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NMR Spectra of Pyridine, Picolines and Hydrochlorides and of Their Hydrochlorides and Methiodides

by

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In our earlier investigations [1] changes in the molecular structure produced by quaternization of pyridine and its homologues were studied in terms of the infrared spectra of these compounds. NMR spectra of pyridine, picolines and of their hydrochlorides and methiodides are now explored to establish the changes in chemical shift associated with the formation of hydrochlorides and quaternary salts.

Experimental

The hydrochlorides of pyridine and of the three picolines were prepared in the conventional way. The methiodides were prepared by reacting pyridine and picolines with methyl iodide in the mole ratio 1 : 1.1. Each salt was purified by crystallization from absolute alcohol. The m.p. and analysis data are collected in Table I. The NMR spectra of aqueous 10% solutions of the substances were taken in a Varian HR-60 spectrometer at 60Mc/s and 27°C. The spectra were calibrated by the side-band technique (±1 c./s.). The signal of water was used as the internal standard. A value of 5.20 p.p.m. was added to each chemical shift to obtain results relative to the tetramethylsilane signal in τ units. The spectra are presented in Figs. 1 and 2 and in Table II.

TABLE I

Compound	M.p., °C	Formula	N, %	
			required	found
Py hydrochloride	84	C_5H_6NCl	12.1	12.25
Py methiodide	116—117	C_6H_8NI	6.3	6.3
α-P hydrochloride	80	C_6H_8NCl	10.8	10.85
α-P methiodide	224	$C_7H_{10}NI$	5.9	6.1
β-P hydrochloride	80	C_6H_8NCl	10.8	10.95
β-P methiodide	80	$C_7H_{10}NI$	5.9	5.7
γ-P hydrochloride	93	C_6H_8NCl	10.8	10.95
γ-P methiodide	158	$C_7H_{10}NI$	5.9	6.1

Py — pyridine, P — picoline.

TABLE II

Chemical shifts, τ p.p.m.

Compound	Hα	Δα	Hβ	Δβ	Hγ	Δγ	N—CH_3	C—CH_3	ΔCH_3
Pyridine	1.48		2.60		2.17				
Py hydrochloride	1.29	—0.19	2.00	—0.60	1.52	—0.65			
Py methiodide	0.90	—0.59	1.63	—0.97	1.15	—1.02	5.27		
α-Picoline	1.56		2.67		2.17			7.68	
α-P hydrochloride	1.34	—0.22	2.35	—0.32	1.80	—0.37		7.34	—0.34
α-P methiodide	1.10	—0.46	1.92	—0.75	1.45	—0.72	5.35	6.96	—0.72
β-Picoline	1.82		2.84		2.50			7.85	
β-P hydrochloride	1.49	—0.33	2.10	—0.74	1.65	—0.85		7.44	—0.41
β-P methiodide	1.20	—0.62	1.84	—1.00	1.40	—1.10	5.44	7.25	—0.60
γ-Picoline	2.09		3.10					7.71	
γ-P hydrochloride	1.45	—0.64	2.17	—0.93				7.40	—0.31
γ-P methiodide	1.14	—0.95	1.92	—1.18			5.47	6.99	—0.72

Py — pyridine, P — picoline.

Results and discussion

The NMR spectra of pyridine and picolines represent complicated spectral systems of types AA'BB'C; ABCD and AA'BB'. The chemical shifts are rather large in relation to the coupling constants; hence, it was possible to determine each chemical shift by estimating the centres of gravity of the multiplets with an accuracy up to ±0.07 p.p.m.

Proton chemical shifts in the pyridine spectrum show considerable differences between positions α, β and γ. According to the literature [2] the chemical shift of aromatic protons in benzene is 2.73 p.p.m. Brügel [3] found the following values of the chemical shift for pyridine: 1.71, 3.23 and 2.85 p.p.m. for protons in positions α, β and γ, and for 30 per cent solutions in DMSO, the values of 1.41; 2.62 and 2.25 p.p.m. for the three positions, respectively. Our values of chemical shift (1.48; 2.60 and 2.17 p.p.m.) slightly different from those given above can be explained by the use of water as solvent. Comparing the chemical shifts of benzene and pyridine we observe that only the chemical shift of protons in position β lies close to the chemical shift of aromatic protons, those in positions α and γ being much lower.

The picolines show a similar arrangement of chemical shifts. In each spectrum the chemical shift of α protons is lower that those of β and γ protons and the chemical shift of β protons is closest to that of aromatic protons.

The NMR spectra of hydrochlorides showed changes in chemical shifts. The τ values for ring and methyl group protons in picolines are shifted towards lower fields. The smallest change was observed for α protons; it could be explained by the paramagnetic effect previously observed [4] in free bases on comparing the chemical shifts of α, β and γ protons.

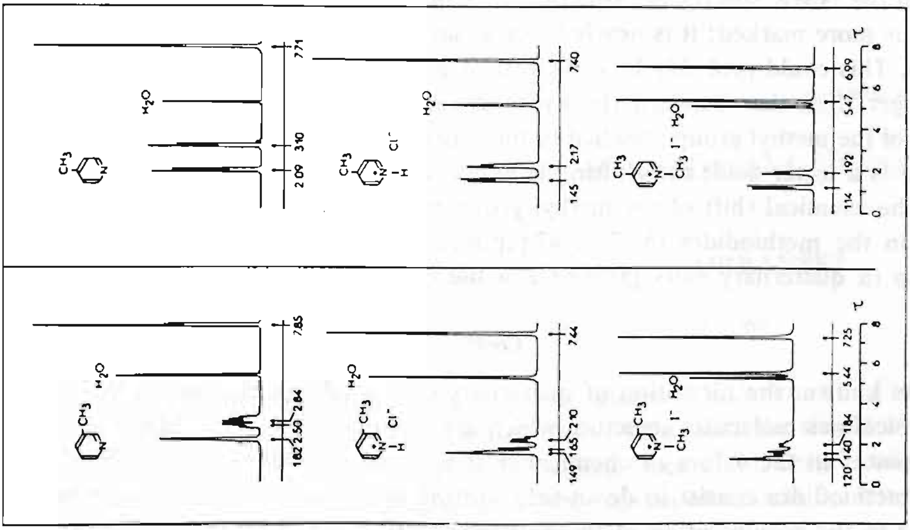
CH3
H2O
2.09
3.10
7.71
CH3
Cl⁻
N–H
H2O
1.45
2.17
7.40
CH3
CH3
I⁻
H2O
1.14
1.92
5.47
6.99
0 2 4 6 8 τ
CH3
H2O
1.82
2.50
2.84
7.85
CH3
Cl⁻
N–H
H2O
1.49
1.65
7.0
7.44
CH3
I⁻
CH3
H2O
1.20
1.40
1.84
5.44
7.25
0 2 4 6 8 τ

Fig. 2

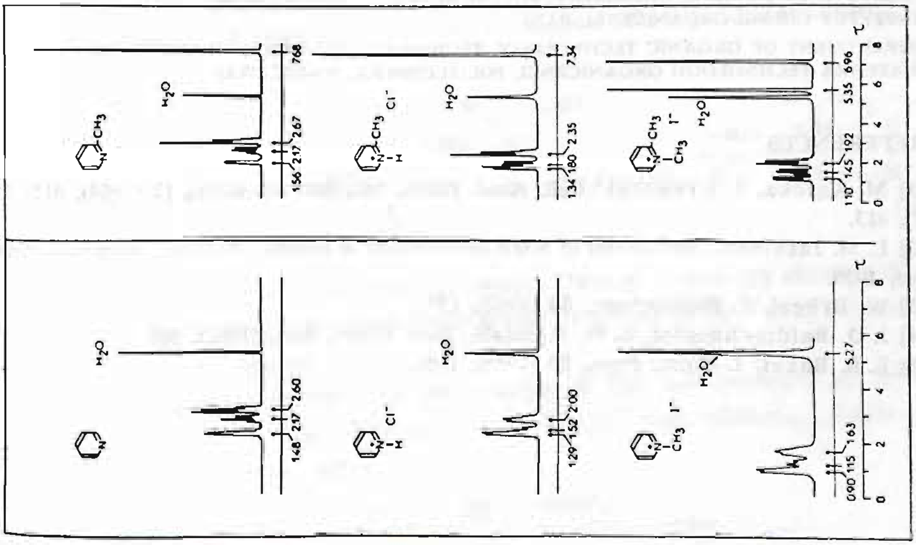
CH3
H2O
1.56
2.17
2.67
7.68
CH3
Cl⁻
N–H
H2O
1.34
1.80
2.35
7.34
CH3
I⁻
CH3
H2O
1.10
1.45
1.92
5.35
6.96
0 2 4 6 8 τ
H2O
1.48
2.17
2.60
Cl⁻
N–H
H2O
1.29
1.52
2.00
I⁻
CH3
H2O
0.90
1.15
1.63
5.27
0 2 4 6 8 τ

Fig. 1

This down-field shift observed for all protons is caused by a decreased electron density on each ring carbon atom as the consequence of a formal positive charge present at the nitrogen atom.

In the NMR spectra of N-methiodides of pyridine and picolines the down-field shift is more marked; it is nearly twice as large as that in the spectra of hydrochlorides. This could probably be explained by a covalent bonding of the methyl group stronger than that between the hydrogen and the nitrogen atoms. The chemical shift of the methyl group attached to the ring carbon atom in picolines is also shifted towards a lower field; the shifting is larger in methiodides than in hydrochlorides.

The chemical shift of the methyl group attached to the nitrogen atom is rather low in the methiodides (5.27—5.47 p.p.m.). The literature data for the $N-CH_3$ group in quaternary salts [5] give a value of *c.* 6.67 p.p.m.

Conclusion

As known, the formation of quaternary salts produces changes in the pyridine and picolines molecular structure which are manifested also in NMR spectra. The differences in the values of chemical shift between free bases, their hydrochlorides and methiodides consist in down-field shifting of all protons. This should be attributed to the accumulation of the positive charge on the nitrogen atom and to the decreased electron density on the ring carbon atom.

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