PROTON, CARBON-13, AND FLUORINE-19 NMR STUDY OF N-ARYLPYRIDINIUM SALTS: ATTEMPTED CALCULATIONS OF THE σ_I AND σ_R^0 VALUES FOR N-PYRIDINIUM SUBSTITUENTS

Rosa Maria CLARAMUNT and José ELGUERO*

Laboratoire de Chimie Moléculaire, Université d'Aix-Marseille III, France

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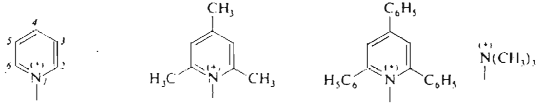
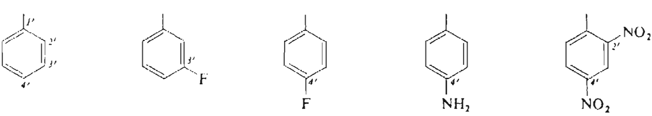
The synthesis and NMR study of fourteen N-arylpyridinium salts have been done. Chemical shifts and coupling constants (^1H—^1H, ^1H—^{13}C, ^1H—^{19}F, and ^{13}C—^{19}F) have been measured in hexadeuteriodimethyl sulphoxide. Conformation about the phenylpyridinium bond is discussed. The electronic properties of the three pyridinium substituents (pyridinium, 2,4,6-trimethylpyridinium, and 2,4,6-triphenylpyridinium) have been determined (Hammett and Tatf's σ values) and compared with those of the trimethylammonium substituent.

Due to the contributions of Balaban[1-3], Dorofeenko[4-6] and, particularly, Katritzky[7,8] the pyrilium salts have become very important synthons for a great variety of organic compounds through their transformation into pyridinium salts. Because of this we have undertaken a ^1H, ^{13}C and ^{19}F-NMR study of a series of N-arylpyridinium salts (pyridinium, *Ia–Ie*; 2,4,6-trimethylpyridinium, *IIa–IId*; 2,4,6-triphenylpyridinium, *IIIb–IIId*) in order to afford some insight into the electronic structure of the N-pyridinium group comparatively to the N-trimethylammonium group (compounds *IVb–IVc*).



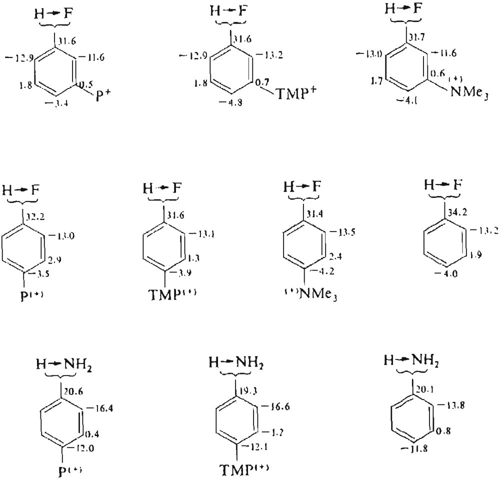
I *II* *III* *IV*



a *b* *c* *d* *e*

* Mailing address: Instituto de Química Médica, C.S.I.C., Juan de la Cierva, 3, Madrid-6, Spain.

The ^{1}H-NMR results of salts *Ia*–*IVc* are gathered in Table I; chemical shifts and coupling constants are obtained from first-order analysis of the 100 MHz spectra. In the case of the 4'-fluoro derivatives, *c*, the fact that J_0 (^{1}H—^{19}F) $\simeq$ $\simeq 2J_m$(^{1}H—^{19}F) has been used for the assignment of protons $H_{2'(6')}$ and $H_{3'(5')}$. In biaryl derivatives, the difference $\Delta\delta = \delta_0 - \delta_m$ is related to the torsional angle between the two rings[9]. This result allows to conclude that the 2,4,6-trimethyl series *II** is more twisted than the unsubstituted pyridinium series *I*: *Ic* ($\Delta\delta$ = 0·57) – – *IIc* ($\Delta\delta$ = 0·14) and *Id* ($\Delta\delta$ = 0·71) – *IId* ($\Delta\delta$ = 0·37). The behaviour of the 2,4,6-triphenyl series, *IIIc* ($\Delta\delta$ = 0·37) and *IIId* ($\Delta\delta$ = 0·74), is more complex since the aromatic protons of the 1-aryl substituent are shielded by the phenyl rings in positions 2 and 6; both phenyl rings appear as singlets whereas the 4-phenyl gives rise to two multiplets. From literature results concerning the geometry of C-phenyl substituents in heteroaromatic compounds[11], we must conclude that the phenyl rings in positions 1, 2 and 6 are almost orthogonal whereas the phenyl ring in position 4 is coplanar with the pyridinium ring.



Scheme 1

* A X-ray study of the 1-phenyl-2,4,6-trimethylpyridinium perchlorate[10] *IIa* shows that the dihedral angle between the two aromatic planes is 83·5°.

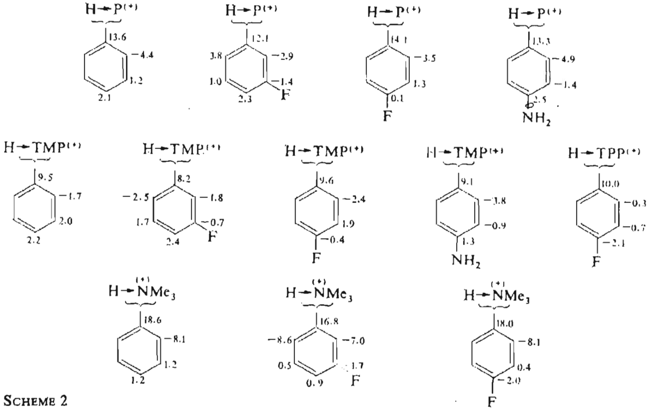
The heterocyclic signals are quite independent on the nature of the substituent in position 1 and this has made easy the assignments of Table I; however minor differences are observed, for instance, when the 4'-amino derivative *Id* and the 2',4'-dinitrophenyl derivative *Ie* are compared ($\Delta\delta \simeq 0{\cdot}25$ ppm). In pyridinium derivatives *I*, the chemical shifts of protons $H_{2(6)}$ and H_4 are related: $\delta H_2 = 1{\cdot}124 + 0{\cdot}943\delta H_4$ ($r = 0{\cdot}96$) including the derivative *Ie* (4'-NH_2 < 3'-F $\simeq$ H $\simeq$ 4'-F < 2',4'-$(NO_2)_2$); thus the *o*-nitro group of *Ie* does not exert a significant anisotropic neighbouring effect upon $H_{2(6)}$, probably because both rings (the pyridinium and the dinitrophenyl ones) are almost orthogonal.

Only twelve salts have been studied in ^{13}C-NMR because the triphenylpyridinium salts would probably give too much complicated spectra; however the spectrum of the 4'-fluoro derivative *IIIc* has been recorded and owing to the ^{13}C—^{19}F coupling constants, some signals have been identified. Chemical shifts are given in Table II.

The substituent chemical shifts (SCS) of the N_1-aryl carbon atoms depend on both substituents (the pyridinium and the fluorine or amino group) but in a first approximation we can discuss them separately.

Fluorine and amino SCS ($P^{(+)}$: pyridinium *I*; $TMP^{(+)}$: 2,4,6-trimethylpyridinium *II*; $TPP^{(+)}$: 2,4,6-triphenylpyridinium *III*) (Scheme 1).

The values are quite similar and coherent with the literature results[13,14], but we must notice that the SCS on carbons *ortho* to the pyridinium substituent have lower values in the trimethyl series *II* than in the unsubstituted one *I*; the trimethylammonium derivatives occupying an intermediate position.



SCHEME 2

Pyridinium and trimethylammonium SCS (δ values of monosubstituted benzenes from references[13,14]), Scheme 2. The values for the trimethylammonium group have been discussed previously[15,16]; those for the pyridinium groups are quite

TABLE I

Chemical Shifts in ^{1}H-NMR Spectra of Compounds *Ia*—*IVc* (δ scale in ppm, tetramethylsilane as standard; in hexadeuteriodimethyl sulphoxide DMSO or trifluoroacetic acid TFAA)

Compound		solvent[c]	Pyridinium			Aryl[a]				
			2,6	3,5	4	2′	3′	4′	5′	6′
Ia,	Cl^- [b]	DMSO	9·58	8·40	8·92	8·02		← 7·75 →		8·02
Ib,	Cl^-	DMSO	9·55	8·39	8·91			← F — 7·8—8·2 →		
Ic,	Cl^-	DMSO	9·56	8·43	8·95	8·16	7·59	F	7·59	8·16
Id,	Cl^-	DMSO	9·33	8·26	8·72	7·56	6·85	NH_2: 6·19	6·85	7·56
Ie,	Cl^-	DMSO	9·59	8·48	9·01	NO_2	9·12	NO_2	9·00	8·57
IIa,	BF_4^-	DMSO	2·30	7·92	2·60			← 7·55—7·8 →		
IIa,	BF_4^-	TFAA	2·43	7·67	2·68			← 7·2 —8·0 →		
IIb,	BF_4^-	DMSO	2·37	7·93	2·63			← F — 7·5 —7·75 →		
IIb,	BF_4^-	TFAA	2·47	7·65	2·70			← F — 7·1 —7·8 →		
IIc,	BF_4^-	DMSO	2·43	7·94	2·63	7·75	7·61	F	7·61	7·75
IIc,	BF_4^-	TFAA	2·48	7·72	2·72	7·53	7·42	F	7·42	7·53
IId,	BF_4^-	DMSO	2·35	7·85	2·58	7·13	6·76	NH_2: 5·68	6·76	7·13
IIf,	2 BF_4^-	DMSO	2·38	7·96	2·63	7·96	7·96	—	7·96	7·96
IIf,	2 BF_4^-	TFAA	2·55	7·73	2·73	7·97	7·97	—	7·97	7·97
IIIb,	BF_4^-	DMSO	7·42	8·54	8·15; 7·70			← F — 7·0—7·55 →		
IIIb,	BF_4^-	TFAA	7·40	8·33	8·00; 7·70			← F — 6·7—7·2 →		
IIIc,	BF_4^-	DMSO	7·45	8·52	8·25; 7·70	7·40	7·03	F	7·03	7·40
IIIc,	BF_4^-	TFAA	7·43	8·33	8·00; 7·65	7·03	6·90	F	6·90	6·90
IIId,	BF_4^-	DMSO	7·42	8·56	8·30; 7·65	6·95	6·21	NH_2: 5·35	6·21	6·95
IIIg,	BF_4^-	DMSO		8·70		7·40	7·40	—	7·40	7·40
IVb,	SO_3Me^- [d]	DMSO	$\overset{(+)}{N}Me_3$: 3·63					← F — 7·35—8·05 →		
IVb,	SO_4Me^- [d]	TFAA	$\overset{(+)}{N}Me$: 3·73					← F — 7·15—7·8 →		
IVc,	SO_4H^-	DMSO	$\overset{(+)}{N}Me_3$: 3·62			8·08	7·43	F	7·43	8·08
IVc,	SO_4H^-	TFAA	$\overset{(+)}{N}Me_3$: 3·75			7·85	7·38	F	7·38	7·85

[a] Coupling constants (in Hz): HH^0 = 8·5—9·0; HH^m = 2·4; HF^0 = 7·5—9·0; HF^m = 4·5. [b] Literature[12] values for this compounds in the same solvent: 9·46, 8·44, and 8·90 ppm. [c] The other phenyl signals appear at 7·50 (s) (10 H), 7·60—7·86 (3 H), 8·20—8·53 (2 H). The NH and the methyl of the acetamide group give singlets at 10·05 and 2·04 ppm, respectively. [d] $SO_4Me^{(-)}$ signal at 3·45 (DMSO) and 3·95 ppm (TFAA).

TABLE II

Chemical Shifts in ^{13}C-NMR Spectra of Compounds *Ia*—*IVc* (δ scale in ppm, tetramethylsilane as standard; measured in hexadeuteriodimethylsulphoxide)

Compound	Pyridinium 2·6	Pyridinium 3·5	Pyridinium 4	Aryl 1′	Aryl 2′	Aryl 3′	Aryl 4′	Aryl 5′	Aryl 6′
Ia, Cl^-	145·0	128·4	146·8	142·7	124·7	130·3	131·2	130·3	124·7
Ib, Cl^-	145·2	128·3	147·2	143·2	113·1	(F) 161·9	118·3	132·1	121·3
Ic, Cl^-	145·2	128·6	147·0	139·2	127·6	117·3	(F) 163·4	117·3	127·6
Id, Cl^-	143·9	128·2	144·8	130·7	125·1	113·9	(NH_2) 151·8	113·9	125·1
Ie, Cl^-	146·2	128·1	148·9	138·8	(NO_2) 143·2	121·4	(NO_2) 149·1	130·2	132·1
IIa, BF_4^-	159·4 CH_3: 21·6	126·0	154·8 CH_3: 21·3	138·6	127·4	131·0	131·3	131·0	127·4
IIb, BF_4^-	159·6 CH_3: 21·4	127·2	154·8 CH_3: 21·4	139·3	114·2	(F) 162·6	118·4	132·8	122·6
IIc, BF_4^-	159·4 CH_3: 21·6	127·3	155·1 CH_3: 21·3	134·7	128·7	117·9	(F) 162·9	117·9	128·7
IId, BF_4^-	158·4 CH_3: 21·5	127·1	155·7 CH_3: 21·1	126·5	126·2	114·4	(NH_2) 150·6	114·4	126·2
IVa, Cl^{-a}	$\overset{(+)}{N}Me_3$: 56·3		—	147·3	120·6	129·9	129·9	129·9	120·6
IVb, SO_4Me^-	$\overset{(+)}{N}Me_3$: 56·3		—	147·9	109·0	(F) 161·6	116·9	131·6	126·5
IVc, SO_4H^-	$\overset{(+)}{N}Me_3$: 56·4		—	143·1	123·0	116·4	(F) 161·3	116·3	123·0
IIIc, BF_4^{-b}	156·1	124·8	155·4	135·1	130·8	115·3	(F) 161·2	115·3	130·8

[a] Values from references[13,14]; [b] other signals: 133·1, 132·3, 132·7, 129·4, 128·6 and 127·9 ppm.

different (mainly on C_{ipso} and C_{ortho}). For the same position, the effect on the fluorine bearing carbon atoms is significantly lower. For one compound, *IIa*, some $^{1}H—^{13}C$ coupling constants have been measured (values in Hz, first order analysis) and they are reported in Table III. For the fluorine derivatives, series *b* and *c*, the $^{13}C—^{19}F$ coupling constants (in Hz) have been measured (Table IV): they are very close to the literature data[13,14].

The ^{19}F chemical shifts of the quaternary salts, *I*–*IV*, and of some selected deriva-

TABLE III

$^{1}H—^{13}C$ Coupling Constants of 1-Phenyl-2,4,6-trimethylpyridinium Fluoroborate

	Pyridinium	
2,6	3,5	4
$^{2}J = 5.5$ (H of CH_3) $^{2}J = 1.1$ (H_5)	$^{1}J = 169.3$	$^{2}J = 5.9$ (H of CH_3)
	Aryl	
1′	2′,6′	3′,5′
$^{3}J = 6.4$ ($H_{3'}$, $H_{5'}$) $^{2}J = 1.4$ ($H_{2'}$, $H_{6'}$)	$^{1}J = 170$	$^{1}J = 166.4$ $^{3}J = 5.8$ ($H_{5'}$)

TABLE IV

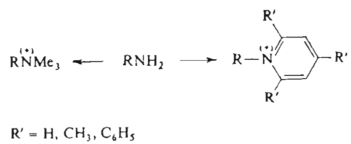
$^{13}C—^{19}F$ Coupling Constants of Compounds *Ib*—*IVc*; Aryl signals

Compound	1′	2′	3′	4′	5′	6′
Ib, Cl^-	9·5	26·9	(F) 246·9	20·9	8·7	3·0
Ic, Cl^-	2·1	9·5	23·7	(F) 249·3	23·7	9·5
IIb, Cl^-	10·1	25·6	(F) 247·8	21·0	9·2	2·5
IIc, Cl^-	3·1	9·3	23·5	(F) 248·5	23·5	9·3
IIIc, BF_4^-	2·8	8·8	23·4	(F) 248·9	23·4	8·8
IVb, SO_4Me^-	9·1	27·9	(F) 246·3	20·2	8·8	masked
IVc, SO_4H^-	broad	8·9	23·2	(F) 248·2	23·2	8·9
Fluorobenzene (ref.[13,14])	(F) 244·0	20·6	8·0	2·5	8·0	20·6

tives, *V–VI*, are gathered in Table V.* The AA'BB'X (series *c*) and the ABCDX (series *b*) systems have not been analysed, but the X multiplet is different in both series; in *c* derivatives the symmetrical multiplet is centered on the most intense peak whereas in *b* derivatives there is no peak on the centre of the multiplet.

Electronic Properties of the Pyridinium Substituent

To compare the electronic properties of the two leaving groups, the trimethylammonium and the pyridinium, corresponding to the two ways of activating an amino group, we have thought of using the Taft's constants[18] σ_I and σ_R^0 (Scheme 3).



SCHEME 3

TABLE V

Chemical Shifts in ^{19}F-NMR Spectra of Compounds *Ib—VIIc* (δ scale in ppm; fluorotrichloromethane as standard; measured in hexadeuteriodimethyl sulphoxide)

Compound	δ	$\int_H^{mX}$	$\int_H^{pX}$	$\Delta\int = \int_H^{mX} - \int_H^{pX}$
V	112·7	—	—	—
VIb	109·5	—3·2	—	7·3
VIc	102·2	—	—10·5	
VIIb	113·3	0·6	—	—15·9
VIIc	129·2	—	16·5	
Ib	107·3	—5·4	—	— 2·2
Ic	109·5	—	—3·2	
IIb	108·5	—4·2	—	— 0·7
IIc	109·2	—	—3·5	
IIIb	111·0	—1·7	—	1·2
IIIc	109·8	—	—2·9	
IVb	108·4	—4·3	—	— 2·9
IVc	111·3	—	—1·4	

V: fluorobenzene; *VIb*: 1-fluoro-3-nitrobenzene; *VIc*: 1-fluoro-4-nitrobenzene; *VIIb*: 3-fluoroaniline; *VIIc*: 4-fluoroaniline.

* Ager and Phillips[17] have described the ^{19}F chemical shifts of compounds *IVc*, *Vv*, *VIc* and *VIIc* in a large series of solvents but not in hexadeuteriodimethyl sulphoxide.

Table VI contains our σ_I, σ_R^0, σ_m and σ_p values for some substituents and the literature ones; our Hammett and Taft constants are related by equations (*1*) and (*2*) (ref.[18]).

$$\sigma_m = \sigma_I + 0.5\,\sigma_R^0 \qquad (1)$$

$$\sigma_p = \sigma_I + \sigma_R^0 \qquad (2)$$

and have been calculated in order to satisfy the experimental results obtained from proton and carbon-13 NMR data.

The protonic amino resonance in *para*-substituted anilino derivatives (in hexadeuteriodimethyl sulphoxide) follows the empirical relationhip[20]:

$$\Delta\delta\,(\text{Hz}) = (\sigma_p - 3{\cdot}06\,.\,10^{-2})/1{\cdot}25\,.\,10^{-2}\,. \qquad (3)$$

Our σ_p values, when introduced in Eq. (*3*) afford calculated $\Delta\delta$ values, identical with the experimental ones:

	Id	*IId*	*IIId*
δ (ppm)	6·19	5·68	5·35
δ (Hz at 60 MHz)	371·4	340·8	321·0
$\Delta\delta$ (Hz) (aniline: 297 MHz)	74·4	43·8	24·0
Calculated from (Eq. (*3*))	74·4	43·8	24·0

Ricci and coworkers[15] showed that for monosubstituted benzene derivatives in hexadeuteriodimethyl sulphoxide solution, the chemical shifts of carbon atoms *meta* and *para* depend on a linear combination of σ_I and σ_R^0:

$$\Delta\delta\,(\text{ppm}) = \delta C_p - \delta C_m = 3{\cdot}6\sigma_I + 23{\cdot}5\sigma_R^0 \qquad (4)$$

Our σ_I and σ_R^0 values were calculated to fit this equation:

	Ia	*IIa*	*IIIa*
Experimental $\Delta\delta$	0·90	0·30	—
Calculated (Eq. (*4*))	0·87	0·30	0·59

The experimental value for compound *IIIa* is not accessible but from the 4'-fluoro derivative *IIIc* it is possible to verify the validity of the calculated value:

	4'-H *a*	4'-F *c*	4'-NH_2 *d*
P^+ (*I*)	0·9	46·1	37·9
TPP^+ (*III*)	(0·6)	45·9	—
TMP^+ (*II*)	0·3	45·0	36·2
$^{(+)}NMe_3$ (*IV*)	0·0[16]	44·9	—

TABLE VI
σ Values

Parameter	H	NO_2	NH_2	$\overset{(+)}{N}Me_3$	$P^{(+)}$	$TMP^{(+)}$	$TPP^{(+)}$
				This work			
σ_1	0·00	0·63	0·10	0·83	1·09	0·67	0·36
σ_R^0	0·00	0·17	—0·47	—0·13	—0·13	—0·09	—0·03
σ_m	0 00	0·72	—0·14	0·76	1·02	0·62	0·34
σ_p	0·00	0·82	—0·37	0·70	0·96	0·58	0·33
				Literature			
σ_1	0·00 (ref.[18])	0·63 (ref.[18])	0·10 (ref.[18])	0·92 (ref.[15])	—	—	—
σ_R^0	0·00 (ref.[18])	0·17 (ref.[18])	—0·47 (ref.[18])	—0·15 (ref.[15])	—	—	—
σ_m	0·00 (ref.[18])	0·70 (ref.[18])	—0·14 (ref.[18])	—	—	0·69 (ref.[1];)	0·63 (ref.[19])
σ_p	0·00 (ref.[18])	0·82 (ref.[18])	—0·38 (ref.[18])	0·68 (ref.[19])	—	0·71 (ref.[19])	0·71 (ref.[19])

For the $\overset{(+)}{N}Me_3$ substituent our values of σ_I and σ_R^0, lead to a calculated $\Delta\delta$ of -0.07 ppm, the experimental value being 0·1 (ref.[15]) or 0·0 ppm (ref.[16]) (Ricci values,[15] $\sigma_I = 0.92$ and $\sigma_R^0 = -0.15$, give $\Delta\delta = 0.21$ ppm).

Taft and coworkers[21,22] have described a very elegant method to calculate σ_I and σ_R^0 from fluorine-19 chemical shifts:

$$\sigma_I = \frac{0.60 - \int_H^{mX}}{7.1}, \tag{5}$$

$$\sigma_R^0 = \frac{\Delta\int}{29.5}, \tag{6}$$

where $\int_H^{mX}$ and $\int_H^{pX}$ are the chemical shifts of *meta* and *para* substituted fluorobenzenes with respect to fluorobenzene itself and $\Delta\int = \int_H^{mX} - \int_H^{pX}$. All the chemical shifts were determined in apolar solvents at infinite dilution.

In our case, the spectra being determined in hexadeuteriodimethyl sulphoxide at ~ 0.5 mol l^{-1} concentration, equations (*5*) and (*6*) have to be calculated again. Moreover, it is by no means evident that this sort of correlation equations applies well to ionic substituents[23]. So, instead of using equations (*5*) and (*6*) to calculate the σ_I and σ_R^0 values of the pyridinium derivatives, we will try to correlate values of Table VI with experimental $\int_H^{mX}$ and $\Delta\int$ ones (Table III, seven substituents, including the proton). The ψ values ($\psi^2 = n(1 - r^2)/(n - 2)$) for equations (*7*) and (*8*) show that the correlations are of medium quality[24].

$$\sigma_I = \frac{0.4 - \int_H^{mX}}{5.7} \quad (r = 0.975,\ \psi = 0.26) \tag{7}$$

$$\sigma_R^0 = \frac{\Delta\int - 1.6}{35.8} \quad (r = 0.991,\ \psi = 0.16) \tag{8}$$

The last remark concerns literature σ values and particularly those of Dorofeenko[19], calculated from the pK_a values of the corresponding anilinium derivatives in acetonitrile. For the $\overset{(+)}{N}Me_3$ substituent, Ricci's values[15] ($\sigma_I = 0.92$, $\sigma_R^0 = -0.15$) and equation (*2*) lead to a $\sigma_p = 0.80$; our value, $\sigma_p = 0.70$, is in better agreement with the Dorofeenkos' one[19] ($\sigma_p = 0.68$). For the $TMP^{(+)}$ substituent, our values and those of Dorofeenko'[19] are comparable, but for the $TPP^{(+)}$ substituent there are considerable differences. Perhaps, our spectroscopy methods suffer, as commented before, from the anisotropic effects of the phenyl rings in position 2 and 6, effects that modify the chemical shifts in a way independent of the electronic properties of the substituent.

TABLE VII
Compounds *Ia*—*IVc*

Compound	Formula (m.w.)	Calculated/Found			M.p., °C[a] yield, %
		% C	% H	% N	
Ia, Cl^-	$C_{11}H_{10}ClN$ (191·7)	68·94 68·91	5·26 5·13	7·31 7·29	105—107 57
Ib, Cl^-	$C_{11}H_9ClFN$ (209·7)	63·02 62·88	4·33 4·62	6·68 6·51	oil 49
Ic, Cl^-	$C_{11}H_9ClFN$ (209·7)	63·02 62·81	4·33 4·57	6·68 6·60	oil 52
Id, Cl^-	$C_{11}H_{11}ClN_2$ (206·7)	63·93 64·07	5·36 5·65	13·56 13·82	253—255 (dec) 27
Ie, Cl^-	$C_{11}H_8ClN_3O_4$ (281·7)	46·91 46·90	2·86 2·83	14·92 14·87	200 (dec) 96
IIa, BF_4^-	$C_{14}H_{16}BF_4N$ (285·1)	58·98 58·73	5·66 5·42	4·91 4·75	90—91 82
IIb, BF_4^-	$C_{14}H_{15}BF_5N$ (303·1)	55·48 54·83	4·99 5·07	4·62 4·28	145—147 84
IIc, BF_4^-	$C_{14}H_{15}BF_5N$ (303·1)	55·48 55·39	4·99 5·11	4·62 4·47	125—127 87
IId, BF_4^-	$C_{14}H_{17}BF_4N_2$ (300·1)	56·03 56·15	5·71 5·49	9·33 9·42	152—154 83
IIf, 2 BF_4^-	$C_{22}H_{26}B_2F_8N_2$ (492·1)	53·69 54·02	5·33 5·01	5·69 5·93	>320 22
IIIb, BF_4^-	$C_{29}H_{21}BF_5N$ (489·3)	71·19 71·20	4·33 4·30	2·86 2·73	255—257 89
IIIc, BF_4^-	$C_{29}H_{21}BF_5N$ (489·3)	71·19 71·81	4·33 4·42	2·86 2·85	199—200 81
IIId, BF_4^-	$C_{29}H_{23}BF_4N_2$ (486·3)	71·62 71·44	4·77 4·98	5·76 5·67	~240 79
IIIg, BF_4^-	$C_{31}H_{25}BF_4N_2O$ (528·4)	70·47 70·51	4·77 4·91	5·30 5·33	169—171 38
IVb, SO_4Me^-	$C_{10}H_{16}FNO_4S$ (265·3)	45·23 45·14	6·08 5·97	5·28 5·67	132—133 85
IVc, SO_4H^-	$C_9H_{14}FNO_4S$ (251·3)	43·02 43·15	5·62 5·44	5·58 5·58	169—170 91

[a] Some salts have already been described but with different anions, for instance the perchlorates of *IId* (ref.[5]), *IIId* (ref.[5]), *IIf* (ref.[6]), *IIIg* (ref.[6]); *Ia*, Cl^-, m.p. 105—106°C (ref.[28]); *Ie*, Cl^-, m.p. 200°C (dec)[28].

The values of Table VI show that the inductive withdrawing effect diminishes a great deal from a pyridinium to a 2,4,6-triphenylpyridinium substituent whereas the slightly donating resonance effect is quite similar. The trimethylammonium group is comparable to the pyridinium one in its σ_R^0 values, but is less powerful as inductive withdrawing group. However it must be reminded that the leaving group ability is not related in a simple way to the σ values and that other factors, specially steric decompression, could play an important role.

EXPERIMENTAL

Temperature data are uncorrected. For properties of compounds *I*—*IV* see Table VII. ^{1}H-NMR chemical shifts are reported in ppm downfield from tetramethylsilane as internal reference. They were measured on a Varian XL-100 instrument (working at 28°C) in hexadeuteriodimethyl sulphoxide at 0·1 mol l^{-1} concentration. The ^{13}C-NMR proton-noise-decoupled spectra and fully proton-coupled spectra were determined on a Varian CFT-20 (t = 30°C) operating at 20 MHz for 0·2—0·8 mol l^{-1} solutions, depending on the solubility of the compounds. Field-frequency control (lock) was effected by means of the deuterium resonance of hexadeuteriodimethyl sulphoxide. Chemical shifts are reported in ppm downfield from tetramethylsilane and were determined with an accuracy of ±0·1 ppm. The coupling constants were obtained with an accuracy of ±0·25 Hz for the long range couplings and ±1 Hz for the direct couplings. ^{19}F-NMR chemical shifts in ppm have been measured from the internal reference (Freon 11: $CFCl_3$) on a Varian XL-100 spectrometer (t = 28°C). The solvent used was hexadeuteriodimethyl sulphoxide and the concentration used 60 mg/0·5 ml; the chemical shifts are slightly dependent on the concentration (for compound *IVc*: 111·2 to 111·4 ppm).

Pyridinium Chlorides *I*

The pyrilium perchlorate has been described[25,26] in the literature, but as starting material for the preparation of the C-unsubstituted pyridinium derivatives *I*, it has two major inconveniences: it gives complex mixtures with amino nucleophiles and is very dangerous to handle. An alternative procedure uses N-cyano[27] or N-2',4'-dinitrophenylpyridinium salts[28], thus Zincke[28] prepared *Ia* by the reaction of *Ie* and aniline. Using Zincke's method, we obtained compounds *Ia*, *Ib*, *Ic*, *Id* and *Ie*.

2,4,6-Trimethylpyridinium Fluoroborates *II*

Compounds *IIa*, *IIb* and *IIc* were obtained from the 2,4,6-trimethylpyrilium fluoroborate[29] and the corresponding aniline under reflux in acetic acid[30]. With 1,4-diaminobenzene as amino component and acetic acid as solvent we obtained the double condensation product *IIf*, 1,4-bis-(2',4',6'-trimethylpyridin-1-ium)benzene whose ^{1}H-NMR chemical shifts are assembled in Table I. To obtain the monocondensation product *IId* we used ethanol as the solvent.

2,4,6-Triphenylpyridinium Fluoroborates *III*

Using the same method indicated for the preparation of compounds *II*, but starting from 2,4,6-triphenylpyrilium fluoroborate[31], we obtained compounds *IIIb* and *IIIc*. In the case of 1,4-diaminobenzene and acetic acid as solvent we isolated the amide *IIIg*: N-4'-acetanilido-2,4,6-triphenylpyridinium fluoroborate whose ^{1}H-NMR chemical shifts are reported in Table I. With ethanol as the solvent we got the non acylated product *IIId*.

Trimethylammonium Salts *IV*

These compounds were obtained by exhaustive methylation[32] of 3- and 4-fluoroanilines with dimethyl sulphate (respectively *IVb* and *IVc*).

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