

Hydrogen-bond Assisted Observation of HCNH ¹H N.M.R. Coupling in *N*-Methylanilines

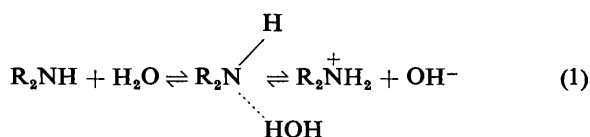
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Proton-proton HCNH coupling in high *pK_a* *N*-methylanilines can be observed in solutions containing strong hydrogen-bond electron donors.

The NH protons of many secondary amines are labile on the n.m.r. time-scale. Under normal conditions proton-proton H-C-N-H spin-spin coupling can only be observed for those compounds with *pK_a* < 3.5¹ while more basic amines require rigorous drying precautions.^{2,3} The most probable mechanism for water-catalysed hydrogen exchange involves initial formation of N ··· HO H-bonds [reaction (1)] and this leads us



to believe that the introduction of H-bond electron donors more powerful than amines should scavenge the water molecules, slow the rate of NH exchange, and hence facilitate observations of HCNH ¹H n.m.r. coupling.

The results of introducing a range of H-bond electron donors into benzene solutions of three *N*-methylanilines (*pK_a* 4.62–5.36) are summarised in Table 1. The variation of *pK_a* limit for observation of coupling correlates well with reported H-bond electron-donor abilities towards OH centres^{4,5} but not with the aqueous basicities of the electron donors.⁴ Fluoride ions are particularly effective and enable coupling to be observed in the highest *pK_a* anilines. No special drying precautions were required to observe the couplings indicated in Table 1 so that the F⁻-18-crown-6 method⁶ compares very favourably in terms of convenience and efficiency with other methods such as those involving exhaustive drying processes with NaK alloy² or dimethylzinc.³ When the KF-18-crown-6-benzene-amine system reagents were dried before use, we observed that coupling is still clearly observed at amine:F⁻ molar ratios of > 50:1 and H₂O:F⁻ molar ratios of up to *ca.* 10:1.

We believe that these results lend weight to our hypothesis that the problem of water-catalysed hydrogen exchange in-

Table 1. Observation of H-C-N-H proton-proton coupling in benzene solutions of *N*-methylanilines.^a

H-Bond electron donor	<i>N</i> -Methyl- <i>o</i> -toluidine (<i>pK_a</i> 4.62)	<i>N</i> -Methyl-aniline (<i>pK_a</i> 4.85)	<i>N</i> -Methyl- <i>p</i> -toluidine (<i>pK_a</i> 5.36)
KF ^b (18-crown-6) ^c	Yes	Yes ^d	Yes
Ph ₃ PO	Yes	Yes	br ^e
Ph ₃ AsO ^t	Yes	br ^e	No
Me ₂ SO	br ^e	No	No
Pyridine	br ^{e,g}	No	No
Dimethylformamide	br ^e	No	No
CHCl ₃	No	No	No

^a A molar ratio of 2 electron donor to 1 amine was used throughout. ^b KF may be replaced by RbF or CsF but not by other non-fluoride salts such as KOAc, KCl, or KI. ^c The ¹H n.m.r. spectrum also shows a peak due to the F⁻-crown complex, the position of which is solvent dependent. ^d Coupling is lost on raising the sample temperature to 350 K although this coalescence temperature is dependent on concentration and the cation so that *T_c* (CsF) > *T_c* (RbF) > *T_c* (KF). ^e Broad, unresolved resonance. ^t Prepared by KMnO₄ oxidation of Ph₃As. ^g Coupling is observed in pure pyridine solution (ref. 1).

hibiting observation of coupling to labile hydrogens may be overcome by control of the H-bonding in the system.

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References

- I. D. Rae, *Aust. J. Chem.*, 1966, **19**, 409.
- K. L. Henold, *Chem. Commun.*, 1970, 1340.
- K. P. Shrestha and K. L. Henold, *J. Am. Chem. Soc.*, 1973, **95**, 6699.
- R. W. Taft, L. J. Gurka, L. Joris, P. v. R. Schleyer, and J. W. Rakshys, *J. Am. Chem. Soc.*, 1969, **91**, 4801.
- J. H. Clark and J. M. Miller, *J. Am. Chem. Soc.*, 1977, **99**, 498; J. Emsley, *Chem. Soc. Rev.*, 1980, 91.
- C. L. Liotta and H. P. Harris, *J. Am. Chem. Soc.*, 1974, **96**, 2250.