CARBON-13 AND NITROGEN-14 NMR SPECTRA OF 1-(SUBSTITUTED PHENYL)PYRIDINIUM SALTS

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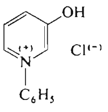
The ^{13}C and ^{14}N-NMR spectra of 1M solutions of 1-(substituted phenyl)pyridinium salts (4-CH_3, 4-OCH_3, H, 4-Cl, 4-Br, 4-I, 3-NO_2, 4-NO_2, 2,4-$(NO_2)_2$ (the ^{13}C-NMR only)) have been measured in heavy water at 30°C. The ^{13}C and ^{14}N chemical shifts, the $^{1}J(CH)$ coupling constants, some $^{3}J(CH)$ coupling constants, and values of half-widths Δ 1/2 of the ^{14}N-NMR signals are given. The ^{13}C chemical shifts of $C_{(4)}$ correlate with the σ^0 constants ($\delta C_{(4)} = (1{\cdot}79 \pm 0{\cdot}097)\,\sigma^0 + (147{\cdot}67 \pm 0{\cdot}041)$), whereas no correlation of the nitrogen chemical shifts with the σ constants has been found. The half-widths Δ 1/2 correlate with the σ^0 constants ($\Delta\ 1/2 = (76{\cdot}2 \pm 4{\cdot}9)\,\sigma^0 + (106{\cdot}4 \pm 2{\cdot}2)$) except for 1-phenylpyridinium chloride.

Pyridinium salts were often studied by NMR spectroscopy. The compounds $C_5H_5\overset{(+)}{N}R$ were studied by ^{13}C-NMR spectroscopy (R = H (ref.[1]), CH_3 (ref.[2]), $O^{(-)}$ (ref.[3,4]) and by means of nitrogen NMR spectroscopy (R = H (ref.[5]), CH_3 (ref.[6]), C_2H_5 (ref.[7]), $O^{(-)}$ (ref.[4,8]), OH (ref.[9]), $\overset{(-)}{B}R_3$ (ref.[10]). So far only little attention has been paid to salts carrying phenyl group at nitrogen. Takeuchi and Dennis[2] measured the ^{13}C-NMR spectra of 1-phenyl-3-hydroxypyridinium chloride (*I*) and 1-phenylpyridinium-3-olate (*II*).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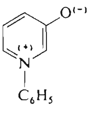
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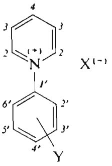

III

This paper gives results of a study of 1-(substituted phenyl)pyridinium salts *III* by means of ^{13}C and ^{14}N-NMR spectroscopy. The aim of the work was to establish the substituent effects on the ^{13}C chemical shifts and ^{14}N-NMR parameters.

EXPERIMENTAL

The used 1-(phenyl, 4-methyl-, 4-methoxy-, 4-chloro-, 4-bromo-, 4-iodo, 2,4-dinitrophenyl)pyridinium chlorides and 1-(3-nitro-, 4-nitrophenyl)pyridinium bromides were prepared according to ref.[11]. 1-Methyl- and 1-ethylpyridinium salts were prepared by reaction of the respective alkyl iodides with pyridine in benzene[12], and 1-pyridinium trifluoroacetate was prepared by mixing equimolar amounts of pyridine and trifluoroacetic acid in heavy water.

The ^{13}C and ^{14}N-NMR spectra were obtained at 25·047 and 7·196 MHz, respectively, using a JNM-FX 100 (JEOL) spectrometer equipped with a multinuclear probe and working in the FT mode. The spectra were recorded for 1M solutions of the pyridinium salts in deuterium oxide and trideuteriomethanol (CD_3OH) at 30°C. The solutions were placed in 10 mm NMR test tubes and D_2O or CD_3OH were used as lock. The carbon chemical shifts were referred to external tetramethylsilane in D_2O or internal tetramethylsilane in CD_3OH, the nitrogen chemical shifts were referred to external neat nitromethane[5]. For obtaining the ^{13}C chemical shifts the following parameters were used: SW 5000 Hz, 8 k, PW 8 μs (23 μs ~ 90°), PR 3 s, proton noise decoupling. For obtaining the coupling constants: SW 1000 Hz, 8 k, PW 20 μs, PR 10 s, gated decoupling. The parameters for obtaining the ^{14}N NMR spectra were as follows: SW 3000 Hz, 4 k, 50 μs (55 μs ~ 90°), PR 0·75 s. We used 8 k points memory for the protonated pyridine, methyl- and ethylpyridinium iodides and 1-phenylpyridinium chloride in CD_3OH.

RESULTS AND DISCUSSION

Tables I to III give the ^{13}C chemical shifts, $^1J(CH)$ coupling constants and some $^3J(CH)$ coupling constants for 1-(substituted phenyl)pyridinium salts. The assignment was carried out on the basis of comparison of the decoupled and coupled spectra, by means of the substituent effects[13] and by comparison with the published

TABLE I

Carbon-13 Chemical Shifts (in ppm from external tetramethylsilane, ±0·05 ppm) for Solution of 1-(Substituted Phenyl)pyridinium Salts in D_2O (1 mol l^{-1})

X	Y	C(2)	C(3)	C(4)	C(1′)	C(2′)	C(3′)	C(4′)	C(5′)	C(6′)
Cl	4′-CH_3[a]	145·02	129·48	147·46	141·26	124·75	132·10	143·51	132·10	124·75
Cl	4′-OCH_3[b]	145·22	129·52	147·36	137·12	126·65	116·81	162·22	116·81	126·65
Cl	H	145·26	129·48	147·75	143·66	125·14	131·67	132·64	131·67	125·14
Cl	4′-Cl	145·36	129·67	148·14	142·29	126·84	131·71	138·20	131·71	126·84
Cl	4′-Br	145·31	129·76	148·23	142·78	127·09	134·78	126·60	134·78	127·09
Cl	4′-I	145·26	129·82	148·28	145·26	127·04	140·83	99·16	140·83	127·04
Br	3′-NO_2	145·70	129·72	148·82	143·95	121·34	149·51	127·43	133·13	132·06
Br	4′-NO_2	145·61	129·91	149·16	147·89	127·43[c]	127·14[c]	150·18	127·14[c]	127·43[c]
Cl	2′,4′-$(NO_2)_2$	146·58	129·72	150·43	139·85	143·95	123·72	150·62	131·96	132·64

[a] $\delta(CH_3) = 21·54$; [b] $\delta(OCH_3) = 57·21$; [c] the assignment can be opposite.

carbon chemical shifts of 1-phenyl-3-hydroxypyridinium chloride (*I*) and 1-phenylpyridinium-3-olate (*II*). In contrast to pyridine (the 1M solution was measured under the same experimental conditions: $\delta(C2) = 149{\cdot}36$; $\delta(C3) = 125{\cdot}33$; $\delta(C4) = 138{\cdot}39$), the absorption of $C_{(4)}$ is shifted downfield as compared with $C_{(2)}$. Values of the chemical shifts of $C_{(4)}$ of the pyridine nucleus are also affected by the benzene

TABLE II

Coupling Constants $^1J(CH)$ (in Hz) for 1-(Substituted Phenyl)pyridinium Salts in D_2O

X	Y	C(2)[a]	C(3)[a]	C(4)[b]	C(2')[b]	C(3')[b]	C(5')[b]	C(6')[b]
Cl	4'-CH_3[c]	194·6	177·7	174·1	165·3	163·1	163·1	165·3
Cl	4'-OCH_3[d]	194·5	176·8	174·2	166·0	165·4	165·4	166·0
Cl	H[e]	191·3	177·7	173·8	165·5	167·8	167·8	165·5
Cl	4'-Cl	192·0	179·4	173·8	168·5	171·6	171·6	168·5
Cl	4'-Br	192·8	179·2	174·1	168·7	174·1	174·1	168·7
Cl	4'-I	195·7	179·7	174·2	168·4	171·8	171·8	168·4
Br	3'-NO_2[f]	193·8	180·7	174·1	172·9	—	172·6	169·2
Br	4'-NO_2	189·9	180·0	168·0	171·1	174·3	174·3	171·1
Cl	2',4'-$(NO_2)_2$	197·5	180·0	174·8	—	179·0	177·7	176·8

[a] ±0·6 Hz; [b] ±0·3 Hz; [c] $^1J(CH_3)$ = 127·2 Hz; [d] $^1J(OCH_3)$ = 145·6 Hz; [e] ^1J(C4′ H) = 164·6 Hz [f] ^1J(C4′ H) = 173·1 Hz.

TABLE III

Coupling Constants $^3J(CH)$ for 1-(Substituted Phenyl)pyridinium Salts in D_2O

X	Y	C(4)[a]	C(2')[b]	C(3')[b]
Cl	4'-CH_3	5·6	4·4	—
Cl	4'-OCH_3	6·0	5·4	5·1
Cl	4'-Cl	6·0	4·6	4·6
Cl	4'-Br	5·6	4·6	5·1
Cl	4'-I	5·0	5·1	6·6
Br	3'-NO_2[c]	6·1	5·9[a]; 5·9[a]	—
Br	4'-NO_2	6·1	4·6	5·6
Cl	2',4'-$(NO_2)_2$[d]	5·6	—	5·0

[a] ±0·5 Hz; [b] ±0·3 Hz; [c] ^3J(C9′ H) = 8·0; 4·9 Hz; ^3J(C7′ H) = 7·8; 4·4 Hz; [d] ^3J(C5′ H) = 5·4 Hz.

ring substituents more than those of $C_{(2)}$, and they correlate with the σ^0 constants according to Eq. (*1*):

$$\delta(\text{C4}) = (1{\cdot}79 \pm 0{\cdot}097)\,\sigma^0 + (147{\cdot}67 \pm 0{\cdot}041)\,, \quad r = 0{\cdot}9913\,. \qquad (1)$$

From Eq. (*1*) we calculated for the 2,4-dinitro derivative the value $\sigma^0 = 1{\cdot}55$ which approximately equals $2\,.\,\sigma^0_{4\text{-NO}_2}$ (*i.e.* 2 . 0·808). For $C_{(2)}$ there exists a similar dependence on σ^0, however, difference in the chemical shifts of $C_{(2)}$ is 0·68 ppm only, and the error ± 0·05 ppm affects the correlation ($r = 0{\cdot}9260$). Recently the reaction rates of 1-(substituted phenyl)pyridinium salts with nucleophiles were measured[14–16]. The rate constants of the attack at 2 or 4 positions correlate with the σ^0 constants, too.

For the individual carbon atoms of the benzene ring of 1-(substituted phenyl)-pyridinium salts we calculated the substitution chemical shifts with respect to 1-phenylpyridinium chloride and compared them with the values of these shifts of the monosubstituted benzenes[13]. In the case of the 4-substituted phenyl derivatives the absolute values of the differences between the published[13] and the calculated substitution chemical shifts for $C_{(1')}$—$C_{(3')}$ were less than 1·1 ppm, those of $C_{(4')}$ were less than 2·5 ppm. The same situation was encountered with the 3-nitro derivative (the difference for $C_{(3')}$ was 2·2 ppm, for the other it was less than 1·1 ppm). With 2,4-dinitro derivative the greatest difference (3·5 ppm) was found for $C_{(1')}$. The ^{13}C chemical shifts of $C_{(4)}$ of monosubstituted benzenes correlate very well with the σ^+ constants[17]. Changes in the ^{13}C chemical shifts for $C_{(1')}$ of 1-(4-substituted phenyl)pyridinium salts can also be expressed by σ^+ better than by σ^0, but the correlation coefficient is low ($r = 0{\cdot}9515$).

TABLE IV

Nitrogen-14 NMR Parameters (δ in ppm from External Neat Nitromethane, ±0·3 ppm; $\Delta_{1/2}$ in Hz, ±4%) for Solutions of 1-(Substituted Phenyl)pyridinium Salts in D_2O (1 mol l^{-1})

X	Y	$\delta(N^{(+)})$	$\Delta_{1/2}$	σ^0
Cl	4'-CH_3	162·9	92	—0·124
Cl	4'-OCH_3	164·1	102	—0·100
Cl	H	162·6	69	0·000
Cl	4'-Cl	164·0	129	0·281
Cl	4'-Br	166·1	134	0·296
Cl	4'-I	164·5	127	0·298
Br	3'-NO_2	168·2	156	0·709
Br	4'-NO_2	166·3	170	0·808

The ^{14}N chemical shifts and the half-widths of the nitrogen signals ($\Delta\ 1/2$) are given in Table IV along with the σ^0 constants[18] used for the correlations in this paper. The upfield shifts are taken as positive (screening-constant scale[19]). For comparison of the derivatives $C_5H_5\overset{(+)}{N}R$ we measured the ^{13}C and ^{14}N chemical shifts of the compounds with $R = H, CH_3, C_2H_5$ in D_2O (Table V). The ^{14}N chemical shifts for $R = H$ and CH_3 are practically identical (the α effect[20]). The difference in the ^{14}N chemical shifts for 1-methyl- and 1-ethylpyridinium iodides (14·2 ppm) corresponds to the β effect[20] ($\delta(CH_3NO_2) - \delta(C_2H_5NO_2) = 12$; $\delta(CH_3NH_2) - \delta(C_2H_5NH_2) = 19$)[21]. The ^{14}N chemical shifts of 1-phenylpyridinium and 1-ethylpyridinium chlorides are almost the same.The nitrogen chemical shifts of the compounds C_5H_5NR ($R = CH_3, C_2H_5, C_6H_5$) in trideuteriomethanol only differ very little (Table V) from the values found in heavy water. Thus solvation does not markedly affect the nitrogen chemical shifts of the salts studied. Values of the ^{14}N chemical shifts of 1-(substituted phenyl)pyridinium salts do not correlate with the σ constants. Similarly no simple correlation was observed[8] between the ^{15}N chemical shifts of alkylpyridinium salts with the calculated electron densities. The half-widths $\Delta\ 1/2$ of the nitrogen signals correlate (except for $\Delta\ 1/2$ of 1-phenylpyridinium chloride) with the σ^0 constants according to Eq. (*2*):

$$\Delta\ 1/2 = (76{\cdot}2 \pm 4{\cdot}9)\,\sigma^0 + (106{\cdot}4 \pm 2{\cdot}2)\,, \quad r = 0{\cdot}9900\,. \tag{2}$$

TABLE V

The NMR Parameters of Solutions of Compounds $C_5H_5\overset{(+)}{N}R\ X^{(-)}$ in D_2O or CD_3OH (1 mol l^{-1})

Carbon-13 chemical shifts in ppm from external tetramethylsilane in D_2O or from internal tetramethylsilane in CD_3OH; ±0·05 ppm. Nitrogen-14 NMR parameters: δ in ppm from external neat nitromethane; ±0·1 ppm and $\Delta_{1/2}$ in Hz; ±1 Hz.

R	X	Solvent	$\delta(^{13}C)$			$\delta(^{14}N)$	$\Delta_{1/2}$
			C(2)	C(3)	C(4)		
H	CF_3COO	D_2O	142·15	128·55	148·34	178·6	20·5
CH_3[a]	I	D_2O	146·48	129·28	146·63	178·2	14·5
CH_3[b]	I	CD_3OH	147·21	129·28	147·15	178·0	13·6
CH_2CH_3[c]	I	D_2O	145·16	129·57	146·72	164·0	13·5
CH_2CH_3[d]	I	CD_3OH	146·37	130·24	147·54	163·5	12·0
C_6H_5[e]	Cl	CD_3OH	145·76	130·48	148·66	162·7	47·0

[a] $\delta(CH_3) = 50{\cdot}04$; [b] $\delta(CH_3) = 80{\cdot}29$; [c] $\delta(CH_2) = 58{\cdot}62$; $\delta(CH_3) = 17{\cdot}30$; [d] $\delta(CH_2) = 59{\cdot}24$, $\delta(CH_3) = 17{\cdot}82$; [e] $\delta(C1') = 145{\cdot}09$, $\delta(C2') = 126{\cdot}34$, $\delta(C\ 3') = 132{\cdot}48$, $\delta(C4') = 133{\cdot}46$.

The half-width Δ 1/2 of 1-phenylpyridinium chloride is markedly smaller, which can be due to different influence on the η value (the η value describes deviation of the gradient of electric field from axial symmetry) exerted by the proton at 4′ position as compared with the other substituents or to various contributions of different relaxation mechanisms.

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