TABLE OF CONTENTS

DECLARATION BY THE SCHOLAR
SUPERVISOR’S CERTIFICATE
ACKNOWLEDGEMENT

Synopsis i

LIST OF ACRONYMS & ABBREVIATIONS iii
LIST OF SYMBOLS v
LIST OF FIGURES vi
LIST OF TABLES viii
LIST OF PUBLICATIONS ix

CHAPTER 1

INTRODUCTION 1
1.1 INTRODUCTION 1
1.2 COMPUTATIONAL METHODS TO STUDY THE CHEMICAL SYSTEMS 2
  1.2.1 AB-INITIO METHODS 2
  1.2.2 SEMI-EMPIRICAL METHODS 9
  1.2.3 MOLECULAR MECHANICS 11
1.3 APPLICATION OF COMPUTATIONAL CHEMISTRY 12
1.3.1 VIBRATIONAL SPECTROSCOPY ANALYSIS 12
1.3.2 HYPERPOLARIZABILITY AND NONLINEAR OPTICAL BEHAVIOR 16

CHAPTER 2

THEORETICAL ASPECTS 18

2.1 INTRODUCTION 18

2.2 AB-INITIO METHODS 18

2.2.1 THE BORN-OPPENHEIMER APPROXIMATION 19
2.2.2 VALENCE BOND THEORY 20
2.2.3 MOLECULAR ORBITAL THEORY 21
2.2.4 HARTREE-FOCK APPROXIMATION 24

2.3 DENSITY FUNCTIONAL THEORY 25

2.3.1 THE HOHENBERG-KOHN THEOREMS 25
2.3.2 THE KOHN-SHAM EQUATIONS 27
2.3.3 EXCHANGE CORRELATION ENERGY FUNCTIONALS 29
2.3.4 TIME-DEPENDENT DENSITY FUNCTIONAL THEORY (TDDFT) 33

2.4 BASIS SET 34

2.4.1 SLATER TYPE ORBITALS 35
2.4.2 GAUSSIAN TYPE ORBITALS 35
2.4.3 CLASSIFICATION OF BASIS SETS 36

CHAPTER 3

MOLECULAR STRUCTURE AND VIBRATIONAL ANALYSIS OF 2-AMINO- 5-(m-NITROPHENYL)-1, 3, 4-THIADIAZOLE BY DFT CALCULATIONS 39

3.1 INTRODUCTION 39
3.2 COMPUTATIONAL DETAILS
3.3 RESULTS AND DISCUSSION

3.3.1 GEOMETRY OPTIMIZATION
3.3.2 POTENTIAL ENERGY SCAN STUDIES
3.3.3 NATURAL BOND ORBITAL ANALYSIS
3.3.4 MOLECULAR ELECTROSTATIC POTENTIAL
3.3.5 HOMO-LUMO ANALYSIS
3.3.6 VIBRATIONAL SPECTRAL ANALYSIS

3.4 CONCLUSIONS

CHAPTER 4
VIBRATIONAL SPECTRAL ANALYSIS AND NONLINEAR OPTICAL BEHAVIOR STUDIES ON 3-(3,4-DIMETHOXYPHENYL)-1-(PYRIDINE-2-YL)PROP-2-en-1-one

4.1 INTRODUCTION
4.2 EXPERIMENTAL

4.4.1 CRYSTAL GROWTH
4.4.2 SPECTRAL MEASUREMENT

4.3 COMPUTATIONAL DETAILS
4.4 RESULTS AND DISCUSSION

4.4.1 GEOMETRY OPTIMIZATION
4.4.2 CONFORMATIONAL ANALYSIS
4.4.3 NATURAL BOND ANALYSIS
4.4.4 VIBRATIONAL ASSIGNMENTS
4.4.5 FIRST HYPERPOLARIZABILITY CALCULATION
4.4.6 MOLECULAR ELECTROSTATIC POTENTIAL
4.4.7 FRONTIER ORBITAL ANALYSIS

4.5 CONCLUSION

CHAPTER 5

QUANTUM CHEMICAL COMPUTATION BY DFT APPLICATION OF NLO MOLECULE 2-AMINO PYRIDINIUM p-TOLUENESULFONATE

5.1 INTRODUCTION

5.2 COMPUTATIONAL DETAILS

5.3 RESULTS AND DISCUSSION

5.3.1 GEOMETRY OPTIMIZATION

5.3.2 MOLECULAR ELECTROSTATIC POTENTIAL

5.3.3 NATURAL BOND ANALYSIS

5.3.4 VIBRATIONAL ASSIGNMENTS

5.3.5 NONLINEAR OPTICAL BEHAVIOR

5.3.6 FRONTIER ORBITAL ANALYSIS

5.3.7 UV-VISIBLE SPECTRUM

5.3.8 THERMODYNAMIC PROPERTIES

5.3.9 MULLIKEN ATOMIC CHARGE DISTRIBUTION

5.4 CONCLUSIONS

CHAPTER 6

A THEORITICAL STRUCTURAL INVESTIGATION OF NLO MOLECULE 1-[4-(METHYLSULFANYL) PHENYL]-3-(4-NITROPHENYL) PROP-2-EN-1-ONE

6.1 INTRODUCTION

6.2 COMPUTATIONAL DETAILS
6.3 RESULTS AND DISCUSSION

6.3.1 GEOMETRY OPTIMIZATION

6.3.2 POTENTIAL ENERGY SCAN STUDIES

6.3.3 MOLECULAR ELECTROSTATIC POTENTIAL

6.3.4 NATURAL BOND ANALYSIS

6.3.5 VIBRATIONAL ASSIGNMENTS

6.3.6 NONLINEAR OPTICAL BEHAVIOR

6.3.7 UV-VIS SPECTRUM AND HOMO-LUMO ANALYSIS

6.3.8 THERMODYNAMIC PROPERTIES

6.3.9 MULLIKEN ATOMIC CHARGE DISTRIBUTION

6.4 CONCLUSION

CHAPTER 7

CONCLUSION AND FUTURE SCOPE

7.1 CONCLUSION

7.2 FUTURE SCOPE

REFERENCES