

UV-Visible Spectroscopic Studies of Charge-Transfer Complexes

Shamshad Ahmad Khan

Assistant Professor, Department of Chemistry, DAV Post Graduate College, Siwan, J.P University, Chapra-841301(Bihar), India.

ABSTRACT

Biphenyl is a C-C bridged benzene rings which resonate as a whole. It is symmetric molecule and its resonance structures are defined through the Kekule structures of benzene rings. In the present work, UV-Vis spectroscopic studies of the charge-transfer complexes of biphenyl and its derivatives. Spectral data and the thermodynamic functions ΔG^0 , ΔH^0 and ΔS^0 for the complex formation have been determined. As the solutions of the investigated electron donor acceptor (EDA) complexes were dilute, these complexes did not exhibit their own colours. Furthermore, C-tmethylbz11, C-methylbz41, C-4-OHBP, C-BP, C-BrBP and C-4,4'-DIOHBP have absorption maxima similar to the absorption maximum of 4,4'-DNBP. It may be possible that the complexes are dissociated to their low pure compounds in solution. In this case the donor components are not visible because of their low concentrations to the complexes. UV, being a concentration sensitive method, failed to detect the components with low contribution in the complex. The C-C tmethylbz11 was the only complex where the donor component is equivalent with 4,4'-DNBP and as such it was expected to observe two absorption maxima, one belonging to tmethylbz and one to 4,4'-DNBP. Only C-BZ shows a significant 5 nm difference from the original 4,4'-DNBP absorption which may be seen as an interaction, H-bonding between the NO_2 and NH_2 functional groups is possible. The H-bonding will necessitate the partial shift of more electrons to the oxygen atoms in the nitro groups thereby reducing the double bond character of the 4,4'-DNBP, and as a result absorption maximum of the 4,4'-DNBP components of the C-BZ will appear at a shorter wavelength.

Keywords: Biphenyl, charge-transfer complexes, UV-VIS spectroscopy, thermodynamic, structural

1. INTRODUCTION

There is a growing interest for simulation of the chromophore-chromophore interactions in the solid state. Nowadays, the molecular exciton model and super molecular approach have been extensively adopted to predict the changes in optical absorption and luminescence properties of conjugated molecules in the condensed phase. In the exciton theory, the excited state wave functions of the molecules in the solid state are computed only considering the electrostatic interaction. Such an approximation is expected to be valid for weak interchain interactions. In the strong interaction limit, the excited state wave function would spread out over several molecules and a suitable description of the electronic structure requires the building of delocalized wave functions. Charge-transfer phenomena was introduced by Mulliken and Widely discussed by Foster to define a new type of adducts. A charge-transfer complex or electron-donor-acceptor complexes is an association of two or more molecules, in which a fraction of electronic charge is transferred between the molecular entities. The resulting electrostatic attraction provides a stabilizing force for the molecular complex. The source molecule from which the charge is transferred is called the electron donor and the receiving species is called the electron acceptor. An electron donor may be defined as a molecule possessing a relatively high localized electron density. Conversely, an electron acceptor is relatively deficient in electrons. The nature of the attraction in a charge-transfer complex is not a stable chemical bond, and its much weaker than covalent forces. The attraction is created by an electronic transition into an excited electronic state, and is best characterized as a resonance. The excitation

energy of this resonance occurs in the visible region of the electro-magnetic spectrum, which produces the usually intense color characteristic for these complexes. These optical absorption bands are often referred to as charge-transfer (CT) bands. Optical spectroscopy is a powerful technique to characterize charge-transfer bands. The characteristic of a charge-transfer complex is the appearance of an additional electronic absorption bands, separate from the absorption bands of the both acceptor and donor molecules. The charge-transfer band occurs in the visible region of the electromagnetic spectrum, which produces the characteristic intense color for complexes. Charge-transfer complexes exist in many molecules. Organic, inorganic and in all phases of matter. Charge-transfer complexes do not experience d-d transitions. Thus, these rules do not apply and the absorptions are generally very intense. The classical example of a charge-transfer complex is that between iodine and starch to form an intense purple colour. This has wide spread use as a rough screen for counterfeit currency. Unlike most paper, the paper used in USA currency is not sized with starch. Thus, formation of this purple colour on application of an iodine solution indicates a counterfeit. The first molecular complexes, now to be of the charge-transfer type, were aromatic hydrocarbon picric acid complexes isolated by Fritzsche. The donor-acceptor approach was reintroduced by Bryce, and it was assumed that the complex was essentially ionic. Stabilization of the complex was considered to be a result of the complete donation of an electron from the donor to the acceptor. It has been known that iodine dissolves in various solvents giving of different colours. Toscano first demonstrated that iodine solutions fall into two classes brown and violet. The former is now known to be $n \rightarrow \pi^*$ or $\pi \rightarrow \sigma^*$ charge-transfer complexes. The brown solutions were considered to contain chemically iodine bound in some way to the solvent, and it was recognized that the brown solvents are electron donating species evidence for solvent binding was obtained by Mayer showed that in brown solutions iodine had a non-zero dipole moment. Benesi and Hildebrand's observations led Mulliken to suggest that the new band in the benzene iodine complex was an intermolecular absorption band and to characterize these complexes as charge-transfer in nature. The charge-transfer complexes exist in two states ground state and an excited state. The two molecules composing the charge-transfer complex undergo the normal physical forces expected between two molecules which are in close proximity to each other in the ground state. These forces include London dispersion forces and any electrostatic interactions, such as between dipole moments. In addition to these normal forces, a small amount of charge is transferred from the donor to the acceptor. The excited state of the complex occurs when the ground state complex absorbs a photon of light having the appropriate frequency. In the excited state the electron which had only been slightly shifted toward the acceptor in the ground state is almost totally transferred. Depending on the structural features of both the donor and acceptor the wavelength of light absorbed may be in the visible range of the electromagnetic spectrum. In many cases, therefore, charge-transfer complexes are coloured. Mulliken was responsible for the development of what has been the most successful theoretical treatment of charge-transfer complexes. The absorption of ultraviolet and visible radiation in organic molecules is restricted to certain functional groups that contain valence electrons of low excitation energy. The absorption occurs when the electrons of these chromophores are excited from lower energy molecular orbitals to higher levels. The UV-VIS spectrometers can rapidly scan the electronic region of the spectrum and provide evidence of the existence of characteristic chromophores. The major limitation imposed is that the compound to be detected must have a characteristic UV-VIS absorbance in the range of 220-770 nm. The absorption of energy in this region is associated with promotion of electrons to higher energy states. In the organic molecules, absorption of energy in this region usually requires the presence of functional groups or multiple bonds, especially two or more such bonds in conjugation. The saturated molecules do not absorb significantly in this region. The amount of an intermediate which can be detected depends on how strongly it absorbs relative to other components of the reaction systems. In favourable cases, concentration as low as 10^{-6} M can be detected. The spectra of π -molecular complexes are to a good approximation presented by the sum of spectra of the individual components. An additional absorption band which is assigned to the charge-transfer band by some authors occurs in the near UV, visible or near IR region between about 5000 and 30000 cm^{-1} . The nature of the ground state, whether ionic or non-ionic, can be determined by overall compression of the spectrum of the molecular complex with the spectra of the individual components which ionizing and neutral conditions. In the absence of any major interactions it can be concluded to be most likely dipole-dipole interaction. The dipole-dipole interaction is an interaction is an intermolecular interaction between molecules having permanent dipoles. This is a type of Vander Waals interactions. The goal of this discussion is to outline the most important theories of electronic spectra, so that the experimental results can be more fully understood. The valence bond treatment of Mulliken and the molecular orbital description of electron donor acceptor complexes are discussed here, alternative descriptions of weak donor/acceptor interactions are given elsewhere.

2.EXPERIMENTAL

The spectra of all the compounds were obtained on a Perkin Elmer 25 in the region 700 nm at room temperature. The complexes were studied in both the solid state and in solution using acetonitrile as solvent. The solid-state experiments did not produce any noticeable absorption, most likely due to the low quality produced.

Valence bond model: -

According to the valence bond model of electron donor acceptor complexes, the ground state or normal state wavefunction for a weak complex is written as-

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

Where $\Psi_0(D \dots A)$ is the so-called no-bond wavefunction and corresponds to the structure of the complex in which the bonding occurs as a result of dipole-dipole forces, London dispersion forces. Etc. The $\Psi_1(D^+ \dots A^-)$ represents the dative or charge-transfer wavefunction and characterizes the complex in which an electron has been transferred from the donor to the acceptor. For weak complexes, such as the π - π complexes studied in the present research project, $a \gg b$. The coefficients a and b determine the relative contributions of the normalized no-bond and dative wavefunctions. These coefficients satisfy the normalization condition:

$$(a^2 + abS) + (b^2 + abS) = 1 \quad (2)$$

Where the overlap integral S is defined by,

$$S = \int \lambda \Psi_0^*(D \dots A) \Psi_1(D^+ \dots A^-) dT \quad (3)$$

And is proportional to the overlap integral between the highest occupied molecular orbital of the donor and the lowest unoccupied molecular orbital of the acceptor. According to the overlap and orientation principle, the donor and acceptor molecules tend to orient themselves so as to make S a maximum. The quantity $(b^2 + abS)$ is a measure of the extent of charge transfer in the ground electronic state. The excited state of the complex has as its wavefunction

$$\Psi_E(DA) = a^* \Psi_1(D^+ \dots A^-) - b^* \Psi_0(D \dots A) \quad (4)$$

Where the coefficient a^* and b^* satisfy a normalization relation analogous to equation (2). In the excited state, the complex has a high degree of ionic character, i.e., $a^* \gg b^*$. The wavefunctions in equation (1) and (4) may also contain contributions from locally excited donor or acceptor states, such contributions are ordinarily insignificant for Ψ_N , but can be important in the case of Ψ_E especially when the energy of the locally excited state is comparable to that of Ψ_1 . The energy levels of the electron donor acceptor complex which emerge from this resonance structure theory are shown in figure-1. The intermolecular charge-transfer transition energy $h\nu_{CT}$ is given by the equation:

$$h\nu_{CT} = I_D - (E_A + G_1 + G_0) + X_1 - X_0 \quad (5)$$

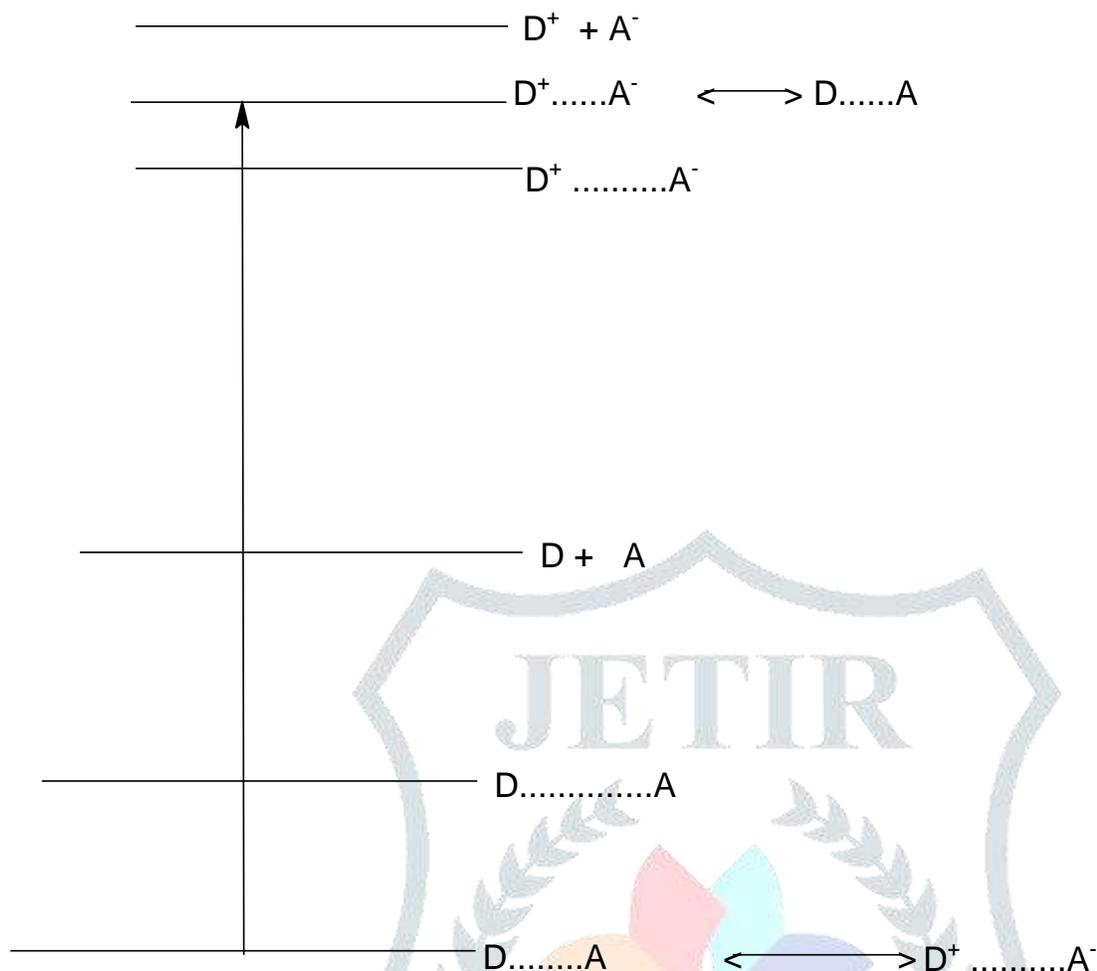


Fig-1. Energy level diagram of an EDA complex

Where I_D is the vertical ionization potential of the donor, E_N is the electron affinity of the acceptor, G_0 is the sum of ground state no-bond terms electrostatic energy and Vander Waals energy, G_1 is the sum of dative state terms including the coulomb interaction x_0 and x_1 are the resonance energies between the no-bond and the dative structures in the ground and excited states respectively. Because of these resonance energies, $h\nu_{CT}$ is not simply equal to the energy required to transfer an electron from the donor to the acceptor, instead, it is the energy of the transition between the states whose wavefunctions are Ψ_N and Ψ_E . The sum $G_0 + X_0$ equal the binding energy i.e the energy given up when two molecules interact and form a complex in the ground electronic state. This intermolecular binding energy is the thermodynamic quantity (H). For $\pi-\pi$ complexes such as those studied here, I_D is the dominant term in equation (5), because of this, for a series of complexes having the same acceptor, $h\nu_{CT}$ has an almost linear relationship with the ionization potentials of the donors. The dependence of the energy of the CT band of the donor ionization potential has been discussed extensively elsewhere.

Charge-transfer absorption bands: -

Electronic absorption or UV-VIS spectroscopy is widely used for the study of charge-transfer complexes, since charge-transfer interactions involve the transfer of an electron from a ground to an excited state. In fact, the observance of an extraneous absorption band in spectra of iodine dissolved in aromatic hydrocarbons by Benesi and Hildebrand in 1949 led, several years later, to Milliken's valence bond treatment for complex formation between electron donor and acceptors. In general, the spectrum of a charge-transfer complex retains the individual absorption bands of its donor and acceptor components, possibly in a somewhat modified form. In addition, however, there are one or more absorption bands due to the complex as a whole. In cases where more than one charge-transfer band is present, the multiplicity may be caused by electron donation from more than one energy level in the donor, from acceptance at more than one energy level in the acceptor, from differences in interaction energies, or from combinations of all of these. In all cases, these Charge-transfer absorption bands are unique to the complex and characteristic for it. Charge-transfer absorptions are usually intense, broad and featureless. Molar

absorptivity may be as high as 50000 but as low as 500 or less. Charge-transfer bands are frequently asymmetrical, being broader on the high frequency side. For complexes having multiple charge-transfer bands, the individual charge-transfer bands may overlap, making spectrum appear as a single band with an abnormally large half width. For intermolecular complexes, however the concentration of the complex and therefore, its absorbance is dependent upon its equilibrium constant.

Factors influencing charge-transfer absorption bands: -

(a) Effect of substituents: - The charge-transfer energy (E_{CT}) is a function of the ionization potential of the donor and the electron affinity of the acceptor. Both the ionization potential and electron affinity are, in turn, a function of the substituents attached to the respective donor and acceptor. Several quantitative relationships relating the frequency of the charge-transfer absorption maximum (ν_{CT}) to the ionization potential of the donor (I_D) and the electron affinity of acceptor (E_A) have been proposed. A simple linear equation is given by equation (6).

$$E_{CT} = h\nu_{CT} = I_D - E_A - W \quad (6)$$

In this equation, h is Planck's constant and W is the dissociation energy of the charge-transfer excited state. A more detailed consideration has led to the following parabolic equation, relating to the frequency of charge-transfer absorption to the ionization potential of the donor:

$$h\nu_{CT} = I_D - C_1 + C_2 / I_D - C_1 \quad (7)$$

Equation (7) is used for a series of complexes involving different donors but having a common acceptor species. In this equation, C_1 and C_2 are constants for a given acceptor. Substituent groups alter the electronic properties of a molecule. Electron releasing substituents increase the donor properties but decrease the accepting properties of a given molecule, electron withdrawing substituents act in the opposite manner. The position of the maximum charge-transfer absorbance shifts to higher frequencies with increasing ionization potential of the donor.

(b) Effect of solvent: - The ground and excited states of charge-transfer complexes usually have different dipole moments, due to this difference in dipole moments different polarity solvents have effect on the charge-transfer absorption band. Solvent effects may be summarized in the following manner. As the solvent polarity increases a blue shift of the charge-transfer band is observed if the ground state of the complex is ionic while the excited state is not ionic, a red shift of the CT band is observed when the ground state is not ionic and the excited state is ionic. Blue or red shifts are observed when both the ground and excited states are ionic. Solvents may also affect the intensity of the CT band, the general trends observed for shifts in position of the CT band with solvent are also true for intensities of the bands.

(c) Effect of temperature: - The charge-transfer interactions are greatly enhanced at low temperature or in frozen solutions. On the other hand, these interactions are diminished at higher temperatures. The CT electronic absorption band also mimics these trends with temperature. As the temperature decreased, thermal motion decreases and results in less inhibition of charge-transfer.

(d) Effect of pressure: - The sensitivity of electron donor acceptor complexes to external pressure is in accord with Mulliken's theory, the stability of charge-transfer complexes and the energy of the CT absorption are sensitive to changes in the orbital overlap of the molecular orbitals of the donor and acceptor. The general trends observed for pressure effects on weak charge-transfer complexes in short, CT absorption maxima shift to longer wavelengths, while the intensities of CT bands increase with increasing pressure.

(e) Association constants: - The stability of a charge-transfer complex is given by its association constant (K).

$$K = [(D:A)] / [D_0 - (D:A)] [A_0 - (D:A)] \quad (8)$$

Where D_0 and A_0 are the initial concentrations of donor and acceptor before interaction, and $(D:A)$ is the concentration of the complex. The association constant may be determined from UV-VIS spectra. In order to do this, the molar absorptivity of the complex is needed and may be obtained from equation (9).

$$\epsilon_{CT} = \log(I_0/I) / l[(D:A)] \quad (9)$$

Where ϵ_{CT} is the molar absorptivity of the CT band, l is the cell path length and $\log(I_0/I)$ is the absorbance.

(f) **Thermodynamic parameters:** - The interactions of donors and acceptors in solution are normally accompanied only small changes in enthalpies and entropies. The thermodynamic constants are obtained by investigating the temperature changes have on the spectrometrically determined equilibrium constants. The enthalpy of dissociation can be determined from equation (10).

$$\ln K_{T_2} / \ln K_{T_1} = - \Delta H^0 / R (1/T_2 - 1/T_1) \quad (10)$$

Standard free energy (G^0) and entropy (S^0) may be obtained from equations (11) and (12).

$$G^0 = - RT \ln K \quad (11)$$

$$G^0 = H^0 - TS^0 \quad (12)$$

In general, H^0 and S^0 become more negative as the equilibrium constant for complex formation increases.

3.RESULTS AND DISCUSSION

The results from the solution spectra are tabulated in Table-1.

Comparison of parent compounds with the components in the EDA complexes

Parent compounds	$\lambda_{\max}(\text{nm})$	Molecular compounds	$\lambda_{\max}(\text{nm})$
4,4'-DNBP	308		
BZ	288	C-BZ	303
tmethylbz	310	C-tmethylbz11	309
4-OHBP	261	C-4-OHBP	308
BP	244	C-BP	308
4-BrBP	255	C-BrBP	308
4,4'-DiOHBP	263	C-,4,4'-DiOHBP	307

As the solutions of the investigated electron donor acceptor (EDA) complexes were dilute, these complexes did not exhibit their own colours. Furthermore, C-tmethylbz11, C-methylbz41, C-4-OHBP, C-BP, C-BrBP and C-4,4'-DIOHBP have absorption maxima similar to the absorption maximum of 4,4'-DNBP. It may be possible that the complexes are dissociated to their low pure compounds in solution. In this case the donor components are not visible because of their low concentrations to the complexes. UV, being a concentration sensitive method, failed to detect the components with low contribution in the complex. The C-C tmethylbz11 was the only complex where the donor component is equivalent with 4,4'-DNBP and as such it was expected to observe two absorption maxima, one belonging to tmethylbz and one to 4,4'-DNBP. Only C-BZ shows a significant 5 nm difference from the original 4,4'-DNBP absorption which may be seen as an interaction, H-bonding between the NO_2 and NH_2 functional groups is possible. The H-bonding will necessitate the partial shift of more electrons to the oxygen atoms in the nitro groups thereby reducing the double bond character of the 4,4'-DNBP, and as a result absorption maximum of the 4,4'-DNBP components of the C-BZ will appear at a shorter wavelength.

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