

Hydrogen bonds of 2-aminothiazoles in intermolecular complexes (1:1 and 1:2) with proton acceptors in solutions

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Abstract

IR spectra of the free molecules of 2-aminothiazole and 2-aminobenzothiazole and their H-bonded complexes of 1:1 composition with acetonitrile, dioxane, tetrahydrofuran, dimethylformamide, dimethylsulfoxide and hexamethyl-phosphoramide in CCl_4 were studied in the range of stretching and deformational vibrations of the amino group. The complexes of 1:2 compositions were studied in undiluted aprotic solvents.

The absorption band spectral characteristics of monomers and complexes were determined: $M^{(0)}$ —zero spectral moment (integrated band intensity B), $M^{(1)}$ —first spectral moment (band gravity center) and effective half-width $(\Delta\nu_{1/2})_{\text{eff}}$ which is related to the second central moment $M^{(2)}$: $(\Delta\nu_{1/2})_{\text{eff}} = 2(M^{(2)})^{1/2}$.

The temperature influence on the absorption band spectral characteristics of the amino group stretching vibrations for monomers and 1:1 complexes were studied in the interval 283–323 K. It was shown that within the range mentioned above, spectral characteristics have practically linear dependence on temperature. Parameters of the linear regression equation $Y = aT + b$ ($Y = B, M^{(1)}, 2(M^{(2)})^{1/2}$) were determined. It was stated that the temperature sensitivity $a = \partial Y / \partial T$ of spectral characteristics for 1:1 complexes of 2-aminothiazoles with proton acceptors is approximately 10 times higher than for monomers.

The monomer-complex equilibrium constants $K(T)$ (1:1) were calculated and the thermodynamical characteristics $-\Delta H$ and ΔS were determined, based on Vant-Hoff equation.

For free (R-NH_2 , R-NHD , R-ND_2) and H-bonded (1:1 and 1:2, with various proton acceptors) molecules of 2-aminothiazoles, the vibrational and electro optic problems were solved in the approximation of the six-coordinate valence force field model. The valence angles $\gamma(\text{HNH})$, force constants $K(\text{NH})$, electro optic parameters $\partial\mu/\partial q$ (derivative of the dipole moment by the length of NH-bond) and $\partial\mu/\partial q'$ (derivative of the dipole moment by the length of the neighboring NH-bond) were determined. The correlations were stated between spectral, geometrical, force and electro optic parameters of free and bonded molecules.

In the approximation of DFT-B3LYP/6-31G** and ab initio MP2/6-31G**, the atom charge distribution (according to Mulliken), geometrical and force characteristics and dipole moments μ_0 of 2-aminothiazoles were calculated.

The quantum mechanical calculations, valence force field calculations and the experimental results were shown to be in good agreement. © 2005 Elsevier B.V. All rights reserved.

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1. Introduction

The ability of the molecule to act as proton donor or acceptor in hydrogen bonding (H-bond) is determined by its composition and electron shell structure.

As a result, one of the important tasks in H-bond nature research is to study force constants and electro optical parameters (dipole moments, polarizability and its natural coordinate derivatives) in free molecules and H-bonded complexes, since these parameters reflect the peculiarities of electron shell structure and their evolution in complex forming.

Studying the dynamics of the spectral changes occurred during transition from free to H-bonded molecules, as well as studying the physical parameters of interacting molecules allows to establish the correlations between them and to

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obtain the more detailed representation of the intermolecular interaction mechanism.

One of the attractive objects for investigation as proton donors in intermolecular H-bonded complexes is primary aromatic amines. The ability of aromatic amines to form 1:1 and 1:2 H-bonded complexes with proton acceptors allows to study peculiarities of the hydrogen bonds in different composition complexes.

A significant influence on the electron density distribution in amino group localization area of primary aromatic amines in free and H-bonded molecules is made by various substituents, which differ in the value and sign of inductive, mesomeric, and field effects (action through space), ability to form intramolecular H-bond.

The comparative analysis of geometrical, dynamic and electro optic parameters of amino group in free and H-bonded molecules of different composition complexes allows to obtain the information on their static and dynamic polarization and to state the correlations between physical parameters of the molecules and their spectral characteristics.

The research of dynamic and electro optic non-equivalency of NH bonds of amino group in 1:1 complexes helps to state the effects of amino group polarization and electron free pair polarization in proton acceptor on absorption band intensity of amino group.

In [1–12] we performed experimental and theoretical investigation of different composition complexes of aniline and many substituted anilines with various proton acceptors. Regularities were established in the changes of geometrical, dynamical, electro optical and energetical characteristics of complexes depending on donor and acceptor properties and on the composition of complex.

It is important to take systematic investigation on influence of hetero-substitution in aromatic ring on proton donor ability and amino group parameters of primary aromatic amines. Heterocyclic compounds are widespread in nature and are a part of numerous biologically active molecules, medical products and dye-stuff. The results of these investigations might be interesting for researchers working in medicine, biology, physics and chemistry.

Previously we studied free molecules and H-bonded 1:1 and 1:2 complexes of aminopyridines [13] and aminopyrimidines [14,15] with various proton acceptors.

In the present work, 2-aminothiazole and 2-aminobenzothiazole were selected as the object of the investigation.

The present study is part of the research program, related to hetero substitution influence on proton-donor properties in intermolecular H-bond, spectral characteristics and amino group parameters in free and bonded molecules. The research results allow to determine both general behavior and individual difference of correlations between physical parameters of amino group and molecule spectral characteristics, which is important to study the nature of H-bond.

Thiazole and its derivatives are heterocycles, which play very significant part in vital functions, generally in the animal kingdom. This fact explains the increased interest to thiazole derivatives. The thiazole cycle appears in molecules of thiamine (vitamin B₁), penicillin, carboxylase ferment and other natural substances. Thiazole derivatives are widely used in the synthesis of the medical products such as sulfathiazole (norsulfazole)—well known antibiotic. Benzothiazoles are used for production of cyanine dyes, which have photosensitizing properties [16].

2-Aminothiazoles are able to tautomerize and can exist in either amino- or imino-form. Numerous examinations [17–21] show that amino form is prevalent for both non-substituted compounds in normal conditions.

The vibration spectra of free molecules and self-associates of 2-aminothiazole were studied in [22]. H-bonded 1:1 complexes of 2-aminobenzothiazole with hexamethylphosphoramide (HMPA) were previously studied in [23].

2. Experiment and calculations

Spectral examination of 2-aminothiazole (**I**) and 2-aminobenzothiazole (**II**) in the range of the amino group stretching (3000–3600 cm⁻¹) and deformation (1550–1750 cm⁻¹) vibrations were performed, using spectrophotometer Specord 75IR (made by Carl Zeiss Jena) with some modernizing modifications such as automated spectrum registration and preliminary processing by a computer (IBM AT compatible was used).

The spectra were registered in optimal conditions [24] with appropriate selection of slit program, scanning speed and device time constant. The absorbing layer thickness, needed to reach necessary photometric precision, was determined by the following condition:

$$\ln(I_0/I)_{\max} = 0.8 \div 1.6 \quad (1)$$

Operating in optimal conditions lets us to minimize the spectrum distortion. To avoid accidental error, each experiment was repeated at least five times with the concentration variation of either donor or acceptor. Sectional cuvettes with CaF₂ windows and standard fixed-thickness cuvettes with NaCl and KBr windows were applied.

The compound studied due to poor solubility in CCl₄ was powdered to fine-dispersive state, using agathic mortar. The solutions of the required concentration were composed by weighing of dry substance in densimeters calibrated by the distilled water at room temperature and followed by filling the densimeter volume with solvent. The concentration of aminothiazoles in solutions during the investigation of 1:1 complexes was 0.005–0.010 mol/dm³. The concentration of compounds in aprotic solvents (1:2 complexes) reached 0.03–0.30 mol/dm³.

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