QUANTUM CHEMICAL STUDIES OF QUADRATIC POTENTIAL FUNCTIONS USING CNDO/FORCE METHOD AND COMPLIANCE CONSTANT FORMALISM

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A thesis submitted to the
Indian Institute of Technology, Delhi
for the award of the Degree of
DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, DELHI
1982

CERTIFICATE

This is to certify that the thesis entitled "Quantum Chemical Studies of Quadratic Potential Functions using CNDO/Force Method and Compliance Constant Formalism", being submitted by Shoba Ranganathan, to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by her. Mrs. Shoba Ranganathan has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted, in part or in full, to any other University or Institute for the award of any degree or diploma.

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ACKNOWLEDGEMENTS

I would like to place on record my deep sense of gratitude to Dr. A.S.N. Murthy, Assistant Professor, for his invaluable help and guidance throughout the course of these studies. I thank the Head, Department of Chemistry, for giving me the opportunity to carry out this research work.

I am thankful to Dr. Latha Surendra for useful discussions. I am indebted to Dr.T.K.K. Srinivasan, IIT, Madras for providing me with an important computer program.

The assistance provided by the Computer Centre, IIT, Delhi and the Fellowship awarded by the NCERT, New Delhi are sincerely acknowledged.

I am grateful to Mr. T.S.R. Iyer for carefully preparing the manuscript and to Miss Neelam for typing the mathematical portions.

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ABSTRACT

The potential functions of a few representative molecules and donor-acceptor systems have been obtained by a combined use of a semiempirical quantum chemical (CNDO/ Force) and compliance constant methods. The compliance constant formalism has recently been found to be advantageous over the conventional force constant approach in determining quadratic potential functions as the transferability of compliance constants among related chemical systems is more valid than that of force constants.

The combined CNDO/F and compliance constant methods have initially been applied successfully to a few simple test cases such as water, ammonia and methane. Subsequently, the method has been applied to formaldehyde, acetaldehyde, acetone, carbonyl fluoride, formyl fluoride, formamide, formic acid and carbon suboxide. The carbonyl compliant constants have been linearly related with Taft's substituent constants.

This approach has also been found to be highly satisfactory in predicting the frequency shifts and new vibrational transitions in the vibrational spectra of systems involving ion-molecule interactions. Also, the changes in the vibrational spectra due to hydrogen bond formation in water dimer and formic acid dimer have been well predicted.

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