

# Vibrational and quantum chemical investigation of weak interactions

Ph.D. theses

Andrea Szabó

Supervisor: Dr. Attila Kovács



M Ű E G Y E T E M 1 7 8 2

Budapest University of Technology and Economics  
Department of General and Analytical Chemistry  
2003

## 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 too small to distinguish them, or the given quantitative data have higher deficiency. Due to the developments of computer techniques 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 phenol 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

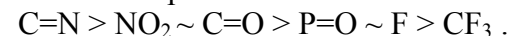
### I. STRUCTURAL CHARACTERISTICS OF INTRAMOLECULAR HYDROGEN BONDING IN BENZENE DERIVATIVES

Structural, vibrational characteristics and energetics of intramolecular hydrogen bonding of some *orto*-substituted phenol derivatives have been investigated. Various proton acceptor groups (C=N, NO<sub>2</sub>, C=O, P=O, F, CF<sub>3</sub>) 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:



$$35 \text{ kJ/mol} - 7 \text{ kJ/mol}$$

– Characteristic changes of geometrical properties of donor and acceptor groups

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

$$\Delta(\text{O-H}): \text{C=N} \gg \text{P=O} > \text{C=O} > \text{NO}_2 \gg \text{F} > \text{CF}_3$$

$$\Delta(\text{C=O}): \text{C=N} > \text{P=O} \sim \text{C=O} > \text{NO}_2 \gg \text{F} > \text{CF}_3$$

$$\Delta(\text{B-Y}): \text{CF}_3 \gg \text{F} > \text{NO}_2 > \text{C=O} \sim \text{P=O} \gg \text{C=N}$$

$$\Delta(\text{C-B}): \text{C=O} \gg \text{C=N} > \text{P=O} \gg \text{CF}_3 \sim \text{NO}_2$$

This nonsystematic variation of the bond lengths shows no close relationship with the hydrogen bonding energy.

– Impacts of hydrogen bond on benzene ring geometry

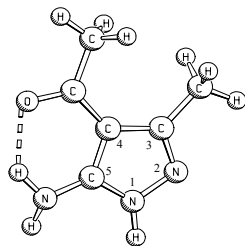
The changes are most pronounced in 2-phosphinylphenol, while the weakest appears in 2-trifluoromethylphenol. Again, there is no direct correlation with the computed hydrogen bond energies, nor with the geometrical changes of the donor and acceptor groups.

– 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-fluorphenol 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 characteristics.



4-acetyl-3-amino-5-methylpyrazole

– Tautomerism, conformation, structure

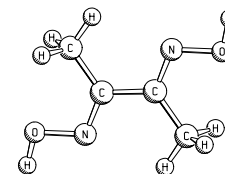
Our survey of the PES resulted in two stable conformers for each tautomer. The 5-amino-3-methyl tautomer is more stable than the 3-amino-5-methyl form, however, the difference is only 2 kJ/mol at the B3LYP/6-311++G\*\* level of theory. The most stable conformer of each tautomer is the hydrogen bonded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



Dimethylglyoxime

#### – Structure and conformation

The potential energy surface (PES) of the dimethylglyoxime was elucidated by calculations using B3LY/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 interaction, viz. by steric and conjugation effects as well as in a few structures by N(O)···H intramolecular hydrogen bonding.

#### – Vibrational analysis

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.

#### – Vibrational analysis

The molecular vibrations of the bis(dimethylglyoximato)-nickel(II) complex have been determined using FT-IR and FT-Raman spectroscopy and scaled quantum mechanical analysis. The initial harmonic force field was evaluated at the B3LYP/6-311++G\*\* theoretical level and was scaled using scale factors

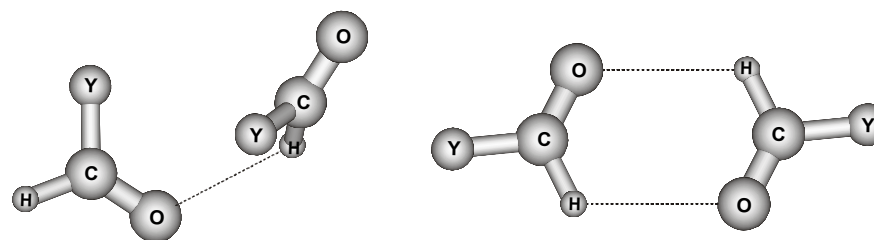
optimized for this level. Based on the present scaled quantum mechanical force field 45 of 87 fundamentals of the molecule have been assigned.

#### 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 ( $\nu_{XH}$ ).

Our goal was the investigation of the weak interactions in the dimers of formaldehyde derivatives  $\{(CHOY)_2, Y=H, CH_3, F, Cl, Br, I\}$ . 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

#### 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  $\sigma^*_{\text{CH}}$  orbitals and alterations in the intramolecular charge-transfer effects as the primary reason of the C–H contraction.

#### ACKNOWLEDGEMENTS

I thank gratefully to Attila Kovács, supervisor, for the patience, guiding and support. I would like to thank Sándor Gál, István Hargittai, György Pokol and the József Varga Foundation for support. I am deeply grateful to my colleagues, family and friends.

#### PUBLICATIONS RELATED TO THE THESES:

1. A. Kovács, A. Szabó, I. Hargittai: Structural characteristics of intramolecular hydrogen bonding in benzene derivatives, *Accounts of Chemical Research*, 2002; 35: 887-894.
2. A. Szabó, V. I. Češljević, A. Kovács: Tautomerism, hydrogen bonding and vibrational properties of 4-acetyl-3(5)-amino-5(3)-methylpyrazole, *Chemical Physics*, 2001; 270: 67-78.
3. A. Szabó, A. Kovács: Structure and molecular vibrations of dimethylglyoxime, *Journal of molecular structure*, in press.
4. A. Szabó, A. Kovács: Vibrational analysis of the bis(dimethylglyoximato)-nickel(II) complex, *Journal of Molecular Structure*, in press.
5. A. Kovács, D. Nemcsok, A. Szabó, I. Hargittai: Blue-shifting C-H...Y (Y=O; Hal) hydrogen bonds in the dimers of formaldehyde derivatives, *Journal of Physical Chemistry A*, 2002; 106:5671-5678.

#### PRESENTATIONS AND POSTERS RELATED TO THE THESES:

1. A. Szabó, A. Kovács: Structure, bonding and molecular vibrations of the bis(dimethylglyoximato)nickel(II) complex (presentation, Hungarian) 43. Magyar Spektrokémiai Vándorgyűlés, Zalaegerszeg, 2000. June 26-28.
2. A. Kovács and A. Szabó: Structure, bonding and molecular vibrations of the bis(dimethylglyoximato)nickel(II) complex (poster) 3rd European Conference on Computational Chemistry (EUCCO-CC3), Budapest, 2000. September 4-8.
3. A. Kovács, A. Szabó: Conformational analysis of glyoxime and dimethylglyoxime (poster) 3rd European Conference on Computational Chemistry (EUCCO-CC3), Budapest, 2000. September 4-8.
4. A. Kovács, I. Hargittai, S. D. Nemcsok, A. Szabó: Dimer formation of fluoroformaldehyde (poster) 3rd European Conference on Computational Chemistry (EUCCO-CC3), Budapest, 2000. September 4-8.
5. A. Kovács and A. Szabó: Structure, bonding and molecular vibrations of the bis(dimethylglyoximato)nickel(II) complex (poster) International School of Crystallography, 32nd Course: Strength from weakness: Structural consequences of weak interactions in molecules, supermolecules and crystals, Erice, Italy; 23 May-3 June 2001.

#### **OTHER PUBLICATIONS:**

1. A. Kovács, A. Szabó: Comparison of ab initio and Density Functional Methods for TeF<sub>6</sub>, Chemical Physics Letters, 1999; 305 . 458-464.
2. A. Kovács, A. Szabó: Hydrogén bonding and molecular vibrations of 2,5-dihydroxy-1,4-benzoquinone, Journal of Molecular Structure, 1999; 510: 215-225.
3. A. Kovács, A. Szabó: Vibrational analysis of perflouroadamantane, Journal of Molecular Structure, 2000; 519: 13-19.
4. M. Lein, A. Szabó, A. Kovács, G. Frenking: Energy decomposition analysis of the chemical bond in main group and transition metal compounds, Faraday Discussions közlés alatt.

#### **OTHER PRESENTATIONS AND POSTERS:**

1. A. Kovács, A. Szabó: Comparison of ab initio and density functional methods for the vibrational analysis of TeF<sub>6</sub> (poster)  
XXIV. European Congress on Molecular Spectroscopy, Prága, 1998., Augustus. 23-28.
2. A. Kovács, A. Szabó: Vibrational characteristics of TeF<sub>6</sub> based on quantum chemical methods (poster, Hungarian)  
41. Magyar Spektrokémiai Vándorgyűlés, Budapest, 1998., September 1-4.
3. A. Kovács, A. Szabó: Vibrational analysis of 2,5-dihydroxy-1,4-benzoquinone (presentation, Hungarian)  
41. Magyar Spektrokémiai Vándorgyűlés, Budapest, 1998., September 1-4.
4. A. Kovács, A. Szabó: Vibrational analysis of perfluoro-adamantane (poster)  
7<sup>th</sup> Austrian-Hungarian International Conference on Vibrational Spectroscopy, Balatonfüred, 1999. April. 7-9.