INTRODUCTION

Somewhat less questions has been answered about weak interactions. The small effects of this weak interactions are close to the experimental deficiencies. The difference between the interacting system and the reference model is to small to distinguish them, or the given quantitativ data have higher deficiency. Due to the developments of computer technics the theoretical methods play an increasing role in researches on molecular structures and other chemical-physical properties, providing reliable data useful as additional information for investigation of experimental results, or provide as accurate as, or more accurate data than the experimental methods in suitably smaller molecular systems.

The experimental methods usually determine the global minimum structure of a molecule, while the quantum chemistry is well suited to scan the complete potential energy surface, investigating among others the electronic structure of bonds or weak interactions, the conformational analysis, molecule-dynamics.

The aims of my work:

– Structural investigation of weak interaction systems based on quantum chemical calculations.
– Structural and vibrational analysis of intramolecular hydrogen bonded systems.

In this thesis the results of systematic study of structural, vibrational and bond characteristics of various hydrogen bonded systems is presented. The characteristics of intra- and intermolecular, strong and weak hydrogen bonds and van der Waals interactions have been determined investigating over 30 molecules.
My results are partitioned for five main topics:

1. Structural and vibrational properties of intramolecular hydrogen bonding in orto-substituted fenol derivatives. Characteristic structural effect and hydrogen bonding ability of different acceptor groups were determined by quantum chemical calculations.

2. Structural and vibrational analysis of 4-acetyl-3(5)-amino-5(3)-methylpyrazole is presented. The complex tautomerism and conformational equilibrium of the molecule have been studied by calculations. Using joint theoretical and experimental information the FT-IR and FT-Raman spectra of solid 4-acetyl-3-amino-5-methylpyrazole form have been assigned. Our vibrational analysis based on the computed harmonic force field. The deficiencies of the computed harmonic force field were corrected by selective scale factors according to the scaled quantummechanical method (SQM).

3. The conformational space of dimethylglyoxime have been elucidated at the same way and the vibrational (SQM) analysis of the most stable conformer have been performed.

4. The structural and vibrational characteristics are really different in complex formations of dimethylglyoxime and metal ions. We determined the molecular vibrations of nickel complex. There is not only a coordination interaction between the metal ion and the ligands but a very strong intramolecular hydrogen bond between the two ligands.

5. Hydrogen bonding and van der Waals interaction in formaldehyde derivatives have been analysed on the bases of quantum chemical calculations. Structural, vibrational properties and hyperconjugation effects were presented.

**Theses, results**

**I. STRUCTURAL CHARACTERISTICS OF INTRAMOLECULAR HYDROGEN BONDING IN BENZENE DERIVATIVES**

Structural, vibrational characteristics and energetics of intramolecular hydrogen bonding of some orto-substituted phenol derivatives have been investigated. Various proton acceptor groups (C=N, NO₂, C=O, P=O, F, CF₃) form different type (weak and strong) of hydrogen bonding were chosen.

We present an analysis of the following:

- Energetics of hydrogen bonding

  The calculated energy of hydrogen bond between the phenolic OH group and different acceptors are ranked as follows:

  \[ C=N > NO₂ \sim C=O > P=O \sim F > CF₃ \]

  \[ 35 \text{ kJ/mol} \sim 7 \text{ kJ/mol} \]

- Characteristic changes of geometrical properties of donor and acceptor groups

  The changes of bond lengths in single substituted derivatives are ranked as follows:

  \[ \Delta(O–H): C=N \gg P=O \gg C=O \gg NO₂ \gg F > CF₃ \]

  \[ \Delta(C=O): C=N > P=O \sim C=O \gg NO₂ \gg F > CF₃ \]

  \[ \Delta(B–Y): CF₃ \gg F > NO₂ > C=O \sim P=O \gg C=N \]

  \[ \Delta(C–B): C=O \gg C=N > P=O \gg CF₃ \sim NO₂ \]

This nonsystematic variation of the bond lengths shows no close relationship with the hydrogen bonding energy.
– Impacts of hydrogen bond on benzene ring geometry

The changes are most pronounced in 2-phosphinylphenol, while the weakest appears in 2-trifluoromethylphenol. Again, there is no direct correlation with the computed hydrogen bond energies, nor with the geometrical changes of the donor and acceptor groups.

– Vibrational properties

The very small geometrical differences between the nitrophenol derivatives are reflected in the vibrational spectra. There are only marginal effects in the spectral properties of 2-fluorophenol and 2-trifluorophenol pointing to the weak nature of these intramolecular hydrogen bonds.

II. STRUCTURAL AND VIBRATIONAL PROPERTIES OF 4-ACETYL-3(5)-AMINO-5(3)-METHYLPYRAZOLE

Due to the collaboration with Mészáros-Szécsényi to investigate metal complexes formed with this compound the determination of the ligand before was necessary. Our goal was the investigation of tautomerism, structural, conformational and vibrational characteristic.

– Tautomerism, conformation, structure

Our survey of the PES resulted in two stable conformers for each tautomer. The 5-amino-3-methyl tautomer is more stable than the 3-amino-5-methyl form, however, the difference is only 2 kJ/mol at the B3LYP/6-311++G** level of theory. The most stable conformer of each tautomer is the hydrogen bonded form.

– Vibrational analysis

We perform a joint theoretical and experimental analysis of the FT-IR and FT-Raman vibrational spectra of the molecule using the scaled quantum mechanical method. The hydrogen bonding is strengthen the conjugation of the NH2 and C=O groups with the pyrazole ring.

III. STRUCTURE AND MOLECULAR VIBRATIONS OF DIMETHYLGLYOXIME

In spite of the important analytical application and strong complex formation capability of the dimethylglyoxime, our knowledge about its properties is far from being complete. Structural and conformational characteristics, investigation of stabilization interactions, more precise vibrational characterisation of the molecule based on scaled computed force field.
The potential energy surface (PES) of the dimethylglyoxime was elucidated by calculations using B3LYP/6-31+G** level of theory, determined the most stable conformers. In spite of the possible intermolecular hydrogen bonding interaction in several syn conformers, the global minimum on the PES is the anti/trans conformer, found previously in the crystal. The conformation of the molecule is determined by three important interactions, viz. by steric and conjugation effects as well as in a few structures by N(O)…H intramolecular hydrogen bonding.

The vibrational analysis of dimethylglyoxime was performed utilizing a scaled computed B3LYP/6-31G*. With the help of this technique we were able to complete the assignment of the vibrational spectra of the compound.

IV. BIS(DIMETHYLGLYOXIMATO) NICKEL(II) COMPLEX

The interesting about this complex from a structural point of view: beside the donor-acceptor interaction with the metal the two anion ligands are connected by a pair of very strong intramolecular hydrogen bonds. Our goal was the investigation of the complete vibrational analysis based on quantum chemical calculations and FT-IR, FT-Raman spectra.

V. BLUE-SHIFTING C–H···Y (Y=O, HALOGEN) HYDROGEN BONDS IN THE DIMERS OF FORMALDEHYDE DERIVATIVES

The blue-shifting types of hydrogen bonds is really different in its characteristics from classical form. Due to the contraction of X–H bond (increasing in classical type) there is a blue shifting of XH stretching frequency (νXH).

Our goal was the investigation of the weak interactions in the dimers of formaldehyde derivatives {(CHOY)2, Y=H, CH3, F, Cl, Br, I}. Halogen substituents on the formaldehyde skeleton represent a second proton acceptor in the molecular system giving rise to a more complex PES, i.e. to additional dimer structures possessing CH···halogen interactions. The characteristics determined by MP2/6-311++G** calculations as follows:

- dimerization energy
- geometrical characteristics
- charges
- vibrational frequencies

Two of eight different dimer structures

optimized for this level. Based on the present scaled quantum mechanical force field 45 of 87 fundamentals of the molecule have been assigned.
Conclusion:
– Eight minima have been found on the PES. Interactions are weak, the dimerization energies are low (9-17 kJ/mol).
– The computations revealed the importance of dispersion forces in the dimer formation, while only a lesser role of the weak intermolecular hydrogen bonding was found.
– The most characteristic geometrical property of the dimers is the shortening of the C–H bond. This is the reason of blue shifting of the vibrational frequencies.
– A natural bond orbital analysis pointed to a slight decrease in the population of the contacting $\sigma_{CH}^*$ orbitals and alterations in the intramolecular charge-transfer effects as the primary reason of the C–H contraction.

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PUBLICATIONS RELATED TO THE THESES:


PRESENTATIONS AND POSTERS RELATED TO THE THESES:

OTHER PUBLICATIONS:


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