CHAPTER I

INTRODUCTION
1. INTRODUCTION

The physics of Solid State embraces experimental investigations and theoretical interpretation of different physical properties of matter in the solid phase. Although there is no unique way of classifying all the solids found in nature, the division can be based upon a survey of chemical, thermal, electrical and magnetic characteristics of the matter. Briefly solids are classified in four ideal types — metallic, ionic, valence and molecular crystals.

Out of the various solids the physics of molecular crystals is least understood. Molecular crystals are formed by inactive atoms such as the rare gases or saturated molecules such as hydrogen and methane held together by weak Vanderwaal Forces. They are characterized by low melting point.

For long the organic molecular solids have been viewed upon as insulators. It was only four decades ago that it was first realized that the electronic conduction might be observed in them. Within the last decade there has been rapid increase in the work on electrical properties of organic substances. The rising interest in bio-physical processes and their relations to the electrical phenomena occurring invivo also spurred investigation of electrical properties of organic compounds.
The existence of semiconducting property has been demonstrated in a variety of different classes of organic compounds, such as molecular crystals, polymers and charge-transfer complexes.

The classical example of molecular crystal is \textit{anthracene}, which is probably the most studied element since 1906. It belongs to a group of aromatic compound, which consists of plane molecules having relatively large size. All these compounds have valence electrons (\textit{\pi} electrons) which can move through the molecular plane. It may be presumed that the molecular orbitals of electrons are diffuse and they overlap slightly on neighbouring molecules. This is expected for large sized molecules. In such cases one should expect a shift of properties towards those of a border line solid.

Charge-transfer complexes are nearly metal like in many respects with small negligible activation energies. It is interesting to note that there exists perfect analogy between the donor-acceptor action of chemical groups in the molecular complexes and the behaviour of impurity atoms in germanium and silicon. Recently great attention has been given to measure the conductivities of various charge-transfer complexes. In several papers\textsuperscript{4} it has been established that the resistivities of charge-transfer complexes are generally lower than those of conventional organic solids and that one can cover the range of poor insulator to nearly metallic behaviour by
suitable chemical and structural modifications of these complexes. Very low conductivities exhibited by certain complexes is marked by Akamatu, Inokuchi and Matsunaga\(^5\) in the study of organic semiconductors.

In molecular crystals, binding arises from dipolar forces between the atoms or molecules of the crystal. Even when an atom or molecule has no average dipole moment, it will in general have an instantaneous fluctuating dipole moment arising from the instantaneous positions of the electrons in their orbitals. Since the molecular crystals are loosely bound aggregates of saturated atoms or molecules, many of their properties are determined primarily by the internal molecular structure rather than by solid binding. The principal source of intermolecular cohesion in non-polar molecular crystal and in many polar molecules, is the Vanderwaal forces.

Many attempts have been made to describe precisely the binding forces between the components of the charge-transfer complexes. Mulliken has integrated the various opinions which have been expressed to provide a theory which seems compatible with the known chemical and physical properties of complexes.

\[ \text{1.A Types of charge-transfer complexes.} \]

Complexes between molecules acting as electron donors and molecule acting as electron acceptor have been studied extensively.\(^6\)
The substances which serve as donor components can be grouped into two general categories. The first category includes alkenes, alkynes, aromatic hydrocarbons and their substitution products. These are classed as \( \pi \) donors (i.e. the electron available for sharing are those contained in \( \pi \) molecular orbitals), and the adducts which they form are called \( \pi \) complexes.7

The second major class of donor comprises a large group of substances in which there are non-bonded electrons (lone pairs) available for coordination. Typical examples of these so-called \( n \) donors are alcohols, organic sulfides, organic iodides and nitrogen bases in which the lone pairs in question are located respectively in atomic orbitals of oxygen, sulfur, nitrogen and iodine atoms.

The substances which serve as acceptor component can be grouped as :

1. Inorganic acceptors
2. Hydroxylic substances.

A host of examples might be listed of cases in which 'n' donors interact with hydroxylic organic substances with the formation of hydrogen bonds between the two components.

(iii) \( \pi \) Acids and other organic acceptors.

Many of the so called \( \pi \) acid type acceptors
are ethylenes which are substituted with highly electronegative substituents.

The nitro-group is strongly electron attracting, and as a result both poly-nitro aliphatic and poly-nitro aromatic substances have acceptor properties. The polynitro-aromatics as well as other aromatic substances which have strongly electron withdrawing ring substituents can be classified as $\Pi$ acids.

A great many colored solids adducts of polynitro-aromatic compounds with aromatic acceptors have been prepared. Picric acid has been used widely in analytical work in the preparation of solid derivatives of aromatic hydrocarbons. Recently $2,4,7$ trinitro-fluorenone $8$ has been used to prepare solid adducts of a wide variety of donors.


A considerable amount of efforts has been devoted in the last two decades in constructing a satisfactory model describing the weak interactions responsible for the stabilization of weak electron donor-acceptor complexes. $9$

(a) The Covalent-bond theory.

In discussing the structure of complexes of aromatic substances with nitro compounds Bennett and Willis $10$
rejected the Pfeiffer\textsuperscript{11} concept of interaction through saturation of residual valence fields in favour of a theory of covalent bonding between components. The covalent bond was presumed to link the nitrogen atom of a nitro group to a carbon of the aromatic ring.

Above structure is supported by the facts that the complexes were formed in simple molecular ratios and were colored, neither of the facts seemed to be consistent with the picture of residual valence. This suggestion which was upheld for a time\textsuperscript{12,13} became reasonable when it was discovered\textsuperscript{14–16} that the separation distance between components in crystalline complexes were much larger than are observed for covalent-bonding.

(b) The Polarization aggregate theory.

Briegeleb\textsuperscript{17,18} has formulated the complexes of nitrocompounds and aromatic hydrocarbons as products of interaction resulting from electrostatic attraction between molecules with permanent dipoles and non-polar molecules which can be polarized by induction.\textsuperscript{17,18} Actually the heats evolved on formation of series of S-trinitrobenzene complexes decrease as the polarizabilities of the several aromatic hydrocarbon donors decrease [anthracene $>$ phenanthrene $>$ naphthalene $>$ benzene]. The early Briegleb explanation cannot be invoked in general sense.
since a number of substances, such as, iodine, which lack even partial moments interact with aromatic hydrocarbons. Furthermore some efforts have been made to explain the intense colors of aromatic-nitro complexes in terms of the dipole-dipole interaction theory.\textsuperscript{19} However, the opinion has often been expressed \textsuperscript{20-24} that Brijgleb binding forces should not produce sufficient transfer between the interacting components to account for the marked changes in light absorption phenomenon which accompany with another, in which the attractive forces are probably truely of the dipole-dipole type (between nitro group) is not accompanied by pronounced color changes.\textsuperscript{25}

(c) The view of Gibson and Loeffler and Hammick.

Gibson and Loeffler\textsuperscript{21} and Hammick and Yule\textsuperscript{23} have expressed the view that color-producing collisions between components of a complex in solution are comparable to normal impacts between liquids molecules except for added restrictions in the orientations of the colliding molecules. It is presumed that color phenomena are associated with the drift of electrons from one component to the other when the reactive centers are appropriately located. This interaction theory is supported by the observation\textsuperscript{21} that the colors of solutions of aromatic amines in nitro aromatics are intensified when the system are subjected to increase in hydrostatic pressure at constant
temperature or to increase in temperature at constant volume. The greater frequency of collision and the deeper intermolecular penetration during collision which are associated with these changes are believed to facilitate the color producing drift of electrons from amino to nitro groups.

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

(d) The ionic complex theory.

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

\[ D^+ + A \rightarrow [D.]^+ + [.A]^− \]  \ldots (1.1)

He explains the characteristic complex colors on the basis that the ions \( D^+ \) and \( A^- \) are odd molecules, which, in general require only low excitation energies like Gibson and Loeffler as well as Hammick and Yule, he feels that these colors as well as the dielectric polarizations of certain solid complexes \(^{27}\) cannot be explained in terms of Vanderwaal's bonding. It is also concluded by Weiss that the stability of a complex increases as the ionization potential of the donor decreases and as the electron affinity of the acceptor increases.

Complexes between dienes and dienophiles have also been formulated as ion pairs resulting from transfer of a single electron. The term "intermolecular semipolar bond" has been used to describe the bonds between the complex components.

(e) The concept of complex resonance.

Various aspects of Weiss arguments have received unfavourable criticism.\(^{20,29}\) The heats of formation are, for example, of much lower magnitude than is ordinarily found for processes of salt formation. The Brackmann \(^{30}\) concept of complex resonance which requires only a partial ionic character for a
complex, appears to be more in accord with the known properties of most aromatic donor acceptor interaction products. According to this theory the donor compound can share an electron pair with the acceptor by a process comparable to Lewis acid-base interaction. The complex structure is regarded as a resonance hybrid:

\[ D : A \leftrightarrow D^+ A^- \quad \cdots \cdots \quad (1.2) \]

to which no-bond and dative structure contribute.

(f) **Mulliken theory.**

The description of the donor-acceptor type molecular complex which is now generally accepted is that presented by Mulliken.\(^{31-33}\) This is in some respects a composite of many of the ideas of the earlier theorists. Mulliken describes a 1:1 donor-acceptor complex in the ground state in terms of the wave-function \( \Psi_N \).

\[ \Psi_N \approx a \psi_0 (D, A) + b \psi_1 (D^+ - A^-) \quad \ldots \quad (1.3) \]

A loosely bound molecular complex \( (a^2 > b^2) \) is regarded as a resonance hybrid receiving major contribution from a no-bond form and minor contribution from a dative form in which an electron has been transferred from the donor to the acceptor. The covalent bond of \( D^+ - A^- \), which might be described as inter-molecular
semipolar bond is not necessarily interatomic in nature.

The complex in excited state is described by:

\[ \psi_E = a^x\psi_1 (D^+ - A^-) - b^x\psi_0 (D, A) \] (1.4)

where \( a^x \approx a \), \( b^x \approx b \) and \( a^2 > b^2 \). The excited state, which presumably can be attained by the absorption of either visible or ultraviolet light, is largely dative in character. The transition \( N \rightarrow E \) which accompanies the absorption of light of appropriate wavelength corresponds to the transfer of an electron from the donor to the acceptor. The corresponding spectrum of the complex, which is considered to be characteristic of the complex as a whole, is called an intermolecular charge transfer spectrum. Recent detailed investigations of complex spectra have helped to strengthen the above theory.

Mulliken stresses the orientational properties of charge-transfer forces as opposed to dispersion forces which are dependent largely on polarizabilities. The orientational properties which along with the electron transfer character of complex formation restrict the combination to simple integral ratios of components, are predicted by considerations of quantum mechanical symmetry of molecular wave functions.

On the basis of group theory symmetry considerations
Mulliken also favours the parallel plane configuration for complexes in which both donor and acceptor molecules are aromatic (or the acceptor are quinoid) in nature. Crystallographic data have been obtained on numerous examples of such complexes;\textsuperscript{35-41} but only in a few cases \textsuperscript{14-16,42,43} they are sufficiently detailed to attest to the correctness of this opinion. In these cases the donor and acceptor molecules are stacked one above the other in parallel plane with little distortion in the bond distances within the component molecules. The plane of the rows are somewhat inclined to the general direction of the rows.

The dipole moment of aromatic-iodine complexes can be ascribed to the partial ionic character of Mulliken-type bond. A quantum mechanical estimate of the dipole of such complexes \textsuperscript{44} is in fair agreement with observed \textsuperscript{45} values. In discussing heats of complex formation Mulliken adopts the Weiss\textsuperscript{26} view that their magnitudes and signs are subject to control by a combination of factors, including the ionization potential of the donor, the electron affinity of the acceptor, the mutual approachabilities of interacting molecules, and effects of the medium.

\hspace{1cm} (g) Other theories.

Shuter\textsuperscript{46} has suggested a model for a $\pi\tau$ type complex in which the $\pi$ electrons of the donor molecule behave as a free
electron gas which must tunnel through a potential barrier to link the donor and acceptor components. The height of barrier is controlled by the ionization potential of the donor and the electron affinity of the acceptor and the width by the Vanderwaals separation of the components. The stability of the complex is determined by the delocalization energy of the interaction, which in turn is determined by the barrier height and width. Recently Shuter has ascribed the high pressure induced shift toward the visible of the major absorption peaks of benzene in the formation of a 1:1 self complex. He estimates the heat of this interaction to be 200 cal/mole through interpretation of these separation changes in terms of the free-electron theory of complex formation.

McConnel, Ham and Plait recall the experiments of Reid who observed that the fluorescence of condensed ring hydrocarbons is quenched by S-trinitrobenzene. The phosphorescence triplet transition of the hydrocarbons are apparently strongly enhanced by complex formation. If singlet triplet transitions were subject to similar enhancement, their intensities might compare in magnitude with those observed for so-called charge transfer transitions.

The view of Dewar and other concerning the role of complexes as intermediates in aromatic substitutions and rearrangements, in spite of some adverse criticism, merit careful attention. These views have been summarized in detail elsewhere. There are probably numerous examples of reactions in which
molecular complex serve as participants in rate controlling steps in organic reactions. The reactions of aromatic has been explained on the assumption that 1:1 aromatic halogen complex is attached by one or more halogen molecule in the slow step. 55-57

1.8 Conduction in organic solids

A complete understanding of conduction mechanism in any organic solid requires a knowledge of the following.

1.8.1 - Carrier generation mechanism
1.8.2 - Carrier recombination and trapping
1.8.3 - Mechanism of carrier transport.

(i) Carrier generation in dark

The dark conductivity data on most of the organic solids shows an exponential temperature dependence of the form:

\[ \sigma^- = \sigma_0 \exp (-E_a/KT) \] \hspace{1cm} (1.5)

Above result led most of the earlier workers to suggest that the carriers were of intrinsic origin and thus experimental activation energy \( E_a \) could be equated to half band gap \( E_g \). Some of the earlier data suggest that \( 2E_a \) is the same as the
energy of the lowest excited singlet state $1E_\text{g}$, while for
several hydrocarbons, the $E_a$ values were close to one half
the lowest excited triplet state energy $3E_\text{g}$. Deriving from
these observations, the tunnel model of electronic conduction
in organic solids was proposed. However, there are two very
severe objections to the singlet or triplet state theories —
(1) Gutmann and Lyons found that when looked for a large
number of organic solids, there is very little agreement between
$2E_\text{g}$ and either $1E_\text{g}$ or $3E_\text{g}$, (2) Theoretically also, there is no
justification why $E_a$ should be related to either $1E_\text{g}$ or $3E_\text{g}$
by equation of intrinsic semiconduction. The definite information
about intrinsic or extrinsic carriers may be obtained from space
charge limited current studies.

(ii) Carrier generation in light.

In contrast to inorganic semiconductors, there is no
similar explanation for photogeneration of carriers in organic
solids. The optical absorption properties of organic solids can
be fully described in terms of Frenkel excitons only, but still
in view of the reported small gain of photo excited carriers,
carrier generation via the low probability mechanism of direct
band to band transition cannot totally be eliminated. Silver and
Sharma have given the theory of this process.

The other important mechanism of carrier generation in the
light involves Frenkel excitations themselves which produce carriers
by dissociation via some several secondary processes. Among the several processes proposed, the most frequently occurring one is that of exciton dissociation at the surface or the electrodes. Carswell and Lyons 61 were the first to suggest the possibility of this mechanism of carrier generation.

The carriers may also be produced via exciton-exciton interactions between two singlet excitons, the sum of whose energies is sufficient to excite an electron hole pair 62 with low intensity laser light of 1.79 eV.

Gealintov and Pope 63 attribute the carrier generation at photon energies of 5.4 eV to the auto ionization of excitons. According to them auto ionization leads to a quasi free electron state which subsequently produces carrier under the influence of temperature or applied field. Recently Hirth 64 reported the generation of electrons and holes in solid and liquid benzene by strongly absorbed light.

There are several suggestions to the involvement of triplet excitons also in the photo-carrier generation processes. Alternatively the carrier generation may proceed by the dissociation of singlet excitons formed in a triplet-triplet annihilation process.

(iii) Carrier generation by contacts.

It has been shown that both the holes and electrons can be
injected into an organic solids through contact. The hole injection in anthracene has been achieved from $\text{I}_2 \text{Ce} (\text{SO}_4)_2$. The energy required for hole injection is:

$$W_E + E_{\text{ext}} > I_C$$  \hspace{1cm} (1.6)

where $W_E$ is the work function of the electrode material, $E_{\text{ext}}$ the energy externally supplied and $I_C$ the ionization energy of the organic solid. Mark and Helfrich could not inject holes into naphthalene and diphenyl which is in keeping with the higher $I_C$ values for these materials so that the energy requirement is not more favourable for hole injection.

An ohmic contact is defined as one which injects carrier so abundantly that the current flowing through the semiconductor on applying voltage is space-charge limited or in other words a contact injecting charge carriers without any restrain is called "ohmic". With this contact a semiconductor exhibits an ohmic current-voltage characteristic at low applied voltages. With one ohmic contact, materials whose intrinsic conductivities are small display a transition from semiconducting to SCLC flow when the applied voltage is increased beyond a certain value.

Ohmic carrier injection into solids has been accomplished either by applying suitable electrode material or by generating carriers in a surface layer with strongly absorbed light. The bending of energy bands depends on the work function of the electrode material and the semiconductor. If the work function
of the electrode material is lower, the bands bend downwards and if the electrode work function is greater, the bands bend upwards and a hole injection contact is formed.

Satisfactory contacts \(44,69-71\) for conductance measurements can often be applied by means of evaporated metal film, metallic paints, graphite layers and some organic liquids. Pressure contacts \(72,73\) are also useful in some cases. Several workers have given different methods of employing electrode contacts to inject charge carriers. \(74-79\) Granacher \(77\) observed that \(I_2\) and chloranil which form charge transfer complex with anthracene, form hole injecting ohmic contact.

(iv) Schottky emission and Poole Frenkel effects.

Schottky emission \(80-82\) of electrons may occur from the metal contact to negative potential into the conduction band of insulator. In the case of current \(I\) limited by the height of the barrier at the electrodes, the current is given by:

\[
I = AT^2 \exp \left( -\frac{\phi}{kT} \right) \exp \left[ \frac{e}{2kT} \left( \frac{eE}{N\epsilon} \right) \right]^{1/2} \quad \ldots (1.7)
\]

where \(e\) - the electron charge, \(K\) - the Boltzman constant, \(T\) - the absolute temperature, \(E\) - the electric field strength, \(\epsilon\) - the dielectric constant, \(\phi\) - the barrier height (eV), \(A\) - the Richardson constant.
Thus, the current I depends both on \( \exp \sqrt{E} \) and temperature \( I \sim T^2 \exp \left(-\frac{\Phi}{KT}\right) \). The equation is valid only for an ideal dielectric (without traps). Now the theory has been developed \(^{83}\) for dielectrics with traps. Thus the Schottky emission especially for the highest fields, cannot be completely excluded and must be considered as a process cooperative with the thermal injection of charge carriers.

Recent observations are by Lengyel, \(^{84}\) O'Dwyer, \(^{85}\) Shrivastava and Tomar. \(^{86}\) Large number of amorphous appearing insulators are known which in a thin film form exhibit linearity in Schottky plots. \(^{87}\)

Poole-Frenkel effect \(^{80-82}\) is similar to Schottky emission. The only difference is that the electrons are excited thermally from traps into the conduction band of insulator. Due to immobility of the positive charge associated with the trap barrier lowering in P-F effect is twice of that of Schottky effect. Now the current, I, in this case is given by:

\[
I = AE \exp \left(-\frac{\Phi_b}{2KT}\right) \exp \left[\frac{\epsilon}{KT} \left(\frac{\epsilon E}{\pi \varepsilon}\right)^{1/2}\right]
\]

... (1.8)

where \( A \) is a constant and \( \Phi_b \) is the barrier height.

Jonscher \(^{88}\) has compared the relative probability of observing an enhanced conductivity in extrinsic and intrinsic semiconductors due to the Poole-Frenkel lowering of activation
energy at high electric field with the probability of the competing process of impact ionization avalanche. It is concluded that the Poole–Frenkel process is only likely to be seen in low mobility crystalline solids.

(v) Space-charge limited current.

Space charge limited and volume controlled currents form a special topic in the broad field of injection current. There are the maximum injection currents possible and observed if one or both of the electrodes inject without restrain. The earliest example of SCLC flow is the glowing cathode vacuum tube. In 1940, Mott and Gurney \(^{39}\) pointed out the possibility that space-charge limited current could also be injected in solids. They derived the current voltage relation for trap free insulator. They also marked that the actual current may be much smaller than their calculated value, because traps may immobilize the space charges, leaving only a small temperature dependent fraction of the carriers. Rapid progress has been made both experimentally and theoretically since 1955 when Smith \(^{90}\) and Smith and Rose \(^{91}\) reported space-charge limited electron current in CdS crystal. At the same time, Rose \(^{92}\) published a simple theory of the influence of trapping on SCLC in organic solids were first reported by Mark and Helfrich, \(^ {93}\) who used contacts discovered by Kallmann and Pope \(^{94}\) to inject hole current into anthracene, p-terphenyl, q-quaterphenyl.
The SCLC currents are important because the injected current is independent of the mechanism of carrier generation and depends only on the transport and trapping of the charge carriers within the crystal.

The character and magnitude of SCLC effects may be determined by the presence of localized states which can trap and store charges in equilibrium with the free charges. Study of SCLC yields information about the traps, such as trap density, location in the energy structure (i.e. trap depth) and their capture cross section. Charge carriers may be electrons alone or electrons and holes both.

Given ohmic contact, the current $I_0$ that could be passed in a trap free solid because of injection of charge carriers into either the conduction band or valence band is given by:

$$I_0 = 10^{-13} \mu \varepsilon AV^2 / d^3$$

... (1.9)

where, $\mu$ - the mobility of the carriers, $\varepsilon$ - the relative dielectric constant of the solid, $A$ - the area of the sample, $d$ - the thickness of the sample, and $V$ - the applied voltage. In solids without traps, the current will thus be proportional to square of the applied voltage. Taking shallow localized levels for majority carriers and assuming a fraction of injected charge carriers to be immobile within traps, then trap limited current is,

$$I_t = \theta I_0$$

... (1.10)
where $\theta$ - the fraction of the total charge which remains free, and is given by

$$\theta = \frac{N_c}{N_t} \exp \left( - \frac{E_t}{KT} \right) \quad \ldots \quad (1.11)$$

where $N_c$ - the effective density of states in valence band,
$N_t$ - the concentration of shallow trapping levels which are all assumed to have equal energy so that they are situated $E_t\text{ eV}$ above the top of the valence band. The current density in space-charge limited region is now represented by:

$$I_t = 10^{-13} \frac{\mu e V^2}{d^3} \left( \frac{N_c}{N_t} \right) \exp \left( - \frac{E_t}{KT} \right) \quad \ldots \quad (1.12)$$

If one plots log $I_t$ against $1/T$, the slope then equals

$$(- \frac{E_t}{K})$$

while intercept for the limit of $\frac{1}{T} \to 0$ equals to

$$10^{-13} \left[ \frac{\mu e V^2}{d^3} \right] \left( \frac{N_c}{N_t} \right)$$

from which $\frac{\mu}{N_t}$ and also $N_t$ can be calculated.

The SCIL theory without the assumption of the blocking electrodes was solved by Muller.\textsuperscript{98} Recently, the existence of SCIL and influence of electrode material and that of temperature in many organic solids have been reported by Sworakowski,\textsuperscript{99} Szymanski et al.,\textsuperscript{100} and Thomas et al.\textsuperscript{101} Also, other reports are available for the existence of SCIL in sugar-cane wax,\textsuperscript{102} Naphthalene,\textsuperscript{103} Xanthene,\textsuperscript{104} and Pyrene.\textsuperscript{105}
1.3.2 Carrier recombination and trapping.

Localized energy levels present between the bands trap the carrier, thus reducing the number of free carriers. Such levels situated nearer the conduction band, act as electron traps and may capture a free electron wandering through the crystal. An electron trap is therefore, a region of localized positive potential which could be considered either as a negative ion vacancy or an ionized donor impurity atom embedded in the crystal lattice. Just the reverse is true for the hole traps which occur nearer the valence band. The traps are thus coupled within the lattice and have a number of discrete energy states associated with them. The electron trap could, therefore, allow one or more electrons to be accommodated until the positive charge of the trap is balanced thus resulting in the vanishing of deformation and the charge imbalance. The electron in the trap could be re-emitted at a subsequent time if it gets the necessary energy for the same. The time, that it spends in the trap on an average, depends on the depth of the trap.

In addition to the charged traps, considered above, electrically neutral discontinuities and irregularities in the potential field of the crystal are also capable of trapping charge carriers. The interaction causing trapping is then not coulombian as in the case of charged traps but is due to the polarization forces between the charged particle and temperature.
whereas the filling up of charged traps result in the disappearance of the charged region and thus of the band deformation, the filling up of uncharged trap causes the trapping center to acquire a charge thus causing a deformation of the energy band structure. Such filled traps exhibiting a net charge having the sign of the trapped carrier are particularly effective as recombination center.

A recombination center according to above, is therefore, an electron trap when empty and a hole trap when filled. Therefore if holes are injected in the material having already negatively charged traps, they will be trapped and the excess energy will be released leaving the center empty. The center thus again acts as an electron trap and can capture electron from the conduction band with the release of the excess energy. Thus one electron hole pair is taken out of circulation and the energy liberated is transferred to the lattice. Trapping thus allows the excess momentum of the electron – hole pair to be transferred to the lattice.

Kepler and Coppage studied recombination of carriers generated by pulsed X-rays and deduced that the mean free paths of holes and electrons to be much less than 120 Å. If an electron gets closer to a hole than this critical distance, the possibility of its getting trapped and eventually recombining with the hole increases markedly. Batt et al. have studied carrier recombination through the field dependence of carrier
generation processes and Schott\textsuperscript{108} through ionization by high
energy particles and Mehl and Funk\textsuperscript{109} found radiative
recombination at room temperature.

1.8.3 Mechanism of carrier transport.

In the past decade the hypothesis of electronic
conductivity in organic solids have been widely accepted.\textsuperscript{110-114}
However, the result from the application of the band theory to
organic solids are in disagreement with the experiments. Further
modification of the band model\textsuperscript{96} especially narrow band models
have given a reasonable explanation of the measured mobility
values.

(1) Hopping Model \quad In the hopping mechanism of conduction,
the carrier is transported over the
barrier via an actual activated state. Such a mechanism is
well known in 3d transition metal oxide which have a very low
mobility that increases exponentially with temperature. Due to
small overlap of 3d–orbital the charge carriers spend an
amount of time on a particular carbon which is long compared to
the vibrational frequency of the lattice and this allows the ion
surrounding a charge carrier to be displaced by its electric
field. This displacement creates a field which tend to prevent
the charge carrier from leaving its lattice site, and so the
charge carrier gets trapped itself. Under this condition, the
charge transfer can only occur when random lattice movement causes the energy levels of the carrier site and a neighbouring cation to be equal.

The intermolecular coupling in an organic solid is weak and the observed mobilities small, which suggests the application of hopping model to charge transport in the crystals. 115

(ii) **Tunnel Model** - The tunnel model is a band model in sense only when the potential varies periodically and regularly throughout the crystal. Tunneling is a quantum mechanical approach in which an electron passes through a potential energy barrier without acquiring enough energy to pass over the top of the barrier. Tunnel model has been invoked first by Eley and Parfitt. 116 Later on this model led to proposition of semiconduction in molecular crystals, by Eley et al. 58,117,118 Organic solids other than free radicals have two electrons in the highest occupied molecular orbital, while the orbital just above it is totally empty. Thermal or photo excitation may lead to the elevation of one electron from former to the later orbital leaving a hole in the former. With free radicals, no such excitation is necessary. Under influence of an external electric field, the potential barrier between the molecule is lowered through which the electrons and/or the holes can then tunnel to occupy the corresponding orbitals in the adjacent molecules. Since the model involves the tunneling of a charge
carriers away from an oppositely charged site, the tunneling particle remains bound to hole until the coulombic energy between them has reduced to a value \( \sim KT \). This situation will be obtained after the electron has tunneled over a distance of several lattice spacings.

(III) Electronic Band Model — The electrical conduction phenomenon in organic solids can be explained on the basis of a modified electronic band model of solids. Calculation of the width of the energy bands proceeds by computing overlap integrals between \( \pi \)-electron molecular wave functions on adjacent molecules. Because the intermolecular binding is weak in molecular crystals, the overlap is small and leads to narrow energy bands, which implies small carrier mobilities.

This model postulates that conduction in organic compounds takes place through the overlapping of molecular orbitals of neighbouring molecules. There are several mechanisms by which such overlapping may be achieved. The extent of orbital overlap is a function of molecular structure and hence, if semiconduction activation energy correlates with properties which are also a function of molecular structure, such as molecular ionization energy, electron affinity and excitation energy of ground triplet state transition. \(^{119,120}\) One of the entities which influence these properties is the number of the more easily polarized \( \Pi \)-electron.
Dielectric constant $\varepsilon$ is the basic parameter of a dielectric describing its properties from the viewpoint of the processes of its polarization or propagation of electro-magnetic waves in it, or more generally from the viewpoint of the process of its interaction with an electric field.

There are three basic types of polarization (1) Electronic polarization, (2) Ionic polarization, and (3) Dipolar polarization.

Electronic polarization occurs in all atoms or ions and can be observed in all dielectrics. One specific feature of electronic polarization is the fact that when an external electric field is superposed this type of polarization occurs during a very brief interval of time (of the order of $10^{-15}$ seconds). In non-polar substances dielectric constant arises due to above electronic shift.

Ionic polarization is the mutual displacement of ions forming a heteropolar (ionic) molecule. A short time is required for the process of ionic polarization to set in, but longer than for that corresponding to electronic polarization, i.e. $10^{-13}$ to $10^{-12}$ seconds.

On the whole the process of electronic and ionic polarization have much in common. Both phenomena may be regarded as the varieties of polarization caused by deformation which is a displacement of changes with respect to each other in the direction of the electric field.
Polar dielectric exhibits a tendency towards dipole or orientational polarization. The essence of this kind of polarization can be reduced in a simplified manner, as has been first suggested by Debye to the orientation of the molecules of a polar dielectric having a constant dipole moment in the direction of an electric field.

Process of establishing a dipole polarization under the action of electric field requires a relatively long time as compared to that of practically almost inertialess phenomenon of deformation polarization (electronic, ionic). So that this type of polarization is called relaxation polarization.

Solids consisting of polar molecules i.e. molecules possessing permanent dipole moments commonly behave like those consisting of non-polar molecules, because solidification usually fix the molecules with such rigidity in the lattice that little or no orientation of the dipoles in an externally applied field is possible.

It is thought that the high dielectric constant in some solids may be due to the molecular rotation. The first direct evidence of molecular rotation in a crystal was obtained for the hydrogen halides (L, M), but this was followed soon by measurements on organic solids.

Quite a large number of organic compounds are known to retain high polarizability in the solid state even though many of
them do not show dipolar polarizability on being frozen. In these compounds, some degree of rotational freedom of dipoles appears to persist down to temperature well below the freezing point.

\textit{t - butyl chloride, bromide and iodide possess so much molecular orientational freedom that their dielectric constant rises on solidification and continue to rise with decreasing temperature until the solid phase undergoes transition to a non-rotator phase.}

Although rotation apparently consists of rotational jumps from one potential energy minimum to another, it is convenient to call it a solid phase, in which such rotation occurs, a "rotator phase" and the transition between a "rotator phase" and a "non rotator phase" is called a rotational transition. These rotational jumps give rise to dipole orientation in an applied field with consequent dielectric constant and loss behaviour more or less like that of the liquid state. Evidence of such dipole orientation in an applied field has been obtained for many solids material, for some of which the dielectric relaxation process has been observed through measurements in the frequency region of dispersion.

A complete theoretical account of the dielectric behaviour of all classes of material is a tremendously difficult task and is never likely to be possible. Using these models, theory
predicts certain properties or variation of parameters which can be tested experimentally, and the degree of closeness with which the experimental results are predicted is a measure of the success of the model. Once the theoretical model based on the atomic and molecular structure of the material is successful it will provide the knowledge on which the search for new materials may be founded, and may also be used to deduce the probable behaviour of the dielectric in different electrical environments.

Dielectric Loss : The amount of power losses in a dielectric under the action of the voltage applied to it is commonly known as dielectric losses.

Process of deformation polarization is practically unaffected by the temperature of the dielectric and is not connected with an irreversible dissipation of energy. The electric energy required to polarize a molecule is completely returned to the electric energy source after voltage is removed. For this reason deformation polarization does not entail any dielectric loss.

As distinct from deformation polarization, dipole polarization and also other kinds of relaxation polarization dissipate electric energy which transforms into heat in a dielectric i.e. this energy causes dielectric losses.
The angular frequency for which the loss factor is a maximum is called the critical frequency and given by:

\[ \omega_c = \frac{1}{\tau} \]

where \( \tau \) is the relaxation time.

Most of the dielectric losses, \( \varepsilon'' \), occur with a frequency range of about a decade on each side of the mentioned critical angular frequency \( \omega_c \) for which the loss factor is maximum. The present accepted interpretation of dielectric constant and loss of un-ionized materials is based upon the theory of Debye \(^{121}\) and subsequent modifications.

Wikstrom \(^{122}\) studied the polarized and unpolarized carnauba wax and found no change in dielectric constant and loss tangent. The dielectric constant of high polymers has been surveyed by many workers. \(^{123-127}\) Dubey et al. \(^{128}\) have produced a relation to correlate the dielectric constant of powder and bulk material. This relation has given accurate results both at radio and microwave frequencies.

1. D

Ultra-violet and Infra-red spectrum.

Spectroscopy provide an experimental method for determining the structure and dynamics of atoms and small molecules. It is also widely used as an analytical tool in structural studies of large molecules. It has provided quick and accurate method of analysis for guidance in research and
process control, it has contributed to fundamental knowledge about chemical bonding and it has facilitated the unravelling of complex molecular structure so that more useful substances could be synthesised, such as synthetic plastics, textiles, rubbers, etc. For reporting the preparation or isolation of a new compound, the standard procedure to-day is not only to give its melting point or boiling point but to give some of its spectral characteristics as a means of its future identification. The literature abounds with material on each type of spectroscopy and now thousands of spectra are on file for making comparisons in the identification of compounds or for chemical analysis.

No molecules absorb radiation over the whole range of electro-magnetic radiation instead absorption tends to concentrate in relatively narrow spectral regions so that the sub-division of the spectrum into ultra-violet, visible, infra-red etc., is useful for quick reference.

1. D.1 Ultra-violet and visible spectra.

The term " electronic spectra " and " ultra-violet and visible spectra " are synonymous and cover the range approximately 200 - 800 m\(\mu\). For practical purpose, the limits of visual perception can be taken as 750 m\(\mu\). Experimentally every part of this extensive region is not workable. In a spectrometer with a fused silica prism there is no difficulty for measurements above about 190 m\(\mu\). But below 190 m\(\mu\) the
transparency of silica falls off sharply whilst the constituents of air especially oxygen begin to absorb strongly, thereby necessitating a complete change in technique. This instrumental boundary effectively divides the ultra-violet into two parts; known as the near ultraviolet (\( \geq 190 \text{ m\&\#39;u} \)) and far or vacuum ultraviolet (\( \leq 190 \text{ m\&\#39;u} \)). Thus the near ultra-violet region is arbitrarily defined as the region from about 200 - 400 m\&\#39;u and is widely used by organic chemists both for qualitative and quantitative analysis. The absorption spectra of a molecule in the visible and ultraviolet region is complex but is characteristic of the molecule. The basic group responsible for this absorption in the near ultraviolet region is termed as "chromophore" which may be an unsaturated linkage, a radical or a grouping with an unshared pair of electrons, are therefore potential chromophore and also will be their numerous like and unlike combinations in conjugation. The presence of conjugation of chromophore in a molecule shifts the absorption towards the longer wavelength.

In discussing the absorption of visible and ultraviolet light by a loosely bound donor-acceptor complex in terms of charge transfer theory of component interaction, Mulliken\(^{129}\) noted that absorption bands characteristic of free donor and acceptor as well as several charge-transfer bands corresponding to various excited states of \( D^+ \) and \( A^- \) may be observed in the spectrum of the complex itself. Often the spectrum of a
complex which is partially dissociated in solution is obscured somewhat by the overlapping absorption of the free components. While such overlap occurs to some degree in solutions of aromatic hydrocarbon-halogen complexes, it is generally not sufficient extreme to prevent the ready determination of the general shape of the complex absorption curve.

Recent detailed investigations of complex spectra have helped to strengthen the charge-transfer theory. A linear relation is found to exist between the ionization potentials of eighteen donor molecules (including aromatic and ethylenic substances, diethyl ether, cyclo-propyne and tert-butyl alcohol) and the charge transfer absorption frequencies of the corresponding iodine complex. A linear correlation between absorption frequencies of charge transfer and donor ionization potentials for halogen and other complexes is also reported by Vandestolpe who also notes a linear relation between the equilibrium constants of a series of methylated benzene system. The charge-transfer absorption bands of donor-acceptor complexes frequently appear in the visible rather than the ultraviolet region of the spectrum. This is commonly the case when the acceptors are \( \pi \) acids given the typical charge-transfer spectra for solutions of tetracyanoethylene in aromatic hydrocarbon solvents. The absorption bands characteristic of the solid molecular complexes of tetracyano-ethylene are
attributed to the charge-transfer interaction between tetracyano-ethylene and donor molecules. The absorption spectra of four chloroform solutions containing picric acid and m-dinitrobenzene were examined from 320 to 460 mμ at 25°C. It is observed that in the case of picric acid and naphthalene in chloroform, the absorption in the range 450-500 mμ for mixture was greater than sum of absorption of the two individuals.


Coblentz published his excellent collection of infra-red spectrum of 135 organic compounds as early as 1905. Coblentz was able to show that correlation of molecular structure with infra-red spectra was possible. But it was not until the early 1940's that there was spread recognition of Coblentz work and the immense power of infra-red method for the solution of structural and analytical problem in organic chemistry. Chemists have studied the infra-red spectra of a variety of compounds and have found systematic correlations with the structure. The absorption by an organic compound in the infra-red region between 2.5 μ and 25 μ is capable of yielding most information about its molecular structure and hence this region is of great practical value. Infra-red radiation promotes transitions in a molecule between rotational
and vibrational energy levels of the ground (lowest) electronic energy state. This is in contrast to the ultra-violet radiation which consist of transition between vibrational and rotational energy level of different electronic levels. The vibrational spectra appear as bands rather than lines. This is quite a wide region and subdivided into three regions.

(i) Near infra-red region - 0.8 to 2.5 \( \mu \)

(ii) Medium infra-red region - 2.5 to 15.3 \( \mu \)

(iii) Far infra-red region - 15.3 to 100 \( \mu \)

The near infra-red region would be very useful in the study of hydrogen bonding, ketoenol isomerisation and hydrolytic equilibria. In recent years, the study of this region has become more active and several reviews have appeared on the subject.\textsuperscript{136,137} The near infra-red spectroscopy is likely to be more useful in quantitative analysis.\textsuperscript{138}

The medium infra-red region is most readily examined and it covers the absorptions due to the fundamental vibrations of nearly all the common groupings of organic chemistry. This region is most ideally suited for structural and analytical studies. This region is further subdivided into two: one is above 1350 cm\(^{-1}\) (below 7.4 \( \mu \)), where many of the stretching vibrations are found and the other below 1350 cm\(^{-1}\) (to be more precise 1350 cm\(^{-1}\) to 900 cm\(^{-1}\)) constituting the so called
"finger print" region is complex and much more difficult to interpret. In this region the bending, stretching and skeletal vibrations take place.

The detailed examination of the spectra of thousands of organic compounds has made it possible to correlate certain frequency ranges with particular groups or bands. The correlation are, of course, quite empiricals. Their validity is statistical in character. There are no rigid rules for interpretation of a spectrum, but certain general observations are helpful. It is observed that certain groups of atoms give rise to vibrational bands at or near the some frequency regardless of the structure of the rest of the molecule. It is this feature that permits the scientist to obtain useful information by simple inspection and reference to generalized charts or characteristic group frequencies. The correlation are more satisfactory in the high frequency region (\( \nu > 1500 \text{ cm}^{-1} \)) where the characteristic frequencies are relatively few in numbers.

In the case of charge-transfer complexes, the increase in bond lengths which results when donor-acceptor interaction takes place are generally accompanied by corresponding decrease in vibrational frequencies of the components. These changes and others which are characteristic of symmetry losses leading to vibrations which are forbidden in free donors and acceptors, are generally apparent in the infra-red spectra of the adducts.
Interactions in which the acceptor molecules actually function as hydrogen donors, e.g., alcohols and phenols, acetylenes and chloroform can often be detected by infra-red spectroscopy. Interaction of aromatic hydrocarbons with halogen is accompanied by an enhancement of the intensity of certain aromatic infra-red absorption bands. The 850 and 992 cm\(^{-1}\) peaks of benzene are enhanced both by bromine and iodine. Their intensity changes are presumed to result because of changes in symmetric ring breathing modes.

Related increases in symmetric methyl stretching modes are reported to accompany iodine-polymethyl benzene interaction. Relatively minor changes in infra-red bands of the donors have been reported to accompany the formation of sulfur-dioxide complexes of benzene and mesitylene. Decrease in the \(C = O\) and \(C - O - C\) vibration frequencies result when ketones and ethers interact with iodine. The interactions of halogens and ICN with nitrogen-containing compounds are accompanied by pronounced changes in infra-red spectra. The absorption bands in the neighbourhood of 1000 cm\(^{-1}\) which are found in the spectra of pyridine and substituted pyridines entirely disappear when halogen complexes are formed and are replaced by strong new bands at somewhat higher frequencies. These changes are characteristic of complexes both in solution and in the solid state. The fact that there is a marked similarity in the spectra of pyridine complexes and the spectra of monosubstituted benzenes in the 1000 cm\(^{-1}\) region serves as the basis for an interesting
discussion of changes in donor vibrational modes which are produced by these interactions.

In general the C – N stretching frequency of the amine is shifted to considerably lower values as a result of complex formation. The infra-red spectra of a series of solid 1 : 1 adducts of acetyl propionyl, and benzoyl fluorides with BF₃, SF₅ and SBF₅ all show strong absorption bands in the region of 2200–2300 cm⁻¹ and only very weak bands in the region in which shifted carbonyl frequencies typical of donor-acceptor complexes should appear. The infra-red spectra of various kinds of solid complexes in which both the donors and acceptors are organic have been reported.

Picric acid forms two different types of solid adducts with nitrogen bases. It reacts with strong bases such as carbazole more highly colored adducts (yellow, orange to red) are obtained. These are similar in color and melting point of 1,3,5-trinitrobenzene complexes of aromatic amines and are identified as donor-acceptor complexes rather than salts. When the salts are formed, bands characteristic of N – H vibration in the free donor (2.8 – 3.3 μ) are shifted to lower frequencies by as much as 900 cm⁻¹, and the O – H stretch of the acceptor molecule is similarly disturbed. The spectra of the two salts, piperidine, HCl and piperidine picric acid, in the 2 – 5 μ region have marked similarities. The yellow picric acid adducts of aniline and β-naphthyl amine also must be salts.
rather than molecular complexes, since the positions of the N-H stretching frequencies of the free amines are strongly affected by the interactions. The spectrum of the carbazole-picric acid molecular complex in the 2-5 μ region, on the other hand, is simply a composite of the spectra of the donor and acceptor.

1. F X-ray Analysis.

The application of X-rays to the study of solids falls into two categories :-

(a) The study of the shape, properties and arrangement of the atoms or molecules within a crystal.

(b) The arrangement and properties of the crystalline aggregates in a polycrystalline material.

The nature of the compounds formed between aromatic polynitro-compounds and other aromatic substances has been much disputed. Some of theories proposed could be tested at once by consideration of the crystal structures of the compounds, but there has been no information as to the relative position of the atoms in their structure. X-ray crystallographic methods have been used to examine a large numbers of these compounds with different degree of completeness of the structure determination for various compounds. The crystal structure of p-Iodoaniline-S-trinitrobenzene has been investigated. 159
Whenever possible, a crystal should be studied by single-crystal method. But there are many instances in which single crystals are not available or difficult to obtain, or in which it is desirable to study a material without altering its form. In such cases the only way to study the crystallographic characteristics of the substance is by the powder method.

There are many applications of the powder method, but two of these are of primary importance. Fundamentally, the powder method provides a way of investigating, within limits, the crystallography of the crystal in the powder. Since the powder diffraction diagram produced by a crystalline substance is a characteristic of that substance, the powder method can be used as a means of identification of crystals.

A somewhat related problem arises when one knows that an aggregate contains crystalline compounds A and B and one wishes to know their relative proportions. In such instances one can make use of the fact that a powder diagram of a mixture of A and B is a mixture of the diagram of A and the diagram of B.

The powder photograph is a diffraction pattern of lines. The reason for this is that, for a given wavelength, the deviation of a particular reflection is $2 \theta$ and therefore corresponding reflection from all crystals in a specimen must lie on a cone, the apex of which is at the specimen, the axis
of which is in the direction of X-ray beam, and the semi-vertical angle of which is 20°. In general there will be many such lines, each representing a set of reflections with the same value of 0, and therefore the powder pattern of a substance is often extremely complicated. In practice, the flat film are readily used; it is preferable to surround the specimen by a narrow strip of film, since this intercepts a greater number of cones of reflections. Only a small part of each cone is recorded, but all reflections except those with 0 just greater than 0° or just less than 90° can reach the film.

1. F Present Problem.

In the past three decades there has been upsurge of research interest in molecular complexes of the donor-acceptor type. This reached the explosive stage after publication of the results of the spectrophotometric studies of Benesi and Hildebrand on iodine complexes of aromatic substances. The formation of donor-acceptor complexes is accompanied by inter-component electron transfer, and corresponding changes occur in the electrical and sometime also in magnetic properties of the components. For quite a few complexes sufficient information is available. Keeping in view the various physical phenomena of these complexes, it is felt that single study will not enable one to explain and correlate the basic electrical properties of substance, so as to understand the underlying mysteries, an extensive study of the material was undertaken as follows:—
1. **Electrical conductivity** - Electrical conductivity measurements disclose various properties of the semiconductor, such as structural defects, impurities, nature of traps, charge carriers and their mobilities, space charge and the nature of transition taking place with the knowledge of the activation energy. From the value of conductivity of complex, it can be seen whether the complex is strongly interacting or weakly interacting.

In the present work, electrical conductivity measurements were carried out in two steps: (a) variation of field at constant temperature, and (b) variation of temperature at constant field.

2. **Dielectric constant** - In order to investigate nature, dipolar mechanism if any in C.T. complexes, dielectric constant and dielectric loss have been measured in thermal equilibrium condition. Studies of temperature and frequency variations of dielectric constant and loss have also been undertaken.

3. **Ultra-violet and Infra-red Spectrum** - Pronounced changes in absorption spectra are often observed to accompany the reaction of two substances to form molecular complexes. With the help of these spectra, it is possible to determine the presence of very weak complex also. For this purpose ultra-violet and infra-red
spectrum of all complexes were taken. Mulliken's original theory of charge transfer complexes predicted a parallel correlation between the binding energy of the complex and the intensity of the C – t band. Thus with the help of C – t band it is possible to calculate the binding energy of the different complex.

4. X-ray Study – In the present investigation powder pattern of naphthalene, phenanthrene, α-Naphthyl-amine, β-naphthyl-amine, α-naphthol, and β-napthol were taken and compared with those reported for these compounds. Powder pattern of the picric acid complex of all above substances and of α-chloro-naphthalene picrate, α-bromo-naphthalene picrate were also studied. Comparison of the powder pattern of complex and its parent substance determine the structural changes when complex is formed.
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