MOLECULAR ORBITAL CALCULATIONS ON SOME METALLOPORPHYRINS AND RELATED SYSTEMS

Abstract

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A THESIS
SUBMITTED IN FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

To

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FEBRUARY, 1985

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I certify that the thesis entitled " MOLECULAR ORBITAL CALCULATIONS ON SOME METALLOPORPHYRINS AND RELATED SYSTEMS " submitted by Mr. Kaushik Kumar Bhattacharjee for the degree of Doctor of Philosophy of the North - Eastern Hill University , Shillong , embodies the record of original investigation carried out by him under my supervision. He has been duly registered and the thesis presented is worthy of being considered for the award of the Ph.D. Degree . This work has not been submitted for any Degree of any other University.

Date : 20.2.85
Place : Shillong

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ABSTRACT

The scope of the thesis is to find rational explanations for some of the observed physicochemical data on metalloporphyrins and related systems, using semi empirical molecular orbital calculations. The thesis consists of four chapters and an appendix.

In the first chapter a brief review is presented on the status of molecular orbital calculations on porphyrins. Emphasis is laid on the literature that has appeared during the past eight years. A comparative evaluation is made on the various methods used for theoretical calculations, based on how well the results of these calculations explain the experimental data. Extended Huckel approach (EHT) and Pariser-Parr-Pople π-electron approach (PPP) have serious limitations. In many situations, the correct ground state is not obtained with these methods. Semi empirical all valence electron methods like CNDO/2, CNDO/3S, INDO are more promising, but the multiplicity of the approach is discouraging the theoretical chemists and it is difficult to choose among the plethora of various modifications of CNDO/2 and INDO formalisms. SCF-X-α approach and ab initio calculations have yielded good results. There are still many problems regarding the physicochemical aspects of porphyrins which deserve, the attention of theoretical chemists. Some of these are mentioned at the end of Chapter I.

One of the intriguing problems in porphyrins is that the redox potentials of metalloporphyrins are very sensitive to the nature of the metal ion but the optical spectra are relatively independent of the metal ion. This aspect has been dealt with in Chapter II. The influence of the effective nuclear charge of the metal ion on the π energy levels of porphyrins is estimated using SCF perturbation theory. CNDO/2 and PPP wave functions of porphine dianion are used as zeroeth order functions. The first order changes in the orbital energies of porphine dianion have been estimated as a function of the perturbing positive charge. The energy levels obtained by this coulombic perturbation are corrected with the observed ionisation potential and redox potential data. The calculations have indicated that the effective nuclear charges of the metal ions in the metalloporphyrins varying from Mg(II) porphyrin to Sn(IV) porphyrin are in the range 1-1.6. The variation in the charges in this range is enough to change the oxidation potentials considerably; but the excitation energies in this range are not affected much.

Many of the tetrapyrrole systems which have biological relevance and are related to porphyrins have not been investigated by semi empirical all valence electron methods or ab initio methods. Some of these systems have been investigated in this thesis using CNDO/2 approach. Comparison of the chemical reactivities of these systems is made with that of porphyrin. In Chapter III, CNDO/2 calculations on phlorin trianion is presented. The CNDO/2 energy levels are compared with those of porphine dianion. Good agreement is obtained with observed trends in the redox potentials. The reactivity parameters, namely frontier electron densities and superdelocalisabilities have bee estimated for various positions in the molecule. The reactivity parameters show good agreement with the observed experimental data.

In Chapter IV CNDO/2 calculations are presented for corrole and tetradehydrocorrin. These systems are related to vitamin B_{12}. The energy levels are checked with the trends in the redox potential data. The observed electrophilic and nucleophilic reactions of these molecules are rationalised in terms of the reactivity parameters.

The listings of two computer programmes are presented in the Appendix. These programmes are used to perform SCF perturbation calculations using CNDO/2 or PPP data for the zeroeth order level. The computer programmes are written in Fortran IV language.
