Chapter I

Introduction
The phenomenon of charge transfer is seen in many day to day things like gemstones such as blue sapphire. Students can recreate this process using iodine and starch. Iodine produces a charge transfer complex with starch, seen as a blue-black color change and in benzene to yield a brown solution was known. The explanation for these colours eluded chemists until Mulliken put forward a comprehensive theory of charge transfer spectra and indicated how weak ground-state interactions could lead to striking spectroscopic phenomena, arising from new type of electronic transition called a charge transfer transition [1].

**Blue Sapphire**

A charge transfer complex (CT-complex) is a combination of a donor (D) and an acceptor (A) which exhibits a special light absorption called a charge transfer transition. A donor may be defined as any molecule capable of losing an
electron and an acceptor is any molecule capable of acquiring an electron. Donors and acceptors interact, according to charge transfer complex theory, to form a complex which, in the simplest case may be expressed as:

\[
D + A \xrightarrow{K} D, A
\]

The CT-complex, (D,A), absorbs light in a way different from either the donor or acceptor alone, in that a new absorption band is present in addition to the originally or slightly modified bands of the components of the complex. In its simplest form, the light absorption process may be written as:

\[
D + A \rightarrow D^{\bullet+}, A^{\bullet-}
\]

The nature of the attraction in a CT-complex is not a stable chemical bond and is much weaker than covalent forces, rather it is better characterized as a weak electron resonance. As a result, the excitation energy of this resonance occurs very frequently in the visible region of the electro-magnetic spectrum. This produces the usually intense colours characteristic for these complexes. These optical absorption bands are often referred to as charge transfer bands, or CT-bands. Hence, optical spectroscopy is a powerful technique to characterize charge transfer bands. Charge transfer complexes exist in many types of molecules, inorganic as well as organic and in all phases of matter, i.e. in solids, liquids and even gases.
According to Mulliken [2, 3], the CT-complex exists in two states, a ground state and an excited state. In the ground state, the two molecules experience the normal physical forces one would expect from two molecules in close proximity i.e. van der Waals forces etc. and in addition a small amount of charge is transferred from the donor to the acceptor which contributes some additional binding energy to the complex. The excited state is promoted when the ground state complex absorbs light of suitable energy. In this excited state, the electron which was only slightly shifted towards the acceptor is almost wholly transferred. It is the transfer of the electron on the absorption of light which gives the characteristic colours of these complexes.

Mulliken has explained this using a valence-bond model [2,3]. The ground state of the complex has a wave function \( \psi_N \) which is a hybrid of two wave functions \( \psi(D,A) \) and \( \psi(D^+-A^-) \). \( \psi(D,A) \) is the no bond function and is the wave function of the two molecules in close proximity with no charge transfer between them. However, it can include contributions from classical electrostatic forces, van der Waals forces and various dispersion forces and dipole interactions. \( \psi(D^+-A^-) \) is called the dative function and is the wave function of the two molecules bound together by an electron being totally transferred from the donor D to the acceptor A. Thus the ground state of the complex is described as:

\[
\psi_N = a \psi_0(D,A) + b \psi_0(D^+-A^-) \quad \text{where } a >> b
\]
and the excited state of the complex is described as:

$$\psi_E = b^* \psi_1(D^+A^-) - a^* \psi_1(D,A)$$

where $b^* >> a^*$

The energy level diagram for a charge transfer complex is shown in Figure 1.1.

Where, $W_0 = \int \psi_0 \psi_0 \, d\tau$; the energy of the no-bond structure

$W_1 = \int \psi_1 \psi_1 \, d\tau$; the energy of the dative structure

$W_{\infty}$ = the energy of the two separated components

$W_N \approx W_0 - [(H_{01} - S_{01}W_0)^2/(W_1 - W_0)]$; the energy of the complex in the ground state

$W_E \approx W_1 + [(H_{01} - S_{01}W_1)^2/(W_1 - W_0)]$; the energy of the complex in the excited state

$H_{01} = \int \psi_0 \psi_1 \, d\tau$; the coulomb integral of the two states $W_0$ and $W_1$

$S_{01} = \int \psi_0 \psi_1 \, d\tau$; the overlap integral for the two states $W_0$ and $W_1$

$G_0$ = the energy stabilizing $\psi_0$ not including resonance

$G_1$ = the energy stabilizing $\psi_1$ not including resonance

$X_0 \approx W_0 - [(H_{01} - S_{01}W_0)^2/(W_1 - W_0)]$; the CT resonance energy of the ground state

$X_1 \approx W_1 + [(H_{01} - S_{01}W_1)^2/(W_1 - W_0)]$; the CT resonance energy of the excited state

In order to be able to identify the CT-band of a complex, it is useful to list some of the properties which have been found empirically. In general these bands are intense, broad and featureless. Extinction coefficients can range as high as 50000 although many of the coefficients listed are as low as 500. There are several
cases reported of multiple charge transfer bands [4]. A probable explanation for this is the presence of close lying filled donor orbitals or unfilled orbitals. So that electron transitions take place from or to more than one orbital, each with its own charge transfer band. If the orbitals are very close together in energy, the charge transfer bands overlap, giving the appearance of a single band with an abnormally large half width.

![Energy level diagram for a charge transfer complex](image)

**Fig. 1.1.** Energy level diagram for a charge transfer complex
The CT-band can be affected by solvents. Weak CT-complex which have little dative character in the ground state, show slight wave length shift of the CT-band maximum which correlate roughly with the polarity dielectric constant or refractive index of the solvent. Strong CT-complexes, with predominantly dative character in the ground state can dissociate into the component ions in solvents of high dielectric constant [5]. So that increasing the polarity of the solvent cause the charge transfer band to be replaced by the spectra of the ions.

1.1 Applications of charge transfer complexes

The formation of electron donor-electron acceptor CT-complexes has long been recognized as an important phenomenon in many biological processes [6-9]. Charge transfer complexes were studied extensively in view of their wide applications and implications in different fields of science and technology [10-17]. CT complexes play an essential role in various fields such as analysis of drugs in pure form or pharmaceutical preparations [18, 19], solar energy storage [20] and surface chemistry [21]. Charge transfer complexes are also known to take part in many chemical reactions like addition, substitution and condensation [22-24]. Other use of CT-systems in molecular recognition in optochemical sensors and in the design of optoelectronic devices in small size scale using CT-model compounds are nowadays important issues in material science [25-28]. Charge transfer complexes are of current importance not only for their occurrence in biological systems, but also as potential materials in organic semiconductors [29-
32], rechargeable batteries [33], photovoltaic cells [34], photocatalysis [35] and in
dendrimer activity [36-38]. Such complexes play significant role in redox
processes and second order non-linear optical activity [39-42]. They are recently
being studied in micro emulsions also [43].

Drugs are organic compounds, and as a result, their activity, their solubility
in plasma and their distribution to various tissues is dependent on their
physicochemical properties. Even the interaction of a drug with a receptor or an
enzyme is dependent on characteristics of a drug molecule, such as ionization,
electron distribution polarity and electronegativity. If we are to understand drug
action, we must also understand the physicochemical parameters that make this
action possible.

In view of the complexities, the knowledge of drug action on a molecular
level is extremely limited. Drugs are usually classified as structurally non-specific
and structurally specific. The activities of the non-specific drugs are not usually
related to chemical structures but are dependent on their particular physico
chemical properties [44] e.g., for anesthetics, air-lipid partition coefficient,
polarizablity and van der Waals’ radii of the drugs are important. In case of
structurally specific drugs, biological activity is very much dependent on the
chemical structures which can bind effectively and interact with the three
dimensional structures of the natural substrate ‘receptor’ to trigger biologic action
[45]. Various physico chemical parameters were utilized and different theories
have been advanced for the quantitative analysis of structure-activity relationship and drug-receptor interactions though the understanding of the mechanism of drug action on the molecular level is yet to emerge [46]. There are various theories of drug-receptor interaction. Paton´s kinetic hypothesis [47], essentially based on diffusion theory, suggested that the activation of the receptor depends on the rate of encounter of a drug at the receptor site to form loose drug-receptor complexes which are capable of dissociation. The activity of the drug requires a high rate of association as well as dissociation to maintain a steady rate of association. The reversible behavior can be achieved by ion association or through H-bonding or by other weak interactions like charge transfer interaction, van der Waals interactions etc. or possibly a combination of such forces [44-46]. Hence, the study of CT-complexes of drug molecules is an interesting area of research and would shed some light on the drug-receptor interactions in real pharmacokinetic situations.

1.2 Significance of quinones

The term quinone refers generally to a 1,4-diketone formally derived from dihydro aromatic compounds in which the two carbonyl groups are connected by a system of conjugated double bond [17]. Since the mid 19th century, chemists have been studying the chemical properties of various quinones. The first synthesized and most common quinone, $p$-benzoquinone was discovered in the late 1830’s in Liebig´s laboratory as the result of the oxidation of guinic acid with manganese
dioxide and sulfuric acid. This reaction involves a dehydration, decarboxylation and oxidation [48].

The chemical compounds having the quinone structure are widely distributed in the nature. Quinones are lipid soluble enzyme cofactors that function as oxidation/reduction intermediaries between assemblies of the membrane-bound proteins of the energy conversion systems of photosynthetic and respiratory systems [49]. Ubiquinone and plastoquinone are biologically significant quinones, which possess alkoxy and alkyl substituents bound to the ring of 1,4-benzoquinone, respectively.

These quinone compounds have various bioactivities and play important roles in the nature. Naturally occurring quinones have captured human attention for thousands of years, initially, by reason of their bright colors with possible uses as dyes and as drugs. Crude preparations of plants, presently known to contain quinones as active ingredients, were prescribed more than 4000 years as purgatives or drugs. Throughout history, several other medicinal benefits have been adding on to the list associated with the use of naturally occurring quinones [48,50].
The reversible oxidation-reduction reaction of biologically active quinones plays a key role in several biological processes. The biological activity of vitamin K$_1$, the oxidation of the reduced form of vitamin K$_1$ is of major important in blood coagulation since a deficiency of this vitamin leads to hemorrhagic bleeding [51]. The reduced form of vitamin K$_1$ reacts, via the enzyme with oxygen and carbon dioxide to generate an interesting 2,3-epoxide intermediate during this process [52]. Other serves as electron acceptors in electron transport chains such as those in photo systems, photo synthesis and aerobic respiration.

Quinones are more important in many fields but they are toxic in nature. Quinone-quinol redox cycles lead to oxidative stress, and some quinones are highly toxic arylating agents, reacting with cellular thiols. They often toxic, featuring a variety of cytotoxic and genotoxic *in vivo* [53] as well as they activate pathophysiologic process such as endoplasmic reticulum stress, inflammation and cancer [54-56]. The study of redox behaviour of quinones, therefore, is an interesting and evergreen area of research.

### 1.3 Literature on the CT-complexes of quinones

Quinones are known to form spectacular CT complexes with variety of donors. The followings are the most common quinones which are used as $\pi$-electron acceptors in the study of CT complexes.
The literature on the spectroscopic studies on the CT-complexes formed by quinones as electron acceptors with wide variety of electron donors is voluminous. Hence, the most important and representative reports on the CT-complexes formed by variety of acceptors containing quinone moieties are listed hereunder.
Mckim et al. [57] have outlined the measurement of the association constants for CT complex formation of a series of methylated benzene donors with tetracyanoethylene, pyromellitic dianhydride, DDQ and 1,2,4,5-tetracyanobenzene acceptors in 1,2-dichloroethane solvent. The evaluation of the position of the CT absorption maximum and the magnitudes of the association constants within a theoretical model is described. These studies showed that non-bonding interactions are important in most complexes while ion-pair interactions play a significant role in a select few of the complexes studied.

Donor-acceptor interactions between the electron donor haloperidol (HPL) and \( \pi \)-acceptors like TCNQ and picric acid (PA) have been studied by El-Habeeb et al. [58]. The CT complexes were discussed in terms of formation constant \( (K_{CT}) \), molar extinction coefficient \( (\varepsilon_{CT}) \), standard free energy \( (\Delta G^\circ) \), oscillator strength \( (f) \), transition dipole moment \( (\mu) \), resonance energy \( (R_N) \) and ionization potential \( (I_p) \). The stoichiometry of these complexes was found to be 1:1 having the formulas \([(HPL)(TCNQ)]\) and \([(HPL)(PA)]\).

Charge transfer complexes of mirtazapine with tetracyanoethylene (TCNE), DDQ and TCNQ have been studied spectrophotometrically in dichloromethane. The stoichiometries of the complexes were found to be 1:1. The equilibrium constants and thermodynamic parameters of the complexes were determined by the Benesi-Hildebrand and van’t Hoff equations. The results indicated that the
formation constants for the complexes depend on the nature of electron acceptors [59].

Spectroscopic and theoretical studies on the CT complexes of methyldopa with \(\pi\)-acceptors (CHA, o-CHL and DDQ) were carried out by Sharma et al. [60]. The physico-chemical parameters of the complexes, composition, association constants and thermodynamic parameters were determined. Oscillator strengths and dipole strengths of the complexes were determined theoretically and experimentally and the limitations of the calculations were outlined.

Bagchi et al. [61] have studied the CT-interactions between the electron donor isoniazid and the acceptors (\(p\)-CHL, CHA and TCNE). The association constants, thermodynamic properties and other related properties were studied and discussed. The energies (\(h\nu_{CT}\)) of the CT complexes were compared with the theoretical values of \(h\nu_{CT}\) of the complexes obtained from HOMO and LUMO of the donor and the acceptors.

Spectroscopic and theoretical investigations on the formation of CT complexes of a designed bisporphyrin with \(C_{60}\), \(C_{70}\) and also the various electron acceptors, viz., DDQ, TCNE, o-CHL and \(p\)-CHL have been reported. Utilizing the CT transition energies for various electron donor-acceptor complexes, the vertical ionization potential of bisporphyrin is determined to be 6.37 eV and the other parameters like degrees of CT, oscillator and transition dipole strengths are computed and interpreted [62].
Shukla et al. [63] have reported the ground state CT complex formation between paracetamol and \( p \)-CHL through Density Functional Theory (DFT) and UV-Vis studies. DFT and Time Dependent Density Functional Theory (TD-DFT) calculations indicated that the C=O bond length of \( p \)-CHL increases on complexation with paracetamol along with considerable amount of charge transfer from the donor to acceptor. TD-DFT calculations have been performed to analyse the observed UV-Vis spectrum of the CT complex and the result indicated that in addition to expected CT transition, a weak symmetry relieved \( \pi \)-\( \pi \) transition in the \( p \)-CHL is also observed.

Charge transfer complexes formed between morpholine as donor with \( p \)-CHL and TCNQ as acceptors have been studied spectrophotometrically by Refat et al. [64]. The synthesis and characterization of the CT-complexes were described. IR, UV-Vis techniques, elemental and thermal analyses were employed to characterize the two CT complexes.

Neelgund et al. [65] have investigated the rapid interaction between DCINQ and \( n \)-butylamine which resulted in the formation of \( 2N(n \)-butylamino)-3-chloro-1,4-naphthoquinone as the final product. The reaction is found to proceed through the initial formation of CT complex as an intermediate. The pseudo first order and second order rate constants at various temperatures for the transformation process were evaluated and discussed.
The CT-interaction of electron acceptors such as CHA, DDQ and TCNQ with the antiviral drug famciclovir has been investigated spectrophotometrically. The 1:1 stoichiometries of the CT complexes reported were based on elemental analysis, IR spectra and thermogravimetric analysis of the solid CT-complexes along with photometric titration measurements for the reactions. Factors affecting the CT-processes such as redox potentials and steric hindrance of reactants are discussed [66].

The charge transfer complexes formed in the reaction of the electron donor 1,4-bis(3-aminopropyl)piperazine with the σ-acceptor iodine and π-acceptors TCNQ, TCNE, DDQ, and 2,4,4,6-tetrabromo-2,5-cyclohexadienone (TBCHD) have investigated by various spectral techniques. The formation constant, molar extinction coefficient, free energy change, CT energy and the ionization potential of these CT complexes were evaluated and discussed [67].

Magadum and co-workers [68] have studied the charge transfer interaction between 2,3-dicyano-1,4-naphthoquinone with N-ethylaniline which resulted in the formation of the monosubstituted product. The reaction was found to proceed through an initial CT complex intermediate and the equilibrium constants of the π-complex were evaluated in three different medium.

The molecular complexes formed between the electron donor 1-(2-aminoethyl)piperidine with the σ-acceptor iodine and π-acceptors DDQ, TCNQ and TBCHD were studied in chloroform [69]. These complexes were
investigated through UV-Vis, FT-IR, thermal and elemental analysis. The physicochemical parameters like formation constant, molar extinction coefficient, free energy change, CT energy and the ionization potential of these CT complexes were calculated and discussed.

The CT interactions of 4,4′-bipyridine with DDQ, CHA, \( p \)-CHL have been studied by Obaid et al. [70]. The stoichiometries of the reactions were determined from photometric titration methods. The thermal decomposition of the complexes followed first order kinetics. The structural morphology was investigated by Scanning Electron Microscopy and Transmission Electron Microscopy and showed that these molecules are of nano size.

The charge transfer interaction of the interesting mixed nitrogen-oxygen donor 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8,8,8]hexacosane with \( \sigma \)-electron acceptor iodine and \( \pi \)-acceptors TCNE and TCNQ have been investigated spectrophotometrically in chloroform. FT-IR, thermal and elemental analysis measurements were performed for the solid CT-interaction products. The reaction stoichiometries were found to be 1:4, 1:6 and 1:3 donor:acceptor molar ratio for iodine, TCNE and TCNQ reaction systems, respectively [71].

The reaction between DClNQ and \( \text{N,N′-diphenyl thiourea} \) in acetonitrile through the formation of CT adduct as intermediate step with evolution of HCl resulted 2,3-(\( \text{N,N′-diphenylthioureylene} \))-naphtho-1,4-quinone as final product.
The formation constant of the CT adduct and the rate constant of the slow process have been determined at four different temperatures and discussed [72].

The electron donor-acceptor interaction between 2,3-dicyano-1,4-naphthoquinone and 3,4-dimethylaniline was studied by Neelgund and co-workers [73]. The formation constant and molar extinction coefficient values for the formation of CT complex were evaluated in the temperature range of 20-35°C. On the basis of kinetic, analytical and spectroscopic results, a plausible mechanism for the formation of CT complex and its transformation into product was proposed.

Charge transfer complexes of risperidone with PA, DDQ, TCNQ, TCNE, p-BRL and p-CHL have been studied spectrophotometrically by El-Habeeb et al. [74]. The stoichiometries of the complexes were found to be 1:1. The equilibrium constants, molar extinction coefficients and spectroscopic-physical parameters were determined using the modified Benesi-Hildebrand equation.

Charge transfer reactions between sulfadoxine as a donor with iodine, DDQ, p-CHL and PA have been studied in solid and solution forms. The stoichiometry of all the complexes was found to be 1:1 by molar ratio method. The results indicated that the formation constant for the complexes were shown to be dependent upon the nature of electron acceptor, donor and polarity of solvents which were used. IR, $^1$H NMR and UV-Vis spectroscopic techniques, elemental analyses and TG-DTG investigation were used to characterize the four sulfadoxine CT complexes [75].
The interaction of organic acceptors such as \( p \)-FRL, \( p \)-CHL, \( o \)-CHL, \( p \)-BRL, \( o \)-BRL and DDQ with (4-dimethylamino-benzylidene)-(4,6-dimethyl-pyrimidin-2-yl)-amine as donor has been studied spectrophotometrically and fluorimetrically in dichloromethane and trichloromethane. The results revealed that the interaction between the donor and acceptors is due to \( \pi-\pi^* \) transitions by the formation of radical ion pairs. The results of spectrofluorimetric study revealed that the fluorescence quenching obeys the static type mechanism via CT complex formation in the ground state [76].

Saini et al. [77] have investigated the vibrational spectra and density functional theory calculations for \( p \)-CHL, imidazole and their complexes. The experimentally observed infrared and Raman bands have been assigned with the help of calculated vibrational frequencies and potential energy distribution analysis. The theoretical values of the interaction energy of various possible \( p \)-CHL–imidazole interactions suggested that the two molecules interact preferably via N and H atoms of imidazole and C=O group of \( p \)-CHL with their molecular planes almost perpendicular to each other.

Ultrasonic investigation has been carried out on six ternary systems to establish the complex formation between \( p \)-CHL (acceptor) and six aromatic hydrocarbons (donors), namely, benzene, toluene, o-xylene, m-xylene, p-xylene and mesitylene in DMSO. The trends in the acoustical parameters and magnitude
of excess thermo acoustical parameters have been used to identify the existence of strong intermolecular interaction through charge transfer complex formation [78].

Refat et al. [79] have prepared new charge transfer complexes formed from the interactions between o-tolidine and PA or CHA. The $^{13}$C NMR, $^1$H NMR, $^1$H-Cosy, and IR studies showed that the charge transfer chelation occurs via the formation of chain structures O–H⋯N, intermolecular hydrogen bond between 2NH$_2$ groups of the donor molecule and OH group in each acceptor units. Thermal behavior of both the CT complexes showed that the complexes were more stable than their parents. The thermodynamic parameters indicated that the formation of molecular CT complexes is spontaneous and endothermic.

The interaction of the donor La(III)acetylacetonate, [La(acac)$_3$], with iodine as a $\sigma$-acceptor and with DDQ as a $\pi$-acceptor have been studied and the results indicated the formation of 1:1 CT complexes. Far-infrared spectra showed that the triiodide ion is nonlinear with $C_{2v}$ symmetry. Mid infrared spectra suggested that the electron donation from [La(acac)$_3$] to the acceptors I$_2$ or DDQ could mainly take place through the oxygen atoms in addition to the acac ring $\pi$-molecular orbitals [80].

Charge transfer complex of o-toluidine with the $\pi$-acceptor $\rho$-CHL has been synthesized and characterized, along with the products of the elimination reaction of o-toluidine with DDQ and TCNQ. Their properties and structures have been investigated using electronic absorption and IR spectroscopy as well as elemental
analyses of the isolated compounds. Thermodynamic parameters were computed from the thermal decomposition data and discussed [81].

Asker et al. [82] have reported the effects of methyl substituent on the CT complexations of dicarbazolylalkanes with \( p \)-CHL, TCNE and TCNQ. The molar extinction coefficients, equilibrium constants, enthalpies and entropies of the CT complexes were investigated. 1,n-Di(3-methylcarbazolyl)alkanes formed CT complexes with higher equilibrium constants, more negative enthalpies and entropies than 1,n-dicarbazolylalkanes.

Charge transfer complexes formed from the reactions of two N,N´-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide such as N,N´-bis-[2-hydroxyethyl]-1,4,6,8-naphthalenediimide and N,N´-bis-[2-N,N-dimethylaminoethyl]-1,4,6,8-naphthalenediimide with DDQ, \( p \)-CHL, TCNQ, 3,5-dichloro-4-chloroiminocyclohexa-2,5-dienone (DCQ) and 3,5-dibromo-4-chloroiminocyclohexa-2,5-dienone (DBQ) as \( \pi \)-acceptors have been studied. The photometric titration curves for the reactions indicated that the data obtained refer to 1:1 CT complexes. The solid CT complexes have been synthesized and characterized by different spectral methods [83].

Electron donor acceptor complexes of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) with \( \pi \)-acceptors like \( p \)-CHL, \( o \)-CHL, DDQ, TCNQ, DCQ, DBQ, CHA, N-bromosuccinimide (NBS) and PA were spectrophotometrically studied and synthesized in solid form. The charge transfer
interactions were interpreted according to the formation of dative ion pairs [18C6\(^{+}\), A\(^{-}\)], where A is acceptor. All of the resulting charge transfer complexes were isolated in amorphous form and characterized using IR and \(^1\)H NMR spectra [84].

The molecular complexes formed in the reaction of the electron donors imidazole and 1-benzylimidazole with the \(\sigma\)-acceptor iodine and \(\pi\)-acceptors DDQ, TCNE and \(p\)-CHL have been studied by Mostafa et al. [85]. These were investigated through electronic and infrared spectra as well as elemental analysis. The formation constant, molar extinction coefficient, free energy change, CT energy and ionization potential of the CT-complexes were calculated and discussed.

Interaction of thiazolidine-2-thione (T2T) as an electron donor with DDQ as an electron \(\pi\)-acceptor has been studied by using electronic absorption spectral technique in several organic solvents of different polarities. The results indicated that a charge transfer complexation has occurred between T2T and DDQ which led to a redox reaction in which T2T has been oxidized to the corresponding dehydrogenated T2T (T2T-\(2H\)), meanwhile DDQ has been fully reduced to the corresponding hydroquinone (DDQH\(2\)). The obtained formation constant and molar absorption coefficient values indicated that T2T-\(2H\) is a weak CT donor, whereas the formed CT complex has a low stability and it is classified as a contact-type CT complex [86].
The donor-acceptor complexes between 2,3-dichloro-5-nitro-1,4-naphthoquinone and some methyl substituted anilines were investigated by spectrophotometric method. Experimental evidences showed the formation of 1:2 (A:D) complexes but not 1:1 complexes. The thermodynamic and spectroscopic parameters were evaluated and discussed [87].

The charge transfer complex between oxatomide drug and DDQ was studied spectrophotometrically in 10 solvents at different temperature by Pandeswaran and Elango [88]. The donor oxatomide was found to form stable 1:1 CT complex with DDQ and the stoichiometry remained unaffected by change in polarity of the solvents studied. On the other hand the spectroscopic and thermodynamic properties were observed to be sensitive to the nature of the solvent.

Three charge transfer complexes of azelastine as n-donor with π-acceptors, DDQ, CHA and TCNQ were prepared in acetonitrile. They yielded radical anions measured at 456, 520 and 841 nm. The molar absorptivities and association constants for the colored products were evaluated using the Benesi-Hildebrand equation. The methods were successfully applied to the analysis of azelastine in its pharmaceutical preparations [89].

The charge transfer complexes of the donor sulfamethoxazole with iodine, DDQ, p-CHL and PA have been studied by Refat et al. [90]. The stoichiometry of the CT complexes was found to be 1:1 by molar ratio method between donor and
acceptor with maximum absorption bands (CT band). The results indicated that the formation constant for the complexes were shown to be dependent upon the nature of electron acceptor, donor and polarity of solvents which were used.

The rapid interaction between sulphonamides (sulphamethoxazole, sulphaguanidine, sulphaquinoxaline sodium and sulphadimidine sodium) as n-electron donors with DDQ and CHA as \( \pi \)-acceptors resulted in the formation of 1:1 CT complexes as the final products with the formula \([(\text{drug}) \ (\text{acceptor})]\). The final products of the reactions have been isolated and characterized using FT-IR, \(^1\)H NMR, mass spectroscopy and elemental analyses as well as photometric measurements and thermogravimetric analysis [91].

Singh et al. [92] have reported the synthesis and characterization of novel CT complexes of thiazolidine-2,4-dione with sigma acceptor (iodine) and \( \pi \)-acceptors (\( p \)-CHL, DDQ, PA and duraquinone). They also evaluated the thermal and electrochemical properties of the complexes and concluded that complex with sigma acceptors are more conducting than with \( \pi \)-acceptors.

A colored charge transfer host complex has been prepared using racemic 10,10´-dihydroxy-9,9´-biphenanthryl, which has a large and widely \( \pi \)-conjugated phenanthrene ring, as the electron donor and 2,5-disubstituted-1,4-benzoquinone as the electron acceptor. Characteristically, it is possible to tune the color and diffuse reflectance spectra of the inclusion CT complex by changing the type of the component 2,5-disubstituted-1,4-benzoquinone [93].
Fakhroo and co-workers [94, 95] have studied the reactions of the electron donors 1-methylpiperidine and 1-methylpiperazine with \( \pi \)-acceptors TCNQ, TCNE, DDQ, \( p \)-CHL and \( \sigma \)-acceptor iodine spectrophotometrically in chloroform at room temperature. The electronic and infrared spectral results showed that the stoichiometries of the reactions are not fixed and depend on the nature of the acceptor.

Electron donor-acceptor interaction of morpholine with CHA and PA as \( \pi \)-acceptors was found to form stable \( n-\pi^* \) CT complexes. These complexes are easily synthesized and characterized using \(^1\)H NMR, IR, elemental analyses, and UV-Vis techniques. The X-ray crystal structure analysis was carried out to predict the structure of the Donor-PA complex [96].

The kinetics and mechanism of the interaction between DDQ and ketoconazole and povidone drugs has been investigated by Pandeeswaran et al. [97]. The 1:1 CT complex of drug:DDQ has been isolated and characterized by FT-IR and GC-MS techniques. The rate of formation of product has been measured as a function of time in different solvents at three temperatures. The thermodynamic parameters, viz. activation energy, enthalpy, entropy and free energy of activation were computed from temperature dependence of rate constants and discussed.

Mostafa et al. [98] have investigated the CT molecular complexes formed in the reaction of 1-(2-aminoethyl)piperazine with the \( \sigma \)-acceptor iodine and \( \pi \)-
acceptors DDQ, TCNQ, p-BRL and p-CHL in chloroform. The obtained results showed that the formula of the solid CT-complexes are in full agreement with the known reaction stoichiometries in solution as well as the elemental analysis measurements.

Three novel aqueous and solid CT complexes have been synthesized by the reaction of the polynitrogen cyclic n-donor 1,4,8,11-tetraazacyclotetradecane-5,7-dione with the σ-acceptor iodine, the aliphatic π-acceptor TCNE as well as with the aromatic π-acceptor DDQ using chloroform as the solvent. The observed reaction stoichiometries in solution are supported by the elemental, thermal and infrared measurements of the formed CT-solids [99].

Spectroscopic studies revealed that the interaction of cimetidine drug with electron acceptors iodine and DDQ resulted through the initial formation of ionic intermediate to CT complex. The rate of formation of the CT-complexes has been measured and discussed as a function of relative permittivity of solvent and temperature. The influence of relative permittivity of the medium on the rate indicated that the intermediate is more polar than the reactants and this observation was further supported by spectral studies [100].

The kinetics and mechanism of the interaction between DDQ and dextromethorphan and atenolol drugs has been investigated spectroscopically. In the presence of large excess of donor drug, the 1:1 CT complex is transformed into a final product, which has been isolated and characterized. The rate of formation
of product has been measured as a function of time in different solvents at three temperatures. Cyclic voltammetric study supported the observed solvent effect on the extent of CT complexation and the rate with which it is converted into the product [101].

Pandeeswaran et al. [102] have studied the kinetics of formation of CT complexes of pantoprazole with DDQ and iodine. The rate of formation of the product has been measured and discussed as a function of solvent and temperature. The activation parameters ($\Delta G^\#$, $\Delta S^\#$, and $\Delta H^\#$) were obtained from the temperature dependence of the rate constants.

Charge transfer complexes of ofloxacin, chlorpheniramune, azacyclonol and indapamide drugs with DDQ have been investigated spectrophotometrically in different organic solvents at different temperatures. The oscillator and transition dipole strengths of the complexes have been determined from the CT absorption spectra. The ionization potential value of the donors calculated using spectral data are in good agreement with those computed using molecular orbital package MOPAC (PM3) method [103].

The kinetics of electron donor-acceptor complex formation between imipramine and DDQ has been investigated spectrophotometrically using soft- and hard-modeling approaches. From the results of exploratory analysis of kinetic data and the spectral changes a consecutive two-steps reaction with two intermediates
was proposed for the process in acetonitrile and 1,2-dichloroethane media and one with a single intermediate in chloroform solution [104].

Charge transfer complexes formed between 2-amino-4-methoxy-6-methylpyrimidine, 2-amino-4,6-dimethyl-pyrimidine, 3-amino-pyrazole, 3,5-dimethyl-pyrazole, 3-amino-5-methyl-pyrazole, 2-amino-4-methyl-thiazole, 2-amino-5-methyl-1,3,4-thiadiazole, 3-amino-5,6-dimethyl-1,2,4-triazine as electron donors with π-acceptor CHA have been investigated in ethanol. It has been found that the equilibrium constant depends on the pKa of the donors [105].

Shahada et al. [106] have studied the CT-interactions between the electron donor 4,4′-trimethyleneipiperidine and the acceptors p-CHL, DDQ, TCNQ and iodine. The formed solid CT-complexes were isolated and characterized through infrared spectra as well as thermal and elemental analysis. The stoichiometry of the complexes was found to be system dependent.

The electron donor-acceptor interaction between drugs and some π-acceptors has been reported by Ofokansi and co-workers [107]. The stoichiometry of the complex formed was evaluated using the Job’s continuous variation method. Spectrophotometric absorption studies showed evidence of the formation of strongly bonded and highly stable CT-complexes. Salem [108] has investigated the CT-reactions of pregabalin as n-donor with various π-acceptors (TCNQ, DDQ, CHA, TCNE and p-CHL). Different colored CT complexes and radical anions obtained were discussed.
The interactions of the electron donors 2-aminopyridine and 3-aminopyridine with the π-acceptors TCNE, DDQ, 2-chloro-1,3,5-trinitrobenzene and \( p \)-CHL were studied spectrophotometrically in chloroform at room temperature. The stoichiometries of the reactions were found to depend on the nature of both the donor and the acceptor. The molecular structures of the CT-complexes were, however, independent of the position of the amino group on the pyridine ring [109].

Darwish et al. [110] have investigated the reaction between the antidepressant fluvoxamine and 1,2-naphthoquinone-4-sulphonate reagent. In alkaline medium (pH 9), an orange-colored product exhibiting maximum absorption peak at 470 nm was produced. The kinetics of the reaction was investigated and its activation energy was found to be 2.65 kcal mol\(^{-1}\). The stoichiometry of the reaction was determined and a reaction mechanism was postulated.

The complexation of electron donor-acceptor complexes of 8-hydroxyquinoline (8HQ) and \( meta \)-dinitrobenzene (MNB) has been studied spectrophotometrically and thermodynamically in different polar solvents. A new theoretical model has been developed which take into account the interaction between electronic subsystem of 8HQ and MNB. The results indicated that the extent of CT-complex formation to be more in less polar solvents [111].
A coloured, two-component, supra molecular, host system has been developed which uses a CT-complex composed of \((rac\)-1,1\(^\prime\)-bi-2-naphthol and 2,5-substituted 1,4-benzoquinone. This CT host system can selectively include aromatic guest molecules into a channel-like cavity by tuning the packing of the electron-donor and electron-acceptor molecules. Characteristically, the color and diffuse reflectance spectra of the inclusion CT-complex can be tuned by changing the type of the component 2,5-substituted 1,4-benzoquinone [112]. The crystal structures of CT-complexes of the donor with \(p\)-FRL were also reported using X-ray crystallographic analyses [113].

Charge transfer complexes formed in the reactions of 2,9-dimethyl-1,10-phenanthroline with some acceptors such as \(p\)-CHL, PA and CHA have been studied. The results of elemental analysis and infrared spectra of the solid CT-complexes along with the photometric titration studies indicated the formation of 1:1 CT complexes. The formation constants for the complexes were shown to be dependent upon the nature of the electron acceptors used [114].

The solid charge transfer complexes formed in the reaction of the electron donor 1,4,7-trimethyl-1,4,7-triazacyclononane (TMTACN) with the acceptors iodine, TCNE and TCNQ have been isolated. These were characterized through electronic and infrared spectra as well as thermal and elemental analysis. The results showed that the CT-complexes have the formulas \([(TMTACN)I]I_3,\)
[(TMTACN)(TCNE)_3] and [(TMTACN)(TCNQ)_3] in full agreement with the known reaction stoichiometries in solution [115].

Charge transfer complexes formed from the reactions of two \(N,N^\prime\)-bis-alkyl derivatives of 1,4,6,8-naphthalenediimide such as \(N,N^\prime\)-bis[2-hydroxyethyl]-1,4,6,8-naphthalenediimide and \(N,N^\prime\)-bis-[2-\(N\),\(N\)-dimethylaminoethyl]-1,4,6,8-naphthalenediimide with CHA and PA as \(\pi\)-acceptors, have been studied spectrophotometrically in methanol and chloroform, respectively at 25°C. The solid CT complexes have been synthesized and characterization by different spectral methods [116].

Charge transfer complexes of 1:1 stoichiometry have been found to form between vitamin B\(_6\) and a series of electron acceptors including \(p\)-CHL in water-ethanol mixture. From the trends in the CT absorption bands the vertical ionization potential of vitamin B\(_6\) has been determined to be 8.12 eV. The magnitude of formation constant has been found to decrease noticeably with a decrease in dielectric constant of the medium [117].

The electron accepting properties of the DDQ and iodine and electron donating properties of the drug cilostazole have been studied using the UV-Vis, FT-IR, GC-MS and Far-IR techniques. The interaction of cilostazole with iodine and DDQ resulted via the initial formation of CT complex as an intermediate. The enthalpies and entropies of formation of the complexes have been obtained by determining their rate constant at three different temperature [118].
AlQaradawi et al. [119] have investigated the reactions of the electron donor 1,4,7,10-tetraazacyclododecane with the π-electron acceptors TCNQ, TCNE, DDQ, \( p \)-CHL and TBCHD. The isolated CT complexes were characterized through electronic and infrared spectra as well as elemental and thermal analysis measurements. The formation constants, charge transfer energy, molar extinction coefficients, free energy change, ionization potential and oscillator strength of the formed CT-complexes were obtained and discussed.

Sharma et al. [120] have prepared the CT-complex of \( p \)-toluidine/\( p \)-CHL by solution growth and microwave techniques and characterized by elemental analysis, UV-Vis, IR and \( ^1 \)H NMR spectroscopic data. The results indicated that the CT-interaction is associated with a proton migration from the acceptor to the donor followed by intermolecular hydrogen bonding. The CT-complex was found to behave as semiconductor at room temperature.

Charge transfer complexes of DDQ with \( p \)-acetotoluidide, acetonilide, biphenyl and naphthalene were studied in different solvents and temperature. The spectral characterization of these CT complexes were determined and correlated with the ionization potential of the donor. The variations in thermodynamic parameters were found to be due to change in donor and solvent [121].

Paliwal et al. [122] have prepared and characterized the CT-complex of \( p \)-phenylenediamine and \( p \)-CHL by solution growth, diffusion and microwave methods. Shahdousti et al. [123] have investigated the CT-complexes of
methamphetamine with several acceptors including bromocresol green, bromocresol purple, chlorophenol red and DDQ. The oscillator strengths, transition dipole moments and resonance energy of all the complexes have been calculated and discussed.

The CT-complexes of 2-, 3- and 4-picoline with the π-acceptor DDQ and the σ-acceptor I$_2$ have been investigated by Razzaq et al. [124]. The $\Delta H^\circ$, $\Delta G^\circ$ and $\Delta S^\circ$ values are all negative implying that the formation of the studied complexes is exothermic in nature. Salem [125] has investigated the CT-reactions of gabapentin as n-electron donor with the σ-acceptor: iodine and various π-acceptors: TCNQ, DDQ, CHA, TCNE and p-CHL. Different variables affecting the reactions were studied and optimized.

The temperature dependent electrical conductivity and thermal degradation kinetics of CT-complexes of phenothiazine with p-CHL and PA were reported. These CT-complexes exhibited semiconducting behaviour. The activation energies for these complexes were calculated based on their electrical conductivities measured [126].

Molecular charge transfer complexes of the donor 2,6-diaminopyridine with π-acceptors TCNE, DDQ and p-CHL were studied spectrophotometrically in chloroform at room temperature. All formed complexes exhibited well resolved charge transfer bands in the regions where neither donor nor acceptors have any absorption. The stoichiometries of the reactions were determined from
photometric titration methods. These three complexes were isolated as solids and further characterized by elemental analysis and infrared measurements [127].

Dimer model compounds of polyvinylcarbazoles (1,\textit{n}-di(\textit{N}-carbazolyl)alkanes, where \(n=1–5\)) were synthesized to model the effects of distance and orientation between carbazole groups in polymeric systems. Charge transfer complexes of carbazole, \(N\)-ethylicarbazole and 1,\textit{n}-di(\textit{N}-carbazolyl) alkanes with \(p\)-CHL have been investigated spectrophotometrically in dichloromethane. The colored products are measured spectrophotometrically at different wavelength depending on the electronic transition between donors and acceptor [128].

Interactions of 2-aminopyrimidine with iodine as a typical \(\sigma\)-type acceptor and with a \(\pi\)-acceptor, \(p\)-CHL have been studied spectrophotometrically. Chemical reaction has occurred via prior or initial formation of the outer-sphere CT complex followed by formation of the corresponding anion radicals as intermediates. UV-Vis, \(^1\text{H}\) NMR, Mass, and FT-IR spectra in addition to elemental analysis were used to confirm the proposed occurrence of the chemical reaction and to investigate the synthesized solid products [129].

The interaction of the interesting polynitrogen cyclic base 1,4,7-trimethyl-1,4,7-triazacyclononane with the \(\sigma\)-acceptor iodine and \(\pi\)-acceptors TCNE, TCNQ and \(p\)-CHL has been studied spectrophotometrically and cyclic voltametrically in
chloroform at 20°C. Based on the obtained data, the formed charge transfer complexes were formulated as their respective stoichiometry [130].

AlQaradawi et al. [131] have studied the spectrophotometric properties of the CT complexes formed between 2,3-diaminopyridine (DAPY) with \( p \)-CHL and TCNE in chloroform. The stoichiometry of these CT-complexes is shown to be 1:1, (DAPY:\( p \)-CHL) and 1:3 (DAPY:TCNE). The two complexes were isolated as solids and characterized by elemental analysis and infrared measurements [131].

Raman, UV-Vis, \(^1\)H NMR, FT-IR, mass and fluorescence spectral techniques were employed to investigate the mechanism of interaction of irbesartan drug with DDQ and iodine. The interaction of DDQ with irbesartan was found to proceed through the formation of outer complex and its conversion to the CT complex. Fluorescence quenching studies indicated that the interaction between the drug and the acceptors are spontaneous and the drug-DDQ interaction is found to be stronger than that of the other system [132].

The interaction and colorimetric sensing properties of the calix[4]pyrrole-\( p \)-CHL CT complex with amino acids and amines in CHCl₃/EtOH/H₂O were investigated using UV-Vis spectroscopic techniques. The obvious spectral and visual changes of the complex solution in the presence of basic amino acids and aliphatic amines were observed, and the calix[4]pyrrole-\( p \)-CHL supramolecular assembly, like a ‘signal magnifier’, markedly improves sensing sensitivity and selectivity [133].
The non-covalent charge transfer complex, formed by di(hydroxymethyl)-di-(2-pyrrolyl)methane and TCNQ, may be used as a colorimetric anion sensor for higher sensitive and selective detection of $\text{SO}_3^{2-}$ than other inorganic anions in a neutral buffered aqueous system. The excellent system property is hopeful to be used in the monitoring fields of food products and environmental pollutant [134].

Bhattacharya et al. [135] have reported that the theoretical investigations of the o-CHL/aniline complex in gas phase employing \textit{ab initio} and time-dependent density functional theory methods. The dipole moment vector is directed from aniline to the o-CHL in the complex. The two O atoms of o-CHL are found to be oriented towards the $-\text{NH}_2$ group of aniline and C=O bond length increases upon complexation with aniline. The CT transition energy of the complex corroborates fairly well with the reported experimental value.

Charge transfer complexes formed between aromatic thiol donors and DDQ were investigated by Kalimuthu et al. [136]. On the basis of the energies of LUMO and HOMO, from quantum mechanical calculations, the broad band observed in the visible region was assigned to the $\pi^* (a_2) \leftarrow \pi (b_1)$ transition and a band observed between 300 and 400 nm was assigned to the $\pi^* (a_2) \leftarrow \pi (a_2)$ transition. The solid CT-complexes of the aromatic thiols with DDQ were prepared and characterized by FT-IR spectroscopy.

Bazzi et al. [137] have investigated the interactions of piperazine and N,N'-dimethylpiperazine with the $\sigma$-acceptor iodine and the $\pi$-acceptors TCNE and
DDQ. The results obtained showed that the stoichiometries of the reactions are not fixed and depend on the nature of both the donor and the acceptor. Al-Attas et al. [138] have investigated the CT-complexes formed between pyrimidines and benzyl adenine and CHA. The association constant, molar extinction coefficient, oscillator strength, dipole moment and the CT-energy of the formed complexes were estimated and discussed. The solid CT-complexes have been synthesized and characterized by FT-IR and $^1$H NMR spectroscopy.

Charge transfer complexes between colchicine and $\pi$-acceptors such as TCNE, DDQ and $p$-CHL have been studied spectrophotometrically in dichloromethane. The stoichiometry of the complexes was found to be 1:1 ratio between donor and acceptors. The formation constants for the complexes were shown to be dependent on the structure of the electron acceptors used [139].

The ground-state structure of the charge transfer complex formed by pyridine as electron donor and $p$-CHL as acceptor has been studied by full geometry optimization at the MP2 and DFT levels of theory. The charge distribution of the ground state complex was evaluated with the natural population analysis, showing a net charge transfer from the donor to $p$-CHL. Analysis of the frontier molecular orbitals revealed a $\sigma$-$\pi$ interaction between the partners [140].

Charge transfer complexes of some pyrazole donors (pyrazole, 4-methylpyrazole, 3-methylpyrazole and 3,5-dimethylpyrazole) with DDQ and TCNE as $\pi$- acceptors have been studied. The spectral characteristics and stability
constants of the formed CT complexes were discussed in terms of the nature of donor and acceptor molecular structure, as well as in relation to solvent polarity. It was concluded that the formed CT complexes are of n-π type with 1:1 composition [141].

The ability of some anthraquinones (AQs) as electron acceptors to form CT complexes with well-known electron donor molecules pyrene and hexamethylbenzene has been investigated. The association constants of the formed CT complexes were determined from the NMR data. The extent of interaction between AQs and donors has been computed using molecular mechanics and quantum mechanics. The computed values were compared with the experimental results of association constants [142].

The interaction of DDQ with trimethoprim (TMP) and albenadazole (ALB) was found to proceed through the formation of donor–acceptor complex, containing DDQ radical anion and its conversion to the product. Fluorescence quenching studies indicated that the interaction between the donors and the acceptor are spontaneous and the interaction of TMP–DDQ (binding constant = 2.9 × 10^5 M^-1) was found to be stronger than that of the ALB–DDQ (binding constant = 3 × 10^3 M^-1) system. Also, the binding constant increased with an increase in polarity of the medium indicating the involvement of radical anion as intermediate [143].
Charge transfer complex formation between 2-amino-4-picoline as the electron donor with CHA as the electron acceptor has been studied spectrophotometrically in different polar solvents. The formation constants and molecular extinction coefficients were estimated using Benesi-Hildebrand equation; they recorded high values confirming high stability of the formed complex. Molecular orbital calculations utilizing GAMESS computations were carried out to predict infrared spectra. They also confirmed the presence of proton transfer beside charge transfer in the formed complex [144].

Charge transfer complexes of 4-(dimethylamino)pyridine (DMAP) with iodine as a typical $\sigma$-type acceptor and with typical $\pi$-type acceptor, DDQ, have been synthesized and characterized. The systems DMAP/iodine and DMAP/DDQ are characterized by formation of triiodide ion ($I_3^-$) and DDQ$^-$ anion radical, respectively, which is proposed to occur via initial formation of outer-sphere CT-complexes [145]. Duymus et al. [146] have investigated the CT-complexes of non-steroidal anti-inflammatory drugs, naproxen and etodolac, with some $\pi$ acceptors, such as TCNE, DDQ and $p$-CHL. The equilibrium constants of the CT-complexes and the thermodynamic parameters were calculated and discussed.

Refat et al. [147] have studied the CT-interactions between sodium flucloxacillin and CHA, DCQ, DDQ and TCNQ. Different variables affecting the reaction were studied and optimized. The proposed methods were applied successfully to the determination of the examined drug either in pure or
pharmaceutical dosage forms with good accuracy and precision. The formation of the CT-complexes and the sites of interaction were confirmed by elemental analysis, UV-Vis, IR, $^1$H NMR and mass spectral techniques.

Reddy et al. [148] have prepared the electron donor-acceptor molecular complexes of a few phenolic donors with some quinonoid and TCNE acceptors by two different methods. The $g$ values obtained in ESR spectral studies for all these molecular adducts vary between 2.000 and 2.022, confirming the free radical nature of the adducts. The results indicated that the ease of complexation not only depends on the ionization potential and electron affinities of the phenolic donors and the acceptors but is also structure sensitive.

Cloxacillin sodium was shown to form a CT-complex of 2:1 stoichiometry with riboflavin (Vitamin B$_2$) in aqueous ethanol medium. Pronounced effect of dielectric constant of the medium on the magnitude of association constant has been observed by determining it in aqueous ethanol mixtures of varying composition. This has been rationalized in terms of ionic dissociation of the cloxacillin sodium (D$^-$/Na$^+$), hydrolysis of the anion D$^-$ and complexation of the free acid, DH with riboflavin [149].

The solid and solution interaction studies that were done between the electron donor $p$-toluidine and some $\pi$-acceptors such as $p$-CHL, DDQ and TCNQ were carried out by Refat and Sadeek [150]. The final product of the reactions has been isolated and characterized using UV-Vis, mid IR, $^1$H NMR, mass spectra and
thermal measurements. The molar absorptivities and formation constants of the resulting 1:1 molecular complexes were determined and discussed.

Charge transfer complexes formed through the reaction of (E)-dicyclopentylmethylene(2,5-dimethyl-3-furylethylidene)succinic anhydride and some π-acceptors namely, DDQ, p-CHL and CHA were prepared and characterized by elemental analysis, IR and electronic absorption spectra. Spectral characteristics of the CT-complexes were discussed in terms of donor molecular structure and π-acceptor electron affinity [151].

Refat et al. [152] have reported the CT-complexes formed between piperidine (Pip) as donor and CHA and PA as acceptors. The synthesis and characterization of piperidine CT-complexes of chloranilic acid [(Pip)_2(CHL)] and picric acid [(Pip)(PA)] were described. _1^H-NMR, IR, elemental analysis, mass spectra and UV-Vis techniques were used to characterize the CT-complexes.

Inaba et al. [153] have reported that the DsbB (Escherichia coli plasma membrane protein) bound with quinone undergoes transition to a pink (λ_{max}, ≈ 500 nm, ubiquinone) or violet (λ_{max}, ≈ 550 nm, menaquinone)-colored state during the course of the DsbB enzymatic reaction. Quantum chemical simulations indicated that proper positioning of thiolate anion and ubiquinone in conjunction with positively charged guanidinium moiety of arginine allows the formation of a thiolate-ubiquinone charge transfer complex with absorption peaks at 500 nm as well as a cysteinyl-quinone covalent adduct.
El-Mossalamy [154] has investigated the CT-complexes of substituted thiourea with DDQ, CHA, \( p \)-CHL, \( p \)-BRL and \( p \)-IDL in methylene chloride spectrophotometrically. The solid CT-complexes have been prepared and characterized by IR, electronic, \(^1\)H NMR and ESR spectroscopy. Non acidic acceptors yielded complexes having \( \pi-\pi^* \) and \( n-\pi^* \) bonding. Acidic acceptors yielded complexes having \( \pi-\pi^* \) and proton transfer interaction.

The interaction of the mixed oxygen-nitrogen cyclic base, \( N,N' \)-dibenzyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane with \( \pi \)-acceptors such as PA and DDQ has been studied by Teleb et al. [155]. The results obtained indicated the formation of 1:4 CT-complexes with the general formula (donor):(acceptor),\(_4\). The electronic, infrared and \(^1\)H NMR spectra of the CT-complexes were recorded and discussed. Roy and co-workers [156] have shown that cloxacillin sodium form CT-complexes of 1:1 stoichiometry with a number of electron acceptors in 50% (v/v) aqueous ethanol medium. It has been noted that the reduction of \( o \)-CHL by aqueous ethanol is completely inhibited by cloxacillin sodium, a phenomenon that makes the study of formation equilibrium possible.

Absorption spectrometric and thermodynamic studies of CT-complexes of vitamin \( K_3 \) with series of phenols have been reported in \( \text{CCl}_4 \) medium. The CT-energies of the complexes were found to change systematically with change in the number and position of the \(-\text{OH}\) groups in the aromatic ring of the phenol moiety. Formation constants of the complexes have been determined at four different
temperatures from which the enthalpies and entropies of formation of the complexes have been estimated and discussed [157].

Hasani and Shamsipur [158] have investigated the interaction of DDQ with diaza-18-crown-6 and diaza-15-crown-5 in acetonitrile and chloroform. The results indicated immediate formation of an electron donor-acceptor complex which is followed by two relatively slow reactions. The influence of both the azacrown´s structure and the solvent properties on the formation of the complexes and the rates of subsequent reactions were discussed.

Dimer model compounds of polyvinylanthracenes \{1, n-di(9-anthryl)alkanes, where \( n=1-5 \)\} were synthesized to model the effects of distance and orientation between anthracene groups in polymeric systems. Charge transfer complexes of anthracene, 9-methylanthracene and 1, n-di(9-anthryl)alkanes with \( p \)-CHL have been investigated in dichloromethane. The formation constants, thermodynamic parameters and stoichiometries of the complexes formed were calculated and discussed [159]. A spectrophotometric study concerning the interaction between aza-15-crown-5 and TCNE, DDQ, TCNQ and \( p \)-BRL has been performed in chloroform. All of the resulting complexes were isolated in crystalline form and the effect of complex formation on IR spectra was discussed [160].

Charge transfer complexes formed between 2-amino-1,3,4-thiadiazole and DDQ, \( p \)-CHL, \( o \)-CHL, \( p \)-BRL and CHA have been reported by Gaber and Al-
Shihry [161]. The solid CT-complexes have been synthesized and characterized by different spectral methods. The spectral changes revealed that the CT-interaction depends on the type of the acceptors. The electrical properties for the solid CT-complexes were measured from which the activation energies were calculated.

The fluorescence quenching and complexation behavior of tetraphenylporphyrin with some organic acceptors such as $p$-CHL, 5,5$'$-dithiobis-2-nitrobenzoic acid and tetravalent metal ions such as Th(IV) and Zr(IV) have been studied Azim et al. [162]. The second-order fluorescence quenching rate constants, association constants, molar absorption coefficients and thermodynamic parameters of the complexation process have been evaluated and discussed.

The kinetics of the interaction between 1,3-dimethylbarbituric acid with some quinones, namely $p$-BQ, NQ and $p$-CHL in methyl alcohol-water mixture have been investigated by Medien et al. [163]. The reaction follows overall second-order kinetics, first order each in reactant. From the dependence of the rate constants on temperature, activation parameters have been calculated. The rate of interaction increases with increasing dielectric constant of the medium.

Oza et al. [164] have reported the infrared spectra of six CT-complexes of lead phthalocyanine with $I_2$, TCNQ, DDQ, $p$-CHL, TCNE and 2,4,7-trinitro-9-fluoren (TNF). The results indicated that metal-ligand vibrations between 400 and 700 cm$^{-1}$ lead to indirect transition between the valence and conduction bands and phonon-mediated coupling between metal chains and the side chains.
The interaction of the cyclic base 1,4,10,13-tetraoxa-7,16-diazacyclooctadecae (TODACOD) with different \( \pi \)-electron acceptors, picryl chloride, TCNQ and \( p \)-CHL have been studied by Nour et al. [165]. The results of various spectral studies indicated the formation of 1:4 CT complexes with the general structures \([(TODACOD)(\text{Acceptors})_4]\).

The reaction of ferric(III) acetylacetonate, Fe(acac)\(_3\), with iodine as a \( \sigma \)-acceptor and with other different \( \pi \)-acceptors have been studied spectrophotometrically at room temperature in chloroform. The \( \pi \)-acceptors used in this investigation are DDQ, \( p \)-CHL and TCNQ. The results indicated the formation of 1:1 charge transfer complexes with a general formula, [Fe(acac)\(_3\)(acceptor)]. The proposed structure of this complex is further supported by thermal and middle infrared measurements [166].

Zhang et al. [167] have described a new voltammetric method for the determination of melamine based on the CT interaction between quinones and melamine. Three types of quinones, i.e., \( p \)-CHL, \( p \)-BQ, and vitamin K\(_1\) were employed and the CT interaction activity of quinones with melamine was found to depend on the structure of quinones, of which \( p \)-CHL with four electron-withdrawing chloro groups exhibited the highest interaction activity with melamine.

The charge transfer complexes of bis(N-phenylsalicyladiminato)Cu(II) with organic acceptors like TCNQ, TCNE, TNF, DDQ, \( p \)-CHL, and iodine have been
prepared and studied with FT-IR spectroscopy. The spectra of the donor chelate showed systematic steps in transmission above 2500 cm\(^{-1}\), which were analyzed by its first-derivative. Fine structure was also seen pronounced in the CT complexes. Two or three electronic absorption envelops were identified in all the complexes [168].

Intermolecular charge transfer or proton-transfer complexes between the drug procaine hydrochloride as a donor and quinol, PA or TCNQ as a \(\pi\)-acceptor have been synthesized and studied. Based on elemental analyses and photometric titrations, the stoichiometry of the complexes was determined to be 1:1 for all three complexes. The formation constant, molar extinction coefficient and other spectroscopic data have been determined using the Benesi–Hildebrand method and its modifications [169].

A new charge transfer complex, consisting of dihydroxymethyl-di-(2-pyrrolyl)methane and TCNQ, has been designed to high selectively distinguish cysteine from other amino acids in water/organic solvent mixtures through the visual color change from blue to nearly colorless. The excellent system properties make the supramolecular assembly a highly selective colorimetric probe for monitoring cysteine [170].

The formation of CT complexes of paracetamol and a series of quinones (including Vitamin K\(_3\)) has been studied spectrophotometrically in ethanol medium. The vertical ionisation potential of paracetamol and the degrees of charge
transfer of the complexes in their ground state has been estimated from the trends in the charge transfer bands [171].

The molecular association of 9-vinyl-carbazole (CBZ) with three electron acceptors, \( p \)-CHL, \( p \)-FRL, and TCNQ, has been investigated in acetonitrile and in micellar aqueous solution of sodium dodecyl sulfate (SDS). CBZ and \( p \)-FRL form a 1:2 complex in acetonitrile, but in SDS micelles the association is 1:1 due to size restriction and occupancy statistics in the host aggregates. The results of spectral studies indicated that the bimolecular CT complex of CBZ with TCNQ is stabilized in two distinct environments of the SDS micelles providing two separated CT absorption bands [172].

Charge transfer spectra of the \( \pi-\pi \) complexes formed by several aromatic amines and nitrogen heterocycles with acceptor TCNE and \( p \)-CHL were measured in acetonitrile. Density functional theory calculations were carried out to determine the probable geometric structures of the complexes that are responsible for the absorption bands. On the basis of the calculated results, which are in good agreement with experiment, the nature and origins of the CT spectra of the various molecular complexes were clarified [173].

Shao et al. [174] have prepared a new class of supramolecular assembly of non-covalent calix[4]pyrrole-\( p \)-chloranil complex. The formation of the complex is mainly attributed to the charge transfer interactions between calix[4]pyrrole with electron-rich pyrrole rings and the electron-deficient \( p \)-CHL subunit. As
potential colorimetric anion sensors, the charge-transfer aggregation may be used for effective and selective detection of $F^-$ and $H_2PO_4^-$ by means of dramatic visual color changes.

Thermodynamic studies on the charge transfer complexes of sulfadoxine and pyrimethamine with chloranilic acid in 1,4-dioxan have been investigated by spectrophotometric method. The absorption maxima for sulfadoxine and pyrimethamine were observed at 500 and 520 nm, respectively. The high value of equilibrium constants, negative enthalpy and free energy values indicated that the formations of the complexes are very stable and exothermic [175].

The interactions of 5-hydroxy-1,4-naphthoquinone with three nucleobases (thymine, cytosine, adenine) and one nucleoside (guanosine), investigated by cyclic voltammetry in aprotic solvent, showed significant change in the redox behavior of the quinone group. The interactions of 1,4-benzoquinone and 1,4-naphthoquinone were studied to compare with 5-hydroxy-1,4-naphthoquinone and to propose different interaction modes [176].

Novel charge transfer complexes have been formed in the reaction of the interesting powerful electron donor 1,4,7,10,13,16-hexamethyl-1,4,7,10,13,16-hexaazacyclooctadecane with $\sigma$-electron acceptor iodine and $\pi$-acceptors TCNE and TCNQ. Due to the expected powerful electron donation of the donor, the reaction stoichiometries were found to be exceptionally high equal to 1:6, 1:16 and 1:3 for iodine, TCNE and TCNQ complexes, respectively [177].
Charge transfer interactions of perhydroisoquinoline with DDQ, p-CHL and TCNQ in chloroform as a solvent have resulted in stable complexes with a molar ratio of 1:1 (donor:acceptor). Elemental and thermogravimetric analyses, photometric titration, and electronic, infrared, and \(^1\)H NMR spectra were used to give an idea of the CT interaction between donating and accepting sites. The Benesi-Hildebrand method and its modification were used to determine association constant and molar extinction coefficient [178].

Charge transfer complexes of ferrocenes with 1,4-quinone derivatives have been reported by Mochida and co-workers [179]. Deca- and octamethylferrocene complexes with 1,4-naphthoquinone derivatives were prepared and structurally characterized; these were neutral 1:2 complexes with mixed-stack structures. CT energies and phase transitions in these neutral and other ionic complexes were investigated.

Paracetamol is shown to form charge transfer complex with DCINQ in aqueous ethanol media exhibiting the unusual 2:1 (paracetamol:quinone) stoichiometry. The complexation enthalpy and entropy have been estimated from the formation constant determined spectrophotometrically at five different temperatures. The theoretically calculated vertical ionization potential of paracetamol also agrees with reported experimental value [180].

The charge transfer interactions between 3-aminopyrazole, 3,5-dimethylpyrazole, 3-amino-5-methyl-pyrazole, 2-amino-4-methyl-thiazole, 2-amino-5-
methyl-1,3,4-thiadiazole and 2-amino-5,6-dimethyl-1,2,4-triazine with CHA as \(\pi\)-acceptor have been investigated spectrophotometrically in acetonitrile. Job's method of continuous variation, spectrophotometric and conductometric titrations were used to identify the composition of the formed CT-complexes [181].

Bistable complex formation systems consisting of biphenylene and redox-active organic molecules such as \(p\)-CHL and TCNE have been experimentally and theoretically investigated based on an intermolecular interaction which characteristically occurs in the electrogenerated dianions forming a \(\pi-\pi\) type charge transfer complex. The CT interaction between the dianions and the donor was measured as the positive shift of the second reduction potential with increasing concentrations of the donor [182].

Amine-based donor radicals, such as dimethylamino-, diethylamino- and morpholinonitronyl nitroxides, were synthesized and their donor abilities were examined by cyclic voltammetry. Charge transfer complexes of these donor radicals with \(p\)-CHL or DDQ were prepared and their conducting and magnetic properties were examined and discussed [183].

Molecular and electronic structural properties of the hydrogen-bonded complexes of \(p\)-quinone dianions (\(\text{PQ}^{2-}\)) were investigated by electrochemistry and spectroelectrochemistry of PQ in MeCN combined with \textit{ab initio} MO calculations. The HF/6-31G(d) calculation results showed that the structure of \(\text{PQ}^{2-}\) is characterized by a lengthening of the C=O bonds and a benzenoid ring. It was
demonstrated that this situation is due to the strong n-σ CT interaction in the hydrogen bonds [184].

The complex formation of hexamethylenetetratellurafulvalene with 28 kinds of organic electron acceptors yielded 31 CT complexes. The IR and UV-Vis spectra of the complexes were examined to study the ionicity of their ground states in solid. A plot of CT transition energies and the difference of redox potentials indicated that four complexes have a neutral ground state; four other complexes exhibit characteristic features of a fully ionic ground state and other twenty-three complexes having a partially ionic ground state [185].

Chloranilic acid was found to form a CT complex in a 1:1 stoichiometry with moclobemide with a maximum absorption band at 526 nm. A complete, detailed investigation of the complex formed was made with respect to its composition, association constant, molar absorptivity and free energy change. The method has been applied successfully to the analysis of commercially available moclobemide tablets with good recovery and reproducibility [186].

The molecular interactions between haloperidol and droperidol as electron donors and each of iodine, TCNQ, DDQ, TCNE, TNF and p-BRL as acceptors have been investigated spectrophotometrically. Different variables affecting the reaction were studied and optimized [187].

The interaction between triethylamine and chloranil has been studied in different solvents by electronic absorption spectroscopy. The kinetics and
energetics of the electron transfer reaction in chloroform and acetonitrile leading to the formation of chloranil anion radical and subsequently the product, N,N-diethylaminovinyltrichloro-p-benzoquinone have been estimated. The interaction of chloranil with triisopropylamine and tri-n-butylamine leads only to the formation of chloranil anion radical [188].

The interactions of retinol and retinoic acid with two electron acceptors, TCNQ and p-CHL, were studied in an investigation on the ability of Vitamin A to behave as a donor of electrons. Retinol reacts with TCNQ in polar organic solvents with the formation, as judged by spectral studies, of the radical anion of TCNQ. Retinoic acid behaved similarly to retinol in its reactions with TCNQ and p-CHL, but it appeared to be a weaker electron donor than retinol. It was suggested that the ability of Vitamin A to behave as a donor of electrons may be an important aspect of its biochemical mode of action [189].

Molecular complexes of anilines with p-CHL in chloroform have been found to have characteristic charge transfer absorption bands in the visible region. The equilibrium constants have been determined from the intensity measurements of these bands. Some discussions on the geometrical configurations of the charge transfer complexes were also made [190].

In addition to the CT-complexations, formed between different types of donors and quinones, discussed above, many more such systems have also been reported in literature. The other systems wherein different donors which form CT-
complexes with variety of quinones include: substituted anilines [191-193], ferrocenes [194, 195], 2,2´-bipyridine and 1,10-phenanthroline [196], phosphines [197], N,N-dimethyl anilines [198], pyrimidines [199], pyridine N-oxides [200, 201], pyrazole [202] ethy carbamate [203], triphenylphosphine [204], crown ethers [205-209], methylated pyridines [210], methylnaphthalenes [211], drugs [212-218], aromatic hydrocarbons [219-227], phenols [228-230], N,N´-diphenylthiourea [231], ethenyl and ethinyl[2.2]paracyclophanes [232], S-alkyl-N-aryldithiocarbamates [233], Schiff bases [234, 235], 2-mercaptobenzazoles [236], Michler’s hydride [237], thianthrene [238], benzocaine, procaine and lignocaine [239], aminothiazoles [240, 241], arylidene anthranilic acid derivatives [242], benzanilides [243], cobaltocene and decamethylferrocene [244], indenophanes [245], heterocyclic azines [246], piperidine, piprazine and morpholine [247], piperidines [248], aza-aromatics [249], heterocyclic nitrones [250], aliphatic amines [251, 252], metal chlorides [253], stilbenes and styrenes [254], diphenyldiazomethanes [255], heterocyclics [256], tetratolylporphyrin [257] etc.
1.4 AIM AND SCOPE OF THE STUDY

The survey of the literature revealed that an enormous amount of work has been reported on the charge transfer complexes of organic compounds with variety of acceptors. During recent past scientists have focused their attention on such studies, as they are significant in many fields. Although extensive study on the charge transfer interaction of variety of donors with substituted quinones as electron acceptors have been made spectrophotometrically, there seem very few reports so far in literature on such studies involving drugs as donors.

The drug-receptor interaction depends on the rate of encounter of a drug at the receptor site and several chemical forces may result in a temporary binding of the drug to the receptor. Essentially any bond could be involved with the drug-receptor interaction. Covalent bonds would be very tight and practically irreversible. Since by definition the drug-receptor interaction is reversible, covalent bond formation is rather rare except in a rather toxic situation. The reversible behavior can be achieved by ion association or through hydrogen bonding or by other weak interactions like charge transfer interaction, van der Waals’ interactions etc. or possibly a combination of these forces. Hence, the study of charge transfer complexes of drugs would shed some light on the mechanism of drug-receptor interaction in real situation.

The chemical compounds having the quinone structure are widely distributed in the nature. These quinone compounds have various bioactivities and
play important roles in the nature. The study of quinones for their CT-interactions stems from their possible role in biological reactions. Quinones are one of the well-known electron acceptors that give rise to spectacular CT-complexes with a variety of donors. Thus, the mechanism of the interaction of quinones with drugs, in general, is a research topic of significant interest and hence the present study.

The major objectives of the present work, therefore, are to investigate the equilibrium, spectral, kinetic and thermodynamic aspects of the charge transfer interaction of the following systems.

<table>
<thead>
<tr>
<th>Electron donors</th>
<th>Electron acceptors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ketoconazole</td>
<td>( p )-Chloranil</td>
</tr>
<tr>
<td>Oxatomide</td>
<td>( p )-Chloranil</td>
</tr>
<tr>
<td>Trimethoprim</td>
<td>( p )-Chloranil</td>
</tr>
<tr>
<td>Iron(II) Phthalocyanine</td>
<td>( p )-Chloranil</td>
</tr>
<tr>
<td>Iron(III) Phthalocyanine</td>
<td>( p )-Chloranil</td>
</tr>
<tr>
<td>Azacyclonol</td>
<td>( p )-Chloranil &amp;</td>
</tr>
<tr>
<td></td>
<td>Two series of novel substituted</td>
</tr>
<tr>
<td></td>
<td>1,4-benzoquinones</td>
</tr>
<tr>
<td>Cimetidine</td>
<td>( p )-Chloranil &amp;</td>
</tr>
<tr>
<td></td>
<td>Two series of novel substituted</td>
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<tr>
<td></td>
<td>1,4-benzoquinones</td>
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</tbody>
</table>

Various spectral techniques such as electronic, emission, FT-IR, LC-MS, \(^1\)H NMR, elemental analysis etc. were used to characterize the interaction between the chosen drugs with these acceptors. The physico-chemical parameters like
formation constant, association constant, ionization potential, oscillator strength, dipole moment, dissociation energy etc. of the CT-complexes formed were determined and discussed. The ionization potentials of the donors determined experimentally were compared with that computed theoretically. As the activity of drugs dependent on their physicochemical properties, investigation of such properties of drug molecules is of important in real pharmacokinetics. An attempt was also made to study the effect of solvent on these interactions for which solvents possessing a wide range of relative permittivity have been employed.

Though these chosen substituted 1,4-benzoquinones are known to synthetic organic chemists as intermediates, to the best of our knowledge this is the first systematic investigation on the charge transfer complexes of these quinones as electron acceptors in both aqueous and non-aqueous solvents. In the frame of Density Functional Theory we have also performed the complete optimization of the geometry for these quinones and donors. Attempts have also been made to correlate the experimentally observed formation constants with theoretically computed HOMO-LUMO energy gaps.

The salient features of the study are presented and discussed in the forthcoming pages.