Hindered Internal Rotation in Stable Protonated Benzaldehydes: Nuclear Magnetic Resonance Study

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Summary Protonation of benzaldehydes substantially increases the barrier to internal rotation (about the Ph–CO bond) which can be evaluated by dynamic n.m.r., the proton exchange rates between the acid system (SbF_5–FSO_3H) and the protonated species remaining very low even at temperatures well above coalescence temperature

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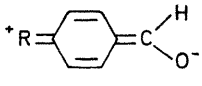
DYNAMIC n.m.r. has been used in the estimation of barriers to internal rotation around σ bonds possessing some π character.[1-3]

It has been shown that boron trifluoride-complexed benzaldehydes have an increased barrier to internal rotation as compared to the free aldehydes.[4] This has been explained, on the basis of the relative ^1H n.m.r. shifts, by stabilisation of the resonance form (I) by complex formation.



(I)

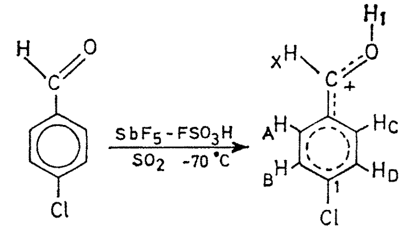
We now report that the energy barrier to internal rotation in benzaldehydes is much increased by protonation in the strong acid system SbF_5–FSO_3H.[5] An increase of 80° of the coalescence temperature is observed for example in the protonated *p*-tolualdehyde ($T_c = +40°$) as compared to the boron trifluoride complex ($T_c = -41°$).[4]

N.m.r. chemical shifts[a] *and free energies of the barriers to internal rotation in stable protonated benzaldehydes*

Benzaldehyde	$C=OH^+$	C–H	Ar–H[b]	CH_3	$\Delta G_c^\ddagger$/kcal mol^{-1}
p-Me	12·51	9·50	8·05	2·62	16·3 (±0·5)
p-Cl	13·08	9·64	8·20		14·8 (±0·5)
p-Br	13·18	9·71	8·20		14·8 (±0·5)

[a] In p.p.m. from external Me_4Si. [b] Centre of the AA'BB' pattern.

When *p*-chlorobenzaldehyde is dissolved in SbF_5–FSO_3H–SO_2 at −70 °C the ^1H n.m.r. spectrum of the ring protons



(II)

(ABCD type) shows the predominance of the planar protonated species (II).

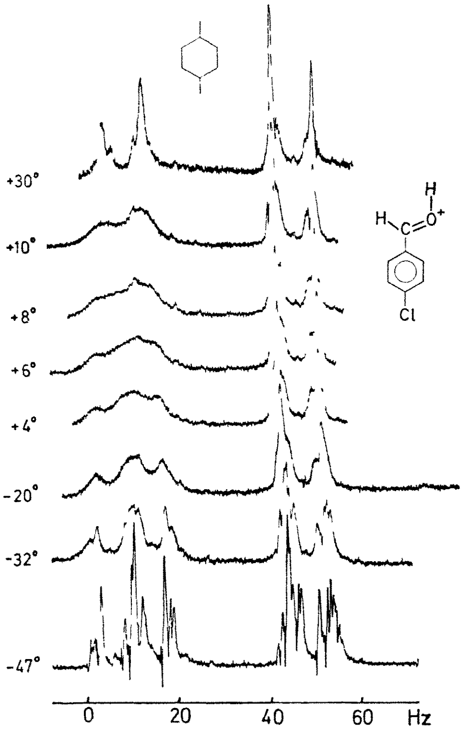


FIGURE 1. *Temperature dependence of* Ar–H *n.m.r. shifts in protonated* p-*chlorobenzaldehyde.*

The chemical shifts indicate charge delocalisation on the aromatic ring. The $C=OH^+$ proton which is known to be highly sensitive to electronic effects of the carbonyl substituent appears (d, $J_{1,X}$ 8·0 Hz) at 13·08 p.p.m. This is 2 p.p.m. upfield from the $C=OH^+$ resonance in protonated acetaldehyde. This shielding effect is also noticed for the aldehyde proton at 9·64 p.p.m. (d of d, $J_{1,X}$ and $J_{X,D}$ = 0·6 Hz). The deshielding of the aromatic ring protons, however (average chemical shift: 8·32 p.p.m.), may be compared to the aromatic proton deshielding in dimethylphenylcarbonium ion.[6] Complete spectral analysis yielded the following: $\delta_A = 8·40$, $\delta_B = 7·85$, $\delta_C = 8·52$, and $\delta_D = 7·81$ p.p.m.; $J_{AB} = 8·3$, $J_{AC} = 2·2$, $J_{AD} = 0·3$, $J_{BC} = 0·4$, $J_{BD} = 2·1$, and $J_{CD} = 8·6$ Hz. The two *ortho*-protons show a chemical shift difference of 7·5 Hz; H_C is probably the most deshielded owing to the anisotropy of the carbonyl group.

When the temperature is raised, the ABCD pattern coalesces to an AA'BB' type (Figure 1). Note that the $C=OH^+$ resonance at 13·08 p.p.m. remains a sharp doublet, showing no line broadening due to exchange even at +30 °C (Figure 2).

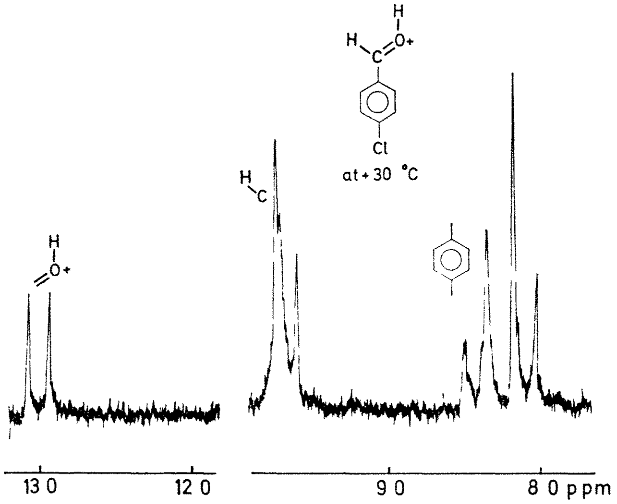


FIGURE 2. *N.m.r. spectrum of protonated* p-*chlorobenzaldehyde in* SbF_5 – FSO_3H – SO_2 *at* + 30 °C.

The free energy of the rate process was calculated from the Eyring equation[7] at coalescence temperature. The values of $\Delta G_c^\ddagger$ for a series of compounds, and the chemical shifts are listed in the Table.

The higher basicity of *p*-tolualdehyde over *p*-chlorobenzaldehyde corresponds to a 40 Hz shielding of the $C=OH^+$ proton and an increase of 1·5 kcal mol^{-1} in $\Delta G_c^\ddagger$ The $C=OH^+$ chemical shifts have been well correlated with the σ^+ and pK_{BH^+} values in protonated acetophenones,[8] and we intend now to investigate the correlation of the barrier to rotation about the Ph–C bond in these protonated species with the Hammett's σ constant.

Though charge delocalisation in the protonated species is shown well by the chemical shifts, the relative importance of this effect on the barrier to internal rotation is not known. Steric effects (presence of the counter ion) and hydrogen bonding of the $C{=}OH^+$ proton with the acid medium should probably be taken in account.

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