

Title: Dynamic effects in compounds with hydrogen bond

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Abstract

The aim of dissertation is study of dynamic effects for compounds with hydrogen bonds in their structures. The compounds are characterized by presence of intramolecular hydrogen bonds and belong to different chemical groups for example Schiff bases, amides or hydroxyacetophenones derivatives.

In the first part of the dissertation the studies of dynamic effects in 5-hydroxy-3-nitro-2-hydroxyacetophenones were introduced. Theoretical and experimental data were obtained. The quantum-mechanical, mainly DFT calculations led to define potential curves for rotation of the nitro-group and isomerization of the hydroxyl group what allowed detection of stable or metastable states of the molecules. Both information about difference of energy between the global and local minimum as well as the barrier made it possible to predict the presence of the most stable conformers. Compounds were studied by using spectroscopic methods such as infrared (IR), Raman spectroscopy, Incoherent Inelastic Neutron Scattering (IINS) and Nuclear quadrupole resonance (NQR), thermal analysis methods such as differential scanning calorimetry (DSC) and thermogravimetry and X-ray. Compound **I** was obtained in two polymorphic forms. Presence of the phase transition for polymorph **I** at 114 K was detected. The reason of phase transition is rotation of the nitro-group. The most sensitive modes under the polymorphic, conformational states and phase transition: $\nu(\text{OH})$ vibrational mode, in-plane $\delta(\text{OH})$ and out-of-plane $\gamma(\text{OH})$ bending modes of the hydroxyl group, $\nu^{\text{as}}(\text{NO}_2)$ and $\nu^{\text{sym}}(\text{NO}_2)$ modes and $\nu(\text{C=O})$ mode were studied by spectroscopic methods. Additionally the use of IINS spectroscopy gave information about the hydrogen bridge ($\nu_{\sigma}(\text{OHO})$) mode. Isotopic effect is very important point in defining the strengthening of hydrogen bond. The question of interaction of chloro-substituents with the phenol ring was discussed on the basis of the NQR measurements.

In the second part investigations of cycle-arranged hydrogen bridges in chosen compounds were introduced. The studied compounds were subdivided into two groups. The first group: 2,4,6-triformylphloroglucinol (**II.1**), (2*E*,4*E*,6*E*)-2,4,6-tris[(methylamino)methylideno]cyclohexane-1,3,5-trione (**II.2**) and (2*E*,4*E*,6*E*)-2,4,6-tris[(methyloamino)methylideno]cyclohexane-1,3,5-trione ^{15}N (**II.3**). Compounds **II.2-III.3** are

tris-aldimines. The synthesis of all compounds were carried out. All compounds were measured by NMR spectroscopy. The proton transfer in hydrogen bridge is present and the NH tautomeric form is dominant (compounds **II.2-II.3**). Compounds **II.2** and **II.3** exist in two isomeric forms. The quantum-mechanical calculations led to define potential curves on the proton transfer and energy barrier high. Using of NMR spectroscopy helped to define isotopic effect ^{15}N .

The second group: 1,1',1''-(2,4,6-trihydroxybenzene-1,3,5-triyl)triethanone (**III.1**), (1*E*)-1-(3,5-diacetyl-2,4-dihydroxy-6-oxocyclohexa-2,4-dien-1-yl)-*N*-methylethaniminium (**III.2**), (1*E*,1'*E*)-1,1'-(5-acetyl-4-hydroxy-2,6-dioxocyclohex-4-ene-1,3-diyl)bis(*N*-methylethaniminium) (**III.3**) and (1*E*,1'*E*,1''*E*)-(2,4,6-trioxocyclohexane-1,3,5-triyl)tris(*N*-methylmethaniminium) (**III.4**). Compounds **III.2-III.4** are *tris*-ketoimines. The synthesis of **III.1** and **III.2** was carried out. Structural properties of obtained compounds were measured experimentally and compared with theoretical data. The impact of the NCH_3 substituent on the bridged hydrogen dynamics and the strengthening of hydrogen bonds were researched by DFT method (potential curves were defined). The prevailing tautomeric form is keto-amine form. The studied compounds contain very short hydrogen bonds. Compound **III.1** and **III.2** were examined by infrared (IR), Raman spectroscopy and Incoherent Inelastic Neutron Scattering (IINS). Modes of the hydroxyl group: $\nu(\text{OH})$ vibrational mode, in-plane $\delta(\text{OH})$ and out-of-plane $\gamma(\text{OH})$ bending were identified on IR and Raman spectra. The isotopic ratio for $\nu_\sigma(\text{XHY})$ vibrations of the hydrogen bridge has been determined from the experimental IR and Raman spectra and equals 1. It was evidence for the presence of strong, short hydrogen bonds. The studies of the hydrogen bridge vibrational modes have been accomplished on the basis of isotopic substitutions and Potential Energy Distribution (PED analysis). The hydrogen bridge ($\nu_\sigma(\text{OHO})$) mode was analysed in far spectral region by IINS spectroscopy. Experimental results were compared with theoretical results obtained by *Car-Parrinello* Molecular Dynamics (CPMD) and DFPT methods.

The third part contains studies of β -hydroxynaphthyl amides: 3-hydroxynaphthalen-2-yl(morpholin-4-yl)methanone (**IV.1**), (3-hydroxynaphthalen-2-yl)(pyrrolidin-1-yl)methanone (**IV.2**), 3-hydroxy-*N,N*-dimethylnaphthalene-2-carboxamide (**IV.3**). Analysis of the conformational state of morpholine, pyrrolidine and dimethylamine groups of β -hydroxynaphthylamides has been carried out on the basis on NMR experimental results and DFT calculations. The potential energy profiles for rotation around CC and CN bond were calculated. The impact of the polarity of the environment and temperature on the strengthening

of hydrogen bonds were studied. The most interesting results were obtained for compound **IV.1**, what is due to conformational changes of the morpholine ring.

The last part of research is devoted to analysis of selected Schiff bases: (1*E*)-1-(5-chloro-2-hydroxy-3-nitrophenyl)ethanone oxime (**V.1**), 3-hydroxy-5-(hydroxymethyl)-2-methylisonicotinaldehyde oxime (**V.2**), 4-hydroxy-6-methyl-3-[(1*E*)-*N*-methylethanimidoyl]-2*H*-pyran-2-one (**V.3**). The compounds were studied by theoretical DFT method and X-ray crystallography. The impact of the kind of substituents on proton transfer and tautomeric equilibrium. For compounds were introduced changes in structures and dynamic of molecules provoked by the steric repulsion between different atoms. The obtained experimental structural parameters were compared with theoretical results. Potential curves for the proton transfer for all compounds were defined. The proton transfer is observed only for compound **V.3**.