

Heterocyclic aromatic amines in H-bonded complexes (1:1 and 1:2 composition) in solutions with various proton acceptors

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Abstract

The influence of the position and number of the nitrogen atoms in the aromatic ring on the proton donation ability in intermolecular H-bond, spectral, geometrical, force, electrooptic and energetic characteristics of the amino group was investigated for free and H-bonded (1:1 and 1:2, with various proton acceptors) molecules of 2-aminopyrazine (I) and 3-amino-1,2,4-triazine (II). Acetonitrile, dioxane, tetrahydrofuran, dimethylformamide, dimethylsulfoxide and hexamethylphosphoramide were used as proton acceptors. Their proton accepting properties vary in a wide range. In the range of the amino group stretching and deformation vibrations, within the temperature interval 285–330 K, IR spectra of free and H-bonded (1:1) molecules of compounds I, II in CCl₄ were studied. Complexes of 1:2 composition were studied in the undiluted aprotic solvents. The following absorption band spectral characteristics were determined: $M^{(0)}$ – zero spectral moment (integrated intensity B), $M^{(1)}$ – first spectral moment (the centre of gravity of the band), $M^{(2)}$ – second central moment related to the effective half width $(\Delta\nu_{1/2})_{\text{eff}} = 2(M^{(2)})^{1/2}$. It was shown that within the explored temperature interval the absorption band spectral characteristics of the monomers and complexes are well approximated by the linear functions $Y = aT + b$ ($Y = B, M^{(1)}, 2(M^{(2)})^{1/2}$). The linear regression parameters for these equations were determined. The vibrational and electro-optic problems for free and H-bonded molecules of compounds I, II were solved in approximation of the R-NH₂ valence force field model. 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 the corresponding bond) and $\partial\mu/\partial q'$ (derivative of the dipole moment by the length of the neighboring bond) were determined. It was shown that the absorption band spectral characteristics of the amino group stretching vibrations of the examined compounds in CCl₄ are most sensitive to the *o*-position of nitrogen atoms in the aromatic ring relatively to the amino group. Increasing the number of the nitrogen atoms in the ring leads to increasing the force constants $K(\text{NH})$, valence angle $\gamma(\text{HNH})$, and electrooptic parameters $\partial\mu/\partial q$ and $\partial\mu/\partial q'$. The linear correlations were obtained between spectral, geometrical, force and electrooptic characteristics of amino group of free and H-bonded (1:1 and 1:2) molecules. The comparative analysis was performed on the dependence of the correlation relations on the position and number of the nitrogen atoms in the aromatic ring. The dependence of the monomer-complex (1:1) equilibrium constants on the temperature was examined. The thermodynamical characteristics of the complex: entropy and enthalpy of the complex formation were obtained on the basis of the Vant–Hoff equation. The H-bond enthalpy in complexes of 1:2 composition was calculated using A.V. Iogansen's "intensities rule". The basic regularities observed in the spectra of free molecules of compounds I, II are confirmed by the quantum mechanical calculations in the DFT-B3LYP/6-31G** approximation and ab initio MP2/6-31G**.

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1. Introduction

Heterocyclic aromatic amines play the important role in the abiocoen and animate nature. They participate in several vital activities as active fragments of the complex

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natural compounds, widely used in the production of the synthetic drugs, natural and artificial dyes and plastic materials [1,2]. The chemical activity of the hetero-substituted aromatic amines substantially depends on the nature, position and number of the hetero atoms in the aromatic ring.

Earlier performed investigations of free and H-bonded molecules of aminopyridines [3], aminopyrimidines [4,5] and aminothiazoles [6] with various proton acceptors revealed the high sensitivity of the amino group spectral, geometrical, dynamical and electrooptic characteristics of free and H-bonded molecules on the nature of the substitution in the aromatic ring. The correlation relations were stated between spectral and other physical characteristics of free and H-bonded molecules. These correlations emphasize the common features of some relations and the individual differences of other relations.

The increase of the electron density asymmetry in the heterocycle is accompanied by the more and more specificity of the chemical behaviour for each atom of the heterocycle. At that, additional non-shared electron pairs localization on the nitrogen atoms appears, opposed from the side of the aromatic system promoting their delocalization. For the six-membered heterocycles with three or more nitrogen atoms, the aromatic properties remain clearly distinct. Regardless of the tautomerization tendency they exist as stable isomers in normal conditions.

We used 2-aminopyrazine (I) and 3-amino-1,2,4-triazine (II) as the study object. Pyrazines and triazines are important compounds for the pharmacology, they are perspective for making the neurotropic medications for the regions with severe environmental pollution. Aminopyrazine is a part of known bactericidal medication – sulphapyrazine. Pyrazine amino-derivatives show all properties of the aromatic amines. They can also exist in two tautomeric forms, however, the equilibrium is completely shifted to the amino form in normal conditions.

Inserting the third nitrogen atom in the six-membered heterocycle does not disturb the aromaticity of the system, however, the inductive effect of the three nitrogen atoms in any combination almost completely overlaps their mesomeric effect.

The steadiest of these compounds is *s*-triazine (symmetric heterocycle), electronic structure of the *as*-triazine is characterized by the irregularity in the electronic density distribution. Currently the properties of *as*-triazines are not enough investigated.

Triazines derivatives are widely used as herbicides and insecticides as well as in the plastic materials manufacture.

In the review [7] the influence of the hetero-substitution on the infrared spectra of the aromatic compounds is discussed. Quantum-mechanical researches of the structure and the electronic density distribution in the crystalline aminopyrazine are performed in [8]. Raman spectra of the 3-aminopyrazine-2-carboxylic acid in the region 100–4000 cm^{-1} are studied in [9]. Geometrical parameters and harmonic frequencies of the molecules are calculated

using semi-empirical (AM1, MNDO and PM3) and ab initio (3-21 G, 6-31G, 6-311G and 6-311**) methods. The spectrum assignment is also performed.

Computer modeling of the resonant structures of 2-amino-1,3,5-triazine and some of its derivatives, as well as calculation of the rotation barriers of the substituted amino group about the triazine N–C bond are presented in [10].

2. Experiment and calculations

In the region of the amino group stretching (3000–3600 cm^{-1}) and deformation (1550–1750 cm^{-1}) vibrations, the spectra of free and H-bonded molecules of 2-aminopyrazine I (Aldrich, 99% of purity) and 3-amino-1,2,4-triazine II (Aldrich, 97% of purity) with various proton acceptors were studied. Acetonitrile (CH_3CN), dioxane, tetrahydrofuran (THF), dimethylformamide (DMF), dimethylsulfoxide (DMSO) and hexamethylphosphoramide (HMPA) were used as proton acceptors. Their proton accepting properties vary in a wide range. All solvents used in work were previously freed from dirt and moisture and kept above molecular sieve 4 Å. All spectra were obtained using the modernized spectrophotometer Specord 75-IR (Carl Zeiss Jena) with automatic spectrum recording by the computer. Spectrum registration was done in optimum conditions under appropriate slit program selected, as well as time constant and spectrum scan speed. The required photometric precision was achieved by fitting of the appropriate thickness of the absorption layer [6,11].

The calculated concentrations of studied compounds in solution were obtained by weighting a dry substance in a densimeter of known volume followed by filling it with solvent. When composing triple solutions (donor–acceptor– CCl_4), the volume occupied by the donor in the measuring cuvette was compensated by the equal volume of CCl_4 in the comparison cuvette.

In the temperature interval 285–330 K, we studied the dependence of the absorption band spectral characteristics of the amino group stretching vibrations on the temperature for free molecules of compounds I, II in CCl_4 . In these researches we used specially designed thermostat, capable to maintain equal temperature in the measuring and comparison cuvettes. Copper-constantan thermocouple firmly attached to the cuvette window was used for the temperature monitoring. The temperature measuring precision is about 0.5 K.

The absorption bands of the amino group stretching vibrations $\nu_c(\text{NH})$ of the H-bonded complexes have complicated structure due to the Fermi resonance between the $\nu_c(\text{NH})$ vibrations and weak-intensive $2\delta_c(\text{HNH})$ overtone. Therefore, instead of usual spectral characteristics – peak position (ν_{max}) and half width ($\Delta\nu_{1/2}$), the following spectral moments were calculated: $M^{(0)}$ – zero spectral moment (integrated intensity B), $M^{(1)}$ – first spectral moment (centre of gravity of the band) and $M^{(2)}$ – second central moment related to the effective half width $(\Delta\nu_{1/2})_{\text{eff}} = 2(M^{(2)})^{1/2}$ [12]. The determination error of

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