Thermodynamic properties of the hydrogen bonded complexes between N-substituted anilines and proton acceptors.

Autorzy

V. E. Borisenko

Yu. A. Zavjalova

T. G. Tretjakova

Z. S. Kozlova

Aleksander Koll

Rok wydania

2004

Czasopismo

Journal of Molecular Liquids

Numer woluminu

109

Strony

125-135

DOI

10.1016/j.molliq.2003.06.003

Kolekcja

Naukowa

Język

Angielski

Typ publikacji

Artykuł

Streszczenie

The influence of temperature, within the range 285–340 K, on spectral characteristics of ν(NH) absorption bands in 'free' *N*-methyl aniline, *N*-ethyl aniline, diphenylamine and *N*-methyl-4-nitroaniline in CCl_4 as well as in their hydrogen bonded complexes with acetonitrile, tetrahydrofurane, dimethylformamide (DMF), dimethylsulfoxide (DMSO) and hexamethylphosphoramide (HMPA) was studied. Spectral moments of ν(NH) absorption bands were determined: $M^{(0)}$—the zero spectral moment (integrated intensity), $M^{(1)}$—the first spectral moment (the centre of band gravity), $M^{(2)}$—the second central moment as well as 'effective' half width of absorption band $(\Delta\nu_{1/2})_{eff}=2(M^{(2)})^{1/2}$. The coefficients of the linear correlation of these parameters with a temperature variation $Y=aT+b$ ($Y=M^{(0)}$, $M^{(1)}$, $2(M^{(2)})^{1/2}$) were calculated for 'free' and hydrogen-bonded molecules. It was demonstrated that these spectral characteristics considerably depend on the character of the N-substitute. The difference in the position of absorption bands ν_m(NH) in the spectra for non-bonded molecules of N-substituted anilines in CCl_4 is caused by σ–π conjugation of alkyl radicals with the N atom and substitute polarization influence. Thermodynamic parameters $-\Delta H$ and ΔS of the complex formation process between amines and proton acceptors were determined from the temperature dependence of the equilibrium constants on the basis of van't Hoff equation. The increase of $-\Delta H$ enthalpy was observed in the rows of proton donors: *N*-alkyl-substituted anilines, diphenylamine and *N*-methyl-4-nitroaniline; and proton acceptors: acetonitrile, tetrahydrofurane, DMF, DMSO and HMPA. The correlations between $-\Delta H$ values and the shift of the first spectral moment $\Delta M_c^{(1)}=M_m^{(1)}-M_c^{(1)}$, on the one hand, and $-\Delta H$ values and the increment of the square root of integrated intensity $\Delta B^{1/2}=B_c^{1/2}-B_m^{1/2}$, on the other hand, were found on passing from free to bonded molecules. However, the proportionality factor α in the equation $-\Delta H=\alpha\Delta B^{1/2}$ depends on individual characteristics of proton donors and remains the same for each proton donor in the row of proton acceptors.

Słowa kluczowe

N-substituted anilines, Thermodynamic parameters, H bond