Correlation Between Hydrogen-bond Shift in Nuclear Magnetic Resonance Spectra and Change in Enthalpy

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Summary If the proton donor is kept fixed the hydrogen-bond shift in the n.m.r. spectrum, $\Delta\delta$, correlates with the enthalpy change, ΔH, for minor structural changes in the proton acceptor.

In hydrogen-bond formation the hydrogen-bond shift in the n.m.r. spectrum, $\Delta\delta$, is defined as the chemical shift of the bonded proton in the complex relative to the chemical shift of the free proton in the monomer.[1] For a constant minimum concentration of the proton donor, dependence of the proton shift, Δ, on the molar concentration of the base, for [B] $\gg$ [proton donor], is given by[2] equation (1)

$$\frac{1}{\Delta} = \frac{1}{\Delta\delta} + \frac{1}{\Delta\delta\, K\, [\mathrm{B}]} \qquad (1)$$

where K is the equilibrium constant and Δ is the chemical shift of the proton in the base–cyclohexane system relative to that of the proton in neat cyclohexane at the same temperature.

The temperature dependence of $\Delta\delta$ gives good linear fit. The results in the Table show that for the same proton donor and a series of closely related bases the $\Delta\delta$ values correlate with the ΔH values. The correlation is remarkably good for the chloroform–ether systems. With the amines the correlation appears to be dependent on the degree of steric hindrance to the approach of the chloroform molecule to the electron-donor site. In NN-dimethylcyclohexylamine and tri-n-propylamine the donor sites are more hindered than in triethylamine and diethylmethylamine, so that the ΔH values are considerably smaller and the temperature variation of $\Delta\delta$ greater for the more hindered

Table. Temperature dependence of $\Delta\delta$ and correlation between $\Delta\delta$ and ΔH for hydrogen bonding of chloroform with various bases in cyclohexane at 60 MHz.

Base	$\Delta\delta^a = f(t)^b$	$\Delta\delta^a$ (34°C)	$-\Delta H^c$	$-\Delta\delta/\Delta H^d$ (34°C)
Di-isopropyl ether	$-0{\cdot}0836t + 65{\cdot}5$	63	14·2	4·4
Tetrahydrofuran	$-0{\cdot}0810t + 53{\cdot}2$	50	10·8	4·6
Tetrahydropyran	$-0{\cdot}0875t + 49{\cdot}4$	48	11·2	4·3
NN-Dimethylcyclohexylamine ..	$-0{\cdot}267t + 100{\cdot}9$	92	13·0	7·1
Tri-n-propylamine	$-0{\cdot}180t + 101{\cdot}3$	95	13·6	7·0
Triethylamine	$-0{\cdot}138t + 109{\cdot}9$	96	16·1	6·0
Diethylmethylamine	$-0{\cdot}135t + 95{\cdot}7$	91	16·4	5·5

[a] Hz at 60 MHz; maximum uncertainty $= \pm$ 1·5 Hz. [b] In $f(t)$, t is in °C; linear correlation coefficient ρ is 0·960—0·998. [c] ΔH kJ mol^{-1}; maximum uncertainty = 0·6 kJ mol^{-1}. [d] Hz mol kJ^{-1} at 60 MHz; uncertainty $= \pm$ 0·4 Hz mol kJ^{-1} at 60 MHz.

amines. The ratio of $\Delta\delta$ to ΔH is therefore greater for the more hindered amine.

This correlation of $\Delta\delta$ with ΔH parallels the i.r. frequency shift $\Delta\nu$ correlation with ΔH.[3] A correlation between $\Delta\delta$ and ΔH has been reported for hexafluoropropan-2-ol and various bases.[4]

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