

Freie Universität Berlin, Institut für Chemie und Biochemie
Takustrasse 3, D-14195 Berlin

Fachbereich Biologie, Chemie,
Pharmazie
Institut für Chemie und Biochemie
Prof. Dr. Hans-Heinrich Limbach
Institut für Chemie und Biochemie
Takustrasse 3
D-14195

Larisa Khrushcheva
Specialist of the Office for Organizational Support of
Dissertation Councils, Administration
Saint Petersburg State University

Telefon
Fax
E-Mail
Internet

Berlin
+49 30 838 55375
+49 30 636 55310
limbach@chemie.fu-berlin.de
www.chemie.fu-berlin.de

Berlin, 11.5.2019

submitted via email to l.khrushcheva@spbu.ru

Review of the Doctoral Thesis of Mrs. Elena Yu. Tupikina

entitled

“NMR and IR diagnostic of geometry, energy and electronic structure of hydrogen bonded complexes”

submitted for defense of the degree of candidate of physical and mathematical sciences, specialization 01.04.05 – Optics.

The present thesis is devoted to the study of how different properties of hydrogen bonded complexes depend on each other. In particular, the aim was the search of correlations between spectroscopic parameters, geometries and energies of hydrogen bonds. The relevance of these studies arises from the significant role of hydrogen bonds in the stabilization of molecular structures, on chemical reactions including proton transfers, on crystal packings, on biological processes. Hydrogen bond correlations are useful because it is very difficult to obtain otherwise hydrogen bond geometries for disordered systems, i.e. liquids, glasses etc. The same is true for the experimental estimation of hydrogen bond energies, in particular for intramolecular hydrogen bonds. Therefore, NMR and IR spectral parameters often appear to be the main source of information about hydrogen bonded complexes.

The Introduction section of the thesis provides an introduction into the relevance of the topic, the aims of the thesis, the methods of research, the scientific novelty and the expected benefits. The following Chapter 1 consists of a review of the relevant scientific literature concerning hydrogen bonds. Particularly, the results of previous experimental and theoretical studies of various hydrogen bonded complexes which predict hydrogen bond energy/geometry correlations base on spectroscopic IR and NMR parameters are discussed. A brief description of commonly accepted quantum-mechanical approaches to the visualization of outer electronic shells of potential hydrogen bond donors and acceptors is given as well. The last subsection is devoted to the review of

theoretical methods that may be applicable for calculations of hydrogen bonded complexes. The literature review covers more than 250 relevant papers.

Chapter 2 presents the results of developing and testing of a novel quantum mechanical method of 3D visualization of outer electronic shells. The main idea of this approach is using the ^3He atom as a numerical spin 1/2 probe. The probed molecule was placed at the point of origin and ^3He atom was moved sequentially through a set of grid points around the investigated molecule. In each point the interaction energy and NMR parameters such as the chemical shift δ_{He} of the helium atom were calculated. It was shown that δ_{He} is sensitive even to electron-rich or electron-poor regions of outer electronic shells. It was also shown, that the maps of the Laplacian of the helium chemical shift $\nabla^2\delta_{\text{He}}$ are the visualize best fluorine lone pairs. The approach proposed has advantages compared to standard quantum mechanical approaches, e.g. the analysis of extrema of molecular electrostatic potential maps, MESP, or the electron localization function, ELF. The Helium chemical shift Laplacian preserves its sensitivity to lone pair regions at significantly larger distances ($>1.5\text{--}2 \text{ \AA}$) as compared to the other methods, and its maximal values could be used to quantitatively estimate the electron-rich character of lone pairs. The novel approach was tested using a series of fluorine containing molecules, i.e. F^- , FH , FHF , $\text{FC}\equiv\text{CH}$, $\text{F}_2\text{C}=\text{CHF}$ and CF_3H . The results of this Chapter 2 were published in two articles.

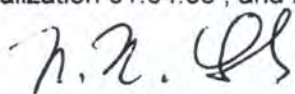
Chapter 3 discusses the possibilities of using spectral IR and NMR parameters for the evaluation of CHX ($\text{X} = \text{O}, \text{N}, \text{F}$), NHN and FHF hydrogen bonds energies and geometries. For that purpose, a set of model objects with homonuclear FHF and NHN hydrogen bonds was considered. The set was chosen so as to cover a wide range of hydrogen bond energies. It was found that the proton H-bond chemical shift changes $\Delta\delta\text{H} = \delta\text{H}(\text{complex}) - \delta\text{H}(\text{free})$ depend in a linear way on the hydrogen bond energies. Therefore, the spectroscopically measurable parameter ($\Delta\delta\text{H}$) may be used for rapid estimations of hydrogen bond strengths. For example, for NHN hydrogen bonds a low-field shift of the H-bonded proton of 1 ppm implies a strengthening of a hydrogen bond of 1.8 kcal/mol. In addition, for NHN hydrogen bonds quite simple equations linking $\Delta\delta\text{H}$ with interatomic distances r_{NH} and r_{NN} are proposed. In the case of FHF hydrogen bonds the validity of Badger-Bauer rule was discussed which predicts a linear dependence between the hydrogen bond energy ΔE and the vibrational frequency shift $\Delta\nu_{\text{FH}}$. Its applicability was verified by using the local mode vibration frequency instead of the normal mode vibrational frequency. Besides, as the alternative to spectroscopic parameters, the applicability of Bader's quantum theory of atoms in molecules (QTAIM) for estimation of hydrogen bond strength is discussed. Numerical values of proportionality coefficients between local electronic kinetic (G) and potential (V) energy densities at hydrogen bond critical point and hydrogen bond energy ΔE for NHN hydrogen bonds are presented.

Finally, complexes with CHX hydrogen bonds ($\text{X} = \text{O}, \text{N}, \text{F}$) formed by 1,1-dinitroethane and trinitromethane as hydrogen bond donors and acetone, pyridine and the fluoride anion as hydrogen bond acceptors as well as proton transfer process in these systems were investigated. The goal

was to track how the geometric and spectroscopic NMR parameters change during the proton transfer. For CHX hydrogen bonds it is shown that the spin-spin coupling constant $^1J_{\text{CH}}$ is of a major diagnostic value. In the first stages of proton transfer from carbon to X, $^1J_{\text{CH}}$ increases surprisingly, but when the r_{CH} distance is further increased, $^1J_{\text{CH}}$ decreases again. The initial effect is explained in terms of initial changes of the carbon hybridization, in particular with an increase of the carbon s-character whereas at later proton transfer stages the dependence on r_{CH} dominates. This interpretation was corroborated experimentally in the case of the ^1H NMR spectra of 1,1-dinitroethane in various aprotic solvents.

Further experimental verification of the computed dependencies was performed by variable temperature NMR experiments of the complex of 1,1-dinitroethane and 2,4,6-collidine. It was shown that energetic barrier for proton transfer reaction is sufficiently high (about 10 kcal/mol) and after proton transfer, the deprotonated form of 1,1-dinitroethane and the protonated form of 2,4,6-collidine in solution are not hydrogen bonded.

The present thesis is written in English, clear and without shortcomings. Mrs Tupikina organized her work very effectively with great discipline. The results have been presented on several international conferences and have led to the publication of five scientific papers, in which Elena Tupikina is the first author. As was mentioned above, the dissertation of Elena Tupikina meets the requirements necessary for the granting of the degree of candidate of physical and mathematical sciences, specialization 01.04.05, and I support it without hesitation.



(Professor Emeritus, Prof Dr. hab., Prof h.c. H. H. Limbach