STUDIES ON MOLECULAR ASSOCIATION

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This is to certify that the M.Phil. dissertation entitled "STUDIES ON MOLECULAR ASSOCIATION", by Syed Muzaffar Ali Andrabi is the original work of the candidate and is suitable for submission.

Pushkin M. Qureshi
Reader
TO MY
MOTHER
FOR HER IMMENSE
LOVE AND SACRIFICE
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M.S.M.A. ANDRABI
ABSTRACT

The dissertation comprises of two chapters. First is the General Introduction which is based on all the relevant literature to date. Among other aspects it gives a detailed description of the spectrometric identification of Charge Transfer Complexes, evaluation of association constants by UV-VIS, IR and NMR spectroscopy. After discussing various other relevant features of these complexes the general introduction concludes with a survey of the recent developments in this important area.

The second chapter deals with the isolation of charge transfer bands for various polynitroaromatic - aromatic amine systems. Even though efforts have been made, these bands could not be isolated before. The charge transfer has been confirmed independently by evaluating association constants. The electron affinities for some polynitroaromatics which are not known have been evaluated from their Charge Transfer bands.
CHAPTER - 1

GENERAL INTRODUCTION
Molecular association is a blanket term which includes all those interactions where no chemical bonds are formed. They extend from hydrogen bonding to proton transfer reactions and include the most important of this family of interactions namely charge transfer complexes or molecular complexes. These complexes are becoming increasingly important in all fields of human endeavour from physics to chemistry and biology to medicine. Currently there is an opinion among some scientists that these complexes are involved somewhere or the other on the reaction profile of all chemical reactions. These are a special case of molecular association and have been most widely investigated.

1.1 THE THEORY OF CHARGE TRANSFER COMPLEXES

It has been known for a long time that hydrocarbons such as naphthalene react with picric acid to form a coloured substance. The nature of these coloured substances has only been recently understood. Briegleb\textsuperscript{1,2} suggested that the hydrocarbon-nitro compound adducts were the result of the electrostatic attraction between the localized dipoles of the nitro groups and the induced dipoles in the hydrocarbons. This theory could explain the bonding energy of a few kilocalories per mole which had been observed.
However, the formation of colour could not be explained by this theory. Pauling\cite{3} suggested that when a hydrocarbon molecule is close to picric acid (at a distance of a 3.5 Å) and also parallel to it then the dielectric constant of the environment of the picric acid molecule is affected. This effect results in greater optical absorption. The distance between the component molecules in a complex was shown by crystallographic measurements to be only slightly less than the van der Waal's distance\cite{4-7}. This observation finally removed the possibility that any sort of normal covalent bonding could be responsible for these complexes. On theoretical considerations too, the instant equilibrium in solution disfavours covalent bonding.

In 1949 Benesi and Hildebrand\cite{8} reported that solutions containing an aromatic hydrocarbon and iodine had an electronic absorption band not present in either component alone. In 1950 Mulliken\cite{9} suggested that complex formation occurs through an intermolecular charge-transfer transition. The detailed theory was put forward by him in 1952\cite{10,11}. As a result of Mulliken's theory there has been a great stimulus to the developments in the study of the charge transfer (CT) complexes. A brief outline of his theory is presented here.
Mulliken's Theory

Mulliken defines a molecular complex between two molecules as an association somewhat stronger than ordinary van der Waal's association, of definite stoichiometry (1:1 for most cases). The partners are very often already closed-shell (saturated valence) electronic structures. In loose complexes the identities of the original molecules are to a large extent preserved. The tendency to form complexes occurs when one partner is an electron acceptor and the other is an electron donor. We abbreviate the term donor acceptor complex to include all such associations and use D for an electron donor and A for electron acceptor. Most studies of complexes thus far have been made in solution, in solvents that are as inert as possible. We may, therefore, assume that the London dispersion interactions which are important between D and A in the vapour state, are very approximately cancelled by losses of solute-solvent dispersion force attractions when complex is formed from free donor and acceptor in solution. Roughly one donor-solvent plus one acceptor-solvent contact is replaced by one donor-acceptor and one solvent-solvent contact. The theory of donor-acceptor complexes and their spectra as presented by Mulliken is a vapour-state theory, except for the omission of the London dispersion attraction terms. This
theory after small correction for solvation energies is essentially valid for solutions in inert solvents. The few studies that have been made on vapour-state complexes are in general agreement with this theory but they show some puzzling features.

The new band found by Benesi and Hildebrand is in the ultra-violet region for a solution of benzene and iodine dissolved in n-heptane. Similar bands also occur in the visible region for many other complexes. To demonstrate this a solution of tetracyanoethylene (TCNE) in methylene dichloride may be added to a series of aromatic hydrocarbons dissolved in methylene dichloride. Benzene gives a yellow solution, xylene an orange, durene a deep red and hexamethylbenzene a deep purple. The \( \pi \)-electron molecules, ethylene and benzene can act either as weak donors or weak acceptors. Other things being equal, donor ability increases with decreasing ionization potential \((I^D)\); the acceptor ability with increasing electron affinity \((E^A)\). Among aromatic hydrocarbons \(I^D\) decreases and \(E^A\) increases with increasing size; graphite with \(I^D = E^A\) is the extreme example and is in fact both a good acceptor and a good donor. Starting with any unsaturated or aromatic hydrocarbon, either its donor or its acceptor capability can be strengthened by the introduction of suitable substituent
groups. The weak donor properties of benzene is fortified by adding more and more electron-releasing methyl groups (inductive effect) whereas the increase of nitro groups greatly fortifies the acceptor capability of benzene. The two kinds of molecular complexes discussed above provide examples of n.v. (strong) and of $\pi-\pi^*$ (weak) complexes. The common types of donors and acceptors are listed in Table-1.

G.N. Lewis\textsuperscript{12} explained coordination compounds or dative compounds (e.g., $R_3N:BCl_3$ which can also be considered as an essentially stable molecular complex) in terms of a structure with sharing of the electron lone pair of the nitrogen atom between the N and B atoms. By this sharing the N atom as well as the B atom are surrounded by a complete octet of outer-shell electrons. This sharing can be expressed in quantum-theory language by an approximate wave function $\psi$ that is a combination of two resonance structures (D here is $R_3N$, A is $BCl_3$):

$$\psi_N(AD) \approx a \psi_o(A,D) + b \psi_o(A^- - D^+) \quad \ldots \quad (1)$$

no-bond \hspace{1cm} \text{dative}

The dative structure corresponds to an ionic plus a covalent bond and has sometimes been called a semipolar double bond. The interpretation of the N-B dative bond in the complex as given by (1) is analogous to the approximate ionic covalent
## TABLE 1

### COMMON TYPES OF DONORS AND ACCEPTORS

<table>
<thead>
<tr>
<th>Donor type</th>
<th>Example</th>
<th>Dative electron(^a) from</th>
<th>Acceptor type</th>
<th>Example</th>
<th>Dative electron goes to</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>(:\text{NR}_3)</td>
<td>Non-bonding lone pair</td>
<td>v</td>
<td>(\text{BCl}_3)</td>
<td>Vacant orbital</td>
</tr>
<tr>
<td>b(\pi)</td>
<td>Benzene</td>
<td>Bonding (\pi) orbital</td>
<td>a(\pi)</td>
<td>TCNE</td>
<td>Antibonding (\pi)-orbital</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a(\sigma^–)</td>
<td>I(_2),HQ(^b)</td>
<td></td>
<td>Antibonding (\sigma^–)-orbital</td>
</tr>
</tbody>
</table>

\(^a\) "Dative electron" refers to the electron transferred from donor to acceptor.

\(^b\) Molecules such as phenol, water, and other molecules that give hydrogen bonding.
The resonance interpretation of the chemical bond in HCl:

\[ \Psi_{\text{HCl}} \approx a \Psi_0 (H^+, Cl^-) + b \Psi_1 (H - Cl) \quad \ldots \quad (2) \]

In both examples \( b >> a \). The inclusion of the no bond structure in (1) is even more important than that of the ionic structure in (2).

Complexes are classified as strong or weak depending on whether the energy of formation and the equilibrium constant (K) are large or small. Increasingly strong donors and/or acceptors form increasingly stable complexes.

\[ A + D \xrightleftharpoons[K]{} A.D \]

Equation (1) shows that the complex is stabilized by resonance between \( \Psi_0 \) and \( \Psi_1 \). The forces involved being called Charge Transfer (CT) forces. However classical electrostatic forces (including induction forces) also contribute to the stability of the complexes and may even be of predominant importance for the stability of the most hydrogen bonded complexes and of the weaker of the complexes of the \( b.\pi - a.\sigma \) and the benzene-iodine \( b.\pi - a.\sigma \) type$^{13}$.

In terms of the resonance structure description of (1) the structure of the ground state of any 1:1 complex is
\[ \Psi_N = a \Psi_o (A,D) + b \Psi_1 (A^- - D^+) \]

This function is normalized as follows:

\[ \int \Psi_N \Psi_N^* d\tau = \int a^2 \Psi_o^2 d\tau + \int b^2 \Psi_1^2 d\tau + \int 2ab \Psi_o \Psi_1 d\tau \quad \ldots (3) \]

Since \( \Psi_N, \Psi_o, \) and \( \Psi_1 \) are all normalized hence

\[ \int \Psi_N^2 d\tau = 1, \int \Psi_o^2 d\tau = 1 \quad \text{and} \quad \int \Psi_1^2 d\tau = 1 \]

Substituting these values in equation (3) we obtain

\[ a^2 + 2ab \int \Psi_o \Psi_1 d\tau + b^2 = 1 \quad \ldots (4) \]

\( \int \Psi_o \Psi_1 d\tau \) is called the overlap integral and is represented by \( S_o \), with the integration carried over all space. If the complex is loose \( S_o \) is small and

\[ a^2 + b^2 \approx 1 \quad \ldots (5) \]

Here \( b^2 \) approximately measures the weight of the dative structure or the fraction of an electron transferred from the donor to the acceptor in the ground state. The term \( 2abS_o \) can easily be as large as \( b^2 \) or larger. Half of this term can reasonably be assigned to the donor and half to the acceptor so that the fractions \( F_o \) and \( F_1 \) in the no-bond and dative structures are:

\[ F_o = a^2 + abS_o, \quad F_1 = b^2 + abS_o \quad \ldots (6) \]
In loose complexes between closed-shell donors and acceptors $b^2 \ll a^2$. For benzene, $I_2$, $b^2$ is perhaps 0.06 or less; for pyridine, $I_2$, $b^2$ is approximately 0.2; for trimethylamine, $I_2$, $b^2$ may be 0.4.

If the ground state structure of the complex (weak or strong) is given by $\Psi_N$ then according to quantum theory principles there must be an excited state $\Psi_E$ where $\Psi_E$ refers to the CT state. $\Psi_E$ is given by

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

The coefficients $a^*$ and $b^*$ are determined by the quantum theory requirement that the excited-state wave function be orthogonal to the ground state function i.e. $\int_\tau \Psi_N \Psi_E d\tau = 0$. The excited state function $\Psi_E$ is normalized as follows:

$$\int \Psi_E^2 d\tau = a^{*2} + b^{*2} - 2a^* b^* S_{01} = 1 \quad \ldots (8)$$

This makes $a^* \approx a$ and $b^* \approx b$. If $S_{01}$ were zero, $a = a^*$ and $b = b^*$ would be true exactly.

For loose molecular complexes the ground state is mostly no-bond that is, $a^2 \gg b^2$. According to the orthogonality requirements the excited state is mostly dative i.e. $a^{*2} \gg b^{*2}$. The excitation of an electron from $\Psi_N$ to $\Psi_E$ essentially amounts to the transfer of an
electron from D to A. The theory further shows that spectroscopic absorption from $\Psi_N$ to $\Psi_E$ should occur with generally high intensity.

Complexes have been studied mostly in solution but some studies have been made in solids\textsuperscript{14-26} and in the case of n.v. compounds and also recently of a few complexes of weaker types in the vapour state\textsuperscript{27,28}. Complexes in solids even when of 1:1 stoichiometry do not always occur in the form of pairwise units. Studies in the vapour state are difficult because $K$ is small and interference of overlapping spectra of the uncomplexed components is often severe. These difficulties are also found for solution studies but they are less troublesome because $K$ is larger. The complete absorption spectrum of a complex consists of absorption due to the following:

1. Locally excited states (states of A or of D, more or less but usually not greatly modified in the complex).

2. CT states [ $\Psi_E$, as in (7) and other CT states involving excited dative structures, for example $\Psi(D^+ - A^\text{-})$, $\Psi(D^+ - A^-)$.]

Figure 1 shows the change that occurs in the spectrum of iodine when it dissolves in n-heptane and then when ethanol is added (ethanol is transparent upto 220 nm).
Fig. 1 The apparent molar absorptivity of $I_2$ vapor and of $I_2$ and EtOH. $I_2$ in n-heptane, Here --- is for $I_2$ vapor, --- for $I_2$ in n-heptane, and ---- for $I_2$ in n-heptane with 3.4 M ethyl alcohol.
The peak of the $\text{C}_2\text{H}_5\text{OH}.\text{I}_2$ CT band is marked in the figure, and the position of the shifted visible absorption band of $\text{I}_2$ in the complex (a transition to a locally excited state) is also indicated. The contact CT band appears as a long wavelength shoulder on the ultra-violet iodine band when $\text{I}_2$ is dissolved in heptane. It is felt by some authors that the importance of CT forces in stabilizing the ground state of such complexes has been exaggerated.

**Dewar's Theory**

Mulliken's theory is a valence bond approximation in which the complex formed by a donor D and an acceptor A is represented as a resonance hybrid of the uncharged aggregate (a) and the ionic structure (b) formed from it by transfer of an electron from D to A. The appearance of a new band in the spectrum of such a complex is ascribed to a transition from the ground state which is mostly (a) mixed with a little (b) to an excited state which is mostly (b) mixed with a little (a). This transition is of CT type and the complexes have accordingly been termed CT complexes.

\[ \text{DA} \quad \text{D}^+\text{A}^- \]

(a) \quad (b)

This problem has been approached in terms of molecular orbital treatment by Dewar and Lepley⁵⁸. The essential features of this treatment are presented below.
The complex DA is represented as a π-complex formed by the interactions of the π-orbitals of D and A. As the interaction is small it may be treated by the perturbation theory. Consider the orbitals of D and A (Figure 2). Interactions between the filled bonding orbitals of D and A lead to no change in their total energy and there is no net transfer of charge between D and A. Interactions of the filled orbitals of D with the empty antibonding orbitals of A depress the former and raise the latter leading to a net stabilization with a simultaneous transfer of negative charge from D to A; interactions of the filled orbitals of A with the empty orbitals of D also lead to stabilization with a net charge transfer in the opposite direction. These interactions are inversely proportional to the difference in energy between the interacting orbitals. In complexes of this kind one component is normally a molecule of donor type (i.e., with filled orbitals of relatively high energy), the other an acceptor (i.e., with empty orbitals of relatively low energy); the main interaction is therefore between the filled orbitals of the donor and the empty orbitals of the acceptor, as indicated in Figure 2; this leads to a net transfer of negative charge from the donor D to the acceptor A.

The heats of formation of complexes of this kind are at least an order of magnitude less than their lowest
Fig. 2 Orbital energies and transitions in a molecular complex formed by a donor D and acceptor A.
transition energies; this suggests that the changes in energy of the orbitals in forming the complex are small compared with the spacing between the filled (bonding) and empty (antibonding) orbitals. The energies of the orbitals in the complex should therefore be little different from those in the separate components. All the possible transitions observed in D and A should therefore appear in the spectrum of DA, and this is commonly the case. Transitions of this type are described as locally excited\(^3\). There should also be CT transitions of electrons from a filled orbital of D into an empty orbital of A and from a filled orbital of A into an empty orbital of D. Figure 2 indicates that transitions of the former kind may occur at lower energies than the locally excited transitions and so lead to the appearance of new absorption bands at lower frequencies. This explains the new bands commonly observed in the spectra of such complexes which are responsible for their colour.

This treatment leads to conclusions similar to those given by the valence bond approach, but it seems preferable for two reasons. First there are cases when more than one new CT band appears in the complex DA; this can be explained in terms of the molecular orbital approach as there should be bands corresponding to transitions between any of the
occupied orbitals of D and empty orbitals of A. Secondly the term "charge-transfer complex" is misleading in that very little charge is transferred in the ground states of such complexes and in that an appreciable part of their stability may be due to back coordination involving interactions between the filled orbitals of the acceptor and the empty orbitals of the donor. The term "π-complex" seems preferable for compounds of this type. If the interactions between donor and acceptor are small, the transition energy \( \Delta E_0 \) for the first CT band should by either treatment be given by

\[
\Delta E_0 = I^D - E^A + \text{constant} \quad \ldots (9)
\]

where \( I^D \) is the ionization potential of D (equal to the energy of the highest occupied molecular orbital in a simple molecular orbital approach) and \( E^A \) is the electron affinity of A (likewise equal to the energy of its lowest unoccupied orbital). If then the acceptor is kept constant, \( \Delta E_0 \) should vary linearly with the ionization potential of the donor; this relation has been observed in a number of cases. In the molecular orbital approach equation (9) is replaced by the more general equation

\[
\Delta E_{ij} = D_i - A_j + \text{constant} \quad \ldots (10)
\]

when \( \Delta E_{ij} \) is the transition energy for the CT band involving the filled orbital \( i \) of D (energy \( D_i \)) and the empty orbital
j of $A_i$ (energy $A_j$). This is equivalent to equation (9) in the case of first CT band, for the ionization potential of the donor should be equal to the energy of its highest occupied molecular orbital. If equation (10) is valid the energies of the CT transitions should be predictable from simple molecular orbital theory. Thus the energies of the first CT transitions of a variety of donors with a given acceptor should be a linear function of the energies of the highest occupied orbitals of the donors.

1.2 MULTIPLE CHARGE-TRANSFER SPECTRA

We can see from Table 2 that the intensity of CT spectra of the iodine-benzene complex is very large and that both the $K$ value and the value of $-\Delta H$ increase proportionately with increasing size of electron donor hydrocarbons. However, the intensity of the CT spectra is inversely proportionate with increasing donor size. In particular, CT spectral intensity of the anthracene-iodine complex seems to be weaker than that expected from the assumption that the CT spectra may borrow much of their intensity from strong absorption bands of the donor itself. This assumption is valid because these catacondensed hydrocarbons have several lower excited states allowed strongly from the selection rule. In connection with this problem Murrell\textsuperscript{32} proposed the
<table>
<thead>
<tr>
<th>Donor</th>
<th>$K_c$ (Temp.)</th>
<th>$\varepsilon_{CT}$ (max) (solv)</th>
<th>$\Delta H$ (solv) K cal mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.15(25°C)$^a$</td>
<td>16.400(292 mp) $(\text{CCl}_4)^a$</td>
<td>-1.3(Hexane)$^b$ $(\text{CCl}_4)^c$</td>
</tr>
<tr>
<td></td>
<td>$\text{CCl}_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>0.25(25°C)$^a$</td>
<td>7.150(360 mp) $(\text{hexane})^b$</td>
<td>-1.8(Hexane)$^b$ $(\text{CCl}_4)$</td>
</tr>
<tr>
<td></td>
<td>$\text{CCl}_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.45(23°C)$^d$</td>
<td>7,100(364 mp) $(\text{CCl}_4)^d$</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>$\text{CCl}_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthracene</td>
<td>3.0(23°C)$^d$</td>
<td>$\sim$550 at 430 mp $(\text{CCl}_4)$</td>
<td>-1.6(430 mp) $(\text{CCl}_4)^d$</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_2\text{Cl}_2,\text{CCl}_4$</td>
<td>(430 mp) $(\text{CCl}_4)$</td>
<td></td>
</tr>
</tbody>
</table>


following discussion. Generally the MO's of aromatic hydrocarbons spread over the whole molecule so that the overlap between the electron donor orbital and the accepting (σ\(^-\), υ of the I\(_2\) molecule) orbital becomes smaller for large hydrocarbons than for smaller ones. As a result, the CT intensity of the iodine complexes with large hydrocarbons results in a weaker intensity compared with that of the complexes with small size hydrocarbons. At the same time the stability of the complexes should decrease with increasing donor size of hydrocarbons as CT theory suggests. Actually, however, K and -ΔH values turn out to be larger with increasing size of hydrocarbons, i.e., complexes become stable, as Table-2 shows.

The main reason for these results may be as follows: When hydrocarbons increase in size there appear many MO's whose energies are not so well separated from one another. Hence it is possible that the charge transfer is also brought about from deeper MO's as well as the highest occupied MO of hydrocarbons. Thus these CT states can interact with the ground non-bonding state, resulting in greater stabilization of the ground state. As a net result the complex becomes more stable as the ring size of hydrocarbon becomes larger. The CT bands caused by the charge transfer from deeper donor orbitals will be hidden.
under the absorption bands caused by the donors or acceptors themselves.

Multiple CT bands, especially two CT bands, have been reported by many workers for various kinds of molecular complexes. A typical example is shown in Figure 33.

1.3 U.V. VISIBLE SPECTRA

In general a complex formed between an electron donor and an electron acceptor still retains the absorptions of the components modified to a greater or lesser extent, together with one or more absorption bands characteristic of the complex as a whole. The recognition of this fact by Brackman34 was important historically because it led to the realization that the absorption is the result of an intermolecular charge transfer transition and not a modified transition of one or other component.

In practice the absorption characteristic of the complex in solution may not be easily observed since the complex will be partially dissociated into its component species. It may be particularly difficult to measure those absorption bands due to "local excitation", when the interaction is between strong donor and strong acceptor. In such cases the transition usually appears as a separate band considerably at longer wavelengths than the absorption of
Fig. 3 Two CT absorption spectra observed on the chloranil-substituted naphthalene \( \pi-\pi \) complexes in \( \text{CCl}_4 \): — naphthalene, —— \( \alpha \)-chlornaphthalene —— —— \( \alpha \)-methylnaphthalene —— —— —— \( \alpha \)-methoxynaphthalene. [Reproduced from A. Kuboyama, J. Chem. Soc. Japan, 83, 376 (1962)].
the component molecules. The intensity of absorption band of a complex is usually determined as the molar absorptivity (extinction coefficient) at the wavelength of maximum absorption. A direct determination of intensity cannot normally be made because the degree of dissociation of the complex in solution is usually significant. Solid charge-transfer complexes have been studied by transmission\(^{35-55}\) and reflection\(^{56-58}\) spectra using specular reflection from a single crystal\(^{58}\). Soon after the publication of Mulliken's charge transfer theory, Nakamoto\(^{35}\) provided an experimental observation which could be well explained in terms of this theory, whereas the absorption of polarized light by oriented crystals and of pure aromatics shows a stronger low energy absorption when the electric vector is parallel than when it is perpendicular to the ring, the opposite obtains for the lowest energy intermolecular charge transfer transition of a complex between the two planar molecules (Figure 4).

If a number of donors are complexed with a single acceptor, a refined parabolic relationship of the form in equation (11) follows

\[
h \sqrt[\frac{C_2}{(I^D - C_1)^2}} = I^D - C_1 + \frac{C_2}{I^D - C_1} \quad \ldots \quad (11)
\]

where \(C_1\) and \(C_2\) are constants for a given acceptor. This equation best correlated the data available then. As the
Fig. 4 The solid complex pyrene-tetracyanoethylene: (a) the polarized absorption spectra of a single crystal: (b) a projection of the crystal structure along the a-axis on the bc plane showing the orientation of the b-and c-axes.
range of donors is increased, some changes in these values can be expected. Slightly prior to the application of equation (11) McConnell et al.\textsuperscript{59} showed that there is an approximately linear relationship between $I^D$ and $\nu_{CT}$ for complexes of iodine with the wide range of relatively weak donors.

$$h \nu_{CT} = I^D - E^A - W$$

... (12)

where $E^A$ is electron affinity of the acceptor and $W$ is dissociation energy of the charge transfer exited state.

Since the publication of that paper, similar linear relationships have been described for complexes of many other acceptors. In general

$$h \nu_{CT} = a I^D + b$$

... (13)

when there is linear correlation between $I^D$ and $h \nu_{CT}$, it is taken as a confirmation of a charge transfer complex, though there is no theoretical justification. There is a similar linear relationship between the electron affinity of series of acceptors, complexed with a single donor and $h \nu_{CT}$ of the type

$$h \nu_{CT} = a E^A + b$$

... (14)

The electron affinity of a number of acceptors has been evaluated from polarographic half wave potential by the equation
\[ E^A = -E_{\text{red}}^A + 1.41 \quad \ldots (15) \]

The energy of charge transfer band is correlated with the Hückel coefficients as follows:

\[ h \mathcal{V}_{CT}(A_1) - h \mathcal{V}_{CT}(A_2) = B_j(A_1) - B_j(A_2) \quad \ldots (16) \]

Kosower\textsuperscript{60-63} has shown that \( \mathcal{V}_{CT} \) for the complex between the iodide ion and a pyridinium ion is extremely solvent sensitive. For complexes in which the components are oppositely charged species, the ground state may be expressed as predominantly an ion pair with a small admixture of a structure involving a pyridinium radical and an iodine atom with the two odd electrons coupled, i.e. \( a^2 << b^2 \) in equation (1), in contrast to the ground state of a weak complex formed of two neutral species where \( a^2 >> b^2 \).

The excited state of the pyridinium complex will be given by equation (1)

\[ \Psi_E = a^# \Psi_0(A,D) - b^# \Psi_1(A^- - D^+) \quad \ldots (17) \]

where \( a^#^2 >> b^#^2 \).

1.4 I.R. SPECTROSCOPY

The CT studies in the solids and in solution state very clearly focus our attention on the differences in the two approaches. Thus infra red measurements provide no information about relative orientation of the donor and
acceptor in the complex solution. Infra red spectrum of the solid bromine - benzene complex has enabled some modifications to be made to the crystal structure description determined by X-ray diffraction. The infra red spectrum which includes a bromine-bromine stretching vibration is inconsistent with the crystal structure having an axial configuration with chains of alternating benzene and halogen molecules, in which the halogens are equidistant from two neighbouring benzene molecules in the chain and are centres of symmetry. Person et al. suggest that these conflicting observations can be reconciled if, in the crystals the halogen molecules are not, in fact, exactly equidistant from their immediate benzene neighbours in the chain, but are somewhat closer to one than the other.

The solid state studies on the tetracyanoethylene (TCNE) and hexamethylbenzene (HMB) system has been very rewarding. Two complexes with a mole ratio of 1:1&1:2 have been prepared. The infra red spectra of the two complexes are given in Figure-5. The spectra of the 1:2 complex may be interpreted in terms of a structure which consists of stacks which contain sequences of D.A.D. D.A.D. D.A.D. D.A.D. D.A.D. D.A.D. molecules. In the 1:1 complex the out-of-plane infra red spectrum shows no absorption at 1295 cm\(^{-1}\) (an absorption assigned to the totally asymmetric C-CH\(_3\) stretching mode of HMB which is forbidden in the free
Fig. 5 Infrared spectra in the 1100-1600 cm$^{-1}$ range for the 1:1 & 2:1 crystalline complexes of hexamethylbenzene and tetracyanoethylene.
molecule). This is to be expected in terms of Ferguson and Matsen's\textsuperscript{68-70} and Person and Friedrich's\textsuperscript{71} theory since the charge oscillation between D and A, characteristic of a vibronic interaction, is effectively zero in symmetrical D.A. .... D.A. ..... D.A. ..... sequence of the 1:1 complex. However, in the 2:1 complex, the lower symmetry of the environment of the donor molecules permits the charge oscillation, and a strong absorption is observed at 1295 cm\textsuperscript{-1}. By contrast, the symmetry of environment of the TCNE molecule should be comparable in the 1:1 and 1:2 complexes. The similar absorption of the totally symmetric double bond mode of TCNE at 1560 cm\textsuperscript{-1} in the two complexes provides support for this conclusion.

The acceptors are generally classified as non acidic and acidic compounds. The former type can only form DA complexes involving electron transfer while the acidic compounds are capable of forming both the electron transfer complexes and those comprising proton donation to the donor. 2,4-Dinitrotoluene (DNT) is a non acidic acceptor and, therefore, it is expected to display the general spectral shifts of $\pi-\pi^*$ complexes\textsuperscript{72}. Since the stability of these complexes arises from a shift of the electron density from the donor to the electron deficient acceptor molecule, the infra red region should record the effect of the change of
electron density in the components upon the vibration of atoms within the individual molecules, study of vibrational spectra may also reveal which parts of the molecules play an active role in complex formation.

1.5 NUCLEAR MAGNETIC RESONANCE (NMR) SPECTROSCOPY

Just like IR, NMR spectrometry of CT complexes gives a summation of the spectra of the individual reactants. However this technique is only applicable to CT complexes between aromatic systems whereby there is a change in their ring current giving rise to an upfield shift of the protons of the acceptor and a low field shift of the protons of the donor. This is because on complex formation electron density is transferred from the donor to the acceptor.

1.6 SPECTROPHOTOMETRIC DETERMINATION OF EQUILIBRIUM CONSTANT AND MOLAR ABSORPTIVITY

The formation constant is defined for the reaction

\[ D + A \rightleftharpoons C, \]

by the expression:

\[ K = \frac{C_C}{C_D C_A} \ldots (18) \]

Here, for example, \( C_D \) is the concentration (in moles per litre) of the donor that exists in the solution at equilibrium. If we take solutions with a fixed total
concentration $C_{D}$ of $D$, equation (18) implies that the concentration $C_{C}$ of the complex $C$ increases as shown in Figure 6. (The absorption observed may be that of the CT band or it could be absorption for a locally excited band of $D$ or $A$, shifted in the complex). Since the absorbance $A_{C}$ due to $C$ in a region in which the complex absorbs is given by Beer's law,

$$A_{C} = \log \frac{I_{0}}{I} = \varepsilon C_{C} l$$

Here $\varepsilon$ is the molar absorptivity of $C$ and $l$ is the length in centimeters of the absorbing path. The value of $A_{C}$ must increase as $C_{D}$ increases, as is seen from Figure-6, depending on how large $K$ is, $C_{C}$ at maximum possible donor concentration (region III of Figure-6, $K > 1.0$) or be limited to region II ($K < 0.1$) or even to region I ($K < 0.01$). (In the latter two cases the $C_{D}$ scale in Figure-6 would, of course, be modified).

As a specific example, the visible spectrum of the complex between pyridine-N-oxide and $I_{2}$ is shown in Figure-7. This figure illustrates the increasing absorbance near 450 nm of the complexed $I_{2}$ and the decreasing absorbance near 520 nm due to the familiar locally excited band of uncomplexed $I_{2}$ as the concentration of donor is increased, with an isobestic point at 490 nm. The existence
Fig. 6 The concentration of complex as a function of donor concentration for a fixed total acceptor concentration $C_A^0$. Region I: $c_C$ is approximately a linear function of $c_D$. Region III: Saturation has been reached, and $c_C$ is constant and equal to $C_A^0$. 
Fig. 7 The visible absorption spectrum of pyridine-N-oxide-iodine in carbon tetrachloride (23°C, 5-cm cell). Curve 1 is for iodine (9.550 x 10^{-5} M). The concentration of pyridine-N-oxide are 4.210x10^{-3} M for curve 2, 8.421x10^{-3} M for curve 3, 16.84x10^{-3} M curve 4 and 33.68x10^{-3} M for curve 5; curve 6 is a calculated curve for the absorption that is due solely to the complexed iodine molecule. [From T.Kubota, J.Am.Chem.Soc., 87, 458 (1965)].
of this point confirms the assumption that only two species in the solution (complexed I\(_2\) and uncomplexed I\(_2\)) absorb in this region of the spectrum.

Figure 7 also illustrates the problem of overlapping absorption of two species which often occurs. In principle a correction is made for the absorbance due to the uncomplexed I\(_2\) in order that the absorbance due to the complex alone may be obtained (illustrated by curve 6 in figure 7). In practice the details of this correction may be somewhat troublesome; for example we determine \(\epsilon_A\) for the acceptor alone in a solvent and compute the correction \(A_A\) to be subtracted from the total absorbance \(A_T\) to obtain \(A_C\), the absorbance of a D.A complex C. In doing so we usually assume that the absorption for uncomplexed A does not change when the solvent is changed by adding D. This assumption is at best questionable in the case of weak complexes, for which \(C_D\) has to be made rather large.

From the corrected absorbance \(A_C\) at a given frequency \(\nu\) for a series of concentrations \(C_D\), the values of \(K\) and \(\epsilon_\nu\) can be obtained using the method of Benesi and Hildebrand. The Benesi-Hildebrand analysis starts from the assumption that only one equilibrium exists in the solution and that the constant is defined as in (18). Then, using a
zero superscript to denote the total concentration \((C_D^0 = C_D + C_C, \text{ etc.})\), we have,

\[
\frac{1}{K} = \frac{(C_D^0 - C_C)(C_A^0 - C_C)}{C_C} = \frac{(C_D^0 - C_C)}{C_C} - \frac{C_A^0 + C_C}{C_C} \quad \ldots (19)
\]

under the usual conditions \((K \text{ small, } A \text{ relatively insoluble})\) \(C_D^0\) is very much greater than \(C_A^0\), in order to form enough complex: \(C_D^0 \gg C_A^0 > C_C\). From Beer's Law \(C_C = \frac{A_C}{\ell \nu L}\); hence to a good approximation,

\[
\frac{1}{K} = \frac{\ell \nu 1C_D^0}{A_C} - C_D^0 \quad \ldots (20)
\]

Dividing by \(C_D^0 \ell \nu\) and rearranging, we obtain the Benesi-Hildebrand equation:

\[
\frac{1C_A^0}{A_C} = \frac{1}{K \ell \nu} + \frac{1}{C_D^0 \ell \nu} \quad \ldots (21)
\]

Here in a given experiment we know \(l, C_A^0\) and \(C_D^0\); \(A_C\) is measured for a series of solutions with varying \(C_D^0\), and the results are plotted as shown in Figure 8. From the slope and intercept the values of \(K\) and \(\ell\) can be obtained.

The above equation is not valid for sparingly soluble compounds because their concentrations cannot be accurately determined, therefore, the Pushkin-Varshney-
Fig. 8 Illustration of the use of the Benesi-Hildebrand equation to obtain $K$ and $\mathbf{E} \cdot \mathbf{V}$ at four wavelengths for the Triethylamine- I$_2$ Complex. The intercept of each line is $1/\mathbf{E} \cdot \mathbf{V}$; the slope is $(1/K \mathbf{E} \cdot \mathbf{V})$. [From S. Nagakura, J. Am. Chem. Soc., 80, 520 (1958)].
Kamoonpuri equation was proposed to solve this problem. This equation takes the form

\[ \frac{1}{A_c} = \frac{1}{K} \varepsilon_n \frac{1}{C_A^{o}} \cdot \frac{1}{C_D^{o}} + \frac{1}{C_A^{o}} \varepsilon_n \]  \hspace{1cm} ... (22)

If a plot is made of $1/A_c$ versus $1/C_D^{o}$ a straight line is obtained and $K$ is evaluated by dividing the intercept by the slope. Therefore $C_A^{o}$ mutually cancels out and is not required for evaluation of $K$. $C_A^{o}$ should be kept constant in all solutions.

1.6.1 DETERMINATION OF OTHER THERMODYNAMIC PROPERTIES

We can obtain $\Delta H^o$ from measurement of $K$ at more than one temperature using the van't Hoff equation

\[ \ln K = - \frac{\Delta H^o}{R} \left( \frac{1}{T} \right) + \frac{\Delta S^o}{R} \]  \hspace{1cm} ... (23)

Assuming that $\Delta H^o$ is constant over the temperature range involved, a plot of $\ln K$ against $1/T$ should then be a straight line whose slope gives $\Delta H^o$ and whose intercept is $\Delta S^o/R$. In this way the enthalpy change $\Delta H^o$ and the standard entropy change $\Delta S^o$ for complex formation can be obtained.
1.6.2 DETERMINATION OF EQUILIBRIUM CONSTANT BY IR SPECTROSCOPY

Though charge transfer complexes have mainly been studied by UV-visible spectroscopy chiefly due to the possible isolation of the charge transfer band, IR spectrometry can give an idea about the geometry of the complex. In most complexes and specially in the weaker ones the IR spectra is merely a summation of the individual spectra. However shifting of peaks may take place to lower or higher frequencies. The regions where there is a greater shift in electron density are the ones that give rise to more prominent peaks, enhanced intensity and greater magnitude in the frequency shifts.

IR spectrometry can also be used to determine the association constants using the usual Benesi-Hildebrand equation (21). For this it is necessary that a peak is chosen which is not overlapped by other peaks and has maximum intensity. The transmittance is measured and converted to absorbance directly. IR spectrometry is a useful tool to distinguish between charge transfer and hydrogen bonding. For example if aniline is involved in hydrogen bonding the N-H vibration in the complex will move to lower frequencies while in the case of charge transfer the reverse will be true. IR is also diagnostic of those CT
complexes where there is almost complete transfer of an electron from the donor to the acceptor and highly conducting organic metals or semiconductors result. In this case there is usually no peak in the entire IR region.

1.6.3 DETERMINATION OF EQUILIBRIUM CONSTANT BY NMR SPECTROMETRY

There is a difference in evaluating association constants by NMR spectrometry than in electronic or IR spectroscopy. In this case the method of Hanna and Ashbaugh is used. The method is as follows: A small amount of the acceptor with a large amount of the donor is dissolved in an inert solvent like CCl. The acceptor concentration is kept constant while the donor concentration is varied. The various shifts are shown schematically below:

![Image of NMR peaks and shifts]

- Acceptor peak
- TMS Signal
- Accepter alone
- Pure Complex (not measurable)
- Equilibrium mixture
The association constant is obtained according to equation:

\[
\frac{1}{\Delta} = \frac{1}{K^{AD}} \cdot \frac{1}{\Delta_o} \cdot \frac{1}{C_D^o} + \frac{1}{\Delta_o} \quad \ldots \quad (24)
\]

where \( \frac{1}{\Delta} \) is plotted against \( \frac{1}{C_D^o} \) and \( K^{AD} \) and \( \Delta_o \) are evaluated from the slope and the intercept.

In addition to this the Qureshi-Varshney-Kamoonpuri equation\(^7\) proposed recently outlines a method for the first time in NMR to ascertain whether the activity coefficients are unity or show deviations. The Qureshi-Varshney-Kamoonpuri equation takes the form

\[
\frac{C_D^o}{\Delta} = \frac{1}{K^{AD}} \cdot \frac{1}{\Delta_o} + \frac{C_D^o}{\Delta_o} \quad \ldots \quad (25)
\]

A plot of \( C_D^o \) Vs \( \frac{C_D^o}{\Delta} \) should yield a straight line with the slope giving \( \Delta_o \) and \( K \) is then obtained from the intercept.
1.7 SOME RECENT DEVELOPMENTS IN CHARGE TRANSFER COMPLEXES

Equilibrium measurements have been used for the evaluation of ionization potentials\textsuperscript{77}. Though such studies leave much to be desired by way of accuracy, nevertheless they are important due to their inherent simplicity. Though space interactions and reactivity have been related by studying the photoelectron and charge transfer spectra of benzobicycloalkenes\textsuperscript{78}. Studies in micellar media are gaining a unique importance in chemistry and therefore it is interesting to note, a recent report showing the effect of micelles on the state and dynamics of some excited charge transfer complexes\textsuperscript{79}. The formation constants of selected charge transfer complexes have been measured using a computer controlled precision polarograph\textsuperscript{80}. It has been
shown that flavin mononucleotide forms charge transfer complexes with phenols. This has been established through the use of resonance Raman spectroscopy\textsuperscript{81}. A single crystal of the charge transfer complex between hexaethylbenzene and tetracyanoethylene was investigated for conformational effects and for charge transfer transitions\textsuperscript{82}. Conducting organic charge transfer complexes are of current importance due to their possible use as organic conductors, semiconductors and therefore it is interesting to note that the charge transfer salts synthesized by the reaction of tetrathiafulvalenes and tetrahalo-p-benzoquinones produced highly conducting organic materials\textsuperscript{83}. It was shown that the complexes of phenylfurans and tetracyanoethylene were $\pi-\pi^*$ complexes\textsuperscript{84}. In an excellent study it has been shown that some charge transfer complexes of tetracyanoquinodimethane can be used to prepare electrochemical electrodes which can be used over a potential region where they serve as inert electrodes\textsuperscript{85}. Most of the organic conductors to date have been based on tetracyanoquinodimethane. Therefore it is very encouraging to note that the charge transfer compounds composed of tetrathiafulvalene and chloranil are perhaps the first highly conducting organic materials that do not contain tetracyanoquinodimethane\textsuperscript{86}. IR spectroscopy has been used to study the degree of charge transfer in organic conductors\textsuperscript{87}, $n-\pi^*$ charge transfer complexes are now systematically being studied due to the paucity of such
studies on this important family of complexes. For example, the interaction of aliphatic amines and benzonitrile has been reported. The solvent effects on the charge transfer spectra of some aminoanthraquinone dyes has been reported in nine different solvents. Surface enhanced Raman scattering shows that there is a charge transfer from tetrathiafulvalene to silver and gold. The formation of a charge transfer complex between quinoline and boron tetrafluoride leads to significant changes in the ordering of electronic levels effecting fluorescence, phosphorescence and inter-system crossing. The mechanism of electron transfer from dihydronicotinamide adenine dinucleotide (NADH) to p-benzoquinone derivatives has been shown to proceed via a charge transfer complex. Picosecond laser photolysis has been used to establish the charge transfer process that occurs in the dibenzocarbazolepyridine hydrogen bonded complexes as a function of structure. The 1:1 and 2:1 complexes of hexamethylbenzene with tetracycnoethylene have been studied by resonance Raman spectroscopy. The colour of (nitrophenyl) anilines has been explained from an x-ray crystallographic study that indicates that the molecules are placed in a "head-to-tail" arrangement resulting in an unusual charge transfer between two molecules of the same compound. Some large electron acceptors based on various substituted quinodimethanes have been designated as
acceptors for molecular metals. The study of vapour-phase charge transfer complexes is rather difficult owing to the sophistication and cost of instrumentation. It is due to this reason that not much progress has been made in this important direction. It is therefore encouraging to note that electron energy loss spectroscopy has been used for the investigation of vapour-phase charge transfer complexes of halogens with n-donors. Graphite coated with viologen polymers behaves as an electrode via a charge transfer process. Charge transfer complexes have been used for the synthesis of organic ferromagnetic materials. The trimethylamine-sulphur dioxide system is the only system for reaction thermodynamics are known both in solution and gas phase. The microwave spectrum of this system has been studied in order to elucidate the structure of the complex. The reaction of azoalkanes with series of donors which are both sacrificial (\(\pi^*, \sigma^*\)) and increvalent gives rise to charge transfer complexation. The fluorescence spectrum of benzenilide exhibits the anomaly that its \(\lambda_{\text{max}}\) occurs at longer wavelengths than that of its phosphorescence emission. It has recently been shown that this anomaly may be due to an intramolecular charge transfer transition. A new approximate procedure for the determination of enthalpy of formation and formation constants of weakly bonded charge transfer complexes has been reported and has
been applied to complexes of molecular iodine and chlorinated benzenes\textsuperscript{103}. The effect of solvent on dipole moment and charge transfer in electron systems has been studied in N,N-dimethyl-p-nitrosoaniline\textsuperscript{104}. \textsuperscript{1}H NMR spectrometry\textsuperscript{105} has been used to evaluate association constants for the electron-donor-acceptor complexes for the complexes of indoles and substituted indoles with 1-(2,4,6-trinitrophenyl) propan-2-one. It has been suggested that both internal and external references may be eliminated in NMR determinations of fast equilibria with special reference to charge transfer complexes\textsuperscript{106}. This study also questions the use of tetramethyilsilane (TMS) as an internal reference due to the possibility that TMS may not be as inert as assumed. A new and simple development for the measurement of charge transfer through fibre optic photometry has been proposed\textsuperscript{107}. The preparation and solid-state characterization and X-ray crystal structure of the 1:1 charge transfer complex of tetrathiafulvalene and m-dinitrobenzene is an important landmark in the study of charge transfer complexes of polynitroaromatics\textsuperscript{108}. 
REFERENCES


CHAPTER -2

ISOLATION OF CHARGE TRANSFER 
BANDS OF SOME POLYNITROAROMATIC – 
AROMATIC AMINE SYSTEMS
INTRODUCTION

Some workers\(^1,2\) have studied the interaction of dinitrobenzenes with anilines but could not satisfactorily isolate the charge transfer bands in these systems.

The reasons could be manifold. Since the complexes are weak the bands may not be observed due to 'local excitations' in the donor, the acceptor or both, or the band may be so close to the absorption of a component so that it is masked. It is also possible that the complex be so weak that though colour formation takes place it may not warrant a separate absorption.

Using a simple technique we have satisfactorily isolated the charge-transfer bands of polynitroaromatics-aromatic amine (diphenylamine) systems.

EXPERIMENTAL

Diphenylamine (BDH Analar), nitrobenzene (Pfizer), o-dinitrobenzene (BDH), m-dinitrobenzene (BDH Analar), p-dinitrobenzene (BDH Analar), 1-chloro-2,4-dinitrobenzene (E. Merck G.R.), 3,5-dinitrobenzoic acid (E. Merck, G.R.), and 2,4-dinitrotoluene (Fluka G.R.) were used. The G.R. and Analar reagents were used as received. Other reagents were recrystallised till their melting points were in agreement
with reported values. Carbon tetrachloride and ethyl alcohol were used as solvents. All measurements were carried out on Bausch and Lomb spectronic 1001 uv-visible spectrophotometer. The association constants were evaluated under the condition that the donor concentration was kept in far excess over the acceptor concentration.

**RESULTS AND DISCUSSION**

Since polynitroaromatics absorb strongly in the region of interest the spectra were recorded by taking an equal concentration of the polynitroaromatics both in the reference and the sample cell. Diphenylamine did not absorb in the region of interest.

Figures 1-7 give the charge transfer spectra for the various polynitroaromatic-diphenylamine complexes. As expected for weak molecular complexes they are broad featureless bands. These charge transfer bands of dinitrobenzene and anilines are perhaps being reported for the first time.

Figure 8 shows the expected dependence of $\tilde{\nu}_{CT}$ on electron affinity. The electron affinities of o-, p- and m-dinitrobenzenes are known. A plot of electron affinities of these dinitrobenzenes against $\tilde{\nu}_{CT}$ gives a straight
Fig. 1 Charge-transfer band for the Nitrobenzene-Diphenylamine system in CCl₄. $\lambda_{\text{max}}$ found 320 nm.
Fig. 2 Charge-transfer band for the o-dinitrobenzene-Diphenylamine system in CCl₄. $\lambda_{\text{max}}$ found 334 nm.
Fig. 3 Charge-transfer band for the m-dinitrobenzene-diphenylamine system in CC\textsubscript{4}. $\lambda_{\text{max}}$ found 320 nm.
Fig. 4 Charge-transfer band for the p-dinitrobenzene-diphenylamine system in $\text{CCl}_4$. $\lambda_{\text{max}}$ found 325 nm.
Fig. 5 Charge-transfer band for the 1-chloro-2,4-dinitrobenzene-diphenylamine system in CCl₄. \( \lambda_{\text{max}} \) found 328 nm.
Fig. 6 Charge-transfer band for the 3,5-dinitrobenzoic acid-diphenylamine system in ethanol. $\lambda_{\text{max}}$ found 318 nm.
Fig. 7 Charge-transfer band for the 2,4-dinitrotoluene – diphenylamine system in CCl₄. 
\( \lambda_{\text{max}} \) 324 nm.
Fig. 8 A plot of $\bar{\psi}_{CT}$ for the o-, m-, and p-dinitrobenzene complexes to diphenylamine and electron affinities of the dinitrobenzenes.
line. The electron affinities of some other dinitrobenzenes (not known till date) have been evaluated from their respective charge transfer bands and are given in Table 1.

Since polynitroaromatics absorb strongly at their charge transfer maxima, a compensation procedure first proposed by Mulliken\(^3\) may produce an optically silent detector. Therefore charge transfer bands alone may not establish charge transfer in these systems but may have to be complemented with an independent data. We have already shown previously (Figure 8) that there is a linear relation between \(\tilde{\nu}_{\text{CT}}\) and electron affinities of those acceptors which are available, this also is indicative of charge transfer. Table 2 reports the association constants of the complexes which show the expected range for similar types of complexes (see inset Table 2).

Equilibrium constant measurements were carried out at 400 nm where the polynitroaromatics do not absorb and the above difficulties do not, therefore, arise. The equation used was, the well known Benesi-Hildebrand equation\(^4\)

\[
\frac{[A]_0}{A} = \frac{1}{K} \frac{1}{\epsilon_{400}} \frac{1}{[D]_0} + \frac{1}{\epsilon_{400}} \quad \ldots (1)
\]

under the condition \([D]_0 \gg [A]_0\). \([D]_0\) in equation 1 signifies the initial concentration of donor (diphenylamine),
<table>
<thead>
<tr>
<th>Nitroaromatic compound</th>
<th>Electron Affinity</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-dinitrotoluene</td>
<td>0.64</td>
</tr>
<tr>
<td>1-chloro-2,4-dinitrobenzene</td>
<td>0.90</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>0.50</td>
</tr>
<tr>
<td>3,5-dinitrobenzoic acid</td>
<td>0.68</td>
</tr>
</tbody>
</table>
$[A]_0$ as initial concentration of acceptor (dinitroaromatic compound) and A is the absorbance of the complex. $[A]_0$ was fixed constant (.01 M) in all the solutions while $[D]_0$ was varied (.1, .2, .3, .4 M ....). A plot of $[A]_0/A$ vs $1/[D]_0$ is linear with the slope equal to $1/K\epsilon_{400}$ and the intercept $1/\epsilon_{400}$. The association constant K is then obtained by dividing the intercept by the slope.

The trend of data in Table 2 further confirms the charge transfer chemistry of these complexes. Nitrobenzene which has only one nitro group can only be a very weak acceptor and so is 2,4-dinitrotoluene which contains a methyl donor group and hence these two have the lowest values of K. o-dinitrobenzene even though having two nitro groups is again a weak acceptor (electron affinity zero). m-dinitrobenzene is a moderately good acceptor and hence has a higher value of K. The slightly higher value of K of the 1-chloro-2,4-dinitrobenzene complex over that of m-dinitrobenzene complex is due to the electron withdrawing nature of -Cl in the former giving it a higher acidity than m-dinitrobenzene. The value for p-dinitrobenzene complex is as expected as it is a strong acceptor than m-dinitrobenzene. The highest K obtained for this series is for 3,5-dinitrobenzoic acid. This is perhaps due to the presence of a permanent charged acidic group in addition to two nitro
groups. This enhances the acidity of the molecule to an extent that it forms the strongest complex (in the present series).
Fig. 9 Benesi-Hildebrand plot for the nitrobenzene-diphenylamine system in CCl\textsubscript{4} at 400 nm.
Fig. 10 Benesi-Hildebrand plot for the o-dinitrobenzene-diphenylamine system in CCl$_4$ at 400 nm.
Fig. 11 Benesi - Hildebrand plot for the m-dinitrobenzene-diphenylamine system in CCl$_4$ at 400 nm.
Fig. 12 Benesi-Hildebrand plot for the p-dinitrobenzene-diphenylamine system in CCl₄ at 400 nm.
Fig. 13 Benesi-Hildebrand plot for the 1-chloro-2,4-dinitrobenzene-diphenylamine system in CCl₄ at 400 nm.
Fig. 14 Benesi-Hildebrand plot for the 3,5-dinitrobenzoic acid-diphenylamine system in ethanol at 400 nm.
Fig. 15 Benesi-Hildebrand plot for the 2,4-dinitrotoluene-diphenylamine system in CCl$_4$ at 400 nm.
### TABLE 2

**EQUILIBRIUM CONSTANTS OF SOME DINITROAROMATIC-DIPHENYLAMINE COMPLEXES AT 400 nm**

<table>
<thead>
<tr>
<th>Complex</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,5-dinitrobenzoic acid/DPA</td>
<td>1.56</td>
</tr>
<tr>
<td>1-chloro-2,4-dinitrobenzene/DPA</td>
<td>1.4</td>
</tr>
<tr>
<td>p-dinitrobenzene/DPA</td>
<td>1.34</td>
</tr>
<tr>
<td>m-dinitrobenzene/DPA</td>
<td>1.225</td>
</tr>
<tr>
<td>Nitrobenzene/DPA</td>
<td>0.8</td>
</tr>
<tr>
<td>2,4-dinitrotoluene/DPA</td>
<td>0.8</td>
</tr>
<tr>
<td>o-dinitrobenzene/DPA</td>
<td>0.15</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Complex</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>pDAB/DNT&lt;sup&gt;1&lt;/sup&gt;</td>
<td>3.9</td>
</tr>
<tr>
<td>DPA/DNT&lt;sup&gt;2&lt;/sup&gt;</td>
<td>0.23</td>
</tr>
<tr>
<td>Ind/DNT&lt;sup&gt;3&lt;/sup&gt;</td>
<td>0.93</td>
</tr>
</tbody>
</table>


DPA = Diphenylamine  
pDAB = p-dimethyaminobenzaldehyde  
Ind = Indole  
DNT = 2,4-Dinitrotoluene
REFERENCES


