SUMMARY

This thesis comprises three chapters:-

1- The frist chapter include the introduction which deals with the chemistry of the molecular compounds, classification of electron donors, acceptors and complexes formed from them. This chapter also includes a literature survery of the work on charge transfer complexes of aromatic nitro-compounds.

2- The second chapter comprise the details for the experimental work including the preparation of the donors, the acceptors used and the methods for obtaning the solid CT complexes. The different spectroscopic technique and the apparatus applied in these studies are described.

3- The third chapter is devoted to the results and discussion of the work carried out on the CT complexes included in the thesis.

The infrared absorption spectra of the CT complexes under investigation are recorded in the solid state as KBr discs, the bands of diagnostic importance are reported. The results show that the γ_{CH} bands of the acceptors display generally a shift to lower wvaenumbers where as those of the donor display an opposite shift, which is characteristic of charge

transfer of the $\pi-\pi^*$ type.

The ir spectra of charge transfer complexes with acidic acceptors (I, II, III and IV) are characterized by a group of bands within the 2400-3000 cm^{-1} range corresponding to the stretching modes of a proton attached to a positive quaternary nitrogen of the group $(H-\overset{+}{N}\Rightarrow)$ which is formed through the transfer of a proton from the acidic center of the acceptor to basic one of the donor.

The symmetric NO_2 bandes in the CT complexes become more broader and show some splitting indicating higher differentation in their energy states. The higher energy asymmetric NO_2 band is either shifted to higher wavenumber or remains at the same position which may be due to $n-\pi^*$ interaction. A substantial support for the results obtained from the ir spectra is gained by considering the changes of the NMR spectra of some molecular complexes under investigation in comparison to those of their constituents. As a matter of fact the signal due to the aromatic protons of the donor parts are shifted downfields while those of the acceptors parts exhibit a reverse displacement. Such shifts are due to the decreased electron density on the ring and its increase on the acceptor ones which results from the intermolecular $\pi-\pi^*$ interaction.

Then in the CT complexes the protons of the donor part are less shielded than in the free donor molecule. On the other hand the protons of the acceptor part are more shielded compared to those of the free acceptor.

The U.V and visible absorption spectra of the charge transfer complexes are recorded using the Nujal mull technique. The electronic absorption spectra of all CT complexes under investigation display only one CT band, which can be assigned to $\pi - \pi^*$ CT interaction. The appearance of one band denotes that no $\pi - \pi^*$ interaction is liable to occure. This is further substituted by calculating the energy of the CT interaction (E_{CT}) using the relation given by Briegleb:-

$$E_{CT} = I_p - (E_A + C)^{\#}$$

The electron affinities of some acceptors are determined from the values of E_{CT}. A plot of E_{CT} as a function of I_p is a more or less linear relation. The value of E_A determined from this plot is comparable to that obtained from Briegleb equation.

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where C is the colomic factor.