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Studies of Nuclear Magnetic Resonance Spectra of Positive Halogen Salts of Pyridine and Substituted Pyridines

S.K. BARUAH* and P.K. BARUAH†
Department of Chemistry, Dibrugarh University, Dibrugarh-786 004, India

In the NMR studies of positive halogen salts of pyridine and substituted pyridines, it is observed that the effect of the substituents on the chemical shift is quite remarkable and perturbed significantly. It appears that in shifting from pyridine to the pyridinium cation, there is quite a large decrease in electron-density at the 4-position and smaller loss at 2- and 3-positions. It is also observed that the unit of electron density corresponds to a shift, which amounts to 0.22, 0.38 and 0.63 in γ-scale at 2-, 3- and 4-position respectively. Examination of the results shows that there is more downfield shift of the ring protons on complexation with bromine than that of its iodine counterpart. Therefore, it would appear to be reasonable to interpret a more prominent downfield shift as arising from the deshielding effect of π-electron density redistribution in the bromine complex which is greater than that of the iodine complex.

Key Words: NMR, Halogen salts, Pyridine, Substituted pyridines.

INTRODUCTION

Salts containing the ions $[Py_2I]^+$ and $[Py_2Br]^+$ have been known for a considerable time[1–4]. These ions are in agreement with the requirements of bicoordination for I^+ and Br^+ species.

NMR spectroscopy has been applied with limited success to the investigation of the structure of molecular complexes of positive halogen salts of pyridine and substituted pyridines. ^1H NMR chemical shifts and coupling constants for series of 2-substituted-5-nitropyridines and 2-substituted 3-nitropyridines, both in the free base and protonated form were reported[5]. The effects of the substituents on the chemical shifts are substantial but not unusual. The coupling constants are less sensitive to the nature of the substituent and are perturbed only slightly when the ring nitrogen is protonated. The contribution to the proton chemical shifts in pyridine due to the magnetic anistropy of the nitrogen atom and the polarization of the (C—H) bonds by the nitrogen lone pair has been calculated. Few reports dealing with the application of NMR technique to donor-acceptor complexes have also been reported[6–8].

In this work, the proton NMR spectra of the complexes of positive halogen

†Department of Chemistry, J.B. College, Jorhat, India.

salts of pyridine and substituted pyridines have been studied in order to get an additional information on the extent and nature of the electronic rearrangement which occurs on complex formation. It is observed that the effect of the substituent in different positions of the ring on the chemical shifts is quite remarkable and perturbed significantly.

EXPERIMENTAL

Materials: The following chemicals are purified as described in the literature[9]. 'AnalaR' pyridine is dried over potassium hydroxide and barium oxide for several days. The liquid is then distilled from fresh barium oxide. The infrared spectra of purified pyridine obtained in this way does not show any bands of picoline. α-, β- and γ-Picoline (BDH), 2,5-lutidine and 2,6-lutidine (Fluka) are dried over potassium hydroxide and barium oxide for 24 h. They are distilled under reduced pressure and kept over molecular sieve 'type 4A'.

Sodium perchlorate (BDH), sodium fluoroborate (Fluka) and silver nitrate (AnalaR) are used as such. Methanol, chloroform all are spectrograde and used without purification. Nujol is kept over molecular sieve 'type 4A' for several days prior to use. Bromine (E. Merck) is used without further purification. Iodine (BDH) is purified by sublimation from mixture of CaO and KI.

Preparation: Preparation of these complexes has been discussed elsewhere[10–12]. Measured quantity of sodium perchlorate in water is directly added slowly by constant stirring whereby a white solid compound is formed. This is then washed with ice-cold distilled water for several times to remove the excess of $AgNO_3$ and the solid is dried over P_2O_5 in a desiccator. The silver complex is then dissolved in a mixture of MeOH + $CHCl_3$ solution (1 : 10). It is then treated with I_2 or Br_2 solution in MeOH whereby silver is precipitated as AgI or AgBr. It is filtered and the filtrate is treated with sodium dried ether and a white compound appears in every case. It is then recrystallized from spectrograde methanol, dried *in vacuo* over P_2O_5. The identification of the compound is established by iodine/bromine analysis and by melting point. Elemental analyses and melting points of the compounds are given in Table-1.

Spectroscopy: The NMR spectra are recorded in the Varian high resolution NMR Spectrometer operating at 299.9486 MHz under conditions which in general comply with the instrument specification noted as: speificc width: 5000.0 Hz; acquired time: 4.0 s; pulse width: 8.0 μs.

RESULTS AND DISCUSSION

The ring proton resonance spectra of the complexes are presented in Figs. 1 and 2. The proton resonance spectra of the free bases and their complexes in $CDCl_3$ have been analyzed to give the chemical shifts (δ) and are reported in Tables 1 and 2, along with the amount of shifts which occur at different ring protons and methyl group protons when complexation takes place.

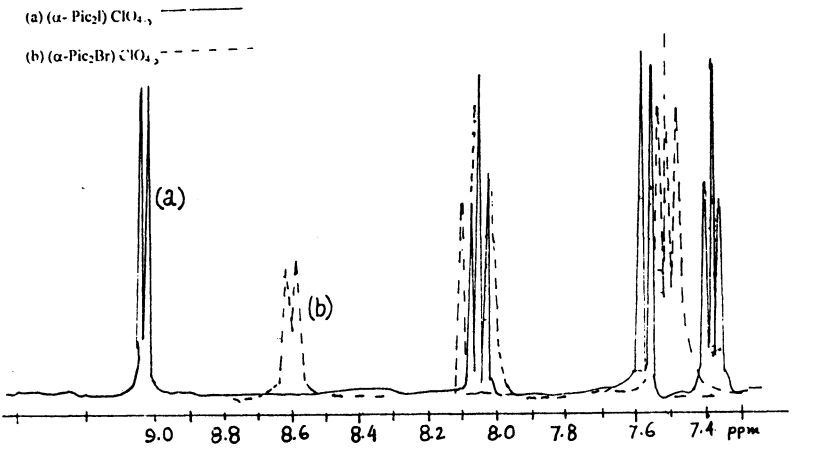


Fig. 1. NMR Spectra of (a) $(\alpha\text{-Pic}_2\text{I})ClO_4$, (b) $(\alpha\text{-Pic}_2\text{Br})ClO_4$

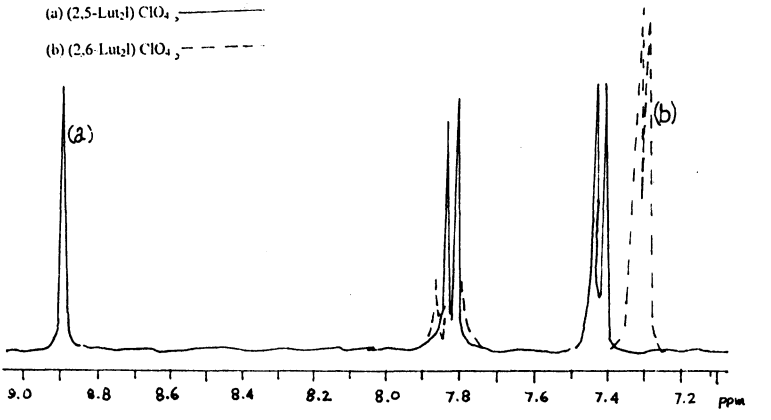


Fig. 2. NMR Spectra of (a) $(2,5\text{-Lut}_2\text{I})ClO_4$, (b) $(2,6\text{-Lut}_2\text{I})ClO_4$

It is now a well established fact that the chemical shift observed in proton resonances reflect differences in the distribution about chemically non-equivalent protons. These shifts arise from the small magnetic fields set up by the electrons, which oppose the applied field and are directly proportional to it. This is commonly called a diamagnetic shielding of the protons by the electrons. The result of these shielding effects on the proton resonance is a set of absorption lines which correspond to the number of non-equivalent protons contained in the molecule. The conclusion that the chemical shifts can be taken as an approximate measure of electron density is subject to the restriction that no important changes in bond hybridization occur. The current theories predict differences in the electron distribution at the α-, β-, γ-positions of pyridine and substituted pyridines. This suggests that under conditions of high resolution differences in chemical shifts may be observable.

TABLE-1
ELEMENTAL ANALYSES AND MELTING POINTS OF THE COMPOUNDS

Compound	Iodine		Bromine		m.p. (°C)
	Calc.	Found	Calc.	Found	
$(Py_2I)ClO_4$	33.03	32.54			180
$(Py_2Br)ClO_4$			20.88	20.02	175
$(\alpha\text{-}Pic_2I)ClO_4$	30.77	29.50			136
$(\alpha\text{-}Pic_2Br)ClO_4$			21.86	20.50	121
$(\alpha\text{-}Pic_2I)BF_4$	31.75	30.87	+		142
$(\alpha\text{-}Pic_2Br)BF_4$			22.66	21.08	140
$(\beta\text{-}Pic_2I)ClO_4$	30.77	30.00			141
$(\beta\text{-}Pic_2Br)ClO_4$			21.86	21.25	135
$(\beta\text{-}Pic_2I)BF_4$	31.75	30.50			145
$(\beta\text{-}Pic_2Br)BF_4$			22.66	21.75	142
$(\gamma\text{-}Pic_2I)ClO_4$	30.77	29.75			165
$(\gamma\text{-}Pic_2Br)ClO_4$			21.86	21.06	154
$(\gamma\text{-}Pic_2I)BF_4$	31.75	31.05			152
$(2,5\text{-}Lut_2I)ClO_4$	28.82	27.45			132
$(2,6\text{-}Lut_2I)ClO_4$	28.81	28.20			136
$(2,5\text{-}Lut_2I)BF_4$	29.67	28.85			140

*Py = Pyridine; Pic = Picoline; Lut = Lutidine

TABLE-2
AMOUNT OF CHEMICAL SHIFTS (Δδ) OF PYRIDINE AND SUBSTITUTED PYRIDINES IN THEIR COMPLEXES IN COMPARISON WITH FREE BASES

Complexes	α-Proton (*o*-proton)		β-Proton (*m*-proton)		γ-Proton (*p*-proton)
	2-H^1	6-H^1	3-H^1	5-H^1	4-H^1
$(Py_2I)ClO_4$	0.22	0.22	0.38	0.38	0.63
$(Py_2Br)ClO_4$	0.29	0.29	0.41	0.41	0.65
$(\gamma\text{-}Pic_2I)ClO_4$	0.13	0.13	0.32	0.32	—
$(\gamma\text{-}Pic_2Br)ClO_4$	0.18	0.18	0.42	0.42	—
$(\gamma\text{-}Pic_2I)BF_4$	0.12	0.12	0.32	0.32	—
$(2\text{-}6\text{-}Lut_2I)ClO_4$	—	—	0.28	0.28	0.39
$(2\text{-}6\text{-}Lut_2I)BF_4$	—	—	0.32	0.32	0.40
$(\alpha\text{-}Pic_2I)ClO_4$	—	0.59	0.52	0.33	0.55
$(\alpha\text{-}Pic_2Br)ClO_4$	—	0.16	0.48	0.48	0.54
$(\alpha\text{-}Pic_2I)BF_4$	—	0.49	0.60	0.38	0.62
$(\alpha\text{-}Pic_2Br)ClO_4$	—	0.45	0.49	0.49	0.54
$(\beta\text{-}Pic_2I)ClO_4$	0.13	0.13	—	0.36	0.55
$(\beta\text{-}Pic_2I)BF_4$	0.12	0.12	—	0.36	0.56
$(2,5\text{-}Lut_2I)ClO_4$	—	0.49	0.32		

The results reported in Tables 1 and 2 show that when the strength of the (N—X) bond between the nitrogen atom of pyridine and halogen cation (X^+) increases, there is a marked shift of the resonance of the β- and γ-protons to lower field strength whereas that of the α-proton shifts relatively little. Similar observations have been made by Smith and Schneider[13] in their studies of the protonation of pyridine by trifluoroacetic acid. Gil and Murrel[14] have interpreted the PMR spectrum of pyridine by proposing that the observed chemical shifts of the ring protons are governed (a) by the magnetic anisotropy of the nitrogen atom and (b) by the influence of the nitrogen atomic dipole. However, no explanations have been offered for the shifts observed on (N—X) bonding.

It is evident that the magnetic anisotropy of an atom can strongly influence the chemical shift of neighbouring protons in the same molecule. The anisotropy is due to the paramagnetic part of the total susceptibility and arises as a result of a mixing of the ground state of the molecule with low-lying excited states under the influence of the applied magnetic field. The rigorous calculation of the magnitude of the paramagnetic contribution, σ_p, to the screening constant of a neighbouring proton required a knowledge of all the excited states of the molecule in question[15].

Pyridine and other nitrogen heterocyclic compounds have low-lying excited states and transitions between their ground states and excited states can be detected in their UV spectra. The lowest energy transition is $n \rightarrow \pi^*$ in which one of the lone-pair (non-bonding) electrons of the nitrogen atom is promoted into the lowest energy antibonding π-molecular orbital of the ring system. It may therefore be assumed that the largest contribution to σ_p is associated with this transition. The field associated with the nitrogen atomic dipole in pyridine can make a large contribution to the screening constants of the ring protons.

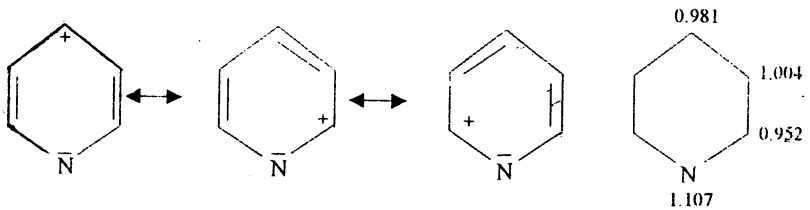
Replacement of the nitrogen lone-pair electrons by an (N—X) bond as in the pyridinium ion leads to a considerable reduction in this effect with the result that all the resonance should move upfield.

Some further information on this point may be drawn by reference to the phenyl-metallic compounds[16]. Here the ionic character of the metal-carbon bond is the greatest in phenyl lithium and least in diphenyl zinc. If dipole effects are important then one would predict that the resonances of all the ring protons would shift to low field in going from phenyl lithium to diphenyl zinc. The observed shifts of the meta- and para-proton resonances in our compounds exhibit the appropriate trend predicted on this basis. Both the effects discussed above lead to the prediction that the resonance of the α-proton of pyridine and its derivatives should shift considerably upfield on complex formation with halogen cation while those of the β- and γ-protons are expected to move in the same direction but to a lesser extent.

These conclusions are in accordance with our observation with a slight difference in γ-protons. Evidently there must also be some other compensating effects, which have not been taken into account.

In the case of the phenylcarbanion only one low-energy valence bond structure can be written. The essential difference in the case of pyridine is that the nitrogen

is more electronegative than carbon and there is a definite tendency for the π-electrons to move on to this atom giving rise to the resonance structure below. The resulting distribution of π-electron density around the ring has also been shown as



The fact that the resonance of both γ- and β-proton can be partially attributed to the importance of the above structures.

It is apparent that, in going from pyridine to the pyridinum cation, there is quite a large decrease in electron density at the γ-position and a smaller loss at the α and β-positions. Assuming that one unit of electron density corresponds to a shift to 10 ppm[17], these shifts amount to 0.53, 0.787 and 1.52 ppm at the α, β, and γ positions, respectively. These figures are incompatible with the observed shifts.

On the basis of this we have observed that in the NMR spectrum of $(Py_2I)ClO_4$ complex, these shifts amount to 0.22, 0.38 and 0.63 in δ-scale at the α, β and γ positions respectively (Table-2). A similar trend is also observed for $(Py_2Br)ClO_4$ complex. Examination of the results in Table-2 shows that there is more downfield shift of the ring protons on complexation with bromine than that of the iodine complex. This result has been interpreted in terms of acceptor power. It would appear to be reasonable to interpret a more prominent downfield shift as arising from the deshielding effect of π-electron density redistribution in the bromine complex which is greater than that of iodine complex.

In $(\alpha\text{-}Pic_2I)ClO_4$, $(\alpha\text{-}Pic_2I)BF_4$ complexes (Table-2) the resonance of both the 6- and 4-protons occurs at lower field with doublet and triplet respectively than that of the 5- and 3-protons. This is quite a good approximate correlation which can be made between the pK_4 values of the bases and the downfield shifts for the β- and γ-protons.

Chemical shift of CH_3-group protons

Examination of the results in Table-3 shows that there is a considerable downfield shift of the methyl group protons on complexation. The shift is relatively greater for the 2-methyl group than it is for the 3- or 4-methyl groups. It seems possible that this larger downfield shift may be due to direct interaction between the halogen cation and the adjacent methyl group when coordination takes place. It can be readily interpreted in terms of inductive effect, which is predominant for the 2-position than the 3- or 4-positions.

TABLE-3
CHEMICAL SHIFT VALUES FOR CH_3-GROUP PROTONS

Compound	Chemical shift values in δ-scale		
	Complex	Free Base	Amount of shift
(α-Pic_2I)ClO_4	2.87	2.56	0.31
(α-Pic_2Br)ClO_4	2.84	2.56	0.28
(α-Pic_2I)BF_4	2.86	2.56	0.30
(α-Pic_2Br)BF_4	2.85	2.56	0.29
(β-Pic_2I)ClO_4	2.50	2.40	0.10
(α-Pic_2I)BF_4	2.51	2.40	0.11
(γ-Pic_2I)ClO_4	2.53	2.30	0.23
(γ-Pic_2Br)ClO_4	2.45	2.30	0.15
(γ-Pic_2I)BF_4	2.52	2.30	0.22
(2,5-Lut_2I)ClO_4	2.79[a] 2.44[b]	2.56[a] 2.32[b]	0.23[a] 0.12[b]
(2,6-Lut_2I)ClO_4	2.77	2.52	0.25
(2,6-Lut_2I)BF_4	2.74	2.52	0.22

a = 2-Methyl group; b = 5-Methyl group.

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