Research Article

Styrylpyrylium Salts: ^1H and ^{13}C NMR High-Resolution Spectroscopy (1D and 2D)

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^1H and ^{13}C NMR high-resolution spectroscopy (1D and 2D) (^1H , ^1H -COSY, HSQC, HMBC) for four styrylpyrylium perchlorates were carried out and signal attributions are reported. Chemical shifts observed on ^{13}C NMR spectra for the styrylpyrylium salts were compared with net atomic charge for carbon obtained by AM1 semiempirical calculations. The position of the styryl group present low effect on chemical shifts for carbon atoms, while the presence of methyl group led to the unshielding of the substituted carbon.

1. Introduction

NMR spectroscopy reports for pyrylium salts from few authors are available [1, 2]. This investigation presents some complexity in the attribution of the chemical shifts to atoms. The data on pyrylium salts NMR spectroscopy with substitution effects analysis are useful to understand various properties well known for pyrylium cations [3–6]. Particularly emission properties (fluorescence and phosphorescence) of styrylpyrylium salts are reported in relation with proton, chemical shifts in ^1H NMR of the pyrylium ring [7, 8]. However carbon chemical shift data relative to pyrylium ring, proton and carbon chemical shift for styryl group remain unknown, as for us.

In this study, we report high-resolution 1D and 2D ^1H and ^{13}C NMR analysis results for four styrylpyrylium salts (Figure 1).

^{13}C chemical shifts of the pyrylium ring, phenyl, and styryl groups are presented with correlation with Austin Model 1 (AM1) theoretical calculations. The substitution effects of methyl, phenyl, and styryl groups and their positions on the pyrylium ring were discussed as regards atomic chemical shifts.

2. Results and Discussion

Spectra are recorded with compounds dissolved in d_6 -DMSO. Proton NMR chemical shifts recording for studied styrylpyrylium salts were reported in Table 1 and those for carbon 13 in Table 2.

On all spectra, we observed general pyrylium salts characteristics and also specific data due to styryl group with its extracyclic double bond. Data are comparable to those of previous work at low resolution obtained by A. R. Katritzky and coll [1]. Here the study at high resolution gives high precision on chemical shifts for proton and carbon and reveals correlation between atoms.

2.1. ^1H NMR Spectra Data Analysis. H_x or C_x : x is the position number of carbon or hydrogen beard by carbon x .

All the protons of the phenyl groups resonate between δ_{H} 7.50 and δ_{H} 8.45. Pyrylium ring proton signals appear as singlets in the range 8.50–9.20. The signals were assigned and compared with data encountered in literature [8–10].

The two protons H_3 and H_5 of compound **1** are isochrones because of the symmetry of this molecule and

FIGURE 1: Structures of studied styrylpyrylium salts.

TABLE 1: ^1H NMR (600 MHz) data: chemical shifts δ in ppm as unit of measurement; multiplicity and constant coupling J given in Hz for four styrylpyrylium salts **1**, **2**, **3** and **4**.

Compounds	δ (multiplicity); J			
	1	2	3	4
H_3	8.92 (s)	—	9.02 (s)	—
H_5		9.17 (s)	8.80 (s)	8.52 (s)
H_7	7.70 (d); 16.2	7.87–7.77 (m)	7.81 (d)	7.72–7.77 (m)
H_8	8.70 (d); 16.2	8.72 (d); 15.9	8.48 (d); 16.2	8.37 (d); 16.2
H_{10}	7.84–7.88 (m)	8.02–8.13 (m)	7.96 (t); 3.6 and 4.2	7.80 (t); 4.2 and 3
H_{11}	7.84–7.88 (m)	7.62–7.64 (m)	7.60 (m)	7.56 (m)
H_{12}	7.62 (m)	7.62–7.64 (m)	7.60 (m)	7.56 (m)
H_{14}	8.44 (d); 7.8	8.02–8.13 (m)	8.61 (d); 7.2	8.08 (d); 7.2
H_{15}	7.79 (t); 7.8	7.87–7.77 (m)	7.85 (t); 7.2 and 7.2	7.72–7.77 (m)
H_{16}	7.62 (m)	7.87–7.77 (m)	7.76–7.79 (m)	7.72–7.77 (m)
H_{18}	8.44 (d); 7.8	8.42 (d); 8.4	8.44 (d); 7.2	7.89–7.91 (m)
H_{19}	7.79 (t); 7.8	7.87–7.77 (m)	7.76–7.79 (m)	7.72–7.77 (m)
H_{20}	7.62 (m)	7.87–7.77 (m)	7.76–7.79	7.72–7.77 (m)
H_{21}	—	2.67 (s)	—	1.90 (s)

(m: massif; t: triplet; d: doublet; s: singlet).

appear at δ_{H} 8.92, whereas in compound **3**, because of the asymmetry of the molecule, they are δ_{H} 9.02 for H_3 and H_5 shifted towards low frequency with δ_{H} 8.80 (Figure 2).

The high chemical shift value corresponding to H_3 may be explained by the fact that it is in a paramagnetic anisotropy field of both phenyl rings, those in positions 2 and 4, while H_5 is impacted by only one phenyl group anisotropy, the one in position 4 [11].

For NMR data analysis, comparison with triphenyl pyrylium: 2,4,6-triphenylpyrylium tetrafluoroborate encountered in the literature [12] shows the signal of the pyrylium ring protons at δ_{H} 8.50. These protons are more shielded than the styrylpyrylium perchlorate due certainly to the mesomeric effects.

The vinylic protons H_7 and H_8 constitute an AX system. Proton H_8 for all the compounds appears like a doublet between δ_{H} 8.37 and δ_{H} 8.72.

FIGURE 2: ^1H NMR spectra of compound 3.

FIGURE 3: HMBC spectrum for compound 3.

The scalar coupling value between the two vinylic protons of each molecule varied between 15.90 Hz and 16.20 Hz. This value is an indication for the (*E*) stereochemistry of the double bond $\text{C}=\text{C}$ of styryl group [13].

In the case of compound 3, H_7 signal appears on the spectrum 2D (HMBC) like doublet at δ_{H} 7.81 (Figure 3).

The allocation of the proton H_7 was confirmed by using proton-proton correlation spectra (COSY). The results show that this proton resonates at δ_{H} 7.80, in a broad peak for 2 and 4. On the 1D ^1H NMR spectrum of 1, proton H_7 resonates in a good resolution as doublet at δ_{H} 7.70 (Figure 4).

When the styryl group is attached in position 4 of the pyrylium ring, the proton H_8 resonates at δ_{H} 8.70 as for 1 and at δ_{H} 8.72 as for 2; when it moves to position 6, H_8 undergoes a slight shielding and resonates at δ_{H} 8.48 as for 3 and δ_{H} 8.37 as for 4.

Protons H_{14} and H_{18} of 1 are isochrones because of the symmetry of the molecule and resonate like doublet at δ_{H} 8.44.

Proton-proton correlation allowed allocation of signal in the form of triplet towards δ_{H} 7.79 to isochrones protons H_{15} and H_{19} .

In compound 3, proton H_{14} is more unshielded than proton H_8 from styryl group (Figure 1 and Table 1). However, on the ^1H NMR spectra of the other compounds, H_8 is more unshielded than all the other aromatic protons.

2.2. ^{13}C NMR Spectra Data Analysis. Carbon chemical shifts attribution for pyrylium cation-carbons were made by

FIGURE 4: Partial view of ^1H NMR spectra of compound 1 (600 MHz). FIGURE 5: ^{13}C NMR spectra of compound 1.

correlation spectra (HSQC, HMBC) and by DEPT. Data are given in Table 2.

Carbons C_2 , C_4 , and C_6 of pyrylium ring are unshielded than phenyl carbon and those of styryl group while carbons C_5 and C_3 are the most shielded as it is shown on Figure 5.

Indeed, the pyrylium cation is a hybrid of resonance between an oxonium form and three carboniums forms (Figure 6).

So, C_2 , C_4 , and C_6 exhibit a positive charge in the main resonance structures. The NMR chemical shifts (calculated by the GIAO method) [14] obtained for carbon atoms of the pyrylium cation are in good agreement with these results.

HMBC correlation spectrum based on the ^1H NMR data observed with compound 3 shows that proton H_8 is coupled with carbon C_6 , C_4 , and C_9 but not with C_7 . Also, H_7 is coupled with C_6 and C_5 but not with C_8 (Figure 7).

Carbon C_7 resonates between δ_{C} 118 and δ_{C} 124 while C_8 resonates between δ_{C} 145 and δ_{C} 149 for all the compounds. This difference is due to the mesomeric forms of the molecule given positive load on carbon 8 (Figure 8).

This mesomeric form is the same for all the compounds. The net atomic charge for carbon atoms obtained by AM1 semiempirical calculation corroborates with allocations made (Table 2). Indeed, the highest is the net atomic charge, and the more unshielded carbon is observed [15].

3. Substitution Effect Analysis

Comparing the pyrylium cation structure and the obtained ^{13}C NMR spectra, we were interested by methyl group

TABLE 2: ^{13}C -NMR data, 9.40 T (100.6 MHz) or 14.09 T (150.9 MHz) of compounds **1**, **2**, **3** and **4**: Chemical shifts δ (in ppm as unit of measurement) and net atomic charge (q) of styrylpyrylium salts carbons.

Carbon	1		2		3		4	
	δ	q	δ	q	δ	q	δ	q
C ₂	168.88	0.213	167.19	0.189	169.12	0.211	169.46	0.192
C ₃	114.90	-0.303	129.07	-0.167	114.29	-0.300	128.39	-0.162
C ₄	163.23	0.162	163.61	0.155	163.69	0.168	167.94	0.156
C ₅	114.90	-0.312	112.75	-0.310	116.93	-0.311	118.34	-0.305
C ₆	168.88	0.220	168.97	0.213	170.15	0.209	169.60	0.205
C ₇	123.77	-0.299	121.18	-0.299	118.86	-0.304	121.01	-0.304
C ₈	148.67	0.000	149.22	-0.007	145.80	0.004	146.40	0.005
C ₉	129.21	-0.140	129.32	-0.139	129.15	-0.141	130.24	-0.142
C ₁₀	129.68	-0.136	130.27	-0.137	129.76	-0.135	129.44	-0.134
C ₁₁	129.36	-0.199	127.52	-0.199	128.71	-0.200	129.14	-0.199
C ₁₂	132.53	-0.136	132.35	-0.138	132.17	-0.135	133.04	-0.135
C ₁₃	134.72	-0.134	129.81	-0.133	134.38	-0.139	135.14	-0.134
C ₁₄	129.97	-0.123	130.35	-0.129	129.96	-0.127	130.65	-0.133
C ₁₅	128.26	-0.197	128.95	-0.192	129.25	-0.195	129.24	-0.193
C ₁₆	134.78	-0.127	134.37	-0.139	134.96	-0.129	132.23	-0.136
C ₁₇	134.72	-0.135	129.70	-0.140	132.53	-0.140	134.26	-0.138
C ₁₈	129.97	-0.124	132.59	-0.127	129.53	-0.135	129.33	-0.146
C ₁₉	128.26	-0.197	127.98	-0.197	129.47	-0.193	129.26	-0.191
C ₂₀	134.78	-0.126	134.90	-0.128	134.87	-0.135	131.88	-0.143
C ₂₁	—	—	15.10	-0.322	—	—	17.63	-0.322

FIGURE 6: Pyrylium cation resonance structures.

FIGURE 7: Pertinent HMBC correlations observed with **3**.

FIGURE 8: Mesomeric forms of **1**.

position in pyrylium ring, effect on the chemical shifts of styryl group and pyrylium ring carbons.

Disturbance made by the electron donating methyl group led to the unshielding of substituted carbon with a gap of about δ_{C} 14, while affecting slightly chemical shifts of the other carbons (Table 3). The effect was noticed with isothiazol, where the presence of methyl group causes the unshielding of substituted carbon by δ_{C} 10 to δ_{C} 15 [16].

Pyrylium ring ^{13}C NMR of the 2,4,6-triphenylpyrylium is given in the literature [17]. When one phenyl group is substituted by a styryl group (formation of **1** or **3**), we observe a shielding of about δ_{C} 4 of carbons C₂ and C₆, and about δ_{C} 6 of C₄. This shielding could be explained by the paramagnetic anisotropy, which is more intense around 2,4,6-triphenylpyrylium which has 3 phenyls groups directly attached to the pyrylium ring.

When styryl group is in position 4, the methyl carbon resonates at δ_{C} 15.10; when the styryl group is bearing in position 6, the carbon resonates at δ_{C} 17.63. This slight unshielding is certainly due to a magnetic anisotropy effect [11].

4. Conclusion

Protons and carbons chemical shifts for four styrylpyrylium perchlorates were allocated notably thanks to correlation spectra and to DEPT. Carbon 13 chemical shift assignments have been confirmed by net atomic charge for carbon obtained by AM1 semiempirical calculation. The scalar

TABLE 3: Gap of chemical shifts of styryl group and pyrylium ring carbons for compounds **1**, **2**, **3** and **4**.

	δ in ppm as compared to non substituted compounds						
	C ₂	C ₃ *	C ₄	C ₅	C ₆	C ₇	C ₈
δ (2)- δ (1)	-1.69	14.17	0.38	-2.15	0.09	-2.59	0.55
δ (4)- δ (3)	0.34	14.10	4.25	1.41	-0.55	2.15	0.60

* Substituted carbon.

coupling value indicates an (*E*) stereochemistry around the double bond C=C of the styryl group.

The effects of the styryl group position in the pyrylium ring and the substitution effects (methyl and phenyl groups) will be compared to their reduction potential obtained by cyclic voltammetry.

5. Experimental Part

Styrylpyrylium perchlorates are prepared as described in literature by Simalty et al. [18] or with a procedure via δ -diketone for compounds **1** and **2** [19].

The NMR spectra were recorded at 298 K in DMSO-*d*₆ on a Bruker Avance spectrometer operating at 7.05 T (300 MHz for ¹H and 75.4 MHz for ¹³C) or Varian VNMRs spectrometers operating at 9.40 T (400 MHz for ¹H and 100.6 MHz for ¹³C) and 14.09 T (600 MHz for ¹H and 150.9 MHz for ¹³C).

The chemical shift scales were calibrated using the signal of the solvent (2.50 ppm for ¹H and 39.5 ppm for ¹³C) [20] or the signal of internal TMS (0.00 ppm).

Mass spectra are recorded using ES ionization with a Waters QTOF2 spectrometer.

Calculations were carried out using the CS MOPAC programs version 5.0. All the structures were completely optimized by the AM1 method [21].

1. 2,6-diphenyl-4-styrylpyrylium perchlorate [18, 19].

Red compound; yield: 31%; Mp: 274°C.

IR (cm⁻¹): 1638.35; 1603.67; 1593.16; 1576.99; 1517.97; 1495.32; 1469.78; 1191.17; 1083.42; 984.77; 776.86; 714.24; 683.39; 646.12; 621.12.

MS ES: *m/z* (%): 337(5); 336(35); 335 [M⁺] (100); 254(11); 253(55); 231(11); 178(21); 157(22); 129(28); 100(5).

¹H-NMR; δ (ppm): 8.94 (s, 2H, pyr H₃ and H₅); 8.70 (d, 1H, =C₈H-); 7.50–8.50 (15H, Ar and 1H, d, -C₇H= at 7.70).

NMR ¹³C: 168.88 (C₂, C₆); 114.90 (C₃, C₅); 163.23 (C₄); 123.77 (C₇); 148.67 (C₈).

2. 3-methyl-2,6-diphenyl-4-styrylpyrylium perchlorate [18, 19]

Red compound; yield: 20%; Mp: 287°C.

IR (cm⁻¹): 1626.16; 1601.89; 1590.82; 1574.97; 1508.48; 1080.41; 978.00; 738.37; 728.39; 698.87; 623.78.

MS ES: *m/z* (%): 350(25); 349 [M⁺] (100); 335(10); 267(11); 254(15); 253(100); 244(5); 159(5); 157(58); 120(8).

¹H-NMR; δ (ppm): 9.17 (s, 1H, pyr H₅); 8.70 (d, 1H, =C₈H-); 7.7–8(m, 16H, Ar and -CH₇=); 2.67 (s, 3H, -CH₃).

NMR ¹³C: 168.97 (C₆); 167.19 (C₂); 163.61 (C₄); 149.22 (C₈); 127.52; 121.18; 112.75.

3. 2,4-diphenyl-6-styrylpyrylium perchlorate [18].

Red compound; yield: 22%; Mp: 213°C.

IR (cm⁻¹): 1629.89; 1592.25; 1504.82; 1492.34; 1467.63; 1215.65; 1092.70; 975.90; 766.67; 679.75; 622.87.

MS ES: *m/z* (%): 337 (5); 336 (30); 335 [M⁺] (100)

¹H-NMR; δ (ppm): 9.02 (s, 1H, pyr H₅); 8.8(s, 1H, pyr H₃); 8.5(d, 1H, =C₈H-); 7–8(m, 16H, Ar and -C₇H=)

NMR ¹³C: NMR ¹³C: 170.15 (C₆); 169.12 (C₂); 163.69 (C₄); 145.80 (C₈); 134.96; 134.87; 134.38; 132.53; 132.17; 129.96; 129.76; 129.53; 129.47; 129.25; 129.15; 128.71; 118.85 (C₇); 116.93 (C₅); 114.28 (C₃).

4. 3-methyl-2,4-biphenyl-6-styrylpyrylium perchlorate [18]

Red compound; yield: 23%; Mp: 208°C.

IR (cm⁻¹): 1626.30; 1606.20; 1594.25; 1504.85; 1091.11; 972.04; 764.06; 698.70; 624.03.

MS ES: *m/z* (%): 350 (12); 349 [M⁺] (45); 244 (15); 243 (100); 179 (12); 101 (6).

¹H-NMR; δ (ppm): 8.52 (s, 1H, pyr H₅) 8.4 (d, 1H, =C₈H-); 7.5–8 (m, 16H, Ar and -C₇H=); 1.9 (s, 3H, -CH₃)

NMR ¹³C: 169.60 (C₆); 169.46 (C₂); 167.94 (C₄); 146.40 (C₈); 135.14; 134.26; 133.04; 132.23; 131.88; 130.65; 130.24; 129.44; 129.33; 129.26; 129.24; 129.13; 128.39; 121.01 (C₇); 118.34 (C₅); 17.63 (CH₃).

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