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Influence of chlorine-substitution in pyrimidine ring on proton donor ability in H-bond and parameters of amino group of 2-amino pyrimidine.

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The stretching and deformational vibrations of amino group in 2-aminopyrimidine **(1**), 2-amino-4-chloro-6-methylpyrimidine (**2**) and 2-amino-4,6-dichloropyrimidine (**3**) as well as its 1:1 and 1:2 complexes with different proton acceptors: CH_3CN, dioxane, tetrahydrofurane, dimethylformamide, dimethylsulphoxide and hexamethylphosphoramide were studied by IR spectroscopy and quantum chemical calculations.The influence of temperature, within the range 285–330 K, in CCl_4 solutions, on the first spectral moment $M^{(1)}$, effective band half width $2(M^{(2)})^{1/2}$ and integrated intensity B, of the stretching vibrations of $–NH_2$ group of the free and 1:1 H-bonded complexes of compounds **1–3** with proton acceptors was studied. Parameters of linear dependency of the spectral moments on temperature were established. The thermodynamic characteristics of the complex formation process were determined.The vibrational and electrooptic problems, in framework of RNH_2 model of valence force field, were solved and the γ(HNH) angle, force constants K(NH) and electrooptic $\partial\mu/\partial q$ parameters for the free and H-bonded molecules of aminopyrimidines **1–3** were calculated.It was found that formation of 1:1 complexes with proton acceptors led to 10–15% decrease of the force constant K_1(NH) of NH bond directly involved into hydrogen bond formation, and only 1% increase of the force constant K_2(NH) for the “free” NH bond. The comparison of K(NH) force constants of H-bonded complexes of different composition showed that H-bond in 1:1 complexes is stronger than in 1:2 complexes.It was shown, that chlorine-substitution in 4,6-positions of 2-aminopyrimidine significantly influences the donor ability of $–NH_2$ group in H-bond, as well as spectral, force, electrooptic and thermodynamic characteristics of amino group of bonded molecules.Theoretical calculations at DFT-B3LYP/6-31+G(d,p) level were performed and atom charge redistribution upon hydrogen bond formation was determined. Charge transfer process between the proton donor and proton acceptor molecules, in dependency on the character of proton acceptor molecule was discussed.The results of quantum chemical calculations for free and H-bonded aminopyrimidines correspond to the results of the experiment and calculation in model of valence force field.

Słowa kluczowe

Hydrogen bond, 2-Aminopyrimidines, IR spectra, Force constants, Charge transfer, Electroptic parameters, Thermodynamics of complex formation

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