Theoretical investigation of H-bond structure and dynamics in molecules of biological interest

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By

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Title of the M. Sc. thesis:

Theoretical investigation of H-bond structure and dynamics in molecules of biological interest

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Abstract

Name: **Ashour Abd-Elaal Mahmoud Ahmed**

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Theoretical investigation of H-bond structure and dynamics in molecules of biological interest

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This thesis is discussing two important research points. First, the equilibrium geometry of sodium dihydrogen triacetate and its anion is calculated quantum mechanically. Second, the geometric hydrogen/deuterium (H/D) isotope effect and cooperativity in the hydrogen bonds of sodium dihydrogen tri acetate (SDHTA) are discussed.

In the first part, a lot of conformers for the dihydrogen triacetate (DHTA) anion are suggested. All conformers are optimized using the density functional theory at different levels of theories to probe the conformer corresponding to the global minimum on the potential energy surface. The minimum is confirmed by calculating the second order Hessian matrix which produces positive eigen values for the minimum. Different minima have been detected and careful analysis of the energetics and geometries, the global minimum has been finally reached. The effect of the presence of sodium ion on the dihydrogen triacetate structure is studied. Moreover, the global minimum on the potential energy surface of sodium dihydrogen triacetate in comparison with the available experimental data is explored.

In the second part, the reduced dimensionality of the potential energy surface is derived from the full-dimensional one by selecting some relevant modes out of 3N-6. Two-dimensional potential energy surfaces in terms of normal modes describing the anharmonic motion in the vicinity of the equilibrium geometry of sodium dihydrogen triacetate (SDHTA) are calculated for the different species, namely, HH, HD, DH, and DD isotopomers. The ground state wave functions and their relation to the geometric H/D isotope effect are discussed. It has been found that the hydrogen bonds in SDHTA are anticooperative, that is, elongation of the deuterated hydrogen bond does not affect the non-deuterated one, i.e no coupling appears between the two hydrogen bonds in case of the asymmetric isotopic substitution (HD and DH isotopomers). It has been surmised that, the double proton transfer in sodium dihydrogen triacetate may proceeds step-wisely. Eventually, the obtained results have been compared with the NMR experimental data.

Key words: DHTA, SDHTA, HF, MP2, DFT, Basis set, cooperativity and geometric isotope effect.

Signature of supervisors:

1- **Prof. Dr. Rifaat Hassan Hilal**

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Chairman of Chemistry Department

Faculty of Science, Cairo University

To my dearest,

MOTHER, FATHER,

WIFE, BROTHERS

AND SON.

May I fulfill the least I owe to you.

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Best regards are forwarded for everyone in **quantum chemistry group**.

Ashour Abd-Elaal Ahmed

Postgraduate courses

Beside the work carried out in this thesis, the candidate has attended passed postgraduate courses in non-organic chemistry including the following topics:

1. Adsorption
2. Inorganic reaction mechanism
3. Electrochemistry
4. Advanced analytical chemistry
5. Nuclear chemistry
6. Molecular structure determination
7. Quantum chemistry
8. Solar energy
9. Thermodynamics
10. Physical chemistry of polymer
11. Statistical thermodynamics
12. Colloidal and catalysis
13. Chelatimetry
14. Metallurgy and molten salts
15. X-ray and thermal analysis
16. Group theory
17. Electrode kinetics
18. advanced inorganic chemistry (complexes)
19. Voltametry
20. German language

He successfully passed on examination in those topics.

Prof. Dr. Rifaat Hassan Hilal
Chairman of the chemistry department

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