

The Proton Magnetic Resonance Spectra of Aromatic Amines and their Charge-transfer Complexes with Iodine and Iodine Monochloride

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ALTHOUGH ^1H n.m.r. techniques have been extensively used to study specific interactions between molecules in solution, only one report¹ deals with the effects, on the spectrum, of charge-transfer complexation with halogen molecules. As an extension to the recent work^{2,3} on the infrared spectra of the aromatic amine-IX ($X = \text{I}$, or Cl) complexes, a study has been made of the proton chemical shift changes which occur when such interaction takes place.

It is expected that the magnitude of the chemical shifts which occur when interaction with a strong electron acceptor like ICl takes place will be largely a measure of the electronic charge redistribution which occurs when charge-transfer is effected from the nitrogen lone-pair (although magnetic anisotropic effects may be of some importance also). The changes of shielding constants, so caused, in pyridine when iodine was used¹ as acceptor are not very large but it is thought that the ICl acceptor should produce more pronounced effects. Also

of interest is the effect of such complexation on the shielding constants of substituent methyl groups, especially in the α -position. There is evidence from the i.r. intensity² and equilibrium constants^{4,5} data that there is considerable steric hindrance to complex formation with 2,6-dimethylpyridine. The $\nu(\text{N-I})$ band intensity² and K_c ⁴ value for 2,6-dimethylpyridine- ICl are both considerably less than the corresponding values for pyridine- ICl . But the $\nu(\text{I-Cl})$ band intensity is essentially the same for these complexes indicating that the amount of actual charge-transfer is not affected by the methyl groups. Finally it is important to study the effect of solvent on these chemical shift changes. In particular, it is thought^{2,6} that specific interaction between the complex molecules and benzene solvent molecules may be responsible for the solubility of the amine- ICl complexes in this solvent, when they have very low solubilities in other non-polar solvents.

Here we report the shifts observed for the methyl

substituent group protons in various solvents. The ring-proton spectral analysis is, of course, more complicated and will be reported later. The results are summarised in the Table. Since the complexes have short life-times in solution,⁷ only average effects are observed.

for the 3- or 4-methyl groups as would be expected if the effect is an inductive one. However, it appears that the shift is much greater for the 2,6-dimethylpyridine than it is for 2-methylpyridine. This is the opposite of what would be expected if charge-transfer were hindered by the adjacent

TABLE

Methyl group proton shifts^a caused by complexation with iodine monochloride and iodine

Solvent ^b	2-Methylpyridine		2,6-Dimethylpyridine		2,3-Dimethylpyridine				2,4-Dimethylpyridine			
	Free base	Base -ICl	Free base	Base -ICl	Free base		Base-ICl		Free base		Base-ICl	
	2-Me	2-Me	2,6-Me	2,6-Me	2-Me	3-Me	2-Me	3-Me	2-Me	4-Me	2-Me	4-Me
Neat liquid ..	2.45	—	2.43	—	2.39	2.06	—	—	2.45	2.14	—	—
Benzene ..	2.42	1.96	2.41	2.19	2.38	1.85	1.97	1.49	2.45	1.89	2.03	1.55
Chloroform ..	2.56	2.74	2.50	2.85	2.50	2.27	2.70	2.40	2.49	2.27	2.69	2.41
Tetrachloroethane	2.54	2.73	2.50	2.81	2.45	2.22	2.70	2.39	2.50	2.30	2.68	2.43
Carbon tetrachloride ..	2.49	— ^c	2.46	2.81	2.47	2.29	2.71	2.38	2.41	2.25	— ^c	— ^c
	Free base	Base-I ₂	Free base	Base-I ₂	Free base		Base-I ₂		Free base		Base-I ₂	
Carbon tetrachloride ..	2-Me	2-Me	2,6-Me	2,6-Me	2-Me	3-Me	2-Me	3-Me	2-Me	4-Me	2-Me	4-Me
	2.49	2.58	2.46	2.54	2.47	2.29	2.54	2.30	2.41	2.25	2.53	2.35

^a Shifts are given in p.p.m. (± 0.02) from the tetramethylsilane signal (internal standard) at 60 Mc./sec. and 33°.

^b Solutions of free base are 10% by volume. Solutions of complex are approximately 0.1 molar.

^c Complex insufficiently soluble in carbon tetrachloride.

A study of the "free" base molecules in various solvents shows quite clearly the diamagnetic anisotropic effect⁸ of benzene solvent molecules in causing a high-field shift of the 3- and 4-methyl group resonances, but very little shift of the 2- and 6-methyl group resonances. These effects have been reported previously for methylpyridines^{9,10} and attempts have been made to interpret the results in terms of specific benzene-solute interactions during which the benzene molecules tend to keep away from the nitrogen lone-pair. When the bases are diluted with chloroform, a low-field shift of the 2-, 3-, 4-, and 6-methyl group resonances is observed, as would be expected when the molecules of base are separated in an aliphatic solvent medium. Since chloroform-aromatic amine hydrogen-bonded complexes are well-known,¹¹ a check was made on the "free" base chemical shifts using carbon tetrachloride as a solvent. The change of shielding constant due to the specific interaction with chloroform or tetrachloroethane is very small.

When the ICl complexes are dissolved in chloroform, tetrachloroethane, or carbon tetrachloride, the methyl resonance signals shift to low field as compared with those for the free bases (in the same solvents). This shift is expected since charge transfer from the lone-pair would be expected to lower the methyl proton shielding constants. The shift is greater for the 2- and 6-methyl groups than

methyl groups in 2,6-dimethylpyridine. It seems possible that this larger down-field shift may be caused by direct interaction between the ICl and the adjacent methyl groups when complexation takes place.

When the complexes are dissolved in benzene there is a large upfield shift of *all* the methyl group resonances. This would appear to indicate definite specific interaction of benzene with the complex molecules (though, the lone pair-benzene repulsion has now been effectively removed). There is also some indication that this effect is somewhat greater for the 2-methyl group than it is for the 3- or 4-methyl groups. This could be interpreted in terms of a benzene-ICl interaction (the ICl being attached to the nitrogen). Attempts at confirming the existence of such specific interactions by observing the effects on the ¹H n.m.r. and i.r. spectra of the benzene molecule have, so far, met with little, if any, success. More data are needed, however, before one can assert that this effect is real.

As can be seen from the Table, the methyl resonance shifts caused by using iodine as the acceptor are much smaller (although only 60—70% of the amine in solution is complexed). In most cases, however, the shift changes are quite real and it appears that even with a relatively weak acceptor, such as iodine, such changes in chemical shift may be used to study the effects of charge-transfer complexation with strong electron donors.

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- ¹ A. Fratiello, *J. Chem. Phys.*, 1964, **41**, 2204.
- ² J. Yarwood and W. B. Person, *J. Amer. Chem. Soc.* to be published.
- ³ R. F. Lake and H. W. Thompson, *Proc. Roy. Soc.*, 1967, *A*, **279**, 440.
- ⁴ A. I. Popov and R. H. Rygg, *J. Amer. Chem. Soc.*, 1957, **79**, 4622.
- ⁵ J. N. Chauduri and S. Basu, *Trans. Faraday Soc.* 1959, **55**, 898.
- ⁶ E. K. Plyler and R. S. Mulliken, *J. Amer. Chem. Soc.*, 1959, **81**, 823.
- ⁷ See, for example, for iodine complexes, V. L. Brownsell and A. H. Price, *Chem. Soc. Special Publ.*, No. 20, 1966, pp. 83-87.
- ⁸ J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, London, 1959, pp. 180-2.
- ⁹ J. Ronayne and D. H. Williams, *Chem. Comm.*, 1966, 712.
- ¹⁰ J. N. Murrell and V. M. S. Gil, *Trans. Faraday Soc.*, 1965, **61**, 402.
- ¹¹ G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Freeman, San Francisco, 1960.