spectroscopic studies of charge transfer complexes from ji- donors containing heterocyclic ring and electronic acceptors of the nitrogenene derivatives

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This thesis comprisesthree chapters:-1- The frist chapter include the introduction whichdeals with the chemistry of the molecular compounds,classification of electron donors, acceptors andcomplexes formed from them. This chapter alsoincludes a -literature survery of the work on chargetransfer complexes of aromatic nitro compounds.2- The second chapter comprise the details for theexperimental work including the preparation ofthe donors, the acceptors used and the methodsfor obtaning the solidspectroscopic techniqueCT complexes. The differentand the apparatus appliedin these studies are described.3- The third chapter is devoted to the results anddiscussion of the work carried out on the CT complexesincluded in the thesis.The infrared absorption spectra of the CT complexesunder investigation are recorded in the solid stateas KBr discs, the bands of diagnostic importanceare reported. The results show that the YCH bandsof the acceptors display generally a shift to lowerwvaenumbers where as thgse of the donor display anopposite shift, which is characteristic of charge1transfer of the 11 - 11* type.The ir spectra of charge transfer complexes withacidic acceptors (I. II. III and IV) are characterizedby a group of bands within the 2400-3000 -1 cm rangecorresponding to the stretching mod~of a proton attachedto a positive quaternary nitrogen of the group(H-N ~ which is formed through the transfer of a protonIfrom the acidic center of the acceptor to basic oneof the donor.The symmetric N02 bande s in the CT complexesbecome more broader and show some splitting indicatinghigher differentation in their energy states. Thehigher energy asymmetric N02 band is either shiftedto higher wavenumber or remains at the same positionwhich may be due to n- 11* interaction. A substantialsupport for the results obtained from the ir spectrais gained by considering the changes of the NMR spectraof some molecular complexes under investigation incomparison to those of their constituents. As a matterof fact the signal due to the aromatic protons ofthe donor parts are shifted downfields while thoseof the acceptors parts exhibit a reverse displacement.Such shifts are due to the decreased electron densityon the ring and itswhich results from theincrease on the acceptor onesintermolecular 11 -11 * interaction.Then in the CT complexes the protons of the donorpart are less shielded than in the free donor molecule.On the other hand the protons of the acceptor partare more shielded compared to those of the free acceptonThe U.V and visible absorption spectra of thecharge transfer complexes are recorded using the Nujalmull technique. The electronic absorption spectraone CT band, which can be assigned toof all CT complexes under investigation display only* CT interaction.The appearance of one band denotes that now-w * interaction is liable to occur-e • This is furthersubstituted by calculating the energy of the CT interaction(ECT) using the relation given by Briegleb:-The electron affinities of some acceptors are determinedfrom the values of ECT· A plot of ECT as a functionof Ip is a more or less linear relation. Thevalue of EA determined from this plot is comparableto that obtained from Briegleb equation.# where C is the colomic factor.