

# ENERGETICS OF MOLECULAR COMPLEXES

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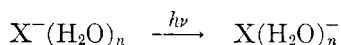
## I. INTRODUCTION

The formation of molecular complexes from many otherwise stable aromatic entities is a well-established phenomenon, and by now a rather intensively investigated one also. The number of books (25, 194) and reviews (8, 26, 63, 187, 236) published on the subject, the importance of such complexing in analytical spot-test procedures (73), and the recent use of picrates for the spectrophotometric determination of adduct molecular weights (53, 224, 227) all attest adequately to the above assertions.

Nonetheless, the reason why complexes form (or, more specifically, the type of intermolecular force which exists between the components of the complex) has been and even still is to some extent a matter of controversy. It is not proposed to consider here the numerous mechanisms of complexing which have been in vogue from time to time. These have been well catalogued and described by Andrews (8) and are now mostly of only historic interest. The object of this review is to consider the *Mulliken theory*, or alternatively the *charge transfer theory* (164, 165, 166, 167, 168, 169, 170, 171, 172), with regard to its predictions and the manner in which these predictions are borne out by

experiment. This theory will, however, be designated by the more common usage: *donor-acceptor interaction theory*. Since in the final analysis the worth of any theory is determined by the conformity of its predictions to experiment, it is felt that the present analysis is necessary.

Since the term "charge transfer (or CT) transition" will be used frequently in the text, it is appropriate that the meaning of this expression be limited. Intramolecular charge transfer transitions (equivalently, electron transfer transitions) which are due to a charge being transferred *from one fragment to another within the same molecule* (140, 181) will not be considered. Such transitions might more accurately be called "charge relocalization transitions." In the case of hydrated anions, Rabinowitch (204) first used the term "charge transfer transition" to describe the relatively very intense absorption due to transitions of the type



where  $\text{X}^-$  is the anion. Such transitions are characteristic of many ligands other than water and of both cationic and anionic systems. They may also be conventionally intramolecular, as in sodium chloride. This type of charge transfer process will not be considered, because of its inorganic connotation.

One might also limit the term "molecular complex" by saying that the complexes to be considered are either wholly or partially organic, that unless specified otherwise they will be assumed to be of 1:1 stoichiometry, and that extensive classified tables of them have been given by Mulliken (168) and Andrews (8). Charge transfer transition will then refer to an *intermolecular* process, whereby an electron is partially or wholly transferred from one component of the complex to the other.

Neither the effect of complexing on reaction rates nor the effect of structure of either donor or acceptor on the stability of the complex will be considered here, as Andrews (8) has treated both these subjects quite fully.

## II. ELECTRON DONOR-ACCEPTOR INTERACTION

The present theory of complexing might be said, with much truth, to have developed not so much in order to explain complexing as to interpret the fact that formation of a complex is usually accompanied by the appearance of a new and characteristic absorption band.

If classical and/or dispersion forces afforded the total binding energy of the complex, then, since the first dispersion force excited state lies at much too high energies (ca. 19 e.v. above the ground state of the complex in the case of the benzene-iodine complex (105)), the new and generally intense electronic transition of the complex must of necessity be attributed to a transition characteristic of some one of the two molecules which comprise the complex. The particular transition would of course be modified by the inclusion of the molecule in the complex and would produce what appears to be the new transition. Following somewhat this line of reasoning Bayliss (13) attributed the strong absorption of the benzene-iodine ( $\text{Bz-I}_2$ ) complex with  $\lambda_{\text{max}} = 2970 \text{ \AA}$ . and of the benzene-

bromine complex with  $\lambda_{\max} = 2920 \text{ \AA}$ . to a strongly shifted halogen molecule transition, which in the free halogens occurs below 2000  $\text{\AA}$ . Similarly, Mulliken (164) at first explained the same absorption as due to the weak 2600  $\text{\AA}$ . absorption of benzene. This latter transition, which is orbitally forbidden in the isolated  $D_{6h}$  benzene molecule, was presumed to become strongly allowed in the postulated  $C_{2v}$  point group of either the benzene-iodine or the benzene-bromine complex. This interpretation, as also a similar explanation of the 3570  $\text{\AA}$ . band of the naphthalene-iodine complex (21), has been rendered questionable by the observation (102) of the 2600  $\text{\AA}$ . transition of benzene unaffected, apart from a very slight intensification, in the spectrum of the benzene-iodine complex.

The possibility of an alternative and more general interpretation of this characteristic absorption band was first noted in complexes of *s*-trinitrobenzene with other aromatics. Weitz (248, 249) formulated the intermolecular binding as an electron donor-acceptor interaction, and was able to explain the effects of substituents in both the nitro and the purely aromatic parts of the complex on its resultant color. These ideas were further developed by Weiss (245), Woodward (254), and especially Brackmann (24). However, only in the last six years has the concept of donor-acceptor interaction (167) been sufficiently developed to give a satisfactory account of molecular complexing.

#### A. THEORETICAL BASIS OF ELECTRON DONOR-ACCEPTOR INTERACTION

According to quantum mechanics the interaction of an electron donor (D) and acceptor (A) may be described by saying that when D and A combine to form a complex, the wave function (WF) for their combination or association may be approximately written (167):

$$\Psi_N(D, A) = a\Psi_0(DA) + b\Psi_1(D^+A^-) \quad (1)$$

In general A or D may be molecules, molecule-ions, or atom-ions, but with the restriction that they are both in their totally symmetric ground states. With these restrictions the principal contributing term in the wave function of the ground state of the complex,  $\Psi_N$ , will usually be that in  $\Psi_0$ .  $\Psi_0$  itself is the wave function corresponding to a structure for the complex in which the binding of the two components is effected by classical intermolecular forces such as dipole-dipole, ion-dipole, dipole-induced dipole interactions, etc., by hydrogen bonding, or by perturbation effects of higher order such as London forces.  $\Psi_0$  is denoted the no-bond wave function.  $\Psi_1$ , the dative-bond wave function, corresponds to a structure of the complex in which an electron has transferred from the donor to the acceptor, and in which, besides all the forces listed above as operative in the structure corresponding to  $\Psi_0$ , there may also be weak chemical binding between the odd electrons now situated on the two components of the complex. If A and D are both neutral species, ion-ion attractive forces may account for a large part of the binding energy of the dative structure.

If the donor is a *weak* base and the acceptor a *weak* acid, then frequently a third term, representing electron transfer from the acceptor to the donor, may

be important (170). In this case

$$\Psi_N(D, A) = a\Psi_0(DA) + b\Psi_1(D^+A^-) + c\Psi_2(D^-A^+) \quad (2)$$

where the coefficient  $c$  will usually be much less than  $b$ . However, a wave function such as given in equation 2 is presumably necessary for a complete description of the ground state of complexes formed between ethylenic systems and ions of transition metals (12, 37, 38, 39, 63).

If the donor is a strong base and the acceptor a strong acid, then the structure  $D^-A^+$  becomes energetically improbable relative to  $D^+A^-$  and equation 2 reduces to equation 1. At the other extreme are the so-called "self-complexes," such as the benzene-benzene complex (167, 225, 226), where now both components have exactly similar donor and acceptor properties. In this case  $b = c$ . The wave function of any other complex will be intermediate between equation 1 and equation 2. It should be noted, however, that dependent on the relative acidity (or basicity) of the two components of a complex whose ground state conforms to equation 1,  $a$  may be greater or smaller than  $b$ . Usually, though,  $a \gg b$ .

A good, although not exact, illustration of the above is given by the diatomic molecules  $H_2$ ,  $HCl$ , and  $HBr$  (170). An approximate wave function of the ground state of the hydrogen molecule in valence-bond theory is

$$\Psi(H_2) = a\Psi_0(H-H) + b\Psi_1(H^+H^-) + c\Psi_2(H^-H^+) \quad (3)$$

where  $\Psi_0$  is the principal contributing term and represents the formation of a covalent bond between the hydrogen atoms.  $\Psi_1$  and  $\Psi_2$  are ionic wave functions and  $c = b < a$ . Equation 3 would correspond to formation of a self-complex between two free radicals, each with one odd electron. For hydrogen bromide  $\Psi_1$  and  $\Psi_2$  correspond to structures  $(H^+Br^-)$  and  $(H^-Br^+)$ , respectively. In this case  $a > b > c$ . However, for hydrogen bromide excited ionic structures are also important. Finally in hydrogen chloride the structure  $H^-Cl^+$  is relatively unimportant, and  $a > b$  with  $c \simeq 0$ . The correspondence of the valence-bond wave functions of these molecules with those of the complexes described would be exact, were it not that formation of a covalent bond is usually associated with the ionic structure of the complex.

For a complex formed from a relatively strong base and a relatively strong acid, equation 1 holds. All contributing structures except those in equation 1 are neglected because the donor-acceptor interaction is to be emphasized, and because the mathematical complexity is considerably reduced. With this restriction the Ritz variation procedure which has been detailed by Coulson (50) may be used for just this type of wave function. It is found that the energy  $E$  associated with the wave function 1 is given by the lower root of the quadratic

$$(W_0 - E)(W_1 - E) = (H_{01} - ES)^2 \quad (4)$$

where

$$W_0 = \int \Psi_0 H \Psi_0 d\tau$$

is the energy associated with the structure DA, and

$$W_1 = \int \Psi_1 H \Psi_1 d\tau$$

is the energy of the structure  $D^+A^-$ .

$$H_{01} = \int \Psi_1 H \Psi_0 d\tau$$

is the interaction energy of structure DA with  $D^+A^-$ , and  $H$  is the exact Hamiltonian of the entire set of nuclei and electrons which comprise the complex.  $S$  is the overlap of the two structures and equals  $\int \Psi_1 \Psi_0 d\tau$ . Since the ground-state energy  $E \equiv W_N$  is not much less than  $W_0$  for the type of complexes under consideration,  $W_0$  may be substituted for  $E$  at every place in equation 4, except in the first bracket on the left where  $W_N$  is substituted, giving:

$$W_N = W_0 - (H_{01} - W_0 S)^2 / (W_1 - W_0) \quad (5a)$$

Similarly, since  $W_E$ , the energy of the excited state, is not much greater than  $W_1$ , one obtains after appropriate substitution:

$$W_E = W_1 + (H_{01} - W_1 S)^2 / (W_1 - W_0) \quad (5b)$$

These are also the equations of second-order perturbation theory (167).

The wave function of energy  $W_N$  is given by equation 1 with

$$b/a = -(H_{01} - S W_0) / (W_1 - W_0) \quad (6a)$$

The excited-state wave function, of energy  $W_E$ , is given by

$$\Psi_E(D, A) = a^* \Psi_1(D^+A^-) - b^* \Psi_0(DA) \quad (7)$$

with

$$b^*/a^* = -(H_{01} - S W_1) / (W_1 - W_0) \quad (6b)$$

The resonance interaction just described is depicted in figure 1, where  $W_0 - W_N$  is the ground-state resonance energy, and will usually be about 0-10 kcal./mole for the complexes being considered. In weak molecular complexes where  $S$  and  $H_{01}$ , and consequently  $W_0 - W_N$ , are small,  $a^* \simeq a \simeq 1$  and  $b^* \simeq b \simeq 0$ .

An essential requirement for resonance between the no-bond and the dative-

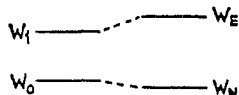


FIG. 1. Representing the resonance of the two structures DA and  $D^+A^-$  of energy  $W_0$  and  $W_1$ , respectively.  $W_N$  is the energy of the ground state of the complex, and  $W_E$  that of the excited state.  $W_0 - W_N$  is the ground-state resonance energy usually of the order of 1-10 kcal./mole. The resonance energy in the excited state,  $W_1 - W_E$ , is such that  $W_E - W_1 > W_0 - W_N$ . In the benzene-iodine complex, for example,  $W_1 - W_0 \simeq 180$  kcal./mole, while  $W_0 - W_N = 1.3$  kcal./mole (232, 234).

bond structures is that  $S$  and  $H_{01}$  be non-zero. Since  $H$  has the total symmetry of the complex, this requires (167) that  $\Psi_1$  and  $\Psi_0$  ( $a$ ) conform orbitally to the same symmetry representation in the point group defined by the complex, and ( $b$ ) be of the same spin type (at least when spin-orbital coupling is weak).

It is supposed that the donor and acceptor species are each in their singlet ground states (i.e., have closed-shell atomic orbital or molecular orbital electron configurations), then  $\Psi_0$  is a singlet wave function belonging to the totally symmetric representation of the point group of the complex. Thus because of ( $a$ ) above,  $\Psi_1$  must also be totally symmetric. If one employs an orbital description of the wave functions corresponding to DA and  $D^+A^-$ , then it may be shown (167) that

$$S = \sqrt{2}S_{DA}/(1 + S_{DA}^2)^{1/2} \quad (8)$$

where

$$S_{DA} = \int \varphi_D \Psi_A d\tau$$

and is the overlap integral between the *highest energy filled* orbital of the donor,  $\varphi_D$ , and the *lowest energy unfilled* orbital of the acceptor,  $\varphi_A$ . Alternatively, it is the overlap of that orbital of the donor from which the electron has transferred with that orbital of the acceptor in which the transferred electron locates in the dative wave function. Since  $S_{DA}$  will usually be fairly small because of the large distance (2.5–3.5 Å.) between the centers of the overlapping orbitals,  $S$  will vary linearly, at least for small values of  $S_{DA}$ , with  $S_{DA}$ .  $H_{01}$  will also vary linearly with  $S_{DA}$ , for small values of  $S_{DA}$ .

Furthermore, the symmetries of  $A^-$  and  $D^+$  will be  ${}^2\Gamma(\varphi_A)$  and  ${}^2\Gamma(\varphi_D)$ , respectively, where the left superscript in usual notation indicates the spin degeneracy and where  $\Gamma(\varphi_i)$  is the representation to which the orbital  $\varphi_i$  conforms in the symmetry point group of the complex. Consequently considerations of resonance may be expressed in terms of the "active orbitals"  $\varphi_A$  and  $\varphi_D$ . This leads to the *overlap and orientation principle* (172), according to which the partners in a donor-acceptor complex tend to assume a relative orientation such as to make  $S$  (or  $S_{DA}$ ) a maximum. For an orientation of the partners such that  $S_{DA}$  is zero,  $b$  also is zero by equations 1 and 8, and charge transfer interaction disappears by equations 5.

It is necessary to stress that the overlap and orientation principle is completely valid only under two restrictions: ( $a$ ) The charge transfer or resonance interaction must afford the primary stabilizing energy of the ground state of the complex. If the no-bond structure is stabilized appreciably, as for example in complexes of trinitrobenzene with polyacenes where dipole-induced dipole interaction may be about 2.5 kcal./mole (29, 30), the positioning of one partner of the complex relative to the other will be a compromise between the maximization of  $S_{DA}$  and the polarization forces (152). ( $b$ ) Equation 1 must hold. The most general equation for  $\Psi_N$  is (172)

$$\Psi_N = a\Psi_0 + \sum_{i,j} b_{ij} \Psi_1(D_i^+ A_j^-) + \sum_{k,l} c_{kl} \Psi_2(D_k^- A_l^+) + \dots \quad (9)$$

where the summations are over all possible states of the two structures  $D^+A^-$  and  $D^-A^+$ , and where the  $+ \dots$  indicates similar summations over all states of more highly ionic structures such as  $D^{++}A^{--}$ , etc., and even over all excited states of the no-bond structure. Although the lowest energy  $\Psi_1$ , assumed in equation 1, is favored by the factor  $1/(W_1 - W_0)$  in equation 5a, it is conceivable that  $S_{DA}$  and  $H_{01}$  might increase so as to outweigh this term for at least some of the excited  $\Psi_1(D^+A^-)$ 's, and that similarly the factor  $1/(W_2 - W_0)$  might be outweighed for one of the  $\Psi_2(D^-A^+)$ 's. If this were the case, the simple overlap and orientation principle based on equation 1 would be invalid. However, there is no good reason for supposing that large increases of the appropriate overlaps occur as  $W_1 - W_0$  or  $W_2 - W_0$  increase; they should rather remain sensibly constant or decrease, so that equation 1 might still be fairly satisfactory.

A somewhat more sophisticated application of the orientation principle, bypassing restriction (b) above, is possible. It will be illustrated on page 1124.

## B. THE OVERLAP AND ORIENTATION PRINCIPLE APPLIED TO SOME SIMPLE COMPLEXES

### 1. The benzene-iodine complex

The molecular orbitals (MO's) of a homonuclear diatomic derived from  $K$ - and  $L$ -shell atomic orbitals (AO's) are depicted in figure 2. Since any halogen atom has seven electrons in its valence shell, the ground molecular orbital configuration of any halogen molecule (see caption to figure 2) may be written as

$$\dots \sigma_g(ns)^2 \bar{\sigma}_u(ns)^2 \sigma_g(np_z)^2 \pi_u(np_x, np_y)^4 \bar{\pi}_g(np_x, np_y)^4 \quad (10)$$

where  $n = 2, 3, 4,$  and  $5$  for  $F_2, Cl_2, Br_2,$  and  $I_2,$  respectively. When iodine functions as an acceptor the donated electron must go into the  $\bar{\sigma}_u(5p_z)$  antibonding molecular orbital, which then corresponds to  $\varphi_A$  of equation 8.

The  $\pi$  molecular orbitals of benzene, derived from the six  $2p_z$  atomic orbitals of the six skeletal carbon atoms, are depicted in figure 3. Since benzene has six  $\pi$  electrons the ground molecular orbital configuration is

$$\dots (a_{2u})^2 (e_{1g})^4, {}^1A_{1g} \quad (11)$$

When benzene functions as a donor, the vacancy will occur in the  $e_{1g}$  molecular orbital, which then corresponds to the orbital  $\varphi_D$  of equation 8. Consequently the overlap of an  $e_{1g}$  molecular orbital of benzene with the  $\bar{\sigma}_u(5p_z)$  orbital of iodine will determine the resonance capability of the dative-bond and the no-bond structures; that is, the relative positions of the iodine and benzene molecules in the complex will be such as to maximize the overlap integral:

$$\int \varphi_{e_{1g}} \varphi_{\bar{\sigma}_u(5p_z)} d\tau$$

Some possible geometric models of the benzene-iodine complex are shown in figure 4. It is seen that by use of some one of the two  $e_{1g}$  molecular orbitals of

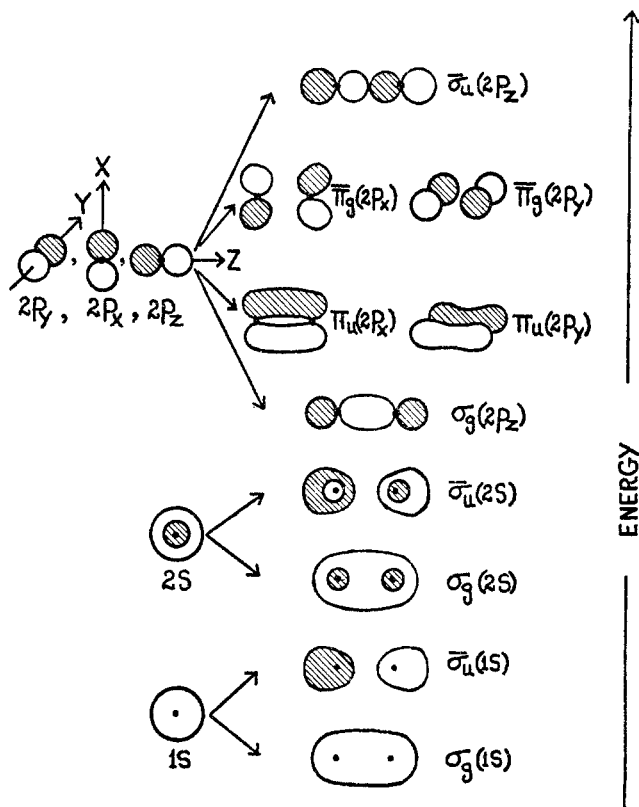


FIG. 2. The lowest-energy molecular orbitals of a homonuclear diatomic formed from atoms of the first or second row of elements in the Periodic Table. The energy scale at the right is not linear; however, the orbitals are arranged vertically in correct order of increasing energy. The atomic orbitals of the isolated atom are on the left; the molecular orbitals of the isolated molecule are on the right. Thus the  $\sigma_g(1s)$  and  $\bar{\sigma}_u(1s)$  orbitals are the molecular orbitals resulting from the bringing together of two  $1s$  atomic orbitals, one on the left (shown) and one on the right (not shown), from infinity to the equilibrium internuclear distance of the molecule being considered.

Antibonding character is denoted by a bar. Hatching signifies negative sign of the wave function, while its absence means positive sign. In the fluorine molecule the  $\sigma_g(1s)$  and  $\bar{\sigma}_u(1s)$  molecular orbitals are virtually nonbonding (i.e., the  $1s$  electrons of the fluorine atom are so tightly bound that there is no appreciable delocalization of them upon forming the fluorine molecule). Similarly in chlorine the molecular orbitals of the  $n = 1$  and  $n = 2$  shells are nonbonding, and one need only specify the molecular orbitals of the valence ( $n = 3$ ) shell. The order of energy and spatial disposition of orbitals are correct as depicted, irrespective of the value of  $n$  in  $ns$  or  $np$ . The number of radial nodes increases as  $n$ ; however, this will not affect any conclusions arrived at by use of the depicted molecular orbitals for considerations relative to the iodine molecule.



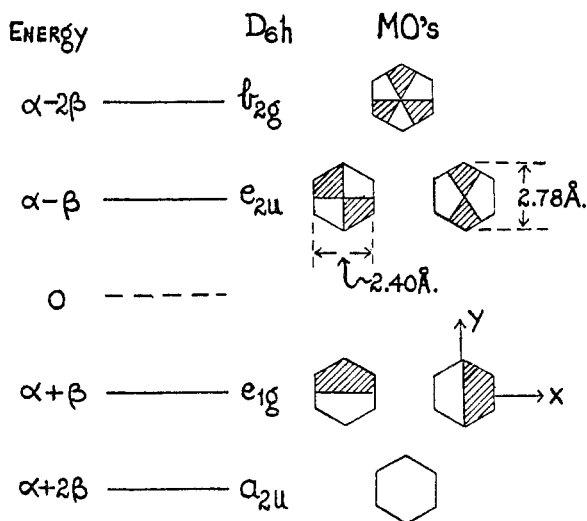


FIG. 3. The  $\pi$  molecular orbitals of benzene. Hatching denotes negative sign of the wave function above the plane of the hexagon. The lines between regions of positive and negative sign are the vertical nodal planes. There is also a horizontal nodal plane in the plane of the benzene hexagon, such that the wave function on the nether side of the ring is of opposite sign to that shown. Energy and representation species are shown on the left.  $\alpha$  is the coulomb integral, and  $\beta$  (a negative quantity) is the resonance integral between nearest neighbor carbons. The  $z$ -axis is perpendicular to the plane of the paper.

benzene the overlap in either of the models  $R_x$ ,  $R_y$ , or  $R'$  is non-zero, while at the same time the model is quite compact so that the interionic attraction in the dative-bond structure (between  $Bz^+$  and  $I_2^-$ ) is quite large. The overlap in model  $R'$  will be slightly smaller than in  $R_x$  or  $R_y$  and consequently this model will represent a small potential maximum between  $R_x$  and  $R_y$ .

The overlap in models  $E_x$  and  $E_y$  is also non-zero but will be slightly smaller than in any of the  $R$  models. Furthermore, the centers of charge in the dative-bond structure will be quite far apart, so that model  $E$  may be neglected as energetically improbable. In model  $A$ , the overlap is zero and thus no-bond-dative-bond resonance is impossible. This model may be neglected. There is an infinity of other possible models, but these may all be rejected as improbable by means of considerations such as those above.

Mulliken (167) chose model  $R_y$  or  $R_x$  as being the more stable, and this particular model has been substantiated to some extent by experiment. It is important to ask, however, if the energy differences between the various  $R$  models are really sufficiently large to inhibit a slightly hindered rotation of the iodine molecule throughout the whole gamut of  $R$  models. Neither is it clear that the energy differences even between the  $E$  and  $R$  models are sufficiently large to prevent a small concentration of complexes of geometry  $E$  from existing at equilibrium at room temperature.

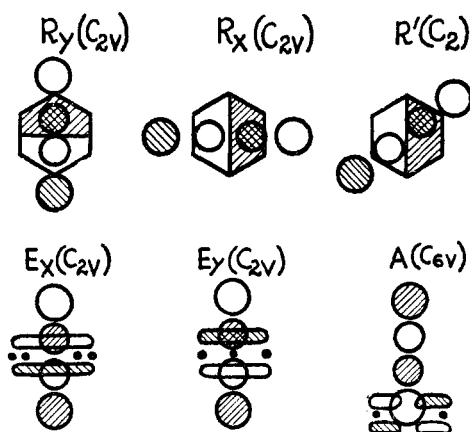


FIG. 4. Overlap integrals for some models of a benzene-iodine complex. Model  $R_x$  has the  $z$ -axis of the iodine molecule parallel to and above the  $y$ -axis of the benzene (see figures 2 and 3), and the sixfold axis of benzene bisects the I—I bond of iodine. Model  $R_y$  may be obtained from  $R_x$  by rotation of the iodine molecule through  $90^\circ$  (or  $30^\circ$ ) about the  $z$ -axis of benzene. Model  $R'$  may be made from  $R_x$  or  $R_y$  by rotation of the iodine molecule about the benzene  $z$ -axis by any angle not equal to  $30^\circ$  or an integral multiple of  $30^\circ$ . Model  $E_x$  has the  $z$ -axis of iodine perpendicular to the benzene plane, with the center of the I—I bond situated on the  $x$ -axis of benzene and removed some 3 Å. from the side of the benzenoid hexagon. Model  $E_y$  is similar to  $E_x$ , except that now the center of the I—I bond is on the  $y$ -axis of benzene. Model A has the  $z$ -axis of benzene coincident with the  $z$ -axis of iodine, with the iodine molecule standing above the benzene ring.

Hatching, whether slanting from right to left or from left to right, denotes a negative wave function. Crosshatching then indicates a region of overlap of two negative wave functions, which makes a positive contribution to the overlap integral. Absence of hatching denotes positive sign of the wave function, and a total whiteness in a region of overlap indicates a product of two positive wave functions and thus a positive contribution to the overlap integral. Hatching in a region of overlap indicates a negative contribution to the overlap integral. The total overlap in model A is then readily seen to be zero, while finite in all the other models shown.

Indeed, the only unambiguous conclusion which may be reached as of the moment is that model  $R_x$  or  $R_y$  is the more probable and will presumably preponderate in whatever mixture of orientation isomers it is that exists at equilibrium. In accord with this an x-ray investigation of the benzene-iodine and the mesitylene-iodine complexes in solution points to a less symmetrical location for the iodine than would be expected from model  $R_x$  or model  $R_y$  (62). High-pressure studies of the intensity of light absorption (89, 90, 100, 101) are also indicative of the presence of more than one geometric type of complex (see page 1148). Infrared evidence is ambiguous and will be considered on page 1132.

## 2. Complexes of transition metals with $\pi$ -bonded systems

Ethylene (Ety) with two  $\pi$  electrons has a ground electron configuration  $(\pi_v)^2$ , as is evident from figure 5. In the ethylene-silver ion complex, when

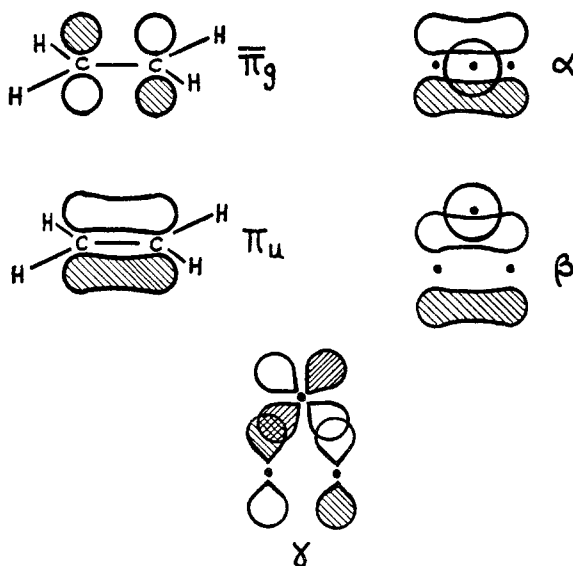


FIG. 5. The  $\pi$  molecular orbitals of ethylene, and the overlap integrals for some models of the ethylene-silver ion complex. The  $\pi$  molecular orbitals of ethylene,  $\pi_u$  and  $\pi_g$ , are indicated on the left. Models  $\beta$  and  $\gamma$  are the same and represent that geometry of the complex in which the silver ion is located above the ethylenic plane directly over the center of the C=C bond. The overlap integral being illustrated in  $\beta$  is

$$\int \varphi_{1s}(\text{Ag}) \varphi \pi_u(\text{Et}\gamma^+) d\tau$$

and in  $\gamma$  is

$$\int \varphi_{4d}(\text{Ag}^{++}) \varphi \pi_g(\text{Et}\gamma^-) d\tau$$

In model  $\alpha$  the silver ion lies in the ethylenic plane opposite the center of the C=C bond, and the overlap integral being depicted is the same as in  $\beta$ . The overlap in models  $\beta$  and  $\gamma$  is finite, and in  $\alpha$  is zero.

ethylene functions as a donor, an electron is transferred from the  $\pi_u$  molecular orbital of ethylene and locates in the  $5s$  atomic orbital of silver ion.  $S_{DA}$  is non-zero when the silver ion is above the ethylenic plane, directly over the carbon-carbon double bond (model  $\beta$ , figure 5), and zero when the silver ion is in the ethylenic plane even though directly opposite the carbon-carbon double bond (model  $\alpha$ , figure 5). Model  $\beta$  will then be the more stable, since it also accords with maximum ion-induced dipole attraction in both the no-bond and the dative-bond structures.

Another structure, initially somewhat improbable, which however becomes more attractive when one considers the large overlap, the large ion-ion attraction, and the larger polarizability of the anionic ethylene, is  $\text{Et}\gamma^-\text{Ag}^{++}$ . This structure is made by transfer of a  $4d$  electron from silver ion to the antibonding  $\pi_g$  molecular orbital of ethylene. The overlap integral here is between a  $4d$  atomic orbital and a  $\pi_g$  molecular orbital and is again non-zero if the silver ion is situated as in model  $\gamma$ , model  $\gamma$  being the same as  $\beta$ .

The ground-state wave function of the ethylene-silver ion complex is

$$\Psi_N(\text{Ety}, \text{Ag}^+) = a\Psi_0(\text{EtyAg}^+) + b\Psi_1(\text{Ety}^-\text{Ag}) + c\Psi_2(\text{Ety}^-\text{Ag}^{++}) \quad (12)$$

This wave function is in accord with recent views of this complex, which presume  $c$  to be appreciable and of the same order of magnitude as  $b$  (37, 38, 39, 63). It discords, however, with older concepts which would make  $c$  zero (196, 243, 251).

If one presumes that the contribution of the structure  $\text{Ety}^-\text{Ag}^{++}$  is necessary in order to obtain a stable complex, then one may understand why such ethylenic complexes are formed only by transition metal ions or atoms. These are Ni, Cu<sup>+</sup>, Ag<sup>+</sup>, Fe, Rh<sup>+</sup>, Ni<sup>++</sup>, Pd<sup>++</sup>, and Pt<sup>++</sup> (37, 40, 41). Cupric ion does not form an isolable complex, presumably because the  $d$  electrons of the cupric ion are sufficiently tightly bound to make the structure  $\text{Ety}^-\text{Cu}^{++}$  energetically improbable (63). The mercuric ion has been reported as forming such a complex, but the evidence here is conflicting (36, 40, 41, 124, 141).

All metals known to form stable olefin complexes do so in valency states which admit of  $dp$  hybridization in the dative  $\pi$  bond (41). It is thus suggested that formation of a stable olefin-to-metal  $\pi$  bond necessitates some  $p$  character on the part of the  $d$  orbitals.

It is interesting to speculate on the extent of resonance interaction between the dative  $\sigma$ -bonded structure and the dative  $\pi$ -bonded structure. In terms of the approximate symmetry in the vicinity of the interaction zone in the molecule this would seem to be rather small, but nonetheless finite. This means that the mesomeric release of electrons from metal to ligand in the dative  $\pi$  bond induces a compensating release of electrons from ligand to metal in the  $\sigma$  bond, thus tending to preserve the electrical asymmetry of the complex. Considerations of redox potentials are in accord (2) with this conclusion.

The benzene-silver ion complex has been studied by Mulliken (167, 170). The principal dative structure here will again be  $\text{Bz}^+\text{Ag}$ . In order that  $S_{\text{DA}} \neq 0$  for this structure, it is necessary (167) that the silver ion be located above and to the side of the benzene ring. Such a structure has been found for the solid benzene-silver perchlorate complex by x-ray means (216). The crystal of course is not a 1:1 complex, but is more nearly  $\infty : \infty$ . Each benzene molecule interacts with two silver ions, one above and one below the benzene plane, and located near diametrically opposite bonds of the benzene. Similarly, each silver ion interacts with two benzene molecules. This, however, does not alter the principal conclusions derived from consideration of the 1:1 complex, even with inclusion of the structure  $\text{Bz}^-\text{Ag}^{++}$ .

### 3. Self-complexes

Examples of this type of complex are the *N*-ethylphenazyl (109), benzene (225, 226), *p*-nitroaniline (1), and iodine (148) self-complexes.

The benzene self-complex has been treated using both free electron (225, 226) and dispersion force (51) theories. Mulliken (167) and Murakami (176) will be followed by considering the benzene-benzene complex, using considerations of donor-acceptor interaction.

The wave function corresponding to the no-bond structure of the benzene-benzene complex is  ${}^1\Psi_0(\text{Bz}_L\text{Bz}_R)$ , where  $\text{Bz}_L$  designates the benzene molecule on the left and  $\text{Bz}_R$  that on the right as the complex is viewed. The dative-bond structure is formed by transfer of an electron from one benzene molecule to the other. By virtue of the symmetry of the problem, electron transfer is equally probable in either direction, and four dative-bond wave functions arise. They are

$$1/\sqrt{2}[{}^1\Psi_1(\text{Bz}_L^+\text{Bz}_R^-) \pm {}^1\Psi_2(\text{Bz}_L^-\text{Bz}_R^+)] \quad (13a)$$

and

$$1/\sqrt{2}[{}^3\Psi_1(\text{Bz}_L^+\text{Bz}_R^-) \pm {}^3\Psi_2(\text{Bz}_L^-\text{Bz}_R^+)] \quad (13b)$$

Since whatever the relative orientations of the partners in the complex the no-bond wave function will be totally symmetric and more or less dissociative, the actual geometric model of a presumed 1:1 stable self-complex will be determined by considerations of the compactness and the overlap in the ionic structure. The overlap in question (see figure 3) will be

$$\int \varphi e_{1g} \varphi e_{2u} d\tau$$

and will be non-zero for a complex of geometry  $D_{3h}$ ,  $C_{3v}$ ,  $C_{2v}$ ,  $C_{1h}$ , or  $C_s$ . Any of the models in which the two benzene rings are superposed one above the other with their sixfold axes coincident, as may be visualized from figure 3, are consequently excepted from consideration. The most probable models are ones in which the benzene rings are superposed, but with the sixfold axes displaced from coincidence, or ones in which the two benzene rings are coplanar and lying side by side. It is difficult to say which of the above two types of model would be more stable.

The ground-state wave function of a 1:1 benzene self-complex would then be

$$a{}^1\Psi_0(\text{Bz}_L\text{Bz}_R) + b/\sqrt{2}[{}^1\Psi_1(\text{Bz}_L^+\text{Bz}_R^-) + {}^1\Psi_2(\text{Bz}_L^-\text{Bz}_R^+)] \quad (14)$$

where only the symmetric combination of the singlet dative-bond wave functions (equation 13a) may be used. Equation 14 is the same as equation 2 with  $c = b \ll a$ .

It is appropriate to stress that if the benzene self-complex exists (and there is really no definite evidence that it does), it will be a rather weak complex and certainly not of 1:1 stoichiometry. The results above are still valid, but are reinterpreted to mean that in a sample of liquid benzene at rather low temperatures and under fairly high pressure there may exist small transient regions of ordered orientations where one has an almost graphitic lattice with planar layers of benzene rings superposed on other layers, each layer being somewhat displaced relative to the ones above and below it.

Similar considerations to those above apply to the self-complexes considered by Hausser and Murrell (109), with just two differences. These self-complexes are formed from radicals; consequently gross considerations of overlap, without actual numerical evaluation, will not determine the kind of model to which

the geometry of the complex conforms. The reason for this is that the covalent binding will occur in what would now, somewhat ambiguously, be called the no-bond structure. It might more reasonably be termed the "non-dative-bond structure." Since both of the orbitals between which binding occurs are group theoretically the same in each isolated radical, they will of necessity transform identically in any model that may be conceived of for their 1:1 complex. This will lead to non-zero overlap for any geometry, except accidentally. It has been supposed, however, that the two radicals are exactly superposed one above the other. The second difference is that the triplet configuration is now also associated with the non-dative-bond structure.

#### 4. Primarily ionic complexes

These are complexes for which  $W_1 < W_0$  and will usually be formed only by partners which are respectively strongly acidic and strongly basic. Other features which will aid in the formation of such complexes are a lack of steric hindrance and a strong directionality of the "active orbitals." This will lead to close approach of the partners, giving rise to large coulombic attractive energy and quite strong chemical bonding.

The ground-state wave function of such a complex will be given by equation 1, with  $b > a$ . Examples of such complexes are the ammonia-boron trifluoride complex (167), the triethylamine-iodine complex (242), and some complexes of the quinhydrone type (116).

### III. MAGNETIC SUSCEPTIBILITY OF MOLECULAR COMPLEXES

Magnetic susceptibility measurements on quinhydrone and its constituents indicate that the Pascal law is approximately obeyed (159). Benzene solutions of iodine (16, 205), however, are more diamagnetic than this additivity would predict; in other words

$$\chi_m(\text{Bz-I}_2) < \chi_m(\text{Bz}) + \chi_m(\text{I}_2)$$

where  $\chi_m$  is the molar susceptibility in cubic centimeters. Sahney, Aggarwal, and Singh (218) have also found increases in diamagnetic susceptibility of the order of  $3.55\text{--}16.8 \times 10^{-6}$  in polyacene-trinitrobenzene complexes. These latter measurements were rather exact and apparently supersede earlier and quite opposite results (17) on somewhat similar nitro complexes. It was found (218) that the increase in diamagnetic susceptibility was in the order: anthracene-trinitrobenzene > phenanthrene-trinitrobenzene > naphthalene-trinitrobenzene. The stability of these complexes, and their donor-acceptor resonance interaction, follow exactly the same order (152).

It is significant that both the benzene-iodine and the polyacene-trinitrobenzene complexes conform to equation 1 with  $a \gg b$  (152, 167). Some potential energy curves for complexes of this type are sketched in figure 6A. It seems reasonable to suppose that in these complexes the most important single factor affecting susceptibility is the increasing delocalization of electrons. Indeed, rough calculation supports the conclusion that the increase in orbital extent due

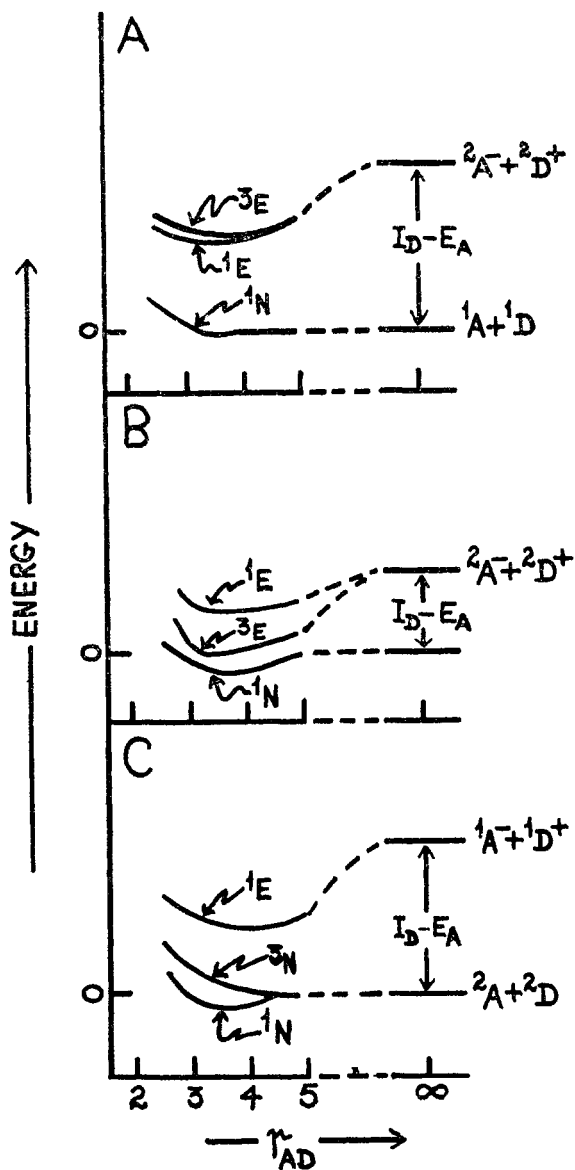


FIG. 6. The potential energy curve arising from resonance of the dative-bond and non-bond structures in (A) polyacene complexes with either iodine (167) or trinitrobenzene (152), (B) radicaloid complexes, and (C) free-radical complexes.  $I_D$  is the vertical ionization potential of the donor, and  $E_A$  the vertical electron affinity of the acceptor.  $r_{DA}$  is the coordinate representing the distance between the two components of the complex, as they approach one another from infinity with relative orientations the same as at the equilibrium intermolecular separation. Left superscripts refer to spin multiplicity.

to the dative-bond-no-bond resonance is the basis for the observed increase in diamagnetism.

In the case of primarily ionic complexes, such as are described on page 1126, two wave functions arise from the dative-bond structure. Of these the triplet wave function will be associated with a higher energy than the singlet (152). If the ionicity of the complex is primarily due to the relative acid-base character of the components and to the ion-ion attractive force rather than to any covalent binding of the dative structure, the singlet-triplet splitting and the dative-bond-no-bond resonance interaction will both be fairly small. The potential energy curves for such a situation are shown in figure 6B.

The ground state of this complex will be a singlet, but there will be a triplet state at only very slightly higher energies. The thermal population of this well-stabilized triplet level may be appreciable, and may give rise to paramagnetism even though both components of the complex are diamagnetic. It will be appreciated that such a complex is almost a diradical; the term *diradicaloid* has been suggested (116). A small paramagnetism has been observed in complexes of various *p*-phenylenediamines with differently substituted *p*-benzoquinones, and has been attributed to the above behavior (116). It would not be expected that the ammonia-boron trifluoride complex, or the outer complex of triethylamine-iodine (see page 1140), would be paramagnetic because of the large covalent stabilization of the dative-bond structure.

Solutions of organic free radicals such as triphenylmethyl usually show large deviations from Curie's law, such deviations being explained by a temperature-dependent equilibrium of a paramagnetic monomer and a diamagnetic dimer. In the solid state such compounds usually exist in the diamagnetic form, but even if the solid does consist of monomeric radicals Curie's law is followed fairly closely.

Some free radicals and radical-ions show deviations from Curie's law at low temperatures in the solid state (106, 107). One of these, the *N*-ethylphenazyl radical, behaves similarly in solution (108), and also exhibits a new intense absorption ( $\lambda_{\max} = 8000 \text{ \AA}$ ,  $\epsilon_{\max} = 10,000$ ) which appears and increases in strength as the paramagnetism decreases. These results are interpreted (109) in terms of an equilibrium between the radical and a 1:1 self-complex in which the plane of one radical is exactly superposed on the other.

The potential energy curves for this type of complex are drawn in figure 6C. There is a triplet level at rather low energies, but it is dissociative, and ineffective except in so far as it may promote equilibrium between the complex and the radicals.

Crystalline polycyclic aromatic hydrocarbons such as perylene or violanthrene are good semiconductors, their electrical resistivity being of the order of  $10^7$ - $10^{12}$  ohm-cm. at 25°C. (3). Their crystalline halogen complexes, however, have a remarkably low resistivity of the order of  $10^0$ - $10^3$  and some 80 per cent of this large conductivity is intrinsically electronic (4, 5). Complexation is also accompanied by a decrease of diamagnetism (4). If it is assumed that the difference between the observed and estimated molar susceptibilities is due to the



paramagnetic contribution of electrons in a triplet state of the complex, the excitation energy of this triplet is calculated (147) as 0.17 e.v. for the violanthrene-2I<sub>2</sub> complex, and corresponds well to the energy gap of 0.15 e.v. for conductivity (4).

The reasons for the changes in susceptibility and conductivity caused by complexing are not known. Suggestive, however, is the fact that such polycyclics are almost certainly diradicaloid (153), and that the energy of the low-lying triplet relative to the singlet might be still further decreased by complexing (153). This would account for the loss of diamagnetism, but it would seem then that the conductivity must also be associated with this triplet because of the similarity in energy gaps. This might be possible by means of a sort of zip-fastener conductive action between polycyclics and iodines such as was envisaged by Reid (208) in accounting for some oxidation-reduction phenomena at large separation of couple. However, it seems more reasonable to presume considerable orbital delocalization over the whole of this macromolecular (and certainly not 1:2) crystalline lattice.

The structure of the violanthrene-2I<sub>2</sub> crystal resembles (4) that which is found among the intermediate phases of metallic systems and among quasi-metallic compounds. Such quasi-metallic nature has also been independently noted (97, 113, 150) in complexes of some aromatic hydrocarbons with electron donors such as the alkali metals and electron acceptors such as the halogens.

#### IV. DIPOLE MOMENTS

In a complex of a nonpolar donor with a nonpolar acceptor, the dipole moment of the no-bond structure will usually be very small and may be zero. However, there will be a dipole moment associated with the dative-bond structure and it will be directed from D to A. Since the actual ground-state wave function of the complex is an admixture of both the no-bond and the dative-bond wave functions, this implies that there will be a dipole moment of the complex, the approximate magnitude of which will depend on  $\mu_1$ , the dipole moment of the dative-bond structure, and on the coefficient  $b$  of equation 1. For the case that one of the partners is initially dipolar, the situation becomes more complicated and the dipole moment of the complex may be either greater or less than that of the dipolar component.

The dipole moment of the complex is given by (167)

$$\mu_M = -e \int \Psi_N \sum_i r_i \Psi_N d\tau$$

where  $e$  is the electronic charge and  $r_i$  the vector distance of the  $i^{\text{th}}$  electron from any suitable origin. For the particular case that  $\mu_0$ , the dipole moment of the no-bond structure, is zero (i.e., benzene-iodine), use of equations 1 and 7 leads to (167):

$$\mu_M = \mu_1(b^2 + abS) \quad (15)$$

If  $\mu_0$  is non-zero, one must use an alternative expression (167). The wave func-

tions 1 and 7 also obey the orthonormality conditions

$$\int \Psi_N^2 d\tau = \int \Psi_E^2 d\tau = 1 \quad \text{and} \quad \int \Psi_N \Psi_E d\tau = 0$$

leading immediately to (28, 167)

$$a^2 + 2abS + b^2 = a^{*2} - 2a^*b^*S + b^{*2} = 1 \quad (16a)$$

and

$$a^*(b + aS) = b^*(bS + a) \quad (16b)$$

$\mu_1$ , with the implied restrictions, is the dipole moment which would result from complete one-electron transfer from  $\varphi_D$  to  $\varphi_A$ . It will approximately equal  $er_{DA}$ , where  $r_{DA}$  is the equilibrium separation of the two components in the complex. Then, knowing  $\mu_M$ ,  $\mu_1$ , and  $S$ , quantities which may be either determined or estimated, one may calculate  $a$ ,  $b$ ,  $a^*$ , and  $b^*$  from equations 15 and 16. The percentage ionic character of the ground state  $\Lambda = 100b^2/(a^2 + b^2)$  may also be calculated. These quantities are tabulated in table 1 for a representative range of complexes.

Despite the general smallness of  $b$ , or of  $\Lambda$ , it must be emphasized that the contribution of the dative-bond structure to the binding energy of the complex can be considerable. This is due to the large binding energy of the dative-bond structure (ca. 100 kcal./mole) compared to the usually almost negligible binding energy of the no-bond structure. In order to clarify this the percentage contribution of the resonance energy to the total binding energy of the ground state has been tabulated in table 1. This quantity is denoted as per cent  $E_r$ .

A finite dipole moment is always observed (27, 28, 56, 71, 72, 133, 241) for a complex formed from nonpolar species. The dipole moment of nitrobenzene, 4.22 D, is however reduced to 3.73 D in the nitrobenzene-naphthalene complex, and that of *m*-dinitrobenzene, 3.79 D, to 3.43 D in its naphthalene complex. It must follow that the resultant of the mesomeric dipole moment of the complex and of the permanent moment of the nitro compound is less than this

TABLE 1  
*Dipole moments, coefficients, and per cent ionic character*

Complex	$M$	$a$	$b$	$a^*$	$b^*$	$\Lambda$	Per Cent $E_r$	References
Hexamethylbenzene-trinitrobenzene	0.87	0.962	0.193	0.986	0.230	3.8	58	(28)
Stilbene-trinitrobenzene	0.82	0.964	0.186	0.988	0.284	3.5	70	(28)
Naphthalene-trinitrobenzene	0.69	0.969	0.168	0.991	0.266	2.8	51	(28)
Durene-trinitrobenzene	0.55	0.975	0.145	0.994	0.244	2.1	47	(28)
Hexamethylbenzene-chloranil	1.00	0.957	0.209	0.983	0.306	4.4	45	(28)
Benzene-iodinet	0.72	0.97	0.17	0.99	0.27	2.8	100	(167, 170)
Benzene-iodinet	1.80	0.93	0.286	0.964	0.381	S.2	100	(28, 133)
Pyridine-iodine	4.5	0.86	0.50	—	—	25	—	(170, 209)
Triethylamine-iodine	11.3	—	—	—	—	59	—	(182, 242)

† The discrepancy here is to be attributed to experimental variations of the apparent dipole moment and the equilibrium constant, and not to any difference in theoretical approach.

latter moment minus the dipole-induced moment in the naphthalene. On the other hand, the dipole moment of pyridine is 2.28 D, whereas that of the pyridine-iodine complex is 4.5 D (130, 133, 233). Such an increase will be primarily due to a large mesomeric moment. For this latter case, as also for the triethylamine-iodine complex, because of difficulty in estimating  $\mu_0$ , the values given in table 1 will be somewhat approximate.

On account of the absence of permanent dipoles in both iodine and benzene, one can imagine the classical binding energy to be very small, or zero. In this approximation of  $W_0 \simeq 0$ , the coefficient  $b$  may be calculated (125) from the experimentally determined  $\Delta H$  value of  $-1.3$  kcal./mole (52, 234), by setting it in correspondence with  $W_N$ .  $b$  so obtained has a value of 0.13, considerably smaller than the values obtained from dipole moment data (see table 1). This lack of agreement has been shown (28) to lead to a virtual absurdity unless one presumes the experimental entities  $\mu_M$  or  $\Delta H$ , or both, to be in error.

In the case of the benzene-trinitrobenzene complex the moments induced by the  $\text{NO}_2$  dipoles in the benzene plane will cancel on account of symmetry. However, there will be a finite but small polarization perpendicular to the plane of the complex in the no-bond structure, and in the same direction as the mesomeric moment. This, when not accounted for, will cause the mesomeric moment to be a little too large, and thus also  $b$ ,  $\Lambda$ , etc., in table 1.

## V. INFRARED AND RAMAN SPECTRA

The importance of DA interaction in stabilizing the complex implies a certain amount of charge transfer in the ground state of the molecular compound. This in turn infers partial removal of an electron from a bonding orbital of the donor (i.e.,  $e_{1g}$  of benzene) to an antibonding orbital of the acceptor (i.e.,  $\bar{\sigma}_u(5p_z)$  of iodine), and a consequent decrease of bond order for at least one bond in each component of the complex (i.e., benzene-iodine). The following effects should then ensue:

(a) There should be an increase in some bond lengths in both the donor and the acceptor. In agreement with this, the normal 2.67 Å. bond length of iodine is increased to 2.85 Å. in the violanthrene-iodine complex (5) and to 2.90 Å. in the pyridine-iodine complex (62).

(b) There should be a decrease in the vibrational frequencies of those modes whose force constants are sensitive to the active orbitals involved in the DA interaction. This decrease will be larger the more localized the particular active orbital or the smaller the molecule.

(c) A decrease of total symmetry is usually associated with complexing. It is to be expected then that some vibrational modes, spectrally unobservable in the isolated donor or acceptor because of a symmetry forbiddenness, will appear in the spectrum of the same species when complexed.

### A. THE DONOR SPECTRUM

The Raman spectra of olefin-silver ion complexes (235) show a general decrease of ca.  $65 \text{ cm.}^{-1}$  in the ethylenic  $\text{C}=\text{C}$  stretching frequency of the isolated

olefin. This large decrease agrees with the localized nature of the  $\pi$  electrons in nonconjugated ethylenic species and with equation 12. The two dative-bond structures invoked in this wave function imply removal from a bonding  $\pi_u$  molecular orbital and transfer into an antibonding  $\pi_g$  molecular orbital, respectively, and a weakening of the C=C bond will result in each case. The small and not really significant frequency shifts which appear in the Raman spectrum of the benzene-silver ion complex are perhaps illustrative of the greater spatial extent of the benzene  $e_{1g}$  molecular orbital.

Effect (c), as well as intensity changes in other previously allowed transitions, has been observed in the infrared spectrum of the benzene-iodine complex. The earlier investigations of this complex, as also of the mesitylene-iodine complex, led to some debate (91, 99, 103, 104, 195) relative to impurity effects and the feasibility of ever distinguishing between weak complex formation and strong solvent perturbations. Such distinction was to some extent considered (99) a matter of convenience. It has now been shown, however, that the infrared spectra of iodine and bromine complexes of benzene and toluene do contain (74) two enhanced bands. The same is true of the hexadeuterobenzene-iodine complex (76) and of other complexes of iodine with various monosubstituted benzenes (77).

In each case the enhanced bands are the  $a_{1g}$  symmetric ring-stretch at 992  $\text{cm.}^{-1}$  and the  $e_{1g}$  fundamental at 850  $\text{cm.}^{-1}$  (76). These are Raman-active vibrations, the increase in intensity of which in the infrared of the complex provides evidence in favor of model A, figure 4. The lowering of symmetry from  $D_{6h}$  to  $C_{6v}$  would cause precisely these two forbidden modes, and no others, to become infrared-allowed (76).

Similar symmetry considerations have been applied to the benzene-antimony trichloride complex (60), which had previously been investigated in the Raman with conflicting results (11, 211). Seven fundamentals of benzene were found to be increased in intensity, one to be decreased, and three to be unobservable in the infrared spectrum of the complex (60). The only model of the complex in which predictions of increased allowedness or forbiddenness agree with the experimental intensity changes is the  $C_{3v}$  (staggered) symmetry species.

Recent applications (61) of this symmetry perturbation method to molecular compounds of known structure such as the benzene-silver ion and the dioxane-antimony trichloride complexes yield geometries at variance with those known. This, of course, renders questionable the previous model (or symmetry point group) deductions (60, 77, 195). This experimental conclusion (61) is validated by recent theoretical findings (78) that an enhancement of infrared absorption bands due to changes in vertical ionization potential or electron affinity is inherent in charge transfer theory. The reason why the symmetry perturbation method fails (61) is clarified, and the earlier objections (77, 195) to Mulliken's model of the benzene-iodine complex are somewhat eased.

Insofar as complexing is concerned it is not the above results but rather a comparison of them with the vibrational spectrum of the donor in inert solvents which is indicative. When benzene is in solution in carbon disulfide or carbon

tetrachloride all observable inactive fundamentals are either enhanced or diminished in intensity in approximately the same manner (75). Similarly, no effects on the vibrational spectrum of saturated hydrocarbons due to halogens are observed (195). This behavior, contrasted with that above, is suggestive of some specificity on the part of the benzene-halogen interaction different in kind as well as magnitude from that with so-called inert species. It is this specificity which is presumed due to DA interaction.

#### B. THE ACCEPTOR SPECTRUM

The fundamental vibrational frequency of iodine chloride (ICl) when complexed with various donors has been observed to decrease with increasing equilibrium constant of the D-ICl complex (191, 192). Similar observations have been made for the iodine-carbon stretching frequency in complexes of iodine cyanide, ICN (193). This behavior is expected, since the larger the equilibrium constant the more partial charge transfer there is in the ground state of the complex to the antibonding molecular orbital of iodine cyanide or iodine chloride. In complexes of oxalyl chloride with aromatics (144, 219) the C=O frequency at  $1700\text{ cm}^{-1}$  and the C—Cl stretch at  $777\text{ cm}^{-1}$  are found (220) in the complex at  $1777$  and  $757\text{ cm}^{-1}$ , respectively, in the infrared. No shifts are observed in the Raman (220), but the  $1078\text{ cm}^{-1}$  C—C stretch of oxalyl chloride is intensified in the complex, as would be expected from the larger polarizability caused by the extra antibonding character.

The  $3.46\ \mu$  fundamental of hydrogen chloride is shifted to longer wavelengths in benzene and other aromatic solutions (47, 94, 198, 250). Although such shifts are observed to parallel increasing dipole moment of the solvent, the magnitude of change is too large to be accounted for solely in those terms. Similar comment might apply to a more recent study of the  $1335\text{ cm}^{-1}$  band of *p*-nitroaniline in acetone-benzene binary solvents (160). The decrement in frequency of the hydrogen chloride fundamental when in solution in solvents containing carbonyl groups has been proposed as a measure of the base strength of the solvents (47, 48). This is a previously used gauge of donor strength (92, 93, 94, 95, 96).

In picrate (134) and other nitroaromatic (33, 206) complexes the nitro asymmetric stretching mode and the out-of-plane CH bending mode are sensitive to complexing. The manner in which these modal fundamentals are changed in intensity and/or in frequency has been used as a criterion of complex type for picrates (134). Three types of complex were distinguished: the  $\pi$ - $\pi$  complex, where  $\varphi_A$  and  $\varphi_D$  are both  $\pi$  orbitals; the  $n$ - $\pi$  complex, where  $\varphi_A$  is a  $\pi$  orbital but where  $\varphi_D$  is a primarily nonbonding orbital localized on some one atom (the nitrogen atom in pyridine); and the  $\pi$ - $\pi$  complex in which there is also a strong localized, presumably dipolar, interaction.

The fundamental vibrational frequency of chlorine, at  $557\text{ cm}^{-1}$  in the isolated halogen, is reduced to  $526\text{ cm}^{-1}$  when chlorine is dissolved in benzene (45). Similarly, the  $321\text{ cm}^{-1}$  frequency of bromine is reduced to  $301\text{ cm}^{-1}$  in

the benzene-bromine complex (64). The larger decrement for chlorine is in agreement with its stronger acceptor nature.

Furthermore, these bands, normally only Raman-active, are now observed in the infrared. Such should not be the case if the benzene-halogen complex belonged to the expected R model of figure 4; it becomes necessary to presume (171) an unsymmetrical geometry for the complex. The discordance of this latter geometry with that predicted could only be attributed to a breakdown of the simple orientation principle caused by a large overlap of a wave function, or wave functions, corresponding to one or another, or perhaps several, of the structures  $D_i^+A_j^-$  or  $D_i^-A_j^+$ , with  $\Psi_0$  (see equation 9). This hardly seems likely (172, 180).

A more reasonable suggestion (180), and one which is in line with more recent ideas of complexing (189), is that in benzene solution any one halogen molecule may be in contact with several benzene molecules. Thus, even though the two halogen atoms are interacting equivalently with one benzene molecule, they may be doing so nonequivalently with another. The resulting induced dipole in the halogen would cause infrared absorption (180). The particular statistically average type of complex envisioned here is no more fictitious nor any more arbitrary than that of Mulliken (172), and should lend itself to much the same kind of conclusion (189).

The band width of the iodine-chlorine, or the iodine-carbon, stretching vibration has been observed (191, 192, 193) to increase with increasing equilibrium constant of the D-ICl, or D-ICN, complex. Such broadening concurs with an increasing spectrum of different geometric and/or electronic types of complex. However, the distribution of types would be expected to decrease with increasing equilibrium constant (189). Accordingly, the broadening of half-width of the infrared band can only be explained if it is assumed that the light absorptivity of the most probable type is decreased relative to that of the less probable types as the type spectrum decreases.

The intensity of the infrared band of iodine chloride or iodine cyanide has been observed (191, 192, 193) to increase as the equilibrium constant of the complex in which the iodine chloride or iodine cyanide is the acceptor increases. No good interpretation of this increase is available.

## VI. THE ELECTRONIC ABSORPTION SPECTRUM

The existence of an intense absorption corresponding to the transition  $\Psi_E \leftarrow \Psi_N$  is now expected (167). Since  $a^2 \gg b^2$  (see table 1), this transition may be viewed as causing an electron to jump from D to A. It is hence called an  $E \leftarrow N$  transition, a charge transfer transition, or simply a CT transition. It is further noted that this transition requires participation of the two species D and A and is hence characteristic only of the complex.

The transition dipole moment is given by

$$\mu_{EN} = -e \int \Psi_E \sum_i r_i \Psi_N d\tau$$

which may be approximately written as (167)

$$\mu_{EN} = a^*b(\mu_1 - \mu_0) + (aa^* - bb^*)(\mu_{01} - \mu_0S) \quad (17a)$$

or

$$\mu_{EN} = ea^*b(\bar{r}_D - \bar{r}_A) + (aa^* - bb^*)eS(\bar{r}_D - \bar{r}_{DA}) \quad (17b)$$

where  $\mu_{01}$  is the transition moment,

$$-e \int \Psi_0 \sum_i r_i \Psi_1 d\tau$$

between the pure no-bond and the dative-bond structures.  $\bar{r}_D$  and  $\bar{r}_A$  denote the average position of an electron in the orbitals  $\varphi_D$  and  $\varphi_A$ , respectively, with respect to some convenient origin, while  $\bar{r}_{DA}$  is the average position of an electron having a charge distribution of the form of the overlap of the orbitals  $\varphi_D$  and  $\varphi_A$ .

The energy of the charge transfer transition is given from equations 5a and 5b as (172):

$$h\nu = W_E - W_N = (W_1 - W_0) \left( 1 + \left[ \frac{H_{01} - SW_1}{W_1 - W_0} \right]^2 + \left[ \frac{H_{01} - SW_0}{W_1 - W_0} \right]^2 \right) \quad (18a)$$

For small overlap  $H_{01}$  will vary approximately as  $S$ , and  $S$  as  $S_{DA}$ , and one may consequently write

$$h\nu = W_1 - W_0 + \frac{d^{*2}S_{DA}^2}{W_1 - W_0} + \frac{d^2S_{DA}^2}{W_1 - W_0} \quad (18b)$$

where  $d^*$  will be larger than  $d$  since  $W_1 > W_0$ .  $W_1 - W_0$  may further be written as (105)  $I_D - E_A - \frac{e^2}{r} + C_{AB}$ , where  $I_D$  is the ionization potential of the donor and  $E_A$  the electron affinity of the acceptor;  $e^2/r$  is the coulombic energy of the dative-bond structure, and  $C_{AB}$  is the difference between all other energy quantities in the dative-bond and no-bond structures with both partners at their equilibrium internuclear separation in the complex. For complexes of a common acceptor the greatest variation will occur in  $I_D$ ; the other quantities, being more or less constant, may be approximated as  $M$ , giving  $W_1 - W_0 \simeq I_D - M$ . This leads from equation 18 to:

$$h\nu = I_D - M + \frac{(d^{*2} + d^2)S_{DA}^2}{I_D - M} \quad (18c)$$

The electronic spectrum may now be considered on the basis of these considerations.

#### A. POLARIZATION OF THE CHARGE TRANSFER TRANSITION

Nakamoto (184) has studied the optical dichromism of single crystals of complexes of hexamethylbenzene-trinitrobenzene and *p*-bromoaniline-picryl chloride, the components of which are packed in the crystal with their benzene

rings parallel. The absorption of light polarized perpendicular to the benzenoid planes was more intense than that polarized in the plane, and the position of maximum absorption was at longer wavelengths in the perpendicularly absorbed light component than in the in-plane component. Both of these features are reversed for ordinary noncomplexed aromatics (183).

The electron transport from D to A which is characteristic of a charge transfer process in a molecular complex can only be brought about by that component of the incident light which is oscillating perpendicular to the benzenoid ring. This may also be seen from equation 17a: If one considers a complex in which the rings are exactly superposed, one above the other, and of which the no-bond structure is nonpolar, one obtains  $\mu_0 = 0$  and  $\mu_{01}$  equivalent to the dipole produced by transfer of an amount of charge  $eS$  from the donor to approximately halfway between D and A. Thus  $\mu_{01} \simeq S\mu_1/2$ , and there results (168):

$$\mu_{EN} = \left[ a^*b + \frac{S}{2} (aa^* - bb^*) \right] \mu_1 \quad (17c)$$

Since dipole moments are vector quantities it follows immediately that  $\mu_{EN}$  and  $\mu_1$  lie in the same direction, that is, perpendicular to the plane of the complex.

#### B. INTENSITY OF THE CHARGE TRANSFER TRANSITION

The oscillator strength of the absorption,  $f$ , may be evaluated from any of equations 17 and data such as are given in table 1.  $f$  may also be determined experimentally; the following equations apply (151):

$$f \text{ (experimental)} = 4.32 \times 10^{-9} \int \epsilon \, d\bar{\nu}$$

$$f \text{ (experimental)} = 1.35 \times 10^{-8} \epsilon_{\max} (\bar{\nu}_{\max} - \bar{\nu}_{1/2})$$

$$f \text{ (theoretical)} = 4.704 \times 10^{-7} \bar{\nu}_{\max} \mu_{EN}^2$$

where  $\bar{\nu}$  is the frequency in  $\text{cm.}^{-1}$  and  $\epsilon$  the molar extinction coefficient.  $\bar{\nu}_{\max}$  and  $\epsilon_{\max}$  are the frequency and molar extinction coefficient, respectively, at peak absorption;  $\bar{\nu}_{1/2}$  is the half-width of the absorption band, and the integral in the top-most equation is carried out only over the absorption band being considered. A comparison of calculated and experimental values is given in table 2, from which it is obvious that remarkably close individual agreement obtains.

TABLE 2

*Comparison of experimental and theoretical oscillator strengths*

Complex	$f$ (experimental)	$f$ (theoretical)	Reference
Hexamethylbenzene-trinitrobenzene .....	0.080	0.116	(28)
Stilbene-trinitrobenzene .....	0.064	0.112	(28)
Naphthalene-trinitrobenzene .....	0.050	0.101	(28)
Durene-trinitrobenzene .....	0.103	0.089	(28)
Hexamethylbenzene-chloranil .....	0.093	0.101	(28)
Benzene-iodine .....	0.30	0.19	(167)



TABLE 3  
*The variation of  $\epsilon_{\max}$  with  $K$ †*

Acceptor	Donor	$K$	$\epsilon_{\max}$	Reference
Maleic anhydride.....	Benzene	0.63	3140	(10)
	Anisole	0.84	2020	(10)
	Dimethylaniline	1.5	1590	(10)
Trinitrobenzene.....	<i>o</i> -Methylbiphenyl	0.7	2000	(35)
	<i>m</i> -Methylbiphenyl	1.2	1300	(35)
	<i>p</i> -Methylbiphenyl	1.6	1000	(35)
<i>p</i> -Quinone.....	Benzene	0.42	2800	(10)
	Phenol	0.93	1200	(240)
	Hydroquinone	0.97	890	(240)

† The relationship of  $K$  to  $\epsilon_{\max}$  should be studied only within each of the three acceptor groups.

Although the results of table 2 might seem conclusive, the situation with regard to intensity ( $f$  or  $\epsilon$ ) is really quite ambiguous. Since the quantity  $S$  will usually be rather small, any of the equations 17 may be approximated by (175):

$$\mu_{EN} = ea^*b(\bar{r}_D - \bar{r}_A) \quad (17d)$$

This latter equation will hold approximately only for complexing of rather moderate strength; it will not hold for either very strong or very weak complexing.

Since  $b$  increases as the resonance interaction increases (equation 6a), one would expect  $\mu_{EN}$ , and thus also  $f$  and  $\epsilon$ , to increase with decreasing ionization potential of the donor or with increasing equilibrium constant of the complex. Not only do these predictions not obtain but, as may be seen from table 3, the exact opposite is the case. Observations of this opposition of theory and experiment are rife in the literature (8, 9, 10, 35, 83, 122, 135, 175, 177, 203, 234, 240); the data in table 3 do not even constitute a remotely representative sampling. From all of this it may be concluded that  $\epsilon_{\max}$  decreases with increasing donor character of D or increasing acceptor character of A, and that this behavior is quite at variance with expectation (178, 179).

A number of solutions to this problem have been proposed. The first assumed the complex in solution to consist not just of one geometric species, but to embrace a whole ensemble of different geometric and/or electronic types (175, 178), but it led to no really satisfactory conclusions. However, some of the features of this latter concept, as also of another developed (180) in connection with infrared intensity, have been incorporated into a new theory which appears eminently capable of accounting for experiment. Since this theory was developed from quite other considerations than those above, it will be considered in some detail.

#### 1. *The concept of contact charge transfer*

Iodine in the gaseous state does not absorb at  $\lambda > 2000$  Å., yet when dissolved in saturated hydrocarbons it absorbs quite strongly up to 2600 Å. (68, 69, 86, 105). Bromine (69), oxygen (68, 173), and tetranitromethane (70, 129)

behave similarly in solution in a saturated hydrocarbon. There is no spectral evidence for complexing in these solutions (68, 69, 105), and indeed all independent (i.e., nonspectral) evidence (114, 132) on solutions of iodine in saturated hydrocarbons mitigates against the presence of any very stable complexed species in these solutions. In view of this, Evans (68, 69, 70) suggested that the absorption might be due to a charge transfer transition which occurred during collisions of an iodine molecule with a saturated hydrocarbon molecule.

Mulliken (172) developed this suggestion further. For a donor contacting with an acceptor one may define an entity called the *var der Waals volume*,  $S_{VDW}$ , the square of which will determine the repulsive exchange forces (165) of the closed-shell electrons of D with those of A.  $S_{VDW}$  will be determined largely by the overlap properties of the outermost *filled* orbitals of both species. However, in charge transfer interaction it is the square of the so-called (172) *electron acceptance volume*,  $S_{DA}$ , which will primarily determine the DA attractive resonance forces. If  $\varphi_A$  is an antibonding orbital, and it usually will be, it will be spatially quite diffuse. In such a case it is to be expected that  $S_{DA}$  will be larger than  $S_{VDW}$ , at least for distances of approach not much smaller than about 3.5 Å., and that  $S_{DA}$  may even be larger for much looser contact than that usually involved in actual complexing.

All of the formulas thus far derived for stable complexes will apply to these contacts. In particular, we have thus far supposed that the first term of equation 17b is the more important for stable complexes; hence equation 17d. If it is supposed, however, that the second term of equation 17b, which increases in importance for weaker complexing, becomes relatively more important than the first for contact charge transfer, then an absorption of moderate intensity with

$$\mu_{EN} \simeq -\sqrt{2}eS_{DA}r_{DA}$$

is predicted, where  $r_{DA}$  is the separation of charge centers of D and A in the contact.

Fairly intense absorption should then be possible for donor-acceptor pairs which are merely close or in contact even if there are not actual molecules of complex present, or, in other words, even if the equilibrium constant for complex formation is zero. The only requirement is that  $S_{DA}$  differ sufficiently from zero at van der Waals contact or, equivalently, that at that distance of approach where repulsive exchange forces set in,  $S_{DA}$  be non-zero. A necessary adjunct to this is that since  $b > 0$  for  $S > 0$ , there will be a small amount of charge transfer from D to A in the wave function descriptive of the pair of contacting molecules. All of this does not imply any stability of the contact pair, since at the van der Waals contact there will be an exact balance of exchange and charge transfer forces. At any distance of separation a little larger than that for van der Waals contact there will be a small stabilization energy of the contact pair, but it will be completely negligible thermally, even at rather low temperatures. Indeed, one may go further and say that the occurrence of contact charge transfer absorption does not depend on the ability of the charge

transfer forces ever to overcome the exchange repulsions, but rather on the occurrence of a non-zero  $S_{DA}$ .

Orgel and Mulliken (189) have examined a model which supposes a solution of benzene and iodine to consist of a definite fraction of close, relatively low energy, relatively favorably oriented, saturated 1:1 complexes, each loosely surrounded by noninteracting benzene molecules, plus a remaining fraction of iodine molecules having loose and random contactual charge transfer interaction, each with  $\alpha$  benzene molecules. In actuality, of course, there must be a continuous gradation from actual complexes of different geometries to loose contacts of different orientations and stoichiometry. The particular fictitious model chosen, however, does represent a reasonable approach to reality.

When the effects of this particular distribution of complexes and contacts on the Benesi-Hildebrand (15) equation, and on the maximum molar extinction coefficient,  $\epsilon_{BH}$ , and the equilibrium constant,  $K_{BH}$ , derived therefrom, are investigated, the following equations result (189):

$$\epsilon_{BH} = \epsilon_{\text{complex}}(1 + \rho/K_{BH}) \quad (19a)$$

$$\epsilon_{\text{complex}} = K_{BH}\epsilon_{BH}/(K_{BH} + \rho) \quad (19b)$$

where  $\rho = \alpha\bar{\epsilon}_{\text{contact}}/\epsilon_{\text{complex}}$ .  $\bar{\epsilon}_{\text{contact}}$  is the mean molar extinction coefficient for all kinds of contacts, and  $\epsilon_{\text{complex}}$  is a weighted average extinction coefficient over all the types of 1:1 complex which exist. All  $\epsilon$ 's refer to the same wavelength.

It is obvious from equation 19a that the larger  $K_{BH}$  the smaller will be the contribution of contactual charge transfer to the intensity in solution, and that finally when  $K_{BH} = \infty$ , all absorption will be due to 1:1 complexes with  $\epsilon_{BH} = \epsilon_{\text{complex}}$ . In this connection, the rate of decrease of  $\epsilon_{BH}$  with  $K_{BH}$  for complexes of iodine with alkylbenzenes is greater than the rate of decrease of a similar series of alkylbenzene-iodine chloride complexes (186). This accords with the greater  $K_{BH}$  values of the iodine chloride complexes and with equation 19a.

If values of  $\rho = 4$  or  $5$  are substituted in equation 19b, then it is found that the values of  $\epsilon_{BH}$  of alkylbenzene-iodine complexes, which increase anomalously as  $K_{BH}$  decreases, yield values of  $\epsilon_{\text{complex}}$  which behave properly, that is, increase with  $K_{BH}$ , or conform to equations 17. If  $\bar{\epsilon}_{\text{contact}} \simeq \epsilon_{\text{complex}}$  then  $\rho \simeq \alpha$ , and values of  $\alpha = 4$  or  $5$  seem reasonable.  $\bar{\epsilon}_{\text{contact}}$  should, of course, be somewhat smaller than  $\epsilon_{\text{complex}}$ , which would make  $\alpha$  larger. However, because of the particular statistical model chosen, and the fact that iodine complexes which are characterized by large  $\varphi_A$  are being considered,  $\bar{\epsilon}_{\text{contact}}$  may not be so much smaller than  $\epsilon_{\text{complex}}$  as to necessitate an unreasonably large  $\alpha$ .

These latter results are gratifying, but not necessarily conclusive. There seems little doubt, however, that the observed anomalous behavior of the  $\epsilon_{BH}$ 's is to be considered due to:

- (a) Contributions from contact charge transfer spectra (68, 69, 70, 180, 172, 189).
- (b) Varying mixtures of orientation isomers (172, 175, 177, 178, 179, 189).
- (c) Deviations from ideality in solution, magnification of experimental

errors, and other factors not properly accounted for by use of the unmodified Benesi-Hildebrand (15) equation.

### C. ENERGY OF THE CHARGE TRANSFER TRANSITION

If one assumes an approximate constancy of the term  $(d^{*2} + d^2)S_{DA}^2$ , equation 18c reduces (105) to:

$$h\nu = I_D - M + 2\beta^2/(I_D - M) \quad (18d)$$

A somewhat different form of this equation has also been used by Briegleb and Czekalla (28); the general prediction (28, 105, 172) is that a graph of the energy of the experimental charge transfer absorption band versus  $I_D$  should yield a parabolic segment. In practice (105) the range of  $I_D$  values is usually fairly small, and the segment consequently so restricted as to be virtually a straight line. One may view this differently. When one considers a series of complexes of the same acceptor with different but closely related donors for which the  $I_D$  range is only a few electron volts, one may write to a good approximation (149)

$$h\nu = I_D - B \quad (18e)$$

where  $B$  is assumed to be a characteristic constant for the complexes of any one acceptor.

Equation 18e, predicting a linear increase of the energy of the absorption band with  $I_D$ , has been found to fit experiment surprisingly well. Such a linear relation exists for eighteen different aromatic-iodine complexes (149) even when the donors are as diverse as benzene, thiophene, dihydropyran, and piperidine (44, 232). Polyacene-trinitrobenzene complexes (151, 152), as well as various other aromatic- and heteroaromatic-trinitrobenzene complexes (18, 19, 28, 125), also fit equation 18e.

It must be emphasized that even for complexes of the one acceptor, the empirical parameter  $\beta$  should vary somewhat unless one is considering a group of very closely related donors, and thus that the observed linearity has no very good foundation in theory (152, 172). It is not surprising then that the energy of the absorption band predicted from equation 18e deviates by 0.7 e.v. from the experimental value in the triethylamine-iodine complex (182). Similar exceptions have been observed for the pyridine-iodine complex (208) and in the pyridine *N*-oxide complex with iodine (44).

It has been concluded (148) that iodine exhibits an amphoteric character in the  $I_4$  complex. This species exhibits a weak absorption band with maximum at 2880 Å. when in solution in inert solvents (68, 115, 119, 121, 142, 164), and at 2670 Å. in the gas phase (131). Nuclear quadrupole absorption spectra in solid iodine point to anomalies (239) perhaps attributable to this self-complex. McConnell (148), on the basis of the rather low ionization potential (163) of the iodine molecule, calculates the energy of a presumed charge transfer absorption band as 4.4 e.v., a value which accords rather well with the observed value (4.7 e.v.). This is suggestive of a charge transfer origin for the iodine-iodine binding in the complex. Such basic behavior by iodine is hardly improbable, since

there does exist some evidence that bromine may actually be functioning as a very weak partial donor (i.e., coefficient  $c$  of equation 2 being small but significantly greater than zero) in some dibenzoquinoline–bromine complexes (97, 113, 150, 228, 229).

Appropriate substitution of the benzene ring will make the two  $e_{1g}$  molecular orbitals of benzene (see figure 3) slightly different in energy. These substituted benzenes should have two slightly different low-energy ionization potentials, conditioned by whether one ionizes an electron from the molecular orbital of upper or lower energy; it is expected that two charge transfer absorptions will result (188). Two such bands attributable with some reservations to the above causes have been observed (230) in some polymethylbenzene–chloranil complexes and also in dimethylaniline–chloranil. Some diaminobenzene–trinitrobenzene (18), anisole–iodine (143), and *p*-dimethoxybenzene–iodine complexes (143) exhibit similar behavior, except that three bands are observed in the last two.

## VII. THE LUMINESCENCE SPECTRA

The emission spectra of complexes of trinitrobenzene with various aromatics have been observed (161, 207) in solid glassy solution at  $-190^{\circ}\text{C}$ . after excitation with radiation of appropriate wavelength. This luminescence exhibited a remarkable similarity to the phosphorescence ( $T \rightarrow S$ ) spectrum of the free uncomplexed donor component of the complex, and on this basis it was postulated (161) that the emission of the complex actually was the phosphorescence of the donor. However, the luminescence of the anthracene–trinitrobenzene complex was anomalous in that it did not resemble, either energetically or vibrationally, the known  $T \rightarrow S$  emission of anthracene. Because of the above induced parallelism between the emission of the complex and the phosphorescence of the donor, the lowest triplet state of anthracene was reassigned an energy of  $19,000\text{ cm.}^{-1}$  (207), the previous assignation of  $14,700\text{ cm.}^{-1}$  (137) being considered in error.

The  $14,700\text{ cm.}^{-1}$  position was later affirmed (43, 151, 152, 192) by vibrational analyses of the phosphorescence spectra of anthracene and seven of its chlorinated derivatives, and the resultant exclusion of the anthracene–trinitrobenzene complex from the induced parallelism raised some doubt about the identification of the emission of the complex as a phosphorescence of the donor. Furthermore, conclusions reached (187) on the basis of a supposed parallelism also became suspect.

It has now been proven that a mirror-image relation exists between the emission spectrum of the complex and its charge transfer absorption band (19, 20, 57, 58). If, for example, it is supposed that the emission is a phosphorescence of the donor, then it should be little affected energetically (152) in complexes of the same donor with different acceptors. If, on the other hand, it is the reverse of the charge transfer (or  $E \leftarrow N$ ) absorption, then as the electron affinity of the acceptor increases and the charge transfer absorption as a consequence moves to longer wavelengths, the emission must do likewise in order to preserve the mirror-image relationship. That the emission does indeed shift to longer wavelengths with increasing  $E_A$  of the acceptor has been proven by the work of Czekalla

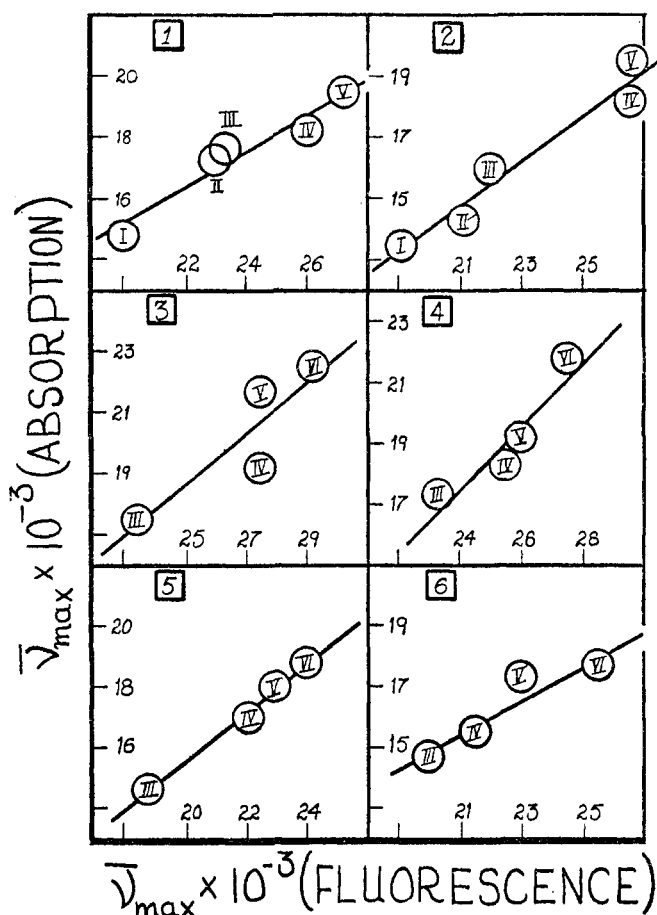


FIG. 7. Plots of  $\bar{\nu}_{\max}$  for absorption versus  $\bar{\nu}_{\max}$  for emission, illustrative of the manner in which an approximate mirror-image relationship is maintained. The plots are as follows: plot 1, durene; plot 2, hexamethylbenzene; plot 3, naphthalene; plot 4, phenanthrene; plot 5, anthracene; plot 6, 1,2-benzanthracene. The points on each plot represent the following acceptors: point I, chloranil; point II, 2,5-dichloroquinone; point III, 2,4,7-trinitrofluorenone; plot IV, trinitrobenzene; plot V, tetrachlorophthalic anhydride; plot VI, trimesyl chloride. This figure is reproduced by gracious permission from the unpublished work of J. Czekalla (57).

(57, 58, 59), a beautiful example of which is given in figure 7. Despite some earlier opposition (231) it may thus be concluded that the emission of trinitrobenzene complexes is  $E \rightarrow N$ , or the reverse of the charge transfer absorption process.

The reason for the correspondence of the  $E \rightarrow N$  emission of a trinitrobenzene complex and the phosphorescence of the donor has also been clarified (151, 152). Phosphorescopic study of the emission spectra of trinitrobenzene complexes of anthracene, naphthalene, phenanthrene, etc. has shown that the observed single

emission band actually consists of two parts: One is a weak emission and corresponds almost exactly to the phosphorescence of the free uncomplexed aromatic in both energy and lifetime. The other, obtained by subtraction of the phosphorescence from the total emission, is a good mirror image of the  $E \leftarrow N$  absorption and has a normal fluorescent lifetime. Since the  $E \rightarrow N$  fluorescence is usually quite structureless, the structure of the total emission is determined by the vibrational characteristics of the phosphorescence. This might explain Reid's original identification (161, 207).

However, a question then arises as to why the phosphorescence and fluorescence occupy the same spectral location in so many trinitrobenzene complexes. It has been suggested (197) that this coincidence is accidental, and is only maintained because of an approximate constancy of the difference in energy of the vertical ionization potential and the lowest triplet state of many aromatic hydrocarbons of ca. 30–35 kcal./mole. The energy of the charge transfer fluorescence is also a function of the electron affinity of the acceptor, and it is to be expected that in complexes with acceptors other than trinitrobenzene there might be a large spectral separation of fluorescence and phosphorescence. Thus in the complex of naphthalene and tetrachlorophthalic anhydride (34) one may distinguish two distinct bands in the total emission spectrum: one of the  $E \rightarrow N$  emission with a half-life of  $10^{-9}$  sec. (27, 54, 55, 59), and the other the phosphorescence of naphthalene with a slightly decreased half-life of a few seconds. Two such bands have also been found in the complexes of tetrachlorophthalic anhydride with anthracene, benzanthracene, phenanthrene, and durene (57).

The mechanistic basis for the observation of two emission spectra has recently been considered (152) on a somewhat theoretical level, using the charge transfer concept. There may be some question as to the advisability of using charge transfer theory for nitroid complexes (29, 42, 112, 175, 177, 178); however, charge transfer interaction, as may be seen from table 1, does account for some 50 per cent of the binding energy of trinitrobenzene complexes, and in view of the ability to account for so many diverse physical and chemical properties on the basis of this charge transfer contribution, its use here seems justified. A derived potential energy diagram for the anthracene-trinitrobenzene complex is given in figure 8. The general conclusions are that immediately following the  $E \leftarrow N$  absorption (process i), there occurs not only the reverse  $E \rightarrow N$  fluorescence (process ii), but also a transfer of energy from the primarily ionic  ${}^1E$  state to a lower-energy triplet state,  ${}^3N^*$ , of the complex. Such energy transfer will occur at or near the juncture (or point of incipient crossing) of the  ${}^1E$  and  ${}^3N^*$  curves, and is called "intersystem crossing." Since the triplet level is dissociative at the energy of the junction point, the complex will probably dissociate to a large extent, yielding trinitrobenzene in its ground state and anthracene in its lowest excited triplet ( ${}^3B_{2u}$ ) state. The anthracene will then return to ground by the observed phosphorescent path (process iii).

Considerations (152) similar to the above have been applied to the benzene, naphthalene, phenanthrene, and carbazole complexes of trinitrobenzene. The only requirement for two emissive paths is that the lowest triplet level of the

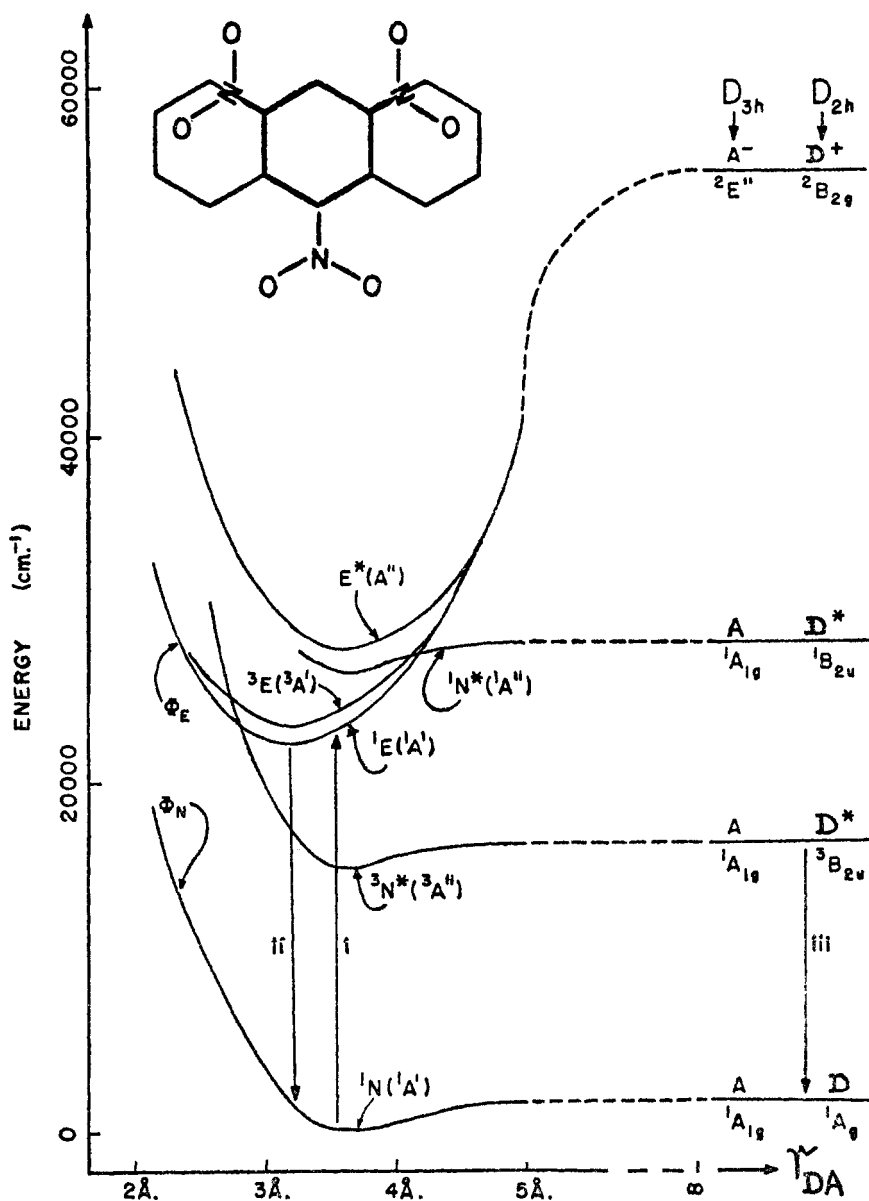


FIG. 8. Potential energy curves for an anthracene-trinitrobenzene complex for which the geometry at the upper left of the figure is assumed. The benzenoid part of the trinitrobenzene is assumed to be positioned parallel to and exactly above the central hexagon of the anthracene. Superposition is indicated in the model at the upper left by a thickening of lines. The symmetry representation species of the acceptor, the donor, and the complex in the point groups  $D_{2h}$ ,  $D_{3h}$ , and  $C_{1h}$ , respectively, are given in columnar form under the appropriate point group symbol or structure. For further detail consult reference 152.



donor be at lower energy than the first excited charge transfer state of the complex; the appearance of the phosphorescence is due to a type of predissociation involving intersystem crossing.

The term "sensitized phosphorescence" has been used to describe the fact that the  $T \rightarrow S$  emission of the donor when complexed is usually more intense than the normal phosphorescence of the free uncomplexed donor species. This term, however, has also been used (237) to describe another and presumably different means of increasing the phosphorescent quantum yield. In this latter case a transfer of energy is presumed to take place directly from the triplet level of one molecule (a sensitizer) to the triplet level of the molecule being observed (65, 66, 237, 238). If this mechanism is correct, then we must note the following differences between the two types of sensitization:

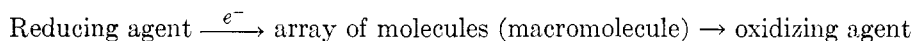
(a) Both components in the cases considered here form stable molecular compounds, whereas in the systems studied by Terenin and Ermolaev (238) there was no evidence of complexing.

(b) The primary exciting light is absorbed in the  $E \leftarrow N$  transition of the complex in one case, and in the  $S' \leftarrow S$  absorption of the sensitizer in the other.

(c) The energy transfer in the cases considered here was intramolecular and  $S \rightsquigarrow T$ , not intermolecular and  $T \rightsquigarrow T$ .

(d) The concentrations at which the type of transfer described by Terenin and Ermolaev becomes effective are much different ( $10^4$  greater) than those necessary for the process described here. If the mechanism described by Terenin and Ermolaev (238) is that which is actually operative in the systems considered by them it might be well to discontinue usage of the term "sensitized phosphorescence" to describe the effects considered here. It would seem, however, that a reinvestigation of the presumed  $T \rightsquigarrow T$  transfer situation is necessitated, since it may very well involve weak, and difficult to establish, complexes. This is especially suggested by (d).

Since energy transfer has been indirectly under consideration, it seems appropriate to consider another type of energy transfer process which may be observed if one can initiate charge transfer at some point in an array of molecules, and which has been invoked (208) in order to account for highly specific biological oxidation-reduction processes. Once initiated such transfer could repeat along the whole array, and an electron would ultimately become available at a point remote from where introduced, thus providing a mechanism for "long-range" oxidation-reduction processes as follows:



It seems significant that just such an array as is required is present in the nucleic acids, where the purine and pyrimidine components may have the role of energy transporters.

### VIII. TRIPLET STATES AND COMPLEXING

The absorption of nitroid complexes, now known to be  $E \leftarrow N$ , was initially considered by Briegleb (25, 28) to be a forbidden transition of the aromatic donor,

the transition probability of which increased when in the dipole field of the acceptor nitro groups. Murakami made a similar suggestion (174), except that here quinone complexes were being surveyed, and the transition which was increased in intensity was thought to be a  $T \leftarrow S$  process of the quinone. Recently it was suggested (149) that charge transfer spectra might be enhanced  $T \leftarrow S$  intercombinations of the aromatic donor. The basis for this last suggestion seems to have been the Reid parallelism already discussed (161, 207) and the solvent perturbation work of Kasha (118). This latter work showed that upon mixing two colorless liquids,  $\alpha$ -chloronaphthalene and ethyl iodide, a yellow color developed instantaneously; subsequent spectroscopic examination showed that the color was caused by an increase in the oscillator strength of the lowest  $T \leftarrow S$  intercombination of the  $\alpha$ -chloronaphthalene, and the effect was attributed to a collisional perturbation of the spin-orbital coupling in the  $\pi$ -electron orbitals of the  $\alpha$ -chloronaphthalene by the heavy iodine atom.

This latter result is admittedly suggestive of a possible origin for the strong new absorption band of molecular complexes, and it consequently seems necessary to consider seriously the suggestion of McConnell, Ham, and Platt (149) and to note its defects. The new absorption bands characteristic of molecular complexes are quite diffuse and not at all similar to the fairly nicely resolved  $T \leftarrow S$  absorptions common to most aromatics. The diffuseness is indeed in accord with charge transfer theory. It is further to be noted that  $\epsilon_{\max}$  values of the absorption of the complex as determined by Benesi-Hildebrand procedures, even when corrected for contact contributions, are still  $10^3$ - $10^2$  times more intense than the  $\epsilon_{\max}$  values of the  $T \leftarrow S$  transitions of the donor component, even when the donor is intramolecularly perturbed (117). It seems certain that in the complex the extent of penetration of the donor  $\pi$  electrons into the field of the heavy atom (or atoms) located in the acceptor is much less than the penetration that can occur when the perturbing atom is actually attached to the  $\pi$  system of the donor by a normal chemical bond. The penetration in the complex will be determined by  $b$  of equation 1 or table 1. On the basis of the collisional hypothesis a similar increase in oscillator strength,  $f$ , of all  $T \leftarrow S$  absorptions of all molecules should occur upon solution of the molecules in any solvent of which the molecules contain an atom of large atomic number. In particular such an increase in the intensity of the  $T \leftarrow S$  (presumed) band of  $\alpha$ -chloronaphthalene should occur in bromide or chloride solvents as well as in iodide solvents, and without any spectral shift of the absorption band. This is well demonstrated by figure 9 where, it might be added, the increments in oscillator strength in the various solvents are proportional to the squares of the atomic spin-orbital coupling factors of Cl, Br, and I, respectively (151). It is significant that, despite expected differences in  $E_A$  of the  $n$ -acceptor (i.e., solvent), no shifts at all are observed.

These facts alone (and there are others) seem sufficient to adjudge invalid the suggestion (151) that the absorptions of complexes are enhanced transitions of the donors. The above reasoning has not been detailed merely to disprove this latter suggestion (151), but because the solvent perturbation of  $T \leftarrow S$  transition probability is of significant interest for quite another reason.

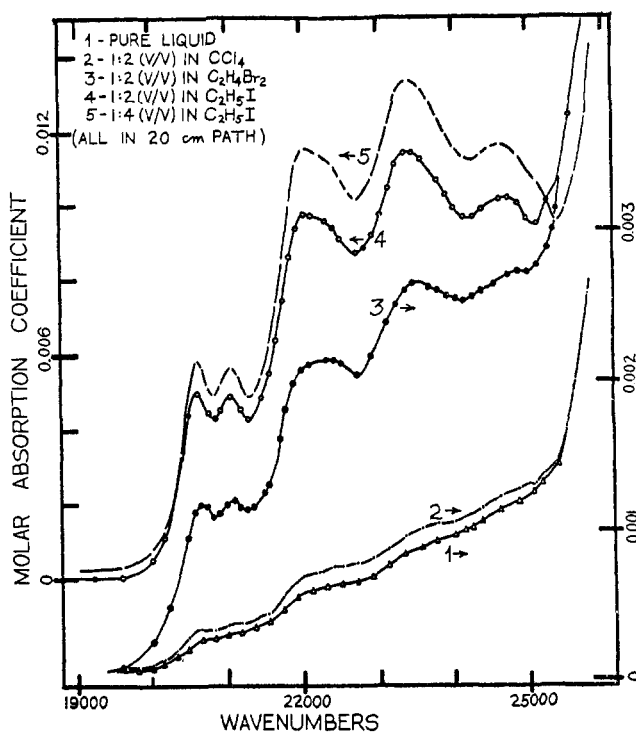


FIG. 9. The effect of solvents of which the molecules contain atoms of high atomic number on the transition probability of the lowest  $T \leftarrow S$  transition of  $\alpha$ -chloronaphthalene. Curves 1, 2, and 3 refer to the scale at the right; curves 4 and 5 to that at the left. The molar absorption coefficient is an apparent coefficient based on the total concentration of  $\alpha$ -chloronaphthalene present.

The interpenetration of the  $\pi$  electrons of  $\alpha$ -chloronaphthalene into the vicinity of the large field of the iodine atom of ethyl iodide which is necessitated by the results of figure 9 obviously implies charge transfer. The question then becomes one of degree: is the charge transfer caused by complexing, contacting, or collision? It is appropriate to differentiate between contact and collision. The former implies that at van der Waals contact  $S_{DA}$  is sufficiently different from zero to predicate the observed results; the latter implies that  $S_{DA}$  is zero at van der Waals contact, and can only become non-zero by virtue of a collision which is more energetic than usual and which can compress the two molecules together to distances of separation sufficiently small to render  $S_{DA}$  sufficiently large. It is to be emphasized that the resulting enhancement of the  $T \leftarrow S$  band is not due to the charge transfer band of the complex, the contact, or the collision pair, but is merely an effect associated with such complexing, contacting, or collision. The charge transfer band should occupy some other, generally different and calculable spectral region.

Since the enhancement of  $T \leftarrow S$  transition probability is due to the extent to which charge transfer occurs, it should be possible to apply Benesi-Hilde-

brand considerations to the increments in oscillator strength observed. This was done (151), the result being that the phenomenon is either contactual or collisional in nature, or equivalently that there was no detectable complexing in the solutions studied.

The effect of pressure and temperature on the intensity of the  $T \leftarrow S$  band of  $\alpha$ -chloronaphthalene when in ethyl iodide solution has been investigated, and it has been found (210) that increase of  $f$  occurred with increasing pressure and temperature, as would be expected if the phenomenon were either collisional or contactual. However, the usefulness of either pressure or temperature effects in distinguishing between stable complexes on the one hand and transitory contacts or collisions on the other seems, as of the moment at least, to be of little value. Thus the intensity of the aniline-trinitrobenzene  $E \leftarrow N$  transition increases as temperature increases (89, 90), despite an expected decreasing stability of the complex. Indeed, this latter result led to rejection of the idea that there were any stable complexes present in these solutions and to the development of a kinetic concept of complexing not dissimilar to that of Orgel and Mulliken, or to that being investigated here. These results have, however, been partially reconciled with expectation for stable complexes (100, 245). The effect of pressure seems also not to be too useful as a discriminatory tool. The light absorptivity of all molecular compounds thus far investigated increases with increasing pressure (89, 90, 100, 101, 226), this being supposed due to the higher pressure increasing the probability of the more compact types of complexes. Since the more compact types will have the higher light absorptivity, the result obtained is reasonable. It would seem, as of now, that one must be wary of viewing the temperature or pressure effects too naïvely.

#### IX. CHARGE TRANSFER ADSORPTION

Mulliken (167) suggested that the adsorption of certain molecules by metals might be due to the formation of a charge transfer complex on the metal surface. Indeed, if one transposes the results of Fairbrother (71, 72) on the dipole moment of the benzene-iodine complex, it seems reasonable that charge transfer adsorption of nonpolar species should give rise to finite surface potentials; the results of Sachtler (217) on benzene adsorbed on platinum confirm this view. One might even use charge transfer theory to predict (32) the sign of the surface potential resulting from adsorbate-adsorbent interaction: A negative surface potential results when the adsorbate functions as a Lewis acid and the adsorbent as a base, and a positive surface potential results when the adsorbate behaves as a Lewis base.

If adsorption on a metallic surface is accompanied by transfer of an electron from the adsorbate to the metal, such transfer would be expected to be endothermic because the ionization potential of the adsorbate,  $I_D$ , is usually larger than the work function of the surface,  $\phi$ . However, charge transfer theory can provide an energy level (the level corresponding to  $\Psi_N$  of equation 1) sufficiently lower in energy than the Fermi level of the metal to make the process exothermic. An expression for this heat of adsorption at zero coverage of the surface,  $X_0$ ,

has been obtained (146) in terms of  $I_D$ ,  $\phi$ , a coulombic image energy, and an interaction integral  $\beta$  related to  $\beta$  of equation 18d. A relation between this  $\beta$  and the surface potential has also been suggested (156), by use of which values of  $X_0$  have been calculated (31) for four different gases adsorbed on various metals, with excellent results.

As a result of the transfer from adsorbate to surface an ionic chemisorption bond is not necessarily formed; all intermediates between pure covalency and ionic bonding are possible. In either case, the quasi-ions generated in the adsorbed layer will repel one another and perhaps account for the observed decrease of heat of adsorption with increasing coverage.

The treatment (146) of adsorption on semiconductors of the  $p$  type is much the same as for metals, with the important difference that the Fermi level of the semiconductor increases considerably in energy with increasing adsorption (247) and will be expected to limit coverage (23, 247). The adsorption of some nitriles, alcohols, esters, and amines on iron powder (49, 98) has been shown to conform (146) to charge transfer adsorption on a semiconductor.

Mignolet has proposed on the basis of an intuitive argument (158) that the double layer at the surface of a metal must be positive, and that adsorbates must function as donors with respect to metals. The concept of a donor adsorbate is based on the debatable supposition (155) that most adsorbates if they functioned as acceptors would have so many nodal planes in their acceptance orbital,  $\varphi_A$ , that  $S_{AD}$  might be expected to be small or zero from (presumably accidental) internal cancellation. Experiment, however, accords with donor behavior on the part of the adsorbate. The negative ions of the inert gases are not very stable (145), and inert gases when adsorbed on bare nickel are strongly polarized with the positive charge outwards from the surface (87, 154); all other films on bare as well as on covered metallic surfaces that have been investigated (22, 155, 157) also have positive surface potentials. Some difficulty arises in the case of oxygen and halogen adsorbates, which are not satisfactorily interpreted on the basis of a positive surface potential (158) but which probably react dissociatively (31, 252).

#### X. THE SPECTROPHOTOMETRIC DETERMINATION OF EQUILIBRIUM CONSTANTS

The Benesi-Hildebrand (15) procedure for the simultaneous evaluation of the equilibrium constant,  $K_{BH}$ , and the extinction coefficient,  $\epsilon_{BH}$ , and some of the limitations inherent in its use have been discussed by Andrews (8). There has been considerable flux in this field recently and it seems that a short review is predicated.

The Benesi-Hildebrand equation which may readily be generalized (127, 128) to take care of the situation where the donor or acceptor, or both, absorb in the region of the  $E \leftarrow N$  transition, is usually written (15)

$$y = \frac{(A)l}{d} = \frac{1}{\epsilon_{BH}} + \frac{1}{\epsilon_{BH}K_{BH}} \left( \frac{1}{x_D} \right) \quad (20)$$

and is applicable only when the absorptions of the complexing species are negligible and the donor is in considerable excess over the acceptor. (A) is the concen-

tration of acceptor in moles per liter,  $l$  is the absorbing path-length, and  $d$  is the optical density, usually maximum, of the  $E \leftarrow N$  absorption band.  $x_D$  is the mole fraction of donor and may be substituted by  $(D)$  with no differences expected other than that caused in  $K_{BH}$  by a change of units.

The usual plot of  $y$  versus  $1/x_D$  is changed by Scott (223) to one of  $yx_D$  versus  $x_D$ . This latter method has the advantage that one extrapolates through regions of increasing dilution to the intercept, and that with precise experimental results one can also determine the initial slope at high dilution. Moreover, if the points do not define a straight line this method gives a more reasonable weighting to the different measurements.

Deviations from ideality in solution have been considered (223) further. Thus the "extinction coefficients" obtained by plotting  $yx_D$  vs.  $x_D$  and  $y(D)$  vs.  $(D)$  are not identical, nor do the two "equilibrium constants" obey the ideal thermodynamic equation  $K_c = V_s K_x$ , where  $V_s$  is the molar volume of the solvent. It is concluded that until some independent means of evaluating the absolute concentration of a complex is obtained, the reported  $K_{BH}$ 's and  $\epsilon_{BH}$ 's must be viewed as subject to considerable error. Of some possible significance here is a reported constancy (120) of the product  $K_{BH}\epsilon_{BH}$  for ethyl iodide-iodine complexes from infinite dilution up to concentrations such that  $(A) + (B) = 0.06$  mole per liter. This latter, however, does not solve the question of which is the more properly considered constant:  $\epsilon_{BH}$  or  $K_{BH}$ .

A discussion by Orgel and Mulliken (189) has clarified the whole question of complexing, and has settled an old controversy already noted in the section on infrared and Raman spectra and recently resuscitated in the ultraviolet field (14) concerning any possible distinction between weak complexing and strong physical perturbations. This discussion presumes ideality of solution, and may be considered in two parts.

If there are several different types of 1:1 complexes present in solution, then each type may have different equilibrium constants and spectra (i.e., they may not necessarily absorb at all at the wavelength at which Benesi-Hildebrand considerations are being applied). Despite this, the determined  $K_{BH}$  is found to be a total equilibrium constant and thermodynamically correct, whereas the extinction coefficient is a weighted-average extinction coefficient and cannot be compared with the results of a theoretical evaluation of  $\mu_{EN}$  unless there is only one type of 1:1 complex present. It is not surprising then that  $K_{BH}$  accords so well with expectation and  $\epsilon_{BH}$  not at all.

Since  $K_{BH}$  measures all complexing in solution it bears on the fact that equilibrium constants as determined by partition methods seem to be larger than those determined spectroscopically. Thus the equilibrium constant of naphthalene picrate in chloroform as determined by partition methods is ca. 2.5 liters per mole (6, 126), whereas  $K_{BH}$  is 0.99 liter per mole (212, 213, 214). Similarly,  $K_{BH}$  is less than  $K(\text{partition})$  for complexes of substituted naphthalenes with picric acid (88). It was initially thought (213) that the presence of at least two kinds of complex was necessary to explain this result, and that  $K_{BH}$  applied only to a light-absorbing type, whereas  $K(\text{partition})$  was inclusive and hence

greater. This conclusion was later retracted (215) and is of course in error, since  $K$  should be the same by both methods. The  $K_{\text{BH}}$  of naphthalene picrate has recently been measured (82) to be 2.4 liters per mole when  $(A) = (D)$  in good correspondence with  $K(\text{partition})$ . However,  $K_{\text{BH}}$  for this complex varies with the concentration of A or D and suggests either thermodynamic nonideality of solution or a concentration-dependent change of the spectrum of D or of A. The equilibrium constants of benzene-iodine complexes determined (253) by both methods do agree, although the measurements reported lack accuracy.

A criterion for the presence of only one type of 1:1 complex is a constancy of  $\epsilon_{\text{BH}}$  (presuming  $E \leftarrow N$  band shape to be Gaussian, and not to shift) with temperature. Alternatively, a plot of  $K_{\text{BH}}$  vs.  $1/T$  should give a straight line if there is only one 1:1 complex present, presuming of course that the heat of formation of this complex is non-temperature-dependent over the range being studied.

If a multiplicity of 1:1 complexes is further complicated by the possibility of contacts which cause absorption in the region being investigated, and if the concentration of such contacts varies linearly as  $1/x_{\text{D}}$ , the Benesi-Hildebrand plot should still yield a straight line. However, as the concentration of complexes decreases this line will tend to go through the origin and  $\epsilon_{\text{BH}}$  will be more and more overestimated, until finally when there are no complexes,  $\epsilon_{\text{BH}}$  becomes infinity. However, if the intercept on the  $1/\epsilon_{\text{BH}}$  axis can be read accurately, the  $K_{\text{BH}}$  values obtained are thermodynamically correct. The  $\epsilon_{\text{BH}}$  values, however, are much too large and cannot be corrected to the value appropriate to the stable complex, or complexes, except by somewhat empirical means.

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