Carbon-13 NMR of *N*-Substituted 2,4,6-Trimethylpyridinium Salts

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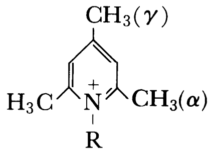
Synopsis. Carbon-13 chemical shifts of twelve *N*-substituted, 2,4,6-trimethylpyridinium (TMP) salts were determined. The data have been used to estimate the relative ring current (RRC) of the *N*-substituents on the pyridinium ring.

Verhoeven et al.[1–5] studying the UV spectra of some substituted pyridinium salts has pointed out that when R=phenyl, their UV spectra display a charge transfer band. Balaban et al.[6,7] utilized the proton NMR spectral data of some *N*-substituted TMP salts to estimate the relative ring current (RRC) of these systems.

Carbon-13 chemical shift, recieved little attention in this respect.[8,9] In this paper twelve new *N*-substituted TMP perchlorates (Scheme 1) were prepared[10] and their carbon-13 chemical shifts have been determined. Equation 2 is suggested for calculating RRC of the R group, using carbon-13 chemical shift of carbons 2 and 4.



Results and Discussion

Proton decoupled, as well as proton-coupled, carbon-13 spectra of the compounds **1**—**12** were recorded. Assignment of the chemical shift of these compounds (Tables 1 and 2) are based on; (i) the application of carbon-13 chemical shift of amines (RNH_2),[11] (ii) by applying the additivity rule, and substitution parameters, for the phenyl,[12,13] and the pyridinium rings,[14] and (iii) using off-resonance spectra of those compounds to determine the quaternary and protonated carbons.

Table 1 shows the trend of carbon-13 chemical shift of carbon 2,6, and the methyl carbons. It demonstrates the pronounced ring current effect of the N-aza aromatic ring on the chemical shift of those carbons.

It is accepted that analogous compounds are not coplanar.[15] Thus the α-methyl and carbons 2 and 6 are exposed to the ring current of the R substituent.

Equation 1[6] has been applied to calculate RRC using ^{1}H-chemical shift of compounds **6**—**12** (Table 3). The results are given in Table 3.

$$\mathrm{RRC}=200\,(D+0.25)-T \qquad (1)$$

where $T=71.7\,x/(1+2.26\,x)$, x=the number of ortho substituents in R.

$$D=\delta_{(\gamma\text{-methyl})}-\delta_{(\alpha\text{-methyl})}$$

Furthermore Eq. 2 is suggested by us, as an extention, to calculate (RRC) using carbon-13 chemical shift of carbons 2 and 4.

Equation 1 was used as a basis to derive Eq. 2 which use carbon-13 chemical shift of carbon 2 and 4 for calculating the RRC. In Eq. 2 T have the same definition as in Eq. 1, and D is given as

$$\delta_{4,2}=D=\delta\,(\text{carbon 4})-\delta\,(\text{carbon 2}). \qquad (1a)$$

When R=H, there is no ring current affecting carbons 2 and 4. The value of δ_4 and δ_2 in 2,4,6-trimethylpyridinium salt is 147.4 and 157.4 ppm,[16] therefore $\delta_{4,2}$ (−10 ppm) in this compound represents a correction factor for the D values in compounds **5**—**12**. Equation 1 could be modified as Eq. 1b by taking into account the above $\delta_{4,2}$ value.

$$\mathrm{RRC}=a\,(D+10)-T. \qquad (1b)$$

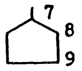
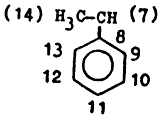
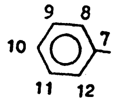
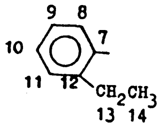
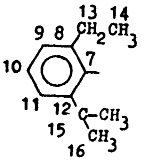
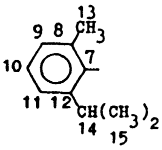
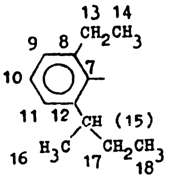
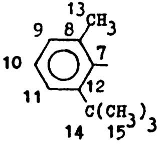
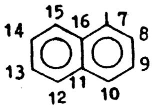
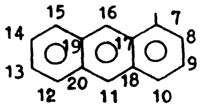
Using compound **5** as a reference (compound) where RRC=100, and D=5.22 ppm (Table 2), applying those values to Eq. 1b, one obtain a value for a=6.57. Thus Eq. 2 could be written as

$$\mathrm{RRC}=6.57\,(D+10)-T. \qquad (2)$$

The calculated RRC values for compounds **6**—**12** are given in Table 3.

As it is expected $\delta_{\text{C-2}}$ and $\delta_{\text{C-4}}$ are affected by the nature of R. The difference between $\delta_{\text{C-2}}$ and $\delta_{\text{C-4}}$ increases in compounds **7**—**9** (Table 1). This increase might be due to a slight change in ring current of R, which shields C-2 in compounds **5**—**12** relative to compounds **1**—**4** (Table 1). These results are consistent with available data, emphasizing the leterature reports that the α-methyl, C-2 and C-6 are oriented in the shielding region of the aromatic ring.[17] It is obvious that the RRC effect decreases when there is one ortho substituent on R (compound **6**), or when there is a bulky substituent (compounds **10**—**12**, Table 1). This might suggest a change of the dihedral angle between the two rings relative to that in compound **5**. It seems that RRC calculated from carbon-13 chemical shift for compounds **6**—**12** is more realistic than that obtained from ^{1}H chemical shift because the steric crowdening will change the dihedral angle thus decrease the RRC. On this basis one expects that the RRC will have a maximum value when R=phenyl (Table 3). This may be explained on the basis that as ortho substituent on R ring increases, the methyl group, carbons 2 and 4 become less exposed to the ring current of R, thus RRC decreases for those compounds relative to compound **5**. A rather interesting case is that of compound **2** whose $\Delta\delta_{4,2}$=0.71 ppm. This value is appreciably different from those of compounds **1**, **3**, and **4** (Table 1). Such apparent inconsistency may be interpreted in terms of the deshielding

Table 1. Chemical Shifts (ppm) of 2,4,6-Trimethylpyridinium

	R	δ_2	δ_3	δ_4	$\delta_{CH_3(\alpha)}$	$\delta_{CH_3(\gamma)}$	$\Delta\delta_{4,2}$	$\Delta\delta_{\gamma,\alpha}$	$\Delta\delta^*_2$	$\Delta\delta^*_4$	$\Delta\delta^*_\alpha$	$\Delta\delta^*_\gamma$
1	$^{7}CH_3$	154.79	127.42	156.83	20.85	21.05	2.04	0.20	0.0	0.0	0.0	0.0
2		156.89	127.91	157.60	20.99	21.53	0.71	0.54	2.10	0.77	−0.14	0.48
3		154.18	129.57	156.90	20.51	22.04	2.72	1.53	−0.61	0.07	0.34	0.99
4		154.67	129.45	158.63	21.16	22.29	3.96	1.14	−0.12	1.80	−0.31	1.24
5		154.03	127.34	159.25	21.34	21.59	5.22	0.25	−0.76	2.42	−0.49	0.54
6		153.85	127.78	159.69	20.86	21.98	5.84	1.12	−0.94	2.86	0.01	0.93
7		153.75	128.32	160.15	20.40	21.27	6.40	0.87	−1.04	3.32	0.45	0.22
8		153.54	128.34	160.12	20.19	21.26	6.58	1.07	−1.25	3.29	0.66	0.21
9		153.86	128.32	160.28	20.51	21.36	6.42	0.85	−0.93	3.45	0.34	0.31
10		154.77	128.44	160.78	20.50	21.59	6.02	1.09	−0.02	3.95	0.35	0.54
11		154.98	127.90	159.98	20.50	21.47	5.00	0.97	0.19	3.15	0.35	0.42
12		154.94	127.98	159.71	20.39	21.44	4.77	1.05	0.15	2.88	0.46	0.39

$\Delta\delta_x=\delta_x$ (compound **1**)$-\delta_x$(other compounds).

Table 2. Carbon-13 Chemical Shift (ppm) of the R Substituents

Compd.	δ_7	δ_8	δ_9	δ_{10}	δ_{11}	δ_{12}	δ_{13}	δ_{14}	δ_{15}	δ_{16}	δ_{17}	δ_{18}	δ_{19}	δ_{20}
1	39.59													
2	36.00	10.95	10.95											
3	64.86	29.85	24.74	24.74	29.85									
4	62.58	136.32	130.30	125.12	128.42	125.12	130.30	17.04						
5	137.71	124.96	130.58	130.73	130.58	124.96								
6	136.81	136.17	131.21	128.27	129.85	125.00	21.98	12.42						
7	141.90	133.81	131.46	125.71	127.19	136.46	23.20	12.35	27.37	22.25				
8	142.04	131.07	131.28	125.78	129.59	134.37	27.19	23.19	16.50					
9	141.41	134.16	131.43	127.22	128.46	136.81	22.37	12.42	34.42	20.25	29.83	11.44		
10	142.72	132.26	130.94	129.79	130.44	134.06	36.45	31.47						
11														
12														

Table 3. Proton Chemical Shifts (ppm) of α and γ Methyl Protons and Relative Ring Current

Compd.	$\delta_{CH_3(\alpha)}$	$\delta_{CH_3(\gamma)}$	$\Delta\delta_{\gamma\text{-}\alpha}$	T	RRC Eq. 1	RRC Eq. 2
1						
2						
3						
4						
5	2.31	2.56	0.25	0	100	100
6	2.25	2.62	0.63	22	84	82
7	2.30	2.64	0.34	26	96	82
8	2.24	2.65	0.41	26	106	83
9	2.28	2.64	0.36	26	96	81
10	2.34	2.63	0.29	26	82	79
11	2.37	2.76	0.39	22	106	99
12	2.41	2.80	0.39	22	104	97

effect of the σ-ring current of the strained cyclopropyl ring on carbon 2.

Experimental

2,4,6-Trimethylpyrylium salts were prepared by reported procedures.[18,19] They were reacted with aliphatic primary amines to produce compounds **1**—**4**,[10] and with aromatic amines to yield compounds **5**—**12**. Carbon-13 spectra were recorded as 20 mol% solution in DMSO-d_6 in 5 mm NMR tubes. Optimum amount of TMS was added to the samples to act as internal reference. The proton-decoupled and proton-coupled carbon-13 NMR spectra were recorded on Varian FT 80 A operating at 20 MHz. The spectral width was 4 KHz, pulse width, 8 μs (θ=45°); aquisition time 1 s, pulse delay 2 s. Chemical shift were accurate to better than 0.06 ppm. The proton spectra were recorded for 5 mol% solution in $CDCl_3$ in 5 mm NMR tubes. TMS was added as internal reference. Varian FT 80 A operating at 80 MHz used to record the proton spectra.

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