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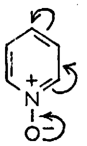
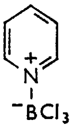
# *N*-Oxides and Related Compounds. Part XXVII.[1] A Proton Magnetic Resonance Investigation of the Interaction of Pyridines with Some Lewis Acids

By A. R. Katritzky, F. J. Swinbourne, and B. Ternai

The variation is discussed of the chemical shifts of ring protons of a series of methyl-substituted pyridines in the following solvents: arsenic trichloride, phosphorus trichloride, sulphur dioxide, carbon tetrachloride, and cyclohexane. The solvent shifts for the first three solvents are shown to be qualitatively similar although quantitatively less than for trifluoroacetic acid. No evidence was found for back-co-ordination in pyridine complexes with arsenic trichloride or phosphorus trichloride.

The back-co-ordination of electrons from the oxygen atom is important in determining the chemical reactivity[2] and physical properties[3] of heterocyclic *N*-oxides, such as pyridine 1-oxide (I). Such an effect is not possible in complexes such as pyridine–boron trichloride (II).[4] But it could occur if the atom adjacent to the ring-nitrogen carried a lone pair of electrons. The present Paper records a proton magnetic resonance study of the interaction of some methylpyridines with phosphorus trichloride and arsenic trichloride, which could form complexes of type (III), and with some other interacting solvents.


(I)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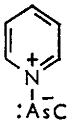
(III)

Complex formation between pyridine and arsenic trichloride has been previously demonstrated;[5] recently, a complex formed between αα′-bipyridyl and arsenic trichloride has been studied.[6] Complexes of alkylpyridines and sulphur dioxide are also quite well known;[7] for a recent discussion of their effect and reactivity at the pyridine nitrogen atom see ref.[8]

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[2] A. R. Katritzky, *Quart. Rev.*, 1956, **10**, 395.

[3] Cf. *inter alia*, A. R. Katritzky, *J. Chem. Soc.*, 1959, 2049.

[4] C. M. Bax, A. R. Katritzky, and L. E. Sutton, *J. Chem. Soc.*, 1958, 1258.

[5] O. Dafert and Z. A. Melinski, *Chem. Ber.*, 1926, **59***B*, 788; W. B. Shirey, *J. Amer. Chem. Soc.*, 1930, **52**, 1720; C. S. Gibson, J. D. A. Johnson, and D. C. Vining, *J. Chem. Soc.*, 1930, 1710; E. Montignie, *Bull. Soc. chim. France*, 1935, **2**, 1365; B. P. Kondratenko, *J. Gen. Chem.* (*U.S.S.R.*), 1934, **4**, 246.

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Although $AsCl_3$ (ref. 9) and $SO_2$ (ref. 10) have both been used as solvents for n.m.r. spectroscopy, the effects of solvent interaction on the spectra of amines has not been previously studied for these systems. However, the effects of other solvents,[11] of co-ordination,[12] of protonation,[13-15] and of counter-ions,[16] on the spectra of alkylpyridines has received attention; some of this work is discussed below.

## EXPERIMENTAL

Pyridines and *p*-disubstituted benzenes were fractionated or recrystallised prior to use, and liquids dried over a molecular sieve. All had m. p. or b. p. in accordance with literature values.

Arsenic trichloride was distilled in a vacuum line. Initially, solutions in this solvent were prepared in the vacuum line, but tests showed that identical results were obtained by making up the n.m.r. tubes in a dry-box. Phosphorus trichloride was treated similarly. Gaseous sulphur dioxide was passed through concentrated sulphuric acid and over calcium chloride and slowly condensed into n.m.r. tubes cooled in acetone–solid $CO_2$, care being taken to exclude moisture.

N.m.r. spectra were obtained on Perkin-Elmer permanent magnet spectrometers at 60 and 40 Mc./sec. with sample spinning and side band calibration. $SiMe_4$ was used as an internal standard in all cases; for $AsCl_3$ the shifts of internal and external $SiMe_4$ showed a difference of 0·72 p.p.m. However, calculation of the correction for bulk susceptibility of $AsCl_3$ gave 0·71 p.p.m., indicating no appreciable interaction between $AsCl_3$ and $SiMe_4$.

Some of the spectra were amenable to first-order treatment, others were analysed by Edsac II computer (Cambridge), using the ABC programme of Banwell and Sheppard.[17]

TABLE 1

Chemical shifts of α-protons (p.p.m.)

| | Solvents | | | | | |
|---|---|---|---|---|---|---|
| Pyridine | $C_6H_{12}$ | $CCl_4$ | $PCl_3$ | $AsCl_3$ | $SO_2$ | $CF_3COOH$ |
| 4-methyl | 1·65 | −0·01 | −0·09 | −0·28 | −0·15 | −0·35 |
| 2,3-dimethyl | 1·81 | 0·0 | −0·12 | −0·24 | −0·01 | — |
| 2,5-dimethyl | 1·77 | +0·01 | −0·12 | −0·23 | +0·06 | — |
| 3,4-dimethyl | 1·80 | +0·01 | −0·08 | −0·30 | −0·09 | −0·36 |
| | 1·82 | +0·01 | | −0·31 | | |
| 3,5-dimethyl | 1·72 | +0·03 | — | −0·17 | — | −0·93 |

Values for cyclohexane solvent are on the τ scale. For other solvents, solvent shift relative to cyclohexane is given, -ve sign indicating down field.

TABLE 2

Chemical shifts of β-protons (p.p.m.)

| | Solvents | | | | | |
|---|---|---|---|---|---|---|
| Pyridine | $C_6H_{12}$ | $CCl_4$ | $PCl_3$ | $AsCl_3$ | $SO_2$ | $CF_3COOH$ |
| 4-methyl | 3·11 | −0·09 | −0·17 | −0·60 | −0·64 | −1·07 |
| 2,3-dimethyl | 3·24 | −0·10 | −0·19 | −0·47 | −0·53 | — |
| 2,5-dimethyl | 3·16 | −0·05 | −0·11 | −0·35 | −0·34 | −1·05 |
| 2,6-dimethyl | 3·19 | +0·15 | −0·02 | −0·26 | −0·26 | −0·97 |
| 3,4-dimethyl | 3·20 | −0·09 | −0·20 | −0·65 | −0·62 | −1·17 |
| 2,4,6-trimethyl | 3·33 | −0·01 | — | −0·52 | −0·24 | −0·89 |

Values indicated as in Table 1.

TABLE 3

Chemical shifts of γ-protons (p.p.m.)

| | Solvents | | | | | |
|---|---|---|---|---|---|---|
| Pyridine | $C_6H_{12}$ | $CCl_4$ | $PCl_3$ | $AsCl_3$ | $SO_2$ | $CF_3COOH$ |
| 2,3-dimethyl | 2·87 | −0·10 | −0·51 | −0·47 | −0·51 | — |
| 2,5-dimethyl | 2·85 | −0·07 | −0·47 | −0·44 | −0·47 | −1·35 |
| 2,6-dimethyl | 2·72 | −0·05 | −0·37 | −0·39 | −0·37 | −1·21 |
| 3,5-dimethyl | 2·80 | +0·05 | — | −0·56 | — | −1·81 |

Values indicated as in Table 1.

## RESULTS AND DISCUSSION

The results are recorded in Tables 1—3. In each of these Tables values for cyclohexane solvent are given on the τ scale. These values are in accordance with literature values.[18] For other solvents, shifts relative

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[13] J. D. Baldeschwieler and E. W. Randall, *Proc. Chem. Soc.*, 1961 303.

[14] V. M. S. Gil and J. N. Murrell, *Trans. Faraday Soc.*, 1964, **60**, 248.

[15] H. Saito, K. Nukada, H. Kato, T. Yonezawa, and K. Fukui, *Tetrahedron Letters*, 1965, 111.

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to those for cyclohexane are recorded. We also compared the intra-ring spin–spin coupling constants, but found [19, 20] that these showed very little solvent variation. We also investigated the chemical shifts of 1-chloro-4-nitrobenzene and 1-methyl-4-nitrobenzene in several of the solvents used in the present work: the ring protons showed variation of $<0{\cdot}15$ p.p.m. We therefore conclude that the interaction causing the variations in chemical shift in the pyridines do not involve the $\pi$-electron cloud, but must be concerned with the nitrogen lone electron pair.

The results in Tables 1—3 show:

(*a*) For a particular compound and solvent, the solvent shift away from the cyclohexane position is greater for the $\gamma$- and $\beta$-protons than for the $\alpha$-proton.

(*b*) For a particular compound and ring position the solvent shifts are in the order: $CF_3CO_2H > SO_2 \sim AsCl_3 > PCl_3 > CCl_4$.

(*c*) For any solvent, the solvent shifts are usually in the order: 4-picoline and 3,4-lutidine > 2,3- and 2,5-lutidine > 2,6-lutidine. This indicates that methyl groups $\alpha$- to the ring nitrogen atom have an unfavourable steric effect on the solvent interaction, as might have been expected.

It may be concluded that the shifts in the other solvents are qualitatively similar, although quantitatively smaller, than those in trifluoroacetic acid.

In trifluoroacetic acid, the pyridines exist completely in the form of the corresponding pyridinium ion. Baldeschweiler and Randall [13] showed that the greater down-field shift of the $\beta$- and $\gamma$-protons on protonation could be accounted for by a mixing in of the $n \longrightarrow \pi^*$ excited state of relatively low energy. Gil and Murrell [14] correlated chemical shifts with $\pi$-electron densities, by considering that the magnetic anisotropy of the nitrogen atom and the local dipole effects of the lone pair were of comparable importance. Their values were in good agreement with the theoretical calculation of Brown and Heffernan.[21] Fratiello and Christie's [12] results for the interaction of pyridine with cations show that for strongly interacting cations, the shift of the $\gamma$- and $\beta$-protons is relatively greater than that for the $\alpha$-protons.

As the results with $AsCl_3$ and $SO_2$ are similar, but smaller than those with $CF_3CO_2H$, the simplest interpretation is that complex formation occurs by simple covalent bonding between the nitrogen electron pair and a solvent molecule as acceptor. The covalent bonding, and thus the transfer of electron density to the acceptor molecules, is less with $AsCl_3$ and $SO_2$ than with a proton, and it is still less for $PCl_3$ as acceptor.

We conclude that our results afford no evidence for significant back-co-ordination of the lone pair on phosphorus or arsenic to the $\pi$-electron system of the pyridine ring.

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[19] For full details see F. J. Swinbourne, Thesis, Norwich, 1965.

[20] For full details see B. Ternai, Thesis, Norwich, 1966.

[21] R. D. Brown and M. L. Heffernan, *Austral. J. Chem.*, 1959, **12**, 554.