excess of boron trifluoride is added (to shift the equilibrium to form the complex to the right by forming BF_4^-) are dependent only on the concentration and not on the structure of the hydrocarbon.

Viscosity measurements sometimes provide evidence of complex formation between the components of binary systems. For normal systems, in which no marked interactions between the components occur, the viscosity isotherms are sagged. For systems in which complexes are formed the isotherms deviate markedly from those of ideal solutions, and in cases in which the extent of the interaction is pronounced, maxima appear in the viscosity-composition curves. The isotherms of sulfur dioxide, thionyl chloride, and sulfuryl chloride in benzene, toluene, xylene, and mesitylene at 25°C. indicate clearly the formation of solute-solvent complexes (199). For solutions of thionyl chloride in mesitylene, in which the deviations from normalcy are extreme, the maximum occurs at approximately a 1:1 mole ratio of the components. The solutions of the sulfur compounds in cyclohexane exhibit normal behavior. Viscosity isotherms for solutions of arsenic trichloride in benzene (281), nitrobenzene, and pyridine (181) also show definite maxima, and a complex $\text{C}_6\text{H}_6 \cdot 2\text{SbCl}_3$ has been detected by viscosity measurements (304).

The existence of complexes in solutions of thionyl chloride or sulfuryl chloride in aromatic hydrocarbons is also suggested by the fact that large positive heats of mixing are observed when such solutions are prepared (199). Kirejew (170) has noted that if heats of mixing are controlled only by physical factors, they are usually zero or negative, whereas the formation of complexes is usually accompanied by positive heat effects such as are observed in the preparation of solutions of chloroform in aromatic solvents. Tamres (290) has found that the magnitudes of the positive heats of solution of chloroform in benzene, toluene, *m*-xylene, and mesitylene increase with increasing methylation of the benzene nucleus. However, the increment changes in these values diminish in the same order. The drop in these increments is even more marked if bromoform is substituted for chloroform. It is suggested that added methyl groups offer steric interference to the formation of a hydrogen bond between the aromatic ring and the haloform. This effect opposes the inductive effects of methyl substitution, which in general results in an enhancement of the basicity of the aromatic nucleus. The chloroform complexes must be of the 1:1 type, since plots of the heats of mixing per mole of solution as a function of solution composition (mole per cent) are symmetrical.

It seems reasonable that the water might also show some tendency for coordination of the hydrogen-bond type with the aromatic nucleus. Some evidence that such interaction may occur has been obtained through the determination of the heats and entropies of solution of benzene and other hydrocarbons in water (35).

It has recently been shown (288) that the products of solvent viscosity and the iodine diffusion coefficient for solutions of iodine in toluene, *m*-xylene, and mesit-

ylene are less than those of solutions of iodine in normal solvents such as hexane and carbon tetrachloride. It is suggested that the existence of iodine-solvent complexes in the aromatic solutions may account for these differences, and it is further suggested that these deviations from normalcy become more marked as the solvent is increasingly methylated.

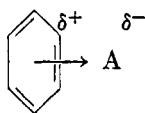
III. TYPES OF ACCEPTORS

Table 1 summarizes the work on aromatic donor-acceptor interaction which has seemed, in the author's opinion, to have been most pertinent in the development of the theory of the structure of molecular complexes. This tabulation is based on a somewhat arbitrary classification of each acceptor molecule as a representative of one of ten general types. This classification forms the framework for a brief discussion of those structural features which confer acidic properties on the acceptor molecules.

Included in this table is a list of the various aromatic donors which are known to interact with these acceptors. Where information is available the mole ratio of donor to acceptor in the complex is also given. It is desirable, from the reader's viewpoint, that a convention be adopted concerning the expression of such ratios. In this report, unless otherwise specified, the relative molar contribution of the donor precedes that of the acceptor. For the convenience of future investigators the methods used in the study of the listed complexes are also reported in the table.

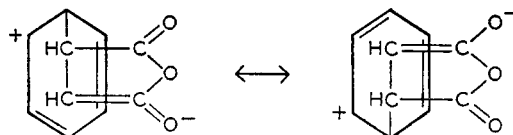
Some valuable references may well have been overlooked in the preparation of table 1, since important contributions to the literature of the field have in many cases been reported only as items of incidental significance in connection with problems of broader scope or of different character. Some references to work on aromatic donor-acceptor interaction which do not contribute materially to the field of molecular complex formation *per se* have been omitted. In particular may be mentioned those which report the use of picric acid and similar substances for the preparation of derivatives of aromatic compounds in connection with problems of organic confirmatory analysis. References to the interaction of amines with polynitrophenols which lead to the formation of picrate salts rather than to π complexes are also omitted. Neither are complexes of diphenylpolyenes or of α,β -unsaturated aromatic carbonyl compounds treated in detail, since their interactions may be more complicated in nature than those of simple aromatic molecules. Data concerning complexes in which azulenes function as donors (240, 241) are also omitted, although it seems likely that such complexes are not fundamentally different in type from those formed by aromatic donors.

Most of the interactions summarized in table 1 can be described by a notation of the Dewar type (76) in which the loose coördinate link involving the electrons of the aromatic nucleus and a vacant orbital of the acceptor molecule (A) is designated by an arrow.



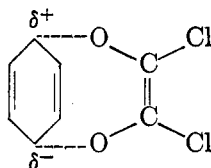
It is perhaps more profitable in attempting to illustrate the inherent capacity of the various acceptor molecules to participate in this electron-sharing process to formulate the complex structures in terms of a more formalized valence-bond notation. As will be considered later in some detail, it must be recognized that any single structure of this kind which one can write vastly overemphasizes the degree of electron transfer between donor and acceptor molecules and implies, probably falsely in most cases, that the acceptor molecule is preferentially coordinated with an individual ring carbon atom.

Section A of table 1 is concerned with acid anhydrides, acid chlorides, and nitriles as acceptors. Among these are listed a series of dienophiles including maleic anhydride, chloromaleic anhydride, and fumaryl chloride. The complexes formed in solutions of these substances in aromatic solvents are probably akin in nature to transitory colored substances observed to form during the course of the Diels-Alder reaction and have been described (12) in terms of structures such as the following:

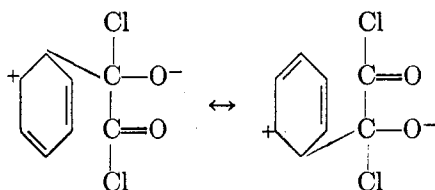


The complexes of quinones (section H of table 1) with aromatic substances in solution must be closely related in type to the maleic anhydride complexes. The structures of solid quinhydrones are undoubtedly modified somewhat by hydrogen bonding between oxygen atoms of benzenoid and quinoid components. Hydrogen bonding is obviously not an essential feature of such complex formations in solution, since the spectra of solutions of complexes of hydroquinone and of its ethers with aromatic substances are similar (207).

A formulation for the benzene-oxalyl chloride complex has been proposed (272) in which the oxygens of the oxalyl chloride molecule are associated at para carbon atoms of the aromatic ring.



In support of this structure are the facts that Raman and infrared absorption data suggest a *cis* configuration for the oxalyl chloride molecule at room temperature and that the O—O distance of the acid chloride approximates the separation distance of para ring carbon atoms. As it is written, this structure seems objectionable in that it requires the destruction of stabilization by ring resonance without compensating for it by resonance stabilization of the complex. Although acetyl chloride is not known to form adducts with aromatic substances, available evidence does not seem to exclude conclusively the possibility that forms of the type



contribute to the structure of the complex. It seems likely that phthalic anhydride, mellitic anhydride, and *s*-tricyanobenzene function as acceptors in much the same fashion as does oxalyl chloride, although information as to intimate details of the process are lacking.

As has been observed previously in the discussion of spectrophotometric studies, the infrared spectra of solutions of methanol in benzene and other aromatics strongly suggest the existence of associations of the hydrogen-bond type involving the hydroxyl hydrogens of the alcohol molecule and the aromatic nuclei. It is probable that the association of benzene with other alcohols and with water (section B of table 1) also is accomplished through hydrogen-bond formation. A similar formulation, supported by infrared absorption studies (107, 247, 324) as described in Section II, may be used to explain the interaction of hydrogen chloride and bromide with aromatic substances (section E of table 1).

Since, as noted in Section II, solutions of anthracene and polymethylbenzenes in hydrogen fluoride are strongly conducting (169, 171), it seems likely that they actually contain high concentrations of fluoride ion and a cationic species ArH^+ . The concentrations of the latter can be increased by the addition of the fluoride ion complexing agent, boron trifluoride (169). The hydrogen halide-aluminum halide complexes (section E of table 1), $\text{ArH}^+\text{MX}_4^-$, are presumed to be similar in nature to those formed in hydrogen fluoride-boron trifluoride solutions. As will be discussed later (Section IV), it has been suggested (49, 52, 53) that the coordination bond of the cationic complex ion formed in these cases is stronger than that of a typical π complex.

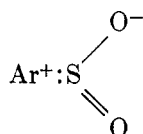
Other association products of aromatic substances such as those with acetic acid (section E) and with triphenylmethane and its derivatives (section J) may also form through participation of the aromatic donor in hydrogen-bond formation. The very interesting triphenylmethane addition products deserve further attention, since no clues are as yet available concerning the nature of the bond between the component molecules.

Evidence has been presented in Section II that chloroform and bromoform (section D of table 1) engage in hydrogen-bond formation with the aromatic nucleus. The complexes of benzene with the carbon tetrahalides and with methylene chloride (also in section D) have not been characterized structurally and require further attention in this regard.

The complexes of halogens and aromatics (section C of table 1) show increasing stability (11, 161) as the polarizability of the halogen component increases ($\text{Cl}_2 < \text{Br}_2 < \text{I}_2 < \text{ICl}$). The same series of relative strengths of halogens as acids has been deduced from studies of the stability of the trihalide ions (275). The suggestion that forms of the type Ar^+X_2^- (alternately formulated by some

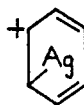
authors as ArX^+X^-) offer some contribution to the structure of the interaction products (9, 11, 76, 88, 160, 161) therefore seems appropriate and is in accord with the fact that solutions of iodine in aromatic solvents show appreciable dipole moments (88). The question of the relative steric orientations of the donor and acceptor portions of the complex is, however, still a matter of some speculation (11, 161, 211, 212, 292). Structures in which the axis of the halogen molecule lies both perpendicular and parallel to the plane of the benzene ring have been suggested. The former viewpoint is supported by the observations that the spectra of the complexes are similar to those of the linear trihalide ions and that the iodine monochloride complexes are more stable than those of iodine, while the latter more compact formulation can be better justified on theoretical grounds.

The complexes of sulfur dioxide and related substances are presumed (section I of table 1) to be close structural relatives of the halogen complexes. Structures of the type



in which the sulfur rather than the oxygen atoms of the sulfur dioxide molecule is most intimately associated with the benzene ring, have been proposed as representative of these complexes (10).

The interactions of silver ion and aromatic nuclei (section F of table 1) have been described (6, 327) in terms of a resonance hybrid structure similar to that suggested for complexes formed from silver ion and olefins (327). Forms of the type,



in which the silver ion is located above the plane and on the sixfold symmetry axis of the ring (293), are presumed to contribute to this resonance hybrid; for the 1:2 complexes the second silver ion has been located on the opposite side of the ring (76). However, on the basis of a preliminary interpretation of the x-ray diffraction pattern of the solid silver perchlorate-benzene complex it is concluded that, in the solid complex at least, the silver ion is located away from the symmetry axis above and between two carbons of the aromatic ring (268). This view is supported by a quantum-mechanical interpretation based primarily on symmetry considerations of the $\text{C}_6\text{H}_6 \cdot \text{Ag}^+$ complex (212). The formation of aromatic addition complexes by metallic halides such as aluminum chloride (also in section F of table 1) constitutes one of many examples of the function of such salts as Lewis acids. Formulations similar to those suggested for halogen and sulfur dioxide complexes may be used to describe these addition products.

The formation of aromatic addition products of nitro compounds (section G of table 1) must be ascribed to the susceptibility of the nitro group to undergo

TABLE 1
The various types of acceptors and the corresponding aromatic donors

Acceptor	Donor (Donor:Acceptor Mole Ratio)	Method of Investigation	References
A. Acid anhydrides, acid chlorides, and nitriles			
Maleic anhydride	Stilbene, biphenyl, indene, 1,1-diphenyl-ethylene, styrene and certain of its para substitution products, and other aromatic substances (probably all 1:1) Benzene, a number of mono- and disubstituted benzenes, polymethylbenzenes, anthracene, styrene and <i>p</i> -substituted styrenes (1:1 and in the case of styrene and <i>p</i> -chlorostyrene also 2:1) Diphenylamine (1:1) Benzene and anisole (1:1) Benzene (1:1)	Color of solutions or fused mixtures Ultraviolet and visible absorption spectra of solutions Melting point-composition diagram Ultraviolet and visible absorption spectra of solutions Ultraviolet absorption spectra of solutions (also infrared and Raman spectra) Colors of fused mixtures	(22, 38, 187, 306) (12, 20, 96) (232) (12) (272) (187)
Chloromaleic anhydride			
Oxalyl chloride			
Phthalic anhydride, phthaloyl chloride, fumaryl chloride, oxalyl chloride	Polycyclic aromatics (?) Naphthalene, anthracene, coumarin, salicylic acid, pyridine, hexamethylbenzene, dibromostyrene, <i>m</i> -dinitrobenzene (all 1:1)	Isolated as solids Isolated as colored solids	(60) (216)
Tetrachlorophthalic anhydride Mellitic trianhydride	Aromatic hydrocarbons and amines (1:1)	Isolated as solids or observed through color of solutions	(29)
Trimesic acid chloride and <i>s</i> -tricyanobenzene			

B. Alcohols and water

Methanol	Benzene (?) Benzene, toluene, <i>m</i> -xylene, mesitylene, pseudocumene, α -methylnaphthalene (?)	Vapor-liquid equilibrium studies Infrared spectra of solutions	(273) (152)
Methanol- <i>d</i>	Nitrobenzene and <i>o</i> -nitrotoluene, <i>o</i> -dichlorobenzene, chloro- and bromobenzenes, α -chloronaphthalene, <i>o</i> -chlorotoluene, benzene, toluene, α -methylnaphthalene, <i>o</i> -, <i>m</i> -, and <i>p</i> -xylenes, and mesitylene (probably all 1:1)	Infrared spectra of solutions	(106, 290)
Cyclohexanol	Benzene (?)	Dipolar absorption bands and viscosity of solutions	(62)
Ethanol and isoamyl alcohol	Benzene (1:3?)	Selective adsorption studies	(257)
Water	Benzene, toluene, ethylbenzene, <i>m</i> - and <i>p</i> -xylenes, naphthalene, biphenyl (?)	Solubility studies and ultraviolet absorption spectra of solutions	(35)

C. Halogen compounds

Chlorine	Benzene and <i>m</i> -xylene (1:1)	Ultraviolet absorption spectra of solutions	(9)
Bromine	Tetraarylethylenes (?) Benzene, toluene, <i>o</i> -, <i>m</i> -, and <i>p</i> -xylenes, chloro-, bromo-, and iodobenzenes, naphthalene (all 1:1) Anisole (1:1?) and tetraarylethylenes (?) Benzene, <i>p</i> -xylene, naphthalene, and biphenyl (?)	Colors of mixtures or solutions Ultraviolet absorption spectra of solutions	(55, 56, 236, 237) (33, 112, 160)
Iodine	Benzene, toluene, <i>o</i> -, <i>m</i> -, and <i>p</i> -xylenes, mesitylene, durene, isodurene, pentamethyl-, hexamethyl-, and hexaethylbenzenes, bromobenzene, naphthalene, styrene, bibenzyl (all 1:1)	Conductivity of solutions Dielectric constant and dipole moment of solutions Ultraviolet absorption spectra of solutions	(55, 215) (68, 88, 183, 210, 325, 326) (11, 28, 33, 66, 112, 292)

TABLE 1—Continued

Acceptor	Donor (Donor:Acceptor Mole Ratio)	Method of Investigation	References
C. Halogen compounds—Continued			
Iodine monochloride	Benzene and toluene (?)	Heats of solution of iodine in the aromatic solvents	(127)
	Toluene, xylene, and mesitylene (?) Benzene, toluene, <i>o</i> -, <i>m</i> -, and <i>p</i> -xylenes, ethyl-, isopropyl-, and <i>t</i> -butylbenzenes, chloro- and bromobenzenes, mesitylene, durene, pentamethyl-, hexamethyl-, and hexaethylbenzenes, naphthalene, and bibenzyl (all 1:1)	Diffusion studies Ultraviolet absorption spectra of solutions	(288) (11, 161)
Cyanogen iodide	Benzene (?)	Dielectric polarization of solutions	(89)
D. Halomethanes			
Chloroform	Benzene, toluene, <i>o</i> -, <i>m</i> -, and <i>p</i> -xylenes, mesitylene, chloro- and bromobenzenes, <i>o</i> -chlorotoluene, α -methyl- and α -chloronaphthalenes (all 1:1)	Heats of mixing	(170, 290)
Bromoform	Benzene, toluene, <i>m</i> -xylene, and mesitylene (probably 1:1)	Heats of mixing	(290)
Carbon tetrachloride	Benzene (1:1, 1:2, and 1:3)	Melting point-composition diagrams	(157, 330)
Carbon tetrabromide	Benzene (4:1)	Selective adsorption studies	(257)
Carbon tetraiodide	Benzene (1:1)	Vapor pressure of benzene over complex	(158)
Methylene chloride	Benzene (1:1)	Evaporation of complex under constant reduced pressure	(257)
	Benzene (1:1, 1:2, and 1:3)	Selective adsorption studies	(257)
E. Hydrogen halides and related acids			
Hydrogen fluoride	Benzene (?) Anthracene (?) and polymethylbenzenes (1:1)	Vapor pressure of solutions Conductance measurements	(282) (169, 171)

Hydrogen chloride	Benzene, toluene, <i>o</i> - and <i>m</i> -xylenes, tetralin, anthracene (?)	Solubility measurements	(172)
	<i>m</i> - and <i>p</i> -Xylenes, mesitylene, hexamethyl- and hexaethylbenzenes (?)	Distribution experiments	(202)
	Benzene (?)	Dielectric polarization of solutions	(87)
	Benzene, chlorobenzene, nitrobenzene, <i>o</i> - and <i>m</i> -nitrotoluenes (?)	Infrared absorption spectra of solutions	(107, 247, 324)
Hydrogen bromide	Benzene, nitrobenzene, <i>o</i> - and <i>m</i> -nitrotoluenes	Vapor pressure measurements	(224, 226, 227, 228)
	Benzotrifluoride, benzene, alkylbenzenes, polymethylbenzenes, halobenzenes, and thiophene (all 1:1)	Vapor pressure of hydrogen chloride over toluene or <i>n</i> -heptane solutions of the hydrocarbons	(49)
	Benzene, toluene, <i>o</i> - and <i>m</i> -nitrotoluenes (?)	Vapor pressure measurements	(159, 225)
	A variety of benzene derivatives and polynuclear aromatic hydrocarbons (?)	Color of solutions	(277)
Hydrogen fluoride-boron trifluoride	Polymethylbenzenes (1:1)	Vapor pressure measurements and batchwise extractions; conductance measurements	(169, 202, 203)
	A variety of aromatic hydrocarbons (?)	Absorption and fluorescence emission spectra	(260)
	<i>s</i> -Triethylbenzene ($\text{Al}_2\text{Cl}_6 \cdot 2\text{Ar} \cdot \text{HCl}$)	Isolated as solid	(221)
	Toluene ($\text{ArH}^+\text{AlCl}_4^-$ and also $\text{ArH}^+\text{Al}_2\text{Cl}_7^-$)	Vapor pressure measurements	(52, 53)
HCl-AlBr_3 and HBr-AlBr_3 HBr-AlBr_3	Benzene, toluene, and xylene (?)	Electrical conductivity measurements	(320)
	<i>s</i> -Triethylbenzene ($\text{Al}_2\text{Br}_6 \cdot 2\text{Ar} \cdot \text{HBr}$), mesitylene ($\text{Al}_2\text{Br}_6 \cdot 3\text{Ar} \cdot \text{HBr}$), pseudocumene ($\text{Al}_2\text{Br}_6 \cdot 3\text{Ar} \cdot \text{HBr}$), toluene (?), and benzene (?)	Isolated as solids or oils	(182, 221, 223)
	Benzene ($\text{Al}_2\text{Br}_6 \cdot \text{HBr} \cdot 6\text{C}_6\text{H}_6$?)	Ultraviolet absorption spectra; vapor pressure and conductance measurements of solutions	(83, 84)
	Benzene, toluene, <i>m</i> -xylene, and mesitylene ($\text{ArH}^+\text{Al}_2\text{Br}_7^-$ and, except for benzene, $\text{ArH}^+\text{AlBr}_4^-$)	Vapor pressure measurements	(54)

TABLE I—Continued

Acceptor	Donor (Donor:Acceptor Mole Ratio)	Method of Investigation	References
E. Hydrogen halides and related acids—Continued			
HBr-AlBr ₃ —Continued	Benzene, toluene, and xylenes [(Ar) ₂ (HBr·AlBr ₃) ₂]	Solubility studies	(16)
Acetic acid	Benzene [Ar·2(CH ₃ COOH) ₂ and Ar(CH ₃ COOH) ₂]	Selective adsorption studies	(257)
Sulfuric acid	Arylethylenes and anthracene (Ar·H ⁺)	Cryoscopic measurements; absorption spectra; distribution studies	(100, 101, 102)
Perechloric and sulfuric acids	Diarylethylenes (1:1)	Colors of solutions	(236, 237)
F. Metallic ions and salts			
Silver ion	Phenol (1:1), aromatic amines (1:1 and 1:2), and cresols (1:1) Benzene and a variety of its mono- and disubstitution products, alkyl- benzenes, and other aromatic hydro- carbons (1:1 and 1:2) Toluene (1:1 and 1:2)	Distribution studies; solubility studies Solubility of aromatics in silver nitrate solution	(103, 104, 163, 327) (6, 7, 8, 11)
Silver perchlorate	Benzene (1:1)	Solubility and ultraviolet absorption spectrum measurements	(162)
Aluminum chloride	Benzene (?) Toluene, xylene, and mesitylene (?)	Crystal structure by x-ray diffraction and Raman spectrum	(268, 263)
Aluminum bromide	Benzene (3:1?) Benzene, <i>m</i> - and <i>p</i> -xylenes (all 1:1) Benzene (?) Benzene (1:1) and benzene, toluene, <i>m</i> -xylene, and mesitylene (Ar·Al ₂ Br ₆) Benzene (1:1), toluene (6Ar·Al ₂ Br ₆ and Ar·Al ₂ Br ₆)	Conductance measurements Heats of formation Conductance measurements Melting point-composition diagrams Infrared absorption spectra of solu- tions Vapor pressure measurements Isolated as solid or oil	(215) (61) (246) (242, 243) (294) (54, 302) (82, 222)

	Benzene (Ar-Al ₂ Br ₃ ?)	Ultraviolet absorption spectra of solutions	(84)
Aluminum iodide	Benzene (?)	Dipole moment measurements	(244)
AlBr ₃ -C ₂ H ₅ Br	Benzene (Ar-Al ₂ I ₆ ?)	Ultraviolet absorption spectra of solutions	(84)
AlBr ₃ -MX (MX = KI, KBr, or KCl)	Hexaethylbenzene [Al(C ₂ H ₅ Br) ₃ (C ₁₈ H ₃₀) ₂][AlBr ₄] ₂	Conductance and transference studies	(328)
AlBr ₃ -Ti	Benzene (MX·2AlBr ₃ ·nC ₆ H ₆)	Isolated as crystalline solids after electrolysis of solutions	(168)
AlBr ₃ -NH ₃	Benzene (Ti·AlBr ₃ ·2C ₆ H ₆)	Isolated as solid from electrolysis of benzene solutions of TiBr ₃ and AlBr ₃	(245)
Ferric chloride	Benzene (AlBr ₃ ·3NH ₃ ·Ar, AlBr ₃ ·5NH ₃ ·Ar) and toluene (AlBr ₃ ·3.5NH ₃ ·Ar)	Isolated as solids	(255)
Arsenic trichloride	Perylene (1:1), <i>cis</i> - and <i>trans</i> -stilbenes (1:2)	Isolated as solids	(40, 85)
Antimony trichloride	Benzene (?)	Ultraviolet absorption spectrum of solution	(84)
	Benzene (1:2)	Viscosity measurements	(281)
	Benzene, biphenyl, diphenylmethane, and phenol (1:2?)	Cryoscopic measurements	(278)
	Benzene and other aromatic hydrocarbons (mainly 1:1 and 1:2)	Melting point-composition diagrams and isolation of solids	(85, 285, 287)
	Benzene (1:2)	Viscosity measurements	(304)
SbCl ₃ -AlBr ₃	Benzene (Ar-AlBr ₃ ·SbBr ₃)	Conductance measurements	(108)
Antimony pentachloride	A variety of polynuclear aromatic hydrocarbons (1:1 and 2:1)	Isolated as solids	(39, 40)
Stannic chloride	Toluene (?)	Viscosity measurements	(72)
	Perylene (1:2), 2,3,10,11-dibenzperylene (1:1), 1,12-benzperylene (1:2), naphthalene (1:2)	Isolated as solids	(39, 40)
Niobium pentachloride	Benzene (1:3 and 1:1? and 1:2?)	Isolated as solids	(95)
Tantalum pentachloride	Naphthalene (1:1) and anthracene (1:1)	Isolated as solids	(95)
Tungsten hexafluoride	Benzene (1:1) and toluene(?)	Color of solutions	(252)

TABLE 1—Continued

Acceptor	Donor (Donor:Acceptor Mole Ratio)	Method of Investigation	References
F. Metallic ions and salts—Continued			
Titanium tetrachloride	<i>cis</i> - and <i>trans</i> -Stilbenes (?) Benzene (1:3)	Isolated as solids Melting point-composition diagram	(37) (67)
G. Nitro compounds			
Tetranitromethane	A variety of substituted benzenes and naphthalenes, anthracene, diphenylmethane, and triphenylmethane (1:1) Unsaturated aromatic ketones (1:1, 1:2, and 2:1), aromatic amines (1:1), stilbene and derivatives (1:1 and 1:2), naphthalene and acenaphthene derivatives (1:1)	Color of solutions (and, in some cases, heats of interaction)	(38, 69, 125, 126)
s-Trinitrobenzene	Benzene (2:1) Fluorene, naphthalene, phenanthrene, anthracene, α - and β -naphthylamines (all 1:1), trinitrotoluene (?) Stilbene (1:2), 1,4-diphenyl-1-butene (1:2), 1-biphenylene-4-phenyl-1-butene (1:1), and diphenylpolyenes (1:2) Styrene and its para substitution products (?) <i>N,N</i> -Dimethylaniline, <i>N,N</i> -dimethyl- <i>o</i> -toluidine, <i>N,N</i> -dimethyl- <i>p</i> -toluidine, and diphenylamine (1:1) Aromatic hydrocarbons (1:1 and 1:2) and aromatic amines Benzene, naphthalene, phenanthrene, anthracene, pyrene, chrysene, 1,2-benzpyrene (all 1:1), and 1,2,5,6-dibenzanthracene (1:2)	Isolated as solids Melting point-composition diagram Thermal analysis with a hot-stage microscope Color of isolated solids Color of solutions Photometric studies and solubility measurements Heats of formation or dissociation in solution by calorimetric methods Ultraviolet absorption spectra of solutions of the complexes	(48, 250, 311, 321) (120) (176, 177, 179) (188) (306) (92, 197) (44, 45, 47, 111, 115) (153, 192)

Picric acid	<p>Dimethylaniline (1:1)</p> <p>Chrysene, 1,2,5,6-dibenzanthracene, pyrene, phenanthrene, 1,2-benzanthracene, 9,10-dimethyl-1,2-benzanthracene (1:1?)</p> <p>Aromatic hydrocarbons, amines, and phenols (probably all 1:1)</p> <p>Naphthalene and monosubstitution products, anthracene, fluorene, benzidine, salol, anthranilic acid, perylene (probably all 1:1)</p> <p><i>p</i>-Iodoaniline, stilbene, perylene and anthracene (all 1:1) and fluorene (3 fluorene: 4 <i>s</i>-trinitrobenzene)</p> <p><i>p</i>-Bromoaniline (1:1)</p> <p>Dibenzoylethylene and derivative (1:2), naphthalene and acenaphthene derivatives (1:1), 2,3,10,11-dibenzperylene (1:2), 1,12-benzperylene (1:1), 1,2-benzanthracene (1:1) and <i>s</i>-trichloroaniline (1:1), 4,4'-dithiolarsenobenzene (1:2)</p> <p>Alkyl, polyalkyl, and hydroxy derivatives of benzene, naphthalene, and other aromatic hydrocarbons (1:1), and 1,4-diphenyl-1-butene and diphenylpolyenes (1:2)</p> <p>Various 1,2-benzanthracenes and benzocyclophenanthrenes (mostly 1:1)</p> <p>Naphthalene, stilbene, and its <i>p</i>-chloro and <i>p</i>-methyl derivatives and ethyl cinnamate (all 1:1)</p> <p>Perylene (1:1 and 1:2), benzene (2:1), and nitronaphthalene (1:1)</p>	<p>Infrared absorption spectrum</p> <p>Fluorescence of the complexes</p> <p>Dielectric properties and dipole moments</p> <p>Magnetic susceptibility and anisotropy</p> <p>Crystal structures by x-ray diffraction</p> <p>Dichroism of crystals</p> <p>Isolated as solids</p> <p>Colors of solid addition products</p> <p>Melting points as criteria of steric effects</p> <p>Solubility measurements; colorimetric studies</p> <p>Melting point-composition diagrams</p>	<p>(59) (259)</p> <p>(186, 271) (18, 270)</p> <p>(130, 136, 143, 251)</p> <p>(217, 295) (30, 39, 48, 185, 321)</p> <p>(21, 188)</p> <p>(229)</p> <p>(13, 266)</p> <p>(40, 120, 154)</p>
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TABLE 1—*Continued*

Acceptor	Donor (Donor:Acceptor Mole Ratio)	Method of Investigation	References
<i>G. Nitro compounds—Continued</i>			
Picric acid— <i>Continued</i>	Fluorene, naphthalene, anthracene, phenanthrene, α - and β -naphthylamines, pyridine (all 1:1)	Thermal analysis with a hot-stage microscope	(178, 179)
	Benzene, alkylbenzenes, and polymethylbenzenes (1:1)	Distribution studies	(4)
	Acenaphthene and anthracene (1:1)	Heats of formation by calorimetric methods	(111)
	Anthracene (1:1)	Dielectric properties	(186)
	4-Bromo-1-naphthylamine and 1-bromo-2-naphthylamine (1:1)	Conductivities in acetone solution	(141)
	Naphthalene, anthracene, phenanthrene, α -methylnaphthalene (all 1:1)	Diamagnetic susceptibilities	(31, 32)
	Naphthalene, α - and β -naphthols, α -bromonaphthalene, anthracene, fluorene, and chrysene (1:1?)	Classification according to crystal structure	(261)
	Benzene (2:1)	Melting point-composition diagram	(120)
	Hexamethylbenzene (1:1)	Absorption spectra of solutions	(264)
	Hexamethylbenzene (1:1)	Changes in vapor pressure on sublimation at constant temperature	(219, 220)
Picryl chloride	Hexamethylbenzene (1:1)	Dichroism of crystals	(217, 295)
	Hexamethylbenzene (1:1)	Crystal structure by x-ray diffraction	(250)
Miscellaneous aromatic nitro compounds:	Substituted benzenes and aromatic hydrocarbons (?)	Colors of mixtures	(38, 51)
	Aromatic hydrocarbons and amines and other substituted aromatics (mostly 1:1)	Colors and melting points of solid addition products	(135)
1. Polynitrobenzenes and nitrobenzene-aluminum chloride mixture			
2. Substituted di- and trinitrobenzenes and phenols			

3. 2,4-Dinitrochlorobenzene	α - and β -Naphthylamines, benzidine, pyridine, naphthalene, fluorene, biphenyl, and α - and β -naphthols (all 1:1)	(58)
4. 2,4-Dinitrobromobenzene	α - and β -Naphthylamines, pyridine, naphthalene, α - and β -naphthols (all 1:1)	(58)
5. <i>p</i> -Nitrochlorobenzene	α -Naphthol (1:1)	(57)
6. 2,4,7-Tritrofluorenone	A variety of aromatic hydrocarbons and derivatives (mainly 1:1 and 1:2)	(230, 231)
7. 4-Nitrobiphenyl and 4,4'-dinitrobiphenyl	<i>N,N,N',N'</i> -Tetramethylbenzidine (1:1)	(258)
8. 2,4,6-Tritroanisole	<i>N,N</i> -Dimethyl- β -naphthylamine, α - and β -naphthylamines, and 4-bromo-1-naphthylamine (all 1:1)	(131, 138)
9. Trichlorotrinitrobenzene	Hexamethylbenzene and naphthalene (probably 1:2)	(119)
10. 2,6-Dinitrophenol	4-Bromo-1-naphthylamine (1:1)	(131)
11. Nitrobenzene	<i>m</i> -Dinitrobenzene (1:1), <i>s</i> -trinitrobenzene (1:2), and dimethylamine (1:1)	(117, 118, 200)
12. Trinitrotoluene	Picryl chloride (1:1)	(109)
13. Dimethyl 4,6,4',6'-tetranitrobiphenate	Aromatic hydrocarbons and nitro compounds (mostly 1:2)	(123)
14. 2,4-Dinitro-2'-methylbiphenyl-6-carboxylic acid	Benzene (1:1 and 1:2)	(124)
15. A variety of mono- and polynitroaromatics	Aromatic hydrocarbons and substitution products including naphthols and naphthylamines (mainly 1:1)	(14, 81, 147, 283, 284, 285)
16. Dimethyl 4,6,4',6'-tetranitrobiphenate	7-Methylacenaphthene (1:2)	(48)
17. <i>d</i> - and <i>l</i> -2,4-Dinitro-2'-methylbiphenyl-6-carboxylic acid	Benzene (1:2)	(195)
18. <i>d</i> - and <i>l</i> -4,6,4'-Tritnitrobiphenic acid	Benzene (1:2)	(121)

Colors and melting points of solid addition products

Melting point-composition diagrams

Isolated as solids

TABLE I—Continued

Acceptor	Donor (Donor:Acceptor Mole Ratio)	Method of Investigation	References
G. Nitro compounds—Continued			
19. 4,6-Dichloro-1,3-dinitrobenzene and 4,6-dibromo-1,3-dinitrobenzene	Naphthalene, naphthols, naphthylamines, and other aromatic hydrocarbons and amines (some 1:1), some 1:2, and some 2:1)	Isolated as solids	(2, 151)
20. Styphnic acid	Perylene (1:1), 2,3,10,11-dibenzperylene (1:2), 1,12-benzperylene (1:1), and 1,2-benzanthracene (1:1)		(39)
21. α -[2,4,6-Trinitrophenoxylpropionic acid ethyl ester	Dimethylaniline (1:1)		(138)
22. A large number of substituted mono- and dinitrobenzenes and derivatives of nitroisophthalic acid	Aromatic hydrocarbons and amines (mainly 1:1, some 1:2)		(29, 30)
23. <i>p</i> -Nitrotoluene and 2,4-dinitrotoluene	Naphthalene (1:1)	Thermal analysis with a hot-stage microscope	(175)
24. 2,4-Dinitrophenol	Phenanthrene (1:1)		(176)
25. <i>p</i> -Dinitrobenzene	α -Naphthylamine (1:1, 3:2, 2:1)		(178)
26. Trinitrotoluene	Carbazole (1:1?)		(178)
27. 2,4,7-Trinitrofluorenone	A variety of aromatic hydrocarbons and derivatives	Distribution experiments	(191)
28. A variety of nitroaromatics including picric acid	A large number of alkylbenzenes and other substituted benzenes and naphthalenes (all 1:1)		(209)
29. Dinitrobenzenes and <i>s</i> -trinitrobenzene	Naphthalene, anthracene, biphenyl, and acenaphthene (all 1:1)	Heats of formation or dissociation by calorimetric methods	(42, 111)
30. <i>o</i> -Chloronitrobenzene and 2,4-dinitrochlorobenzene	Diphenylamine (1:1)		(126)
31. <i>m</i> - and <i>p</i> -Dinitrobenzenes and <i>s</i> -trinitrobenzene	Aniline (1:1 and 2:1)	Visible and ultraviolet absorption spectra of solutions	(190)

32. Nitrobenzene	Aniline (?)	Infrared absorption spectra of solutions	(294)
33. <i>m</i> -Dinitrobenzene	Acenaphthene (?)		(59)
34. Nitrobenzene and related compounds	Aniline, dimethylaniline, diphenylamine, triphenylamine, and related substances (?)	Effects of pressure and temperature changes on light absorption of solutions	(98)
35. Dimethyl 4,6,4',6'-tetranitrobiphenate	Indene (1:2)	Rate of formation and decomposition in carbon tetrachloride solutions	(122)
36. 2,6-Dinitrophenol	4-Bromo-1-naphthylamine (1:1)	Comparative study of solubilities, heats of solution and crystallization phenomena of red and yellow forms	(132)
37. <i>m</i> -Dinitrobenzene and <i>p</i> -dinitrobiphenyl	<i>m</i> -Phenylenediamine (?) and β -naphthylamine (?)	Freezing-point depressions of mixtures in benzene	(23)
38. Various dinitro- and trinitroaromatics	Aromatic hydrocarbons and amines, phenols (?)	Electric polarization and dipole moments	(271)
39. Nitrobenzene, <i>m</i> -dinitrobenzene, and <i>s</i> -trinitrobenzene	Naphthalene (?)		(44)
40. <i>m</i> -Dinitrobenzene	Benzidine, naphthalene, and α -naphthylamine (1:1)	Magnetic susceptibilities	(32)
41. 2,4-Dinitrophenol and 2,4-dinitrochlorobenzene	Aromatic hydrocarbons and amines, phenols (1:1)		(253)
42. 2,6-Dinitrophenol	4-Bromo-1-naphthylamine (1:1)	Crystal structure by x-ray diffraction	(142)
43. 4,6-Dinitro- <i>m</i> -xylene	Acenaphthene (1:1)		(133)
44. 2,4,6-Trinitrochlorobenzene	2,4,6-Trinitrotoluene (1:1)	Chromatography of solutions	(140)
45. Substituted nitrotoluenes	Substituted naphthalenes (1:1?)		(286)
46. Nitrobenzene	Rubrene (1:1?)	Fluorescence-quenching experiments	(36)
H. Quinones			
Benzoquinone	Hydroquinone, hydroquinone dimethyl ether, hydroquinone diethyl ether, hydroquinone methyl ether, phenol, anisole, phenetole, resorcinol, phloroglucinol, benzene (all 1:1)	Absorption spectra in various solvents	(12, 207)

TABLE 1—*Concluded*

Acceptor	Donor (Donor:Acceptor Mole Ratio)	Method of Investigation	References
<i>H. Quinones—Continued</i>			
<i>Benzoquinone—Continued</i>	Hydroquinone (1:1), phenol (2:1), <i>p</i> -cresol (2:1), <i>p</i> -bromophenol (2:1), <i>p</i> -chlorophenol (2:1)	Crystal structure by x-ray diffraction	(5, 93, 307)
	Hydroquinone (1:1)	Dichroism of crystals	(217, 295)
	Hydroquinone (1:1)	Dielectric properties	(186)
	Hydroquinone (1:1)	Vapor pressure measurements, vapor composition studies	(220)
	Hydroquinone (1:1)	Diamagnetic susceptibility	(18, 189, 208)
Chloranil	Hydroquinone (1:1)	Color of solutions	(22, 38, 306)
	Stilbene, indene, styrene, 1,1-diphenylethylene, <i>p</i> -methoxy-, <i>p</i> -methyl-, and <i>p</i> -chlorostyrenes, and other aromatic substances (probably 1:1)		
	Hexamethylbenzene (1:1)	Visible absorption spectra of solutions	(207)
Bromanil	Hexamethylbenzene (1:1)	Dichroism of crystals	(217, 295)
	Hexamethylbenzene (1:1)	Crystal structure by x-ray diffraction	(5)
	Hexamethylbenzene (1:1)	Crystal structure by x-ray diffraction	(5)
Naphthoquinone 2,7-Dinitroanthraquinone	Hydroquinone (1:1)	Crystal structure by x-ray diffraction	(137)
	Fluorene (1:1)	Ultraviolet and visible absorption spectra of solutions	(149)
	Dimethylaniline, hydroquinone dimethyl ether, resorcinol dimethyl ether, durenene, anisole, toluene, mesitylene, <i>p</i> -xylylene, dibenzyl (?)		
Substituted anthraquinones and phenanthrenequinones	A variety of aromatic hydrocarbons (1:1 and 2:1)	Isolated as solids or colorations observed on fusion of mixtures	(134)

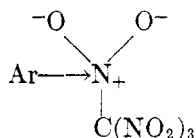
I. Sulfur compounds

Sulfur dioxide	Diphenylamine, naphthalene, biphenyl, diphenyl ether, naphthols	Colors of solutions	(91)
	Benzene (1:1, 1:2, and 1:3), toluene (1:2 and 1:3), mesitylene (1:1), pseudo-cumene (1:1), ethylbenzene (1:1 and 1:2), cymene (1:1 and 1:2), and tetralin (1:1, 1:2, and 1:3)	Melting point-composition diagrams	(70, 71, 205)
	Benzene, toluene, xylene, and mesitylene (?)	Viscosity measurements	(199)
Sulfur trioxide Thionyl chloride Thionyl chloride and sulfuryl chloride	Benzene, toluene, <i>o</i> -, <i>m</i> -, and <i>p</i> -xylenes, mesitylene, chlorobenzene, and styrene (all 1:1)	Ultraviolet absorption spectra of solutions	(10, 19)
	Naphthacene (?)	Color of solutions	(256)
	Biphenyl and stilbene (?) Benzene, toluene, xylene, and mesitylene (?)	Color of solutions Heats of mixing and viscosity measurements	(187) (199)

J. Triphenylmethane and derivatives

Triphenylmethane	Benzene (1:1)	Isolated as solid	(94)
Diaminotriphenylmethane and derivatives	Benzene (1:1)	Melting point-composition diagram	(167)
	A variety of substituted benzenes and aromatic amines, thiophene (largely 1:1)	Isolated as solids	(309)

favorable polarization, as indicated below for tetranitromethane, on the approach of an electron-rich reagent.



It is not yet clear whether the seat of coördination of the donor molecule in such complexes necessarily is the nitrogen atom of a specific nitro group or whether the electron-attracting force of the nitro and similar groups in the acceptor molecule may be exerted through the aromatic nuclei to which they are attached (29). Crystal structure determinations of solid polynitroaromatic complexes (1, 250, 251) seem to provide no definitive answer in this matter but indicate that the interactions between components are weak in character.

IV. STABILITIES OF THE COMPLEXES AS INFLUENCED BY THE STRUCTURES OF THE COMPONENTS

Although the forces of interaction between the components of aromatic donor-acceptor complexes ordinarily are much weaker than those associated with the formation of true chemical bonds, the extent to which these interactions occur in solution is, nevertheless, governed by the mass action principle. Equilibrium constants for complex formation between a large number of donors and acceptors in solution have been determined by a variety of procedures, as outlined in Section II. These constants, which serve as a basis for comparison of the relative stabilities of the complexes, are generally enhanced by the introduction in the aromatic donor component of substituents which increase the electron density of the ring. Favorable electronic influences of these substituents appear in certain cases, however, to be overshadowed by unfavorable steric effects. A detailed consideration of the observations on which these conclusions (and others concerning the influence of changes in donor and acceptor structures on complex stabilities) are based is presented in this section. It should be noted that the classification of the complexes under discussion as products of donor-acceptor interaction is an outgrowth of these observations.

A. Monosubstituted benzenes as donors

The relative stabilities of complexes of a variety of monosubstituted benzenes with silver ion in aqueous solution (6, 7, 8) increase with changes in substituent in the following order (the numbers in parentheses are the equilibrium constants, K_1 , as defined by equation 5 for the formation of 1:1 complexes, $\text{Ag} \cdot \text{Ar}^+$): NO_2 (0.19), F (0.46), COCH_3 (0.54), COOC_2H_5 (0.56), Cl (0.69), Br (0.97), OH (2.19), H (2.41), OCH_3 (2.50), CH_3 (2.63), I (5.00), $\text{CH}=\text{CH}_2$ (18.2). With the exception of the last two substituents this order parallels in a general way the capacity of the substituents to enhance the electron density of the aromatic ring, as measured by their effects on the rates and positions of electrophilic aromatic substitution. It has been shown that the logarithms of these equilibrium constants

give a straight line when plotted (7) against the Hammett σ_{meta} values (116) for the corresponding substituent groups, a fact which may indicate that the relative stabilities of the complexes are controlled primarily by the inductive effect of the ring substituents.

The exceptionally high K_1 value for iodobenzene as compared to that for the other halobenzenes is ascribed to the formation of complexes in which silver ion is preferentially coordinated with the iodine atom rather than with the aromatic nucleus (7). The high value for styrene may indicate that in its complex silver ion is specifically coordinated at the vinyl side chain (8). As might be expected, the K_2 values (equation 6) for the formation of 1:2 complexes, $\text{Ag}_2 \cdot \text{Ar}^{++}$, of these substituted benzenes are much smaller than the K_1 values.

There are other data in the literature which demonstrate the same relative order of stability for complexes of monosubstituted benzenes with various types of acceptors. Among these may be mentioned the equilibrium constants, as determined by spectrophotometric methods, for the interaction of bromine (160), iodine monochloride (161), and sulfur dioxide (10) with aromatic donors. These increase with changes in donor in the order chlorobenzene < benzene < toluene. From measurements of the vapor pressure of hydrogen chloride over solutions of benzene derivatives (49) the stability order of hydrogen chloride complexes is established as benzotrifluoride < chlorobenzene < benzene < toluene. The stabilities of the halobenzene-bromine complexes are in the order chlorobenzene < benzene < bromobenzene < iodobenzene, but of the hydrogen chloride-halobenzene complexes that of iodobenzene is the least rather than the most stable. Bromine may fall into that class of acceptors which show some tendency to coordinate with halogen bound in aromatic compounds.

With some acceptors the magnitudes of the relative stabilities are considerably more sensitive to changes in ring substituents than are those of the silver-ion complexes. The relative stabilities (in parentheses) of tetranitromethane complexes of monosubstituted benzenes in chloroform (125) increase with changes in ring substituent as follows: H (0.05), CH_3 (0.90), OCOCH_3 (1.68), OH (12.28), OC_6H_5 (15.87), OCH_3 (20.41), OC_2H_5 (20.62). Data taken by distribution procedures for picric acid complexes (209) seem anomalous in that the addition products of nitrosubstituted benzenes are more stable than that of benzene itself, even though nitro groups are strongly electron-withdrawing in nature. It is probable that specific interactions between the nitro groups of the two components lead to the formation of these and closely related (109, 117, 118) complexes.

Similar effects of changes in donor substituents are noted for other than monosubstituted benzene systems. The relative stabilities of *s*-trinitrobenzene complexes of a variety of ring-substituted aromatic amines in carbon tetrachloride are roughly parallel to the base strengths of the amines, which in turn are influenced by the ring substituents (115). The stabilities of the picric acid adducts of a series of stilbenes in chloroform (13) are in the order *p*-chlorostilbene < stilbene < *p*-methylstilbene.

Sinomiya (284), through use of his melting-point elevation procedures, has

recorded the following stability series for α -substituted naphthalene complexes of *s*-trinitrobenzene:

α -substituent: $\text{NH}_2 > \text{CH}_3 > \text{OH} > \text{C}_2\text{H}_5 > \text{OCH}_3 > \text{Cl} > \text{Br} > \text{OC}_2\text{H}_5 > \text{H}$

Certain groups, particularly OC_2H_5 and H , seem out of place in this series, a fact which is not surprising, since no more than the most qualitative interpretation of this kind of experimental data seems justified.

The stabilities of the adducts of substituted anilines and 2,4-dinitrochlorobenzene (determined by spectrophotometric methods) in ethanol do not conform in every detail to the anticipated effects of the various substituents on the basicities of the donor molecules (265). It is possible that these stabilities would fall in the expected order if a non-polar medium, in which solvation effects are relatively unimportant, were used in their investigation.

B. Polymethylbenzenes and alkylbenzenes as donors

Sufficient information concerning complexes of polymethylbenzenes and alkylbenzenes is available so that a rather detailed examination can be made of the effects on the stabilities of the complexes of changes in the number and kinds of donor substituents. Table 2 presents a summary of the relative stabilities of addition products of these donors with a number of different acceptors. The stabilities of the *p*-xylene complexes have been chosen as reference standards, and the reported data have been compiled from the results of equilibrium studies which are presumed to be representative of comparative tendencies for 1:1 complex formation.

With all acceptor types except silver ion it is apparent that the donor strength of benzene is enhanced by increasing methyl substitution in the order: toluene < xylenes < mesitylene < hexamethylbenzene. The colors of solid picric acid addition compounds of these benzene derivatives deepen from light yellow to orange yellow in this same order (21). These changes reflect the capacity of a methyl substituent, through induction or hyperconjugation, to increase the electron density of the aromatic nucleus.

For the silver-ion complexes the order of stability is mesitylene < durene < benzene < toluene < xylenes. Two explanations have been advanced to explain the low stability of the mesitylene and durene complexes. In the first it is assumed that water molecules in the hydration sphere of silver ion hinder, through overlap of ring methyl substituents, the close approach of the metallic ion to the aromatic nucleus (6). In the other it is believed that the approach of silver ion to a bonding position near the perimeter of the ring is inhibited in a molecule in which unsubstituted carbon atoms are adjacent to methyl-substituted carbon atoms (212).

Other evidence suggesting that opposing electronic and steric factors affect the donor strength of methylated benzenes is to be found in the previously cited (Section II) reports of the interaction of substituted aromatic hydrocarbons with chloroform and bromoform (290) and with methanol (152). The data of these investigations indicate that even the donor capacity of *m*-xylene is subject to some steric repression.

TABLE 2
Relative stabilities of complexes of polymethylbenzenes and alkylbenzenes (*p*-xylene = 1.00)

Benzene ring substituents	Acceptors										
	Ag ⁺	Br ₂	I ₂	ICl	SO ₂	TNM*	PA†	HCl	HF	HF-BF ₃	Halogenation rate
H.....	0.92	0.46	0.48	0.36	0.35	0.007	0.70	0.61	0.09	—	0.0005
CH ₃	1.00	0.64	0.52	0.58	0.59	0.14	0.84	0.92	0.63	0.01	0.157
<i>o</i> -(CH ₃) ₂	1.20	1.01	0.87	0.82	1.23	1.00†	1.03	1.13	1.1	2	2.1
<i>m</i> -(CH ₃) ₂	1.25	0.96	1.00	0.92	1.11		0.98	1.26	26	20	200
<i>p</i> -(CH ₃) ₂	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
1,2,4-(CH ₃) ₃	—	—	—	—	—	—	—	1.36	63	40	340
1,2,3-(CH ₃) ₃	—	—	—	—	—	—	—	1.46	69	ca. 40	400
1,3,5-(CH ₃) ₃	0.68	—	2.65	3.04	1.57	3.27	1.12	1.59	13,000	2,800	80,000
1,2,4,5-(CH ₃) ₄	0.85	—	2.04	2.82	—	4.10	1.65	—	140	120	1,400
1,2,3,4-(CH ₃) ₄	—	—	—	—	—	—	—	1.63	400	170	2,000
1,2,3,5-(CH ₃) ₄	—	—	—	—	—	—	—	1.67	16,000	5,600	240,000
(CH ₃) ₆	—	—	2.84	4.21	—	5.60	—	—	29,000	8,700	360,000
(C ₂ H ₅) ₆	—	—	4.35	15.0	—	7.81	2.83	—	97,000	—	—
C ₆ H ₅	1.12	—	0.42	0.82	—	—	—	—	—	—	—
<i>n</i> -C ₃ H ₇	1.20	—	—	0.58	—	0.18	0.74	1.06	—	—	0.13
<i>n</i> -C ₄ H ₉	1.25	—	—	—	—	—	0.98	—	—	—	—
<i>i</i> -C ₃ H ₇	1.16	—	—	—	—	—	0.57	—	—	—	—
<i>s</i> -C ₄ H ₉	0.91	—	—	0.58	—	0.13	0.59	1.24	—	—	0.08
<i>t</i> -C ₄ H ₉	0.87	—	—	—	—	—	0.56	—	—	—	—
<i>t</i> -C ₃ H ₇	0.91	—	—	0.58	—	0.24	0.51	1.36	—	—	0.05
References.....	(6, 8, 11, 162)	(160)	(11)	(11)	(10)	(125)	(4)	(49)	(169§)	(49, 202)	(49)

* Tetranitromethane.

† Picric acid.

‡ Based on a mixture of xylenes of unknown composition.

§ Less complete data based on vapor pressure measurements are available in reference 202. The tabulated data are based on equilibrium constants for the formation of ArH⁺ in 0.1 *M* solutions of the hydrocarbons in anhydrous hydrogen fluoride.

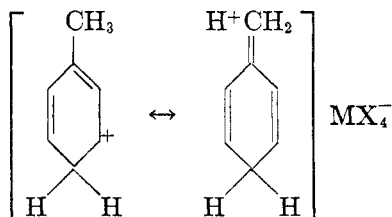
There is no convincing evidence of steric influence of ring substituents on the response of these donors to other types of acceptors except in the cases of the iodine and iodine monochloride complexes of hexamethylbenzene. Of the two most likely structures which have been suggested for benzene-halogen complexes (one in which the axis of the halogen molecule lies on the sixfold symmetry axis of the ring (160) and the other in which the halogen molecule lies parallel to the ring with its center on the sixfold symmetry axis (212)), neither would appear to be less favored sterically by a high degree of donor methylation. On the other hand a consideration of molecular models indicates that in hexaethylbenzene the π electrons of the aromatic nucleus must be shielded to a considerable extent by the alkyl groups (11, 292). Actually (see table 2) the stability of the iodine monochloride complex of hexaethylbenzene is of the same order of magnitude as those of benzene, toluene, and ethylbenzene and is much lower than that of hexamethylbenzene; similar stability relationships are observed for the iodine complexes of toluene, hexamethylbenzene, and hexaethylbenzene.

As the polymethylbenzene-iodine complexes increase in stability the wave length of their primary near-ultraviolet absorption band shifts toward the visible. The hexaethylbenzene complex is exceptional in this regard; its absorption maximum lies further toward the visible than that of any of the other polyalkylbenzene-iodine addition products. Presumably, hexaethylbenzene is inherently a strong base to which halogens which have penetrated the steric barrier are rather tightly held (292).

Other evidences of steric interference of donor methyl substituents have been cited by Orchin (229). For example, of the twelve monomethyl-1,2-benzanthracene picrates all are higher melting than picric acid with the exception of the 9-methyl- and 1'-methyl-1,2-benzanthracene derivatives. In the former hydrocarbon the 9-methyl group must overlap the 1'-hydrogen. Because of this overlap the approach of picric acid to the hydrocarbon plane is hindered, and a low-melting complex of low stability is formed. In the 1'-methyl compound similar methyl-hydrogen overlap must occur. Actually this hydrocarbon forms a dipicrate. Because of steric factors the hydrocarbon may tend to be non-planar and function as two independent naphthalene nuclei with respect to coordination with picric acid. Steric factors are also presumed (229, 321) to account for the low stabilities of picrates and related complexes of the *cis* isomers of stilbenes and 1,2-dibenzoylthylenes. Hydrogen rather than methyl overlap tends to destabilize the picric acid and *s*-trinitrobenzene complexes of 1-phenyl-1- α -naphthylethylene (48). The failure of rubrene to form complexes with *m*-dinitrobenzene and *s*-trinitrobenzene (36) is attributed to steric interference by the four phenyl groups on the naphthalene nucleus of the hydrogen molecule.

Brown and Brady (49) have compared the relative stabilities of the hydrogen chloride and hydrogen fluoride-boron trifluoride complexes of polymethyl- and alkylbenzenes with the relative rates (64, 74) of nuclear halogenation of the aromatic compounds (see the last column of table 2). Alterations in ring substituents produce marked and very similar changes in the susceptibility of the aromatic compounds to ring halogenation and to complex formation with hydrogen fluoride-boron trifluoride. A linear correlation between the logarithms of the relative

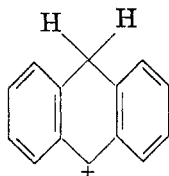
halogenation rates of the donors and the logarithms of the relative stabilities of the corresponding hydrogen fluoride-boron trifluoride complexes has been demonstrated. The hydrogen fluoride-boron trifluoride complexes are therefore regarded as close structural relatives of the transition state intermediates in electrophilic aromatic substitution reactions. These complexes, as well as the hydrogen chloride-aluminum chloride-aromatic addition products, are pictured in terms of a structure in which a proton is specifically coordinated at one of the ring carbon atoms. For the toluene complex a structure of the type



may be written, in which the organic cation is stabilized through methyl group hyperconjugation (49, 202). These interaction products, in which the bonding between the acceptor and ring carbon is of the sp^3 type, are designated as *sigma* (σ) complexes to differentiate them from the less stable π complexes in which the donor molecule accommodates the acceptor probably without the sacrifice of appreciable resonance energy. Recent quantum-mechanical calculations suggest that benzenium ion itself, $C_6H_7^+$ (which is presumably of the σ complex type), should be stabilized to a considerable degree by hyperconjugation (238).

In support of the σ complex structure are cited the facts that the hydrogen fluoride-boron trifluoride and hydrogen chloride-aluminum chloride complexes are highly colored. Also, of the xylene isomers the meta forms by far the most stable adduct, and mesitylene is the most basic of the trimethylbenzenes and is more basic than 1,2,4,5- or 1,2,3,4-tetramethylbenzene. It can readily be demonstrated (202) that hyperconjugative stabilization of protonated polymethylbenzenes of the σ complex type is greatest when methyl substituents are in meta positions relative to each other. In addition, the hexamethylbenzene-hydrogen fluoride-boron trifluoride complex is more stable than that of hexaethylbenzene; and it is observed experimentally that ethylbenzene, which is subject to less hyperconjugative resonance stabilization than is toluene, is halogenated more slowly than is toluene.

Anthracene forms a yellow complex in sulfuric acid to which the structure



is assigned (102). The choice of the meso position as the preferential seat of proton coordination has been justified on theoretical grounds and is supported by the

observation that the spectrum of the complex is closely similar to those of the diarylcarbonium ions formed from diarylethylenes (100, 102) or diarylcarbinols in sulfuric acid solution. Deuterium tracer experiments also show that proton exchanges of anthracene in sulfuric acid occur most readily at the meso position (101).

The spectra of aromatic hydrocarbons in hydrogen fluoride-boron trifluoride solutions (260) show bands at 4000 Å. which are presumed to be characteristic of aromatic carbonium ions and which are similar to those of anthracene in sulfuric acid. Some multi-ring hydrocarbons in hydrogen fluoride-boron trifluoride also show bands at about 4800 Å. which are ascribed to protonated structures in which the positive charge is distributed over the entire ring system. Absorptions in the 300 m μ region of these solutions are tentatively ascribed to Ar·BF₃ complexes.

Although a general enhancement in the relative stabilities of hydrogen chloride complexes with increasing donor methylation is observed, the magnitudes of the changes are by no means as great as those found for the hydrogen fluoride-boron trifluoride adducts. Graphing of the logarithms of the relative stabilities of the hydrogen chloride complexes *versus* the logarithms of the halogenation rates of the corresponding donors does not produce as elegant a linear plot as is obtained for the hydrogen fluoride-boron trifluoride data, largely because the points for ethyl-, isopropyl-, and *tert*-butylbenzenes fall markedly off the line. Unfortunately the stabilities of the hydrogen fluoride-boron trifluoride addition products of these alkylbenzenes are not known. However, if the stabilities of the hydrogen chloride-alkylbenzene complexes were dependent on the capacity of the alkyl group to hyperconjugate with the aromatic nucleus, the reverse of the observed order (toluene < ethylbenzene < isopropylbenzene < *tert*-butylbenzene) would be found. These facts and the fact that the complexes of *m*-xylene and mesitylene with hydrogen chloride are not markedly more stable than those of their isomers led Brown and Brady to conclude that these complexes are of the π type and that their stabilities are influenced by donor substituents in a different way from those of the more stable σ types.

There is obviously some justification for the proposal that a σ complex may have a discrete existence and is not necessarily to be encountered only as a fleeting intermediate in an aromatic substitution reaction. The measurement of an activation energy for the conversion of a π to a σ complex for a given benzenoid donor-acceptor system would provide substantiating evidence for the σ complex theory. There is reason to believe that two different types of pyridine-iodine complexes,⁵ which are separated by an energy barrier, may form (213).

More attention should be given to the fact that the magnitudes of the responses in donor strength to changes in ring substituents vary widely for different acceptors and may be dependent on factors such as the polarizabilities or electron affinities (see Section V) of the acceptors. With hydrogen chloride as the acceptor

⁵ The results of recent work on the interesting pyridine-iodine complexes, in which iodine is probably preferentially coöordinated at the ring nitrogen atom, are available in references 34, 173, 184, 289, and 331.

the increases in complex stabilities with increasing donor methylation are small; they are somewhat greater for iodine and iodine monochloride and are, of course, very large for hydrogen fluoride-boron trifluoride as well as for hydrogen fluoride itself. For the complexes of the weaker acceptors these changes are often not far greater than the experimental errors and may therefore deserve no more than qualitative attention. Large differences in the relative magnitudes of the

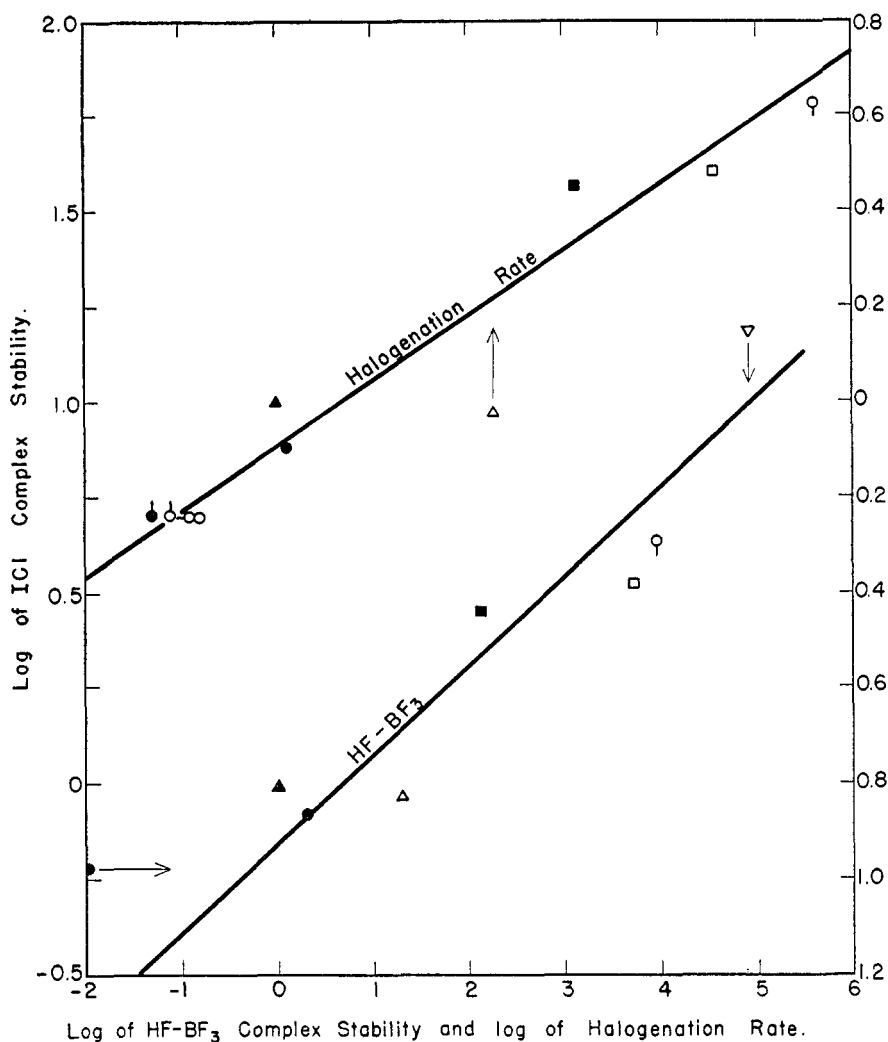


Fig. 1. The relationship between logarithms of the stabilities of iodine monochloride complexes of polymethylbenzenes and of the logarithms of the stabilities of the corresponding hydrogen fluoride-boron trifluoride complexes or of the nuclear halogenation rates of the hydrocarbons. For the upper curve read ordinate values on the right and for the lower curve read ordinates on the left. Benzene ring substituents are indicated as follows: ●, *o*-(CH₃)₂; △, *m*-(CH₃)₂; ▲, *p*-(CH₃)₂; □, 1,3,5-(CH₃)₃; ■, 1,2,4,5-(CH₃)₄; ♀, (CH₃)₆; ▽, (CH₃)₈; ○ or ◐, CH₃; ∞, C₂H₅; ♂, *i*-C₃H₇; ♀, *t*-C₄H₉.

strength of bases with changes in reference acids have been noted for other types of interaction. For example, pyridine is twenty-five times as strong as aniline with respect to antimony trichloride and is five hundred times as strong as aniline in its response to picric acid (180).

The iodine monochloride complexes are very likely of the simple π type, since the equilibrium for their formation in solution is established instantaneously at room temperature. The logarithms of their stabilities, insofar as data are available, show a fair linear correlation with the logarithms of the rates of halogenations and with the logarithms of the stabilities of the hydrogen fluoride-boron trifluoride complexes of the corresponding donor molecules (see figure 1). The data for the complexes of ethyl-, isopropyl-, and *tert*-butylbenzenes, contrary to those obtained using hydrogen chloride as a donor, show no abnormalities when they are analyzed in this manner. Certainly the trends in stability, if not in the magnitudes, for each of the donor-acceptor systems listed in table 2 are similar to the observed trends in halogenation rate of the donors. It seems, then, that the best criterion for distinguishing π and σ complexes,⁶ if they are to be regarded as different structural entities, lies in an examination of the changes in *relative magnitudes* of the stabilities of the complexes with changes in donor substituents.

Anderson and Hammick (4) have made an interesting observation concerning the stabilities of a series of alkylbenzene picrates (see table 2). These vary as the alkyl groups are changed in the order H, C₂H₅, *n*-C₃H₇, *n*-C₄H₉, *n*-C₅H₁₁ in the same zigzag fashion as do the melting points of the straight-chain fatty acids from formic to hexanoic. The stabilities of the complexes in which the alkyl substituents (R) are H, CH₃, C₂H₅, *i*-C₃H₇, *t*-C₄H₉ vary in much the same way as do the melting points of the acids RCOOH. It is suggested that the interaction energies of the complexes in the liquid state are comparable with latent heats of fusion of the acids. Since the latter are presumed to be dependent on the packing arrangement of the alkyl chains, it follows that packing factors may also be of significance in determining the stabilities of the π complex in solution.

C. Multi-ring compounds as donors

Rapson, Saunder, and Stewart (258) have observed that the donor-acceptor ratio in aromatic complexes is usually 1:1 unless two or more structurally independent coordination sites are present in the donor molecule. In the stilbenes (321) and diphenylpolyenes (188), which form 1:2 complexes with *s*-trinitrobenzene, the two benzene rings probably function as separate coordination centers. Since, however, the colors of the complexes are intensified as the length of the polyene chain is increased, the stabilities of the complexes must depend on the extent to which electronic interaction between the aromatic rings of the donor molecule can occur. Even when two such sites are available, steric relationships may be unfavorable for their simultaneous occupancy by an acceptor. The poly-

⁶ Mulliken (213) uses the terms *inner* and *outer* complex more or less synonymously with the terms σ and π complex. He further subtypes these according to structural variations in donor and acceptor molecules. These subclassifications are important to his general theory of donor-acceptor interaction, but will not be treated in detail in this discussion.

nuclear aromatic hydrocarbons, in spite of their large size as compared to simple benzenes, frequently function as single donor units. The donor character of the 1:1 complexes is considerably less from both an electronic and a steric point of view than that of the uncomplexed hydrocarbon. With very large donors such as 1,2,5,6-dibenzanthracene (153) 1:2 complexes are often formed.

There are a number of reports concerning the formation of 1:3 complexes of benzene with acceptors such as carbon tetrachloride (157, 330), methylene chloride (257), and sulfur dioxide (70, 71, 205); these are somewhat surprising considering the steric limitations of benzene as a coordination center. Most of these complexes have been characterized through thermal analysis of binary systems, a procedure which is not always reliable for the determination of the composition of a complex.

In general, in the absence of unfavorable steric factors the stabilities of 1:1 complexes of a given acceptor increase as the number of benzene rings in the donor, or fused rings in a polynuclear donor system, is increased. (As Orchin (229) points out, however, certain complexes are usually stable because of fortunate relationships in the size and shape of the donor and acceptor molecules.) The iodine and iodine monochloride complexes of naphthalene and bibenzyl are more stable than those of benzene (11), as are the anthracene complexes of maleic anhydride (12) and tetranitromethane (125).

Using the equilibrium constants for the formation of 1:1 complexes of silver ion and benzene, Andrews and Keefer (6) have attempted to estimate, on a statistical basis, the formation constants K_1 and K_2 (equations 5 and 6) for 1:1 and 1:2 silver-ion complexes of multi-ring hydrocarbons. In this treatment it has been assumed that each six-membered benzene ring offers two potential sites, one on each side of the plane of the ring, for coordination of silver ion. For biphenyl (observed $K_1 = 3.94$) a K_1 value twice (2×2.41) that for benzene is predicted. In diphenylmethane non-coplanarity of the rings should for steric reasons eliminate one of four potential bonding sites. Thus a K_1 value of $\frac{3}{2} \times 2.41$, only slightly more than the observed value, is predicted. Estimated values for fused ring systems are generally much greater than the observed values, a result which is hardly surprising since polynuclear aromatics do not behave as a group of independent benzenoid components.

A K_2 value for benzene one-fourth that of its K_1 value is predicted if one assumes that the first silver ion does not alter electrostatically the capacity of the aromatic nucleus to coordinate silver ion. The observed value (0.21) is much less than the predicted one. The observed K_2 values for the 1:2 complexes of naphthalene (0.91), biphenyl (1.01), diphenylmethane (1.04), and phenanthrene (1.80), in which the two silver ions may be presumed to be widely separated, are much larger than those for simple benzenes.

D. The acceptor structure

Some of the broader aspects of the influences of changes in the acceptor structure on the stability of the complex have already been discussed. In addition it is of interest to consider in more detail how the stabilities of complexes of quinones

and polynitroaromatics are affected by group substitution in the acceptor molecule. The general rule that those same substituents which enhance the basic character of the donor molecule diminish the acidic properties of the acceptor is illustrated by the relative tendencies for complex formation of a series of quinones which are in the order (149):

duroquinone < xyloquinone < toluquinone < benzoquinone < chloroquinone

In a series of 4-substituted-1,3-dinitrobenzenes the acceptor strength is reported (58) to decrease with changes in 4-substituents in the order $\text{Cl} > \text{Br} > \text{OH} > \text{H} > \text{CH}_3 > \text{NH}_2$. This order has been established qualitatively in terms of the number of solid addition products which can be isolated from each acceptor and a variety of aromatic hydrocarbons, amines, and phenols. The anomalous position of the OH substituent in this series may result from the fact that many of the tested donors are amines, which very likely form picrate-type salts rather than true complexes.

It has long been recognized that *s*-trinitrobenzene forms many more complexes than does picric acid, a fact which reflects the electron-donating properties of the methyl group (relative to hydrogen). The fact that trichlorotrinitrobenzene readily forms solid complexes and colored melts with hexamethylbenzene and naphthalene, while trinitromesitylene does not, may be similarly explained (119).

The stability of the nitroaromatic complexes is enhanced by increasing substitution of nitro or other electron-withdrawing groups on the acceptor nucleus. The complex of α -nitronaphthalene with aniline is much less stable than that of 1,5-dinitronaphthalene (209), and the equilibrium constants for formation of the 1:1 aniline complexes of *m*- and *p*-dinitrobenzenes and *s*-trinitrobenzene in chloroform at room temperature (190) are in the ratio 1:1:7. The effects of the group substitutions in polynitroaromatic acceptors on the stabilities of complexes are reported (29) to fall in the following order (which is representative of the electron-withdrawing power of the groups):



The melting-point elevation data of Sinomiya (284) provide interesting qualitative information concerning the effects of relative placement of nitro and other substituents on the stability of polynitroaromatic complexes. Apparently substitution on a carbon adjacent to a nitro group constitutes a situation which is sterically unfavorable for complex formation. This is particularly noticeable if that substituent is itself a nitro group. The following orders of stability for several series of acceptors are illustrative:

Trinitrobenzenes: 1,3,5 > 1,2,3 or 1,2,4

Trinitrotoluenes: 2,4,6 > 2,3,4 or 2,4,5

Dinitrophenols or dinitrotoluenes: 2,4 or 2,5 or 3,5 > 2,6 > 2,3 or 3,4

It seems probable that for maximum stability of the complex the nitro group must remain in the plane of the acceptor ring, which it cannot do in the presence of sizable ortho substituents. In this regard it is of interest to note that Ross, Bassin, and Kuntz (265) have recently determined equilibrium constants by spectrophotometric methods for the interaction of anthracene with a variety of 1-substituted-2,4,6-trinitrobenzenes in chloroform and have found that the stabilities of the adducts must be controlled by factors other than the electron-withdrawing power of the acceptor substituents.

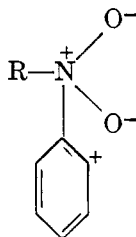
Related examples of repression of complex formation because of unfavorable steric situations in *donor* molecules were reported some time ago (197, 198). On the basis of observations of the colors of solutions or solid addition products of *s*-trinitrobenzene and methyl- and dimethyl-substituted *N,N*-dimethylanilines it was concluded that methyl substituents ortho to the dimethylamino group produce marked destabilization of the complex. These ortho substituents seriously restrict the capacity of the dimethylamino group to engage in resonance with the aromatic nucleus (322). Such resonance, in the case of aromatic amines, appears to be essential for color-producing interactions with nitro compounds. It has, for example, been observed (98) that the colors of solutions of α -phenylethylamine and nitrobenzene, unlike those of aniline and nitrobenzene, are not significantly different from those of the components.

V. THE BOND BETWEEN COMPONENTS OF THE COMPLEXES

As evidence has accumulated from stability studies that a large group of molecular complexes are products of aromatic donor-acceptor interaction, many attempts have been made to describe precisely the binding forces between the components of the complex. Mulliken (211, 212, 213) has recently integrated (from a quantum-mechanical point of view) the various opinions which have been expressed to provide a theory which seems compatible with the known chemical and physical properties of the complexes. The course of this theoretical development during the last quarter of a century is summarized in the following pages.

A. The covalent bond theory

In discussing the structures of complexes of aromatic substances with nitro compounds Bennett and Willis (30) rejected the Pfeiffer (235) concept of interaction through saturation of residual valence fields in favor of a theory of covalent bonding between components. The covalent bond was presumed to link the nitrogen atom of a nitro group to a carbon of the aromatic ring, as indicated below.



In support of such a structure were cited the facts that the complexes were formed in simple molecular ratios and were highly colored, neither of which facts seemed to be consistent with the picture of residual valence. This suggestion, which was upheld for a time (17, 209), became unreasonable when it was discovered (5, 251, 307) that the separation distances between components in crystalline complexes were much larger than are observed for covalent bonding. The rapidity with which equilibria to form complexes in solution are established also is not typical of reactions to form covalent bonds. Of all these equilibria which have been investigated only the reaction between indene and methyl 4,6,4',6'-tetranitrobiphenate (122) has been reported to proceed at a sufficiently slow rate to permit kinetic study.⁷

B. The polarization aggregate theory

Briegleb (41, 43) has formulated the complexes of nitro compounds and aromatic hydrocarbons as products of interaction resulting from electrostatic attraction between molecules with permanent dipoles and non-polar molecules which are subject to polarization through induction. Consistent with this theory is the fact (47) that the heats liberated on formation of 1:1 complexes with *s*-trinitrobenzene decrease with changes in polarizability of the hydrocarbon component in the order: anthracene > phenanthrene > naphthalene > benzene. The heats of formation are generally small ($\Delta H = -4.4$ kcal. for the anthracene complex) and are subject to variations with changes in solvent which result from changes in solvation energies of the complex and its components. The observed trends in heats of formation with changes in components of the complex are probably of some significance if the comparisons are restricted to data on structurally similar complexes contained in the same medium.

The induction energy between a dipole such as the nitro group and a non-polar aromatic hydrocarbon, assuming a separation distance of 3 Å., has been estimated to be about 2 kcal. (42). The observed heats of formation of complexes of *s*-trinitrobenzene and certain of the dinitrobenzenes with naphthalene, anthracene, and biphenyl in carbon tetrachloride, in which solvation energies should be small, are all of this order of magnitude. Similar values ($\Delta H = -1$ to -4 kcal.) have been reported for the heats of formation, in solvents of low polarity, of complexes of aromatic hydrocarbons and amines with a wide variety of acceptors including sulfur dioxide (19), maleic anhydride (20), chloranil (306), polynitroaromatics and tetranitromethane (46, 111, 115, 125, 126), and iodine (66, 301).

Briegleb and Schachowskoy (47) note that the heats liberated in the formation of complexes of acenaphthene increase as the nitro component is changed from

⁷ Some doubt has therefore been expressed (126) as to whether a complex is truly the product of this reaction. Ferguson (90) has suggested that the benzene rings of the nitro compound may have to attain a planar configuration during the process of complex formation. This would require an appreciable activation energy because of overlap of *o,o'*-substituents.

nitrobenzene to *m*-dinitrobenzene to *s*-trinitrobenzene. They conclude that the stability of the complexes is governed by the number of partial moments rather than the overall moment of the acceptor molecule. However, substances such as iodine, which lack even partial moments but which are *susceptible to polarization*, readily form complexes with aromatic hydrocarbons. The fact that solutions of non-polar components such as *p*-dinitro- or *s*-trinitrobenzene in benzene or naphthalene display measurable dipole moments has been offered in further support of the Briegleb theory (44, 193, 194).

C. The views of Gibson and Loeffler and of Hammick

Some effort has been made to explain the intense colors of aromatic-nitro complexes in terms of the dipole-dipole interaction theory (233). However, the opinion has often been expressed (78, 98, 122, 126, 165) that Briegleb binding forces should not produce sufficient transfer between the interacting components to account for the marked changes in light absorption phenomena which accompany complex formation. Indeed, the interaction of one aromatic nitro compound with another, in which the attractive forces are probably truly of the dipole-dipole type (between nitro groups), is not accompanied by pronounced color changes (117).⁸ Gibson and Loeffler (98) and Hammick and Yule (126) have expressed the view that color-producing collisions between components of a complex in solution are comparable to normal impacts between liquid molecules except for added restrictions in the orientations of the colliding molecules. It is presumed that color phenomena are associated with the drift of electrons from one component to the other when the reactive centers are appropriately located. This interaction theory is supported by the observation (98) that the colors of solutions of aromatic amines in nitroaromatics are intensified when the systems are subjected to increases in hydrostatic pressure at constant temperature or to increases in temperature at constant volume. The greater frequency of collision and the deeper intermolecular penetration during collision which are

⁸ In chloroform solution the picryl chloride-hexamethylbenzene complex shows discrete visible absorption. The equilibrium constant for the complex formation can therefore be evaluated by spectrophotometric procedures. The constant thus obtained (264) is about one-tenth as large as that estimated for the interaction on the basis of a study of the repression of the rate of reaction of picryl chloride and triethylamine in chloroform solution by added hexamethylbenzene. The effect on the rate of the addition of the hydrocarbon is attributed to a reduction, through complex formation, of the concentration of free picryl chloride. (Additional examples of the determination of aromatic complex equilibrium constants through kinetic studies have recently appeared (164, 267).) The rate-repressing complex formation presumably encompasses other types of interaction than those measured by the spectrophotometric procedure. It is also of significance that colorimetric studies show no evidence of complex formation between picric acid and *m*-dinitro- or *s*-trinitrobenzene (266), whereas partition studies indicate (209) a strong association between components in such systems. Also the extent of the naphthalene-picric acid interaction, as measured by spectrophotometric procedures, is less marked than partition studies seem to indicate. For these particular systems non-color-producing London interactions or interactions of the dipole-dipole type apparently occur to a significant degree.

associated with these changes are believed to facilitate the color-producing drift of electrons from amino to nitro groups. (Studies of the effects of pressure on the spectra of aromatic-halogen complexes have been reported recently (214), although the results were not available to the author at the time at which this paper was written.)

When solutions of amines and nitro compounds are subjected to temperature increases at constant pressure, color intensity is in some cases increased and in others is decreased. A temperature rise must increase the free volume of molecules in solution and also the energy of molecular impacts. These two effects should oppose each other in determining solution color. In inert solvents such as hexane and carbon tetrachloride interactions between nitro compounds and aromatic amines are always mildly exothermic ($\Delta H = -1$ to -2 kcal.) (126). In these cases the free volume effect must offset the collision force effect. In polar solvents the reactions may be either exothermic or endothermic. The capacity of the solvent to aggregate with itself or with the complex-forming solutes must have a significant influence on the reaction heats in polar media.

D. The ionic complex theory

In discussing interactions involving quinoid or nitro compounds Weiss (310, 311) has described the aromatic donor-acceptor complex as the product of a transfer of a single electron from the donor (D) to the acceptor (A).



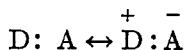
He explains the characteristic complex colors on the basis that the ions D^+ and A^- are odd molecules, which, in general, require only low excitation energies. Like Gibson and Loeffler, as well as Hammick and Yule, he feels that these colors as well as the dielectric polarizations of certain solid complexes (186) cannot be explained in terms of van der Waals bonding. As will be discussed in connection with the Mulliken theory, it is becoming more and more apparent that Weiss was correct when he concluded that the stability of a complex increases as the ionization potential of the donor decreases and as the electron affinity of the acceptor increases.

Complexes between dienes and dienophiles, which may serve as Diels-Alder reaction intermediates, have also been formulated as ion pairs resulting from transfer of a single electron. The term "intermolecular semipolar bond" has been used (329) to describe the bonds between the complex components.

E. The concept of complex resonance

Various aspects of Weiss's argument have received unfavorable criticism (78, 258). The heats of formation are, for example, of much lower magnitude than is ordinarily found for processes of salt formation. The Brackmann (38) concept of complex resonance, which requires only a partial ionic character for a complex, appears to be more in accord with the known properties of most aromatic donor-acceptor interaction products. According to this theory the donor compound can share an electron pair with the acceptor by a process comparable to

Lewis acid-base interaction. The complex structure is regarded as a resonance hybrid



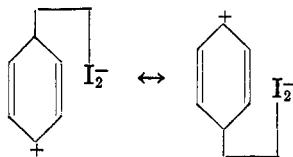
to which no-bond and dative structures contribute.

The crystal structures of the *p*-iodoaniline-*s*-trinitrobenzene (251), quinhydrone (5), and related (217, 307) complexes serve as an indication that the contribution of the dative form is of small but significant structural influence. The benzene rings of the donor and acceptor molecules, which lie in parallel planes, are separated by distances (3.2–3.5 Å.) which are somewhat less (234, 248) than twice the value reported for half the thickness of the benzene ring.

The important novel feature of Brackmann's concept, which is in reality a formalized expression of the views of Hammick and Yule and of Gibson and Loeffler, is the conclusion that the color of the complex is not discretely determined by either component but is a characteristic feature of the complex itself. This opinion is shared by Mulliken (212) and is a major premise of his theory of complex bonding. There is, for example, no correlation between the dipole moments of acceptors such as nitromethane, nitroethane, and nitrobenzene and the colors of their complexes with a specific donor. The pronounced ultraviolet absorption maxima (300 $m\mu$ region) of solutions of halogens in aromatic solvents have been ascribed (24, 25) to a greatly shifted strong halogen transition (which ordinarily lies below 200 $m\mu$). This seems unlikely, since the absorption maxima of complexes of aromatic substances with acceptors such as sulfur dioxide (10) and maleic anhydride (12, 20) also occur in the 300 $m\mu$ region.

F. The Mulliken theory

To explain the appearance of the 300 $m\mu$ region absorption bands in the spectra of the aromatic halogen complexes, Mulliken (211) first suggested that destruction of the symmetry of the benzene ring accompanies the interaction process. The 260 $m\mu$ benzene transition, normally forbidden by selection rules, might thus be allowed and presumably would appear at the higher wave length in the complex spectrum. Structures such as



were proposed to account for this symmetry loss. Although the view that the complex spectrum was determined primarily by the aromatic component received further theoretical attention (33), Mulliken soon rejected it in favor of an alternate interpretation.

According to the revised Mulliken picture (212, 213) the wave function of the ground state of a 1:1 complex, ψ_N , is given approximately by the expression

$$\psi_N \approx a\psi_0(D, A) + b\psi_1(D^+ - A^-) \quad (27)$$

The ψ_0 term designates a no-bond wave function, while the ψ_1 term represents a dative wave function corresponding to the transfer of an electron from D to A with weak covalent-bond formation. This has been termed an "intermolecular electron-pair bond." Although the ratio b^2/a^2 may vary from zero to infinity, it is generally very small in a molecular complex. This present theory is limited in application to situations in which D and A are neutral closed-shell entities with D and A both in symmetrical singlet electronic states. This conception is similar to the Lewis theory of acid-base interaction but lacks the restrictions that electron pairs must be shared between the reactants and that transferred electrons must go from a particular atom in D to a particular atom in A. The bond in the ψ_1 structure of the benzene-iodine complex ($Bz^+-I_2^-$) is said to involve an odd electron in a π molecular orbital of benzene and an odd electron in a molecular orbital of iodine.

The characteristic absorption band of the complex is associated with an excited state of wave function ψ_E ($a^2 \gg b^2$, $a^* \approx a$, $b^* \approx b$).

$$\psi_E = a^*\psi(D^+-A^-) + b^*\psi(D,A) \quad (28)$$

The absorption phenomenon which is presumed to promote the exchange of an electron from D to A is called an "intermolecular charge transfer spectrum." Rough theoretical estimates of the intensity of such transitions are in accord with observed values.

Mulliken stresses the orientational properties of charge transfer forces as opposed to dispersion forces which are dependent largely on polarizabilities. The orientational properties, which along with the electron transfer character of complex formation restrict the combination to simple integral ratios of components, are predicted by considerations of quantum-mechanical symmetry of molecular wave functions. The preferred Mulliken configuration for the benzene-iodine complex, in which the axis of the halogen lies parallel to the plane of the aromatic ring with its center on the ring symmetry axis, is deduced in this manner.

On the basis of group theory-symmetry considerations Mulliken also favors the parallel plane configuration for complexes in which both donor and acceptor molecules are aromatic (or the acceptors are quinoid) in nature. Crystallographic data have been obtained on numerous examples of such complexes (130, 133, 136, 137, 139, 140, 142, 143); but only in a few cases, as previously mentioned, (5, 217, 250, 251, 307) are they sufficiently detailed to attest to the correctness of this opinion. In these cases the donor and acceptor molecules are stacked one above the other in parallel planes with little distortion in the bond distances within the component molecules. The planes of the rows are somewhat inclined to the general direction of the rows. In the *p*-iodoaniline-*s*-trinitrobenzene complex the ring planes make a 30° angle with the face of the unit cell. The 3.1 Å. separation distance between an amino nitrogen and an oxygen atom of a nitro group of a neighboring molecule is the shortest which exists between components in this crystal. In the crystalline self-complex of *p*-nitroaniline a relatively short distance of 2.66 Å. separates the oxygen atom of a nitro group from a carbon atom of an adjacent ring (1). This observation has encouraged the view that the

acceptor centers of aromatic nitro compounds are the nitro groups themselves. In the phenoquinone crystal the plane of the quinone molecule is parallel to its two adjacent phenol molecules, and each phenol forms a hydrogen bond with a quinone molecule in an adjacent column (307). In view of the spectrophotometric work of Michaelis and Granick (207) it is doubtful, as has been mentioned earlier, that the charge transfer forces between the components of quinhydrone are much influenced by such hydrogen-bond formation.

The orientational properties of charge transfer forces have been further illustrated by studies of the dichroism of crystalline complexes such as quinhydrone and hexamethylbenzene-chloranil (217). The long-wave-length spectra of these complexes are polarized, with the larger component perpendicular to and the small component parallel to the planes of the two interacting molecules. In crystals of pure aromatic compounds, however, the density of π electron distribution is larger in the direction parallel to the planes of the aromatic rings. The color intensifications observed on compression of solutions of aniline and nitrobenzene (98) are also indicative of the anisotropic nature of charge transfer interactions.

The dipole moments of aromatic-iodine complexes can be ascribed to the partial ionic character of the Mulliken-type bond. A quantum-mechanical estimate of the dipole moment of such complexes (212) is in fair agreement with observed (88) values. In discussing heats of complex formation Mulliken adopts the Weiss (310) view that their magnitudes and signs are subject to control by a combination of factors, including the ionization potential of the donor, the electron affinity of the acceptor, the mutual approachabilities of interacting molecules, and effects of the medium.

Recent detailed investigations of complex spectra have helped to strengthen the charge transfer theory. A linear relation is found to exist (204) between the ionization potentials of eighteen donor molecules (including aromatic and ethylenic substances, diethyl ether, cyclopropane, and *tert*-butyl alcohol) and the charge transfer absorption frequencies of the corresponding iodine complexes. The energy required (by light absorption) to attain the excited state of a charge transfer complex, in which the donor and acceptor exist as ions, may be expressed by equation 29,

$$h\nu = I_p - E - W \quad (29)$$

where h is Planck's constant, ν is the charge transfer frequency, and I_p , E , and W are, respectively, the donor ionization potential, the acceptor electron affinity, and the dissociation energy of the charge transfer excited state. Using this equation and a value of 1.8 e.v. for the electron affinity of iodine, McConnell, Ham, and Platt (204) estimate, by consideration of the empirical relation between ν and I_p for iodine complexes, that for donors with 8–10 e.v. ionization potentials W is 3.3–3.8 e.v. This value is 1.5 e.v. greater than the Coulomb energy of positive and negative charges separated by van der Waals distances of 3–4 Å. This excess energy has been ascribed either to intermolecular covalent bonding and polarization in the excited state or to solvent effects.

Hastings, Franklin, Schiller, and Matsen (128), who have also investigated the wave lengths of maximum charge transfer absorption for a large number of iodine complexes, suggest the following correlation between the absorption frequency and the donor ionization potential:

$$h\nu = I_p - D + 2\beta^2(I_p - D) \quad (30)$$

where $D = E_A + e^2/r - C_{DA}$, β is the resonance integral, E_A is the electron affinity of the acceptor, e^2/r is the Coulomb energy of the excited state, and C_{DA} is the difference between additional energy quantities in dative and no-bond forms. Frequencies calculated from this equation (for the various iodine complexes) using values of 6 e.v. and 1.3 e.v., respectively, for D and β are in good agreement with experimental values.

A linear correlation between absorption frequencies of charge transfer and donor ionization potentials for halogen and other complexes is also reported by Van de Stolpe (301), who also notes a linear relation between the equilibrium constants and donor ionization potentials of iodine complexes of a series of methylated benzenes. A linear correlation between the extinction coefficients at the complex absorption maxima and the reciprocal of the cube root of the equilibrium constant for complex formation is also reported (292) for iodine-poly-methylbenzene systems. The equilibrium constants for the interaction of iodine with fluorobenzene, *m*-difluorobenzene, and *s*-trifluorobenzene also increase as the extinction coefficients become smaller (291). The extinction coefficients of benzene adducts of iodine, bromine, iodine monochloride, chlorine, *s*-trinitrobenzene, sulfur dioxide, and oxalyl chloride are linearly related to the corresponding wave lengths of charge transfer absorption (300 $m\mu$ region), all of which lie within a 20 $m\mu$ range (204).

Refined experimental procedures have been used (112) to reveal a 260 $m\mu$ absorption band in the spectra of bromine and iodine complexes of benzene. This absorption is attributed to a slight perturbation of the electronic states of the aromatic molecule which account for the 260 $m\mu$ benzene transition. A similar perturbation in the electronic states which produce visible halogen absorption is presumed to account for a slight shift of this band toward the ultraviolet in the spectrum of the complex.

G. Other theories

Shuler (279) has suggested a model for a π -type complex in which the π electrons of the donor molecule behave as a free electron gas which must tunnel through a potential barrier to link the donor and acceptor components. The height of the barrier is controlled by the ionization potential of the donor and the electron affinity of the acceptor and the width by the van der Waals separation of the components. The stability of the complex is determined by the delocalization energy of the interaction, which in turn is determined by the barrier height and width. Recently Shuler (280) has ascribed the high-pressure-induced shift toward the visible of the major absorption peaks of benzene to the formation of a 1:1 self-complex. He estimates the heat of this interaction to be 200 cal./mole through interpretation of these spectral changes in terms of the free-electron theory of complex formation.

McConnell, Ham, and Platt (204) recall the experiments of Reid (259), who observed that the fluorescence of condensed-ring hydrocarbons is quenched by *s*-trinitrobenzene. The phosphorescent triplet transitions of the hydrocarbons are apparently strongly enhanced by complex formation. If singlet-triplet transitions were subject to similar enhancement, their intensities might compare in magnitude with those observed for so-called charge transfer transitions.

The views of Dewar (75, 76, 77, 206) and others concerning the role of complexes as intermediates in aromatic substitutions and rearrangements, in spite of some adverse criticism, merit careful attention. These views, which are beyond the scope of this review, have been summarized in detail elsewhere (78, 79). There are probably numerous examples of reactions in which molecular complexes serve as participants in rate-controlling steps in organic reactions. The high-order rate dependence on halogen concentration of certain halogenation reactions of aromatic hydrocarbons has been explained on the assumption that a 1:1 aromatic-halogen complex is attacked by one or more halogen molecules in the slow step (262, 263, 296).

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