The influence of hetero-substitution in the aromatic ring of amino pyrimidine on amino group characteristic in free and H-bonded molecules.

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Streszczenie

The spectra of free and H-bonded (1:1 and 1:2) molecules of aminopyrimidines with CH_3CN, THF, dioxane, DMF, DMSO, and HMPA were studied in the area of stretching and bending vibrations of amino group. The spectral moments of absorption bands $M^{(0)}$, $M^{(1)}$, $M^{(2)}$ and 'effective' half-width $(\Delta\nu_{1/2})_{eff}=2(M^{(2)})^{1/2}$ were determined.The temperature dependence of spectral moments was studied in the range of 290–330 K. Equilibrium constants K_{298} and enthalpy–ΔH_1 of 1:1 complexes of 2- and 4-aminopyrimidines with DMF, DMSO and HMPA were determined. Valence angles γ(HNH), force constants K(NH), electro optical parameters $\partial\mu/\partial q_{NH}$ and $\partial\mu/\partial q'_{NH}$ were calculated within R-NH_2 model of valence force field for free and H-bonded molecules of aminopyrimidines. The distribution of electron density on C–NH_2 moiety and dipole moments μ_e of aminopyridines were estimated using semi-empirical AM1, PM3 and DFT-B3LYP/6-31G**, ab initio MP2/6-31G** quantum mechanical methods.The comparative analysis stated the influence of heteroatom position and number in the aromatic ring on spectral, geometric, force and energetic characteristics of free and H-bonded molecules in the row of compounds: Aniline, aminopyridines, aminopyrimidines.Correlations between spectral and structural, electrooptic and force characteristics of amino group in aminopyrimidines were established. It was stated that position and number of hetero atoms in the aromatic ring profoundly influence parameters and proton donor ability of amino group in intermolecular H-bonded complexes. However, the parameters of the correlation function change slightly upon the second nitrogen introduction into aromatic ring.Temperature sensitivity of spectral moments $M^{(0)}$ (integrated intensity) and $M^{(1)}$ (center gravity position) of aminopyrimidines compared to aminopyridines shows a great increase.