Introduction
CHAPTER I

INTRODUCTION

The electronic spectra of benzene and its derivatives has been the subject of numerous experimental and theoretical studies. These include absorption and emission measurements of these compounds both in the vapour phase and in the solution phase in different solvents. Most of the studies are performed in UV and visible region although recently data are available in the vacuum ultra violet range also. A number of review articles are available in which information concerning position and intensities of some of the lower energy bands is tabulated. It is now well known that substitution in benzene leads to modification of its lower energy bands both in position and intensity. In some cases the positions of the bands are also reversed on substitution. The shifts in the band positions depend on the nature and place of substituents in the benzene ring and several empirical correlations have been proposed. Qualitatively these shifts have been explained in terms of inductive and mesomeric effects of the substituents. Correlations have also been proposed between band shifts and Hammett, Taft constants. In some molecules the substituent has its own π-electron system which can conjugate with the π-electrons of benzene or it has other local excitations of its own. Spectra of such molecules consist of benzenoid and substituent bands (local Excitations) which depending on the
nature of interactions between the two parts of the molecule results into considerable modification of benzene spectrum. If the substituent is a strong donor (e.g., OH or NH₂) or a strong acceptor (e.g., NO₂) there may be charge transfer to or from the benzene ring and such transitions take place with large increase in dipole moment. In the disubstituted benzenes the two substituents may be weak donors, weak acceptors, strong donors, strong acceptors or one of these may be strong/weak donor and other may be strong/weak acceptor. The variety is further enriched by the usual geometrical isomerism (o, m, p) of the disubstituted benzenes. It is not always easy to characterize the various low energy bands in electronic spectra of such molecules. Experimental studies like solvent effect, fluorescence and phosphorescence, lifetime measurements, photoelectron spectroscopy etc. do help but the assignment is not always unambiguous.

A number of attempts have been made to understand the spectra of these compounds on theoretical basis. Such studies range from ab-initio calculations through semi-empirical methods to simple model calculations. In view of the large computer time required for the ab-initio calculations recourse has been taken to the CNDO/S-CI (semi empirical) method developed by Del Bene and Jaffe which has been found to be most practical. The calculations by this method for a number of disubstituted benzenes have been used successfully for correlation with the experimental results.
The present study is concerned with the experimental and theoretical studies of the electronic spectra of a series of disubstituted benzenes (A-Φ-B) and to find out how the donor and acceptor properties of A and B effect the benzene spectrum. The groups A and B have been so chosen that in some cases their electron donating or accepting power may be changed by protonation or deprotonation. Therefore spectral studies have been made under controlled conditions of pH for such compounds, so that wherever possible the spectra of the anion/cation/zwitter ion of the parent molecule can be obtained. The choice of A and B have been made in such a way that many of these groups possess n electrons also and hence the spectra of AΦB have been further enriched by the nπ* transitions and some local π-π* transitions. It is also one of the aims of the present study to find out how the rm* transitions due to substituent are affected by the nature and position (o,m,p) of the other substituent. The experimental measurements here include supplementing of the existing data regarding absorption and emission spectra of the following set of molecules over a range of experimental conditions.

I. o,m,p-Amino Phenols
II. o,m,p-Nitro Phenols
III. o,m,p-Fluoro Benzoic Acids
IV. o,m,p-Hydroxy Benzoic Acids
V. o,m,p-Amino Benzoic Acids

The effect of solvent has also been studied for these molecules.
The theoretical spectra of the above molecules (including their anions, cations and zwitter ions wherever possible) have been calculated by the CNDO/S-CI method developed by Del Bene and Jaffe. The wave functions have been used to find the charge densities in the ground and the excited states. These have been used for calculating the dipole moments in the ground and excited states. Experimental and theoretical results have been compared and discussed.