Summary

The present thesis include the investigation of the CT complexes which are formed between schiff bases of pyridine, Quinolin and Indolyl derivatives as donors and p-Benzoquinone derivatives as acceptors; it contains five chapters:-

* The first chapter includes the introduction which deals with the chemistry of the molecular compound, classification of electron donors, acceptors and complexes formed from them. This chapter also includes a literature survey of the subjects camed out by previous authors on charge-transfer complexes of p-benzoquinone derivatives.

* In chapter II, the experimental details for the preparation of the schiff bases derived from aromatic aldehydes and amino pyridine amino quinaldine as well as sane aramatic amines and indolyl aldehyde are given. Also the preparation of some halogenated p-Benzoquinones derivatives and their charge-transfer complexes. are included. The working procedures for spectral measurements are as well described, the spectral methods comprise Infrared, ultra violet-visible and proton magnetic resonance. The conductometric titration and elemental analysis are also in cluded.

* The third chapter is devoted to the results and discussion of the work carried on the CT complexes in solution. This chapter is subdivided in to parts, the first post deals with the spectral

behaviour of the CT complexes in different organic solvents; the change in the position of the CT band for different organic solvents are interpreted according to the macroscopic polarity parameters viz dielectric and refractive index the values of λ_{max} of CT band in different solvents are plotted against the dielectric constant and the refractive index, the plots indicate that such parameters affecting on the shift of the band. The secand part includes the determination of the stiochiometry of the charge-transfer complexes so formed by molar ratio (spectrophotometrically) and conductometric titration, the results indicate the formation of 1:1 and 1:2 types of complexes. Confirmation of such conclusion was based on the performance of elemental analysis (C,H,N and X %) for these complexes.

The equilibrium studies are discussed in the theired part the equilibrium constant, molar extinction coefficient, oscillator strength of CT band, transition dipole moment and free energy changes are calculated and depicted in Table (   ).

Chapter IV compases the studies of the solid CT complexes using measurements.

The IR results show that the γ_{CH} bands of the benzal ring display a shift to lower wave numbers whereas thase of the hetero ring display an appasit shift this indicates an intermolecular electron transfer from the hetero to the benzal ring. The presence of substituents on the benzal ring show an interesting effect on the position of the C-H out of plan and deformation (γ_{CH}) of the azomethine -CH=N-; electron with drowing substituents shifts the bands position to lower wavemumbers, while electron donating substituents cause an opposite shift. The acceptors are classified inte acidic and nonacidic ones which has a pronounced on the nature of the CT complex formed. From the results obtained, it was noticed that the acceptor bands disploy a shift to lower wavenumbers where as thase of the donors display a counter shift. Such a behaviour is a criterion for $\pi - \pi^*$ electron transfer of the type ($D_{HOMO} \longrightarrow A_{LÚMO}$). The acidic acceptors exhibit proton transfer interactions, whereby a proton from the acidic centre of the acceptor is located on the basic centre of the donor with the subsequent formation of the $^{+}$N-H group. Such interaction leads to the appearance of a group of bands within the wave number rang 2900 - 2400 cm^{-1} in the IR spectra of the complexes. A substantial support for the results obtained from the ir spectra is gained by considering the changes of the ^{1}H NMR spectra of some molecular complexes under investigation in comparison to thase of their constituents.

As a matter of fact the signal due to the aromatic protons of the donor sarts are shifted down fields while thase of the acceptor parts exhibit a reverse displacement. Such shifts indicate the decreased shielding effect on the proton of the donor ring and its increase on those of the acceptor which results from the intermolecular $\pi - \pi^*$ interaction.

The uv-vis absorption spectra of the prepared complexes were obtained using the Nujol mull technique, the spectra reveal the presence of a new band at the longer wavelength region which was not observed in the spectra of either the free donor or free acceptor molecules. Such band is assigned to the ($D_{HOMO} \longrightarrow A_{LUMO}$) $\pi - \pi^*$ CT interaction. The other band is very brood and of composite nature, this is taken as an indication for the occurance of n- π^* interaction in the complexes. The energies of these CT bands are calculated and their values compared with those obtained experimently, the two sites of values were concordance witheachother to a satesfactary extent .

The ionization potentials of the donors and the electron affinity of acceptor (IDL) are colculated using the Breigleb equation:-

$$E_{CT} = Ip - (E_A + C).$$

Chapter V comprises the general discussion, summary and References.