

Hydrogen bonding in pure base media. Correlations between calorimetric and infrared spectroscopic data

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Abstract

The known correlations between calorimetric and IR spectroscopic data on hydrogen bonding were reinvestigated for hydrogen bond donors (AH) dissolved in pure bases (B). Ninety-five AH...B systems were considered for which the enthalpies of specific interaction due to hydrogen bonding AH...B ($\Delta H_{sp.int. AH/B}$, kJ mol⁻¹), the weight centers of A-H stretching bands (ν , cm⁻¹) and their integral absorption coefficients (a , 10⁴cm mmol⁻¹) had been measured. The relationships between $\Delta H_{sp.int. AH/B}$ and the parameters of the infrared absorption spectra [weight center shifts $\Delta\nu$ and the changes in the square roots of a ($\Delta\alpha^{1/2}$)] were analyzed. It was found that the dependence of $\Delta H_{sp.int. AH/B}$ on $\Delta\alpha^{1/2}$ consists of two nearly parallel straight lines: the first ($-\Delta H_{sp.int. AH/B} = 12.0 \Delta\alpha^{1/2} + 0.4$) corresponds to water and the weak C - H and O - H H-bond donors (chloroethylenes, acetylenes acetonitrile, nitromethane, chloroform, o,o'-di-tert-butylphenol); the second ($-\Delta H_{sp.int. AH/B} = 12.1 \Delta\alpha^{1/2} - 4.2$) corresponds to the stronger N - H and O - H H-bond donors (N-methylaniline, pyrrole, alcohols, phenol, carbon acids). Non-linear dependences of $\Delta H_{sp.int. AH/B}$ on $\Delta\nu$ were obtained for all C - H, N - H and O - H H-bond donors except water [$\Delta H_{sp.int. AH/B} = 59.9 \Delta\nu / (\Delta\nu + 674)$]. Enthalpies of specific interaction for water obey another dependence [$-\Delta H_{sp.int. H_2O/B/2} = 28.5 \Delta\nu / (\Delta\nu + 269)$]. The $\Delta H_{sp.int. AH/B}$ values can be estimated by the above correlations with an accuracy of ± 3 to ± 6 kJmol⁻¹. These relationships obtained for solutions of H-bond donors in pure bases differ from the well known dependences determined for the AH...B hydrogen bonding in carbon tetrachloride medium. © 1996 by John Wiley & Sons, Ltd.
