Chapter Seven

An Overview
In this chapter, an overall summary of the investigations described in the previous chapters is presented. The correlation of structure-activity in organic molecules is a problem of fundamental importance (Sect. 1.1). With the advent of fast and efficient computers the quantum chemical methods employed for describing these molecules at the electronic level are fast coming up (Sect. 1.2). The usefulness of these quantum chemical methods are amply illustrated by the multifarious applications surveyed in Sections 1.3, 1.4, 1.5, and 1.6.

The main aim of the present investigation is to study the electronic structure, spectra and reactivity of some interesting organic molecules. In fact, it is a result-oriented work employing some standard and modified computer calculations without any recourse to changes in the framework of the rigorous theory for the sake of refinements.

Methods Employed

Molecular Orbital techniques suitable for studying the detailed electronic structures of organic molecules are briefly described in Chapter two. In the present investigation Pople's well-known CNDO/2 method is used for
electronic structural calculations (Sect. 2.3.2. A). For the spectral studies, the conventional PPP and a modified PPP method, based on CNDO/2 results, developed by the author are employed (Sects. 2.2.5. C and 2.2.5. D). The molecular electronic indices obtained from the CNDO/2 calculations are correlated with the experimental rate and activation energy values by using a computer plotting technique, again standardised by the author (Sect. 5.2). All the computer calculations are carried out on a DEC-1090 computer system.

Results at a Glance

1) **Electronic Structure**

Chapter three and five exclusively involves the applications of the CNDO/2 method on substituted phenols and substituted alkenes. For the CNDO/2 method, the standard program available in Pople’s book is employed. Geometries of the molecules used for these calculations are all based on either recent X-ray or structure reports.

In Chapter three, three series of substituted phenols (nitrophenols, cresols and hydroxybenzoic acids)
and their parent molecules (phenol, nitrobenzene, toluene, benzoic acid, and benzoate ion) are subjected to molecular orbital calculations. The results are employed to obtain a quantitative picture of the effect of substituent on a skeletal phenyl ring, especially in these cases where there are more than one substituent group present. The electron population data faithfully represent the usual qualitative orienting effects of any particular group attached to the phenyl ring (Sects. 3.3.1, 3.3.2, and 3.3.3). The charged substituent group, $-\text{COO}^-$, in benzoate ion appears to polarise the entire pi-system. And this polarisation effect dominates over any contribution from the pi-inductive and mesomeric effects (Sect. 3.3.3. B). There is a very good similarity between the present CNDO/2 and some of the available ab initio results. A good agreement between calculated and experimental dipole moments is yet another feature to be noted.

In Chapter five, a variety of substituted ethylenes (classified into four) are subjected to the all-electron CNDO/2 calculations. The electron population data in alkenes too indicate that, as in the case of aromatic molecules (Chapter three), the present CNDO/2 results justify completely the well-known substituent effects of the
various groups attached to the double bond (Sects. 5.3.1, 5.3.2, 5.3.3, and 5.3.4). It is to note that the substituent effect as reflected in the values of the derived molecular indices like the total pi-electron density, pi-charges, and pi-bond order, changes according to the substituents attached to the double bond. The electron withdrawing effect of ester groups are more predominant than that due to amide groups. Here also charged groups like -COO(-) is found to polarise the entire pi-system (Sects. 5.3.1, 5.3.3, and 5.3.4). Based on the CNDO/2 results, certain molecular indices capable of reproducing the properties of the double bond are derived. Employing these molecular indices, certain correlations are achieved within different sets of molecules studied using a computer plotting technique, either signifying the class property of a particular molecule or otherwise. In most of these molecules, the total pi-electron density at the double bond and pi-bond order are found to be the most useful molecular indices. Dipole moments also were computed for these types of molecules. However, many of these values could not be compared with those of the experimental ones, as they were not available in the literature. But, there is a fairly good agreement between those reported and calculated values.
2) **Electronic Spectra**

Three series of disubstituted phenols, namely, nitrophenols, cresols and hydroxybenzoic acids are subjected to both conventional and modified PPP CI calculations. Unlike the conventional PPP method, the modified PPP calculations developed by the author, in most of the cases, justify the experimental electronic spectra of disubstituted phenols more accurately (Sects. 4.4.1, 4.4.2, and 4.4.3). In the light of the configuration interaction studies, the observed transition energies are reasonably assigned. Considering the overall results, it is found that nitro- and carboxylate groups (as present in nitrophenols and hydroxybenzoic acids) perturb considerably the electronic spectra of the parent molecule phenol. But the 'pseudo unsaturated' methyl group is found to be less effective in this regard.

3) **Reactivity of the Alkenes**

The CND0/2 based molecular orbital indices developed and discussed in Chapter five for a variety of mono- and disubstituted alkenes are successfully employed in Chapter six, to substantiate some experimental kinetic results of halogen addition to alkenes (Sect. 6.4).
theoretical results could correctly portray most of the experimental data, viz., rates and activation energies. In the light of the correlations (by means of a computer plotting technique) arrived at and other factors, some refinements in the general mechanism of halogen addition to alkenes are suggested. In this respect the quantum chemical calculations can serve as an alternative to the Hammett's type of formulations.

Conclusion

The overall results and observations in the present study indicate that the detailed studies of electronic structures of molecules can, in general, be of great importance in understanding the behaviour of systems under study, be it microscopic or macroscopic.

Moreover, these methods could be extended to the study of aggregates of molecules, polymers, surfaces, and even solids, so that the structure-activity correlations in the most general sense of the term 'activity', meaning the physical, chemical, biological and solid state properties, could be envisaged.
At present any application of quantum chemical methods involves a consideration of their reliability, generality, and sensitivity to changes in the systems. It is suggested here that the semi-empirical MO methods be not merely looked upon as approximate procedures of calculations necessitated by the difficulty in computations, but be treated as a basic approach to tackling the problem of incorporating the environmental effects and experimental conditions into the theoretical treatment, which are clearly outside the scope of the *ab initio* method. It may be expected that in the coming years the evolution of quantum chemical methods; especially the semi-empirical techniques, will have to make a rapid progress in order to cope up with the explosive accumulation of accurate experimental data which are becoming available in diverse and expanding areas of chemical, physical and biological sciences.

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Publications:

1. Structure, Spectra and Reactivity of Nitrophenols.
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2. Cresols - An Investigation into their Electronic
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K.P. Krishnan Namboodiri, S. Viswanathan, R. Ganesan
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3. Electronic Structure, Spectra and Reactivity of
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5. Structure and Reactivity of Monosubstituted Alkenes (to be communicated).


7. Substituent Effect in Alkene Systems (to be communicated).

References: Furnished upon request

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