

Dedicated to Professor Victor-Emanuel Sahini
on the occasion of his 80th anniversary

PYRYLIUM SALTS WITH LONG ALKYL SUBSTITUENTS AND DERIVED PYRIDINIUM SALTS HAVING A TERMINAL FREE AMINO GROUP**

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2,4,6-Trisubstituted pyrylium salts having either one or two linear α -alkyl side chains **3a-6a** reacts with methylamine **2** or triethyltetraamine **7** affording corresponding pyridinium salts N-methyl **3b-6b** or having a free amino group **3c-6c**. All new amphiphiles were fully characterized by ¹H- and ¹³C-NMR (at 400 MHz for protons and 100 MHz for carbons), IR and elemental analysis.

We have examined the surfactant properties of N-triethyl-triaminopyridium perchlorates **3c-6c** and the diagram CMC vs number of carbon atoms of alkyl side chains for these new compounds was also presented.

INTRODUCTION

In the previous paper¹ we described the synthesis and surfactant properties of pyridinium perchlorates with long alkyl substituents having free ethyleneamino terminal group.¹

Pyrylium salts have become easily accessible by diacylation of olefins or their precursors.²⁻⁴ About the same time (1990-2007) similar procedure was used in our laboratory and the 2,4,6-trisubstituted / 2,3,4,6-tetrasubstituted pyrylium salts having either one (or two) linear α/γ -alkyl side chains and derived pyridinium salts were obtained.^{1, 5-15}

These compounds have the advantage of a simple structure, excellent stability and convenience in production and in vesicle formation, hence being of great significance for theory and applications. So, the synthesis of liquid

crystals and the thermotropic liquid crystalline properties of heteroaromatic salts substituted with short (C_n , $n=2,3$) or long (C_n , $n>8$) alkyl side chains were explored systematically by M. Veber and coworkers. They observed that in all cases of cations associated with ClO_4^- anion, the range of mesophase depends on the nature of the heterocycle.¹⁶⁻¹⁸

The present paper describes the synthesis of N-methyl and N-triethyl-triaminopyridium perchlorates derived from 2,6-dipalmitoyl-4-methyl- and 2,6-distearoyl-4-methylpyrylium perchlorates. These new compounds were separated by column chromatography or thin layer chromatography and characterized by elemental analyses, IR, UV-Vis, NMR-spectra. Our surfactant properties and CMC determinations were also presented.

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** This is contribution no. 13 in the series “Pyrylium Salts with Long Alkyl Substituents”. For some previous papers in this series see ref. ^{1, 5-15}

RESULTS AND DISCUSSION

Materials and Methods

The acylation of t-butyl-chloride or mesityl oxide **1** with lauroyl, palmitoyl or stearoyl chloride **2** using SnCl_4 as catalyst, optionally in carbon disulfide as solvent, followed by the treatment of the crude reaction mixture with 70% perchloric acid gave **3a–6a**. Compounds **3a** and **4a** were described previously (Scheme I).^{7, 13, 14}

In previous papers^{7, 10–14} we reported the chromatographic separation of the complex acylation mixture ending in isolation of the pyrylium salts in pure state. This procedure was successfully used for the pyrylium salts **5a** and **6a** as well (see Experimental part).

By reaction between salts **3a–6a** with primary amines CH_3NH_2 , the pyridinium salts **3b–6b** were obtained (Scheme 2).

The N-triethyl-triaminopyridium perchlorate **3c–6c** were obtained by similar procedure. The reaction mixture contains pyridinium and bis-

pyridinium salts. The conditions and the purification procedures for compounds **3a–6a** and **3c–6c** are given in the Experimental part (Scheme 3).

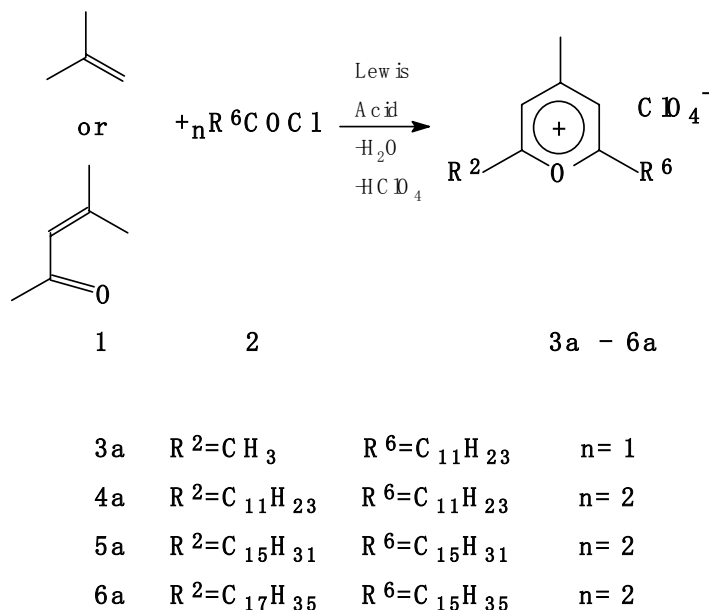
The ^1H and ^{13}C -NMR chemical shifts of pyrylium salts **3a–6a** and of the pyridinium salts **3b–6b** and **3c–6c** were in agreement with the previously reported NMR data on the 2,4,6-trisubstituted homologs.^{1, 7, 10, 12–15}

Table 1 and Table 2 present the ^1H and ^{13}C -NMR chemical shifts respectively for these new compounds.

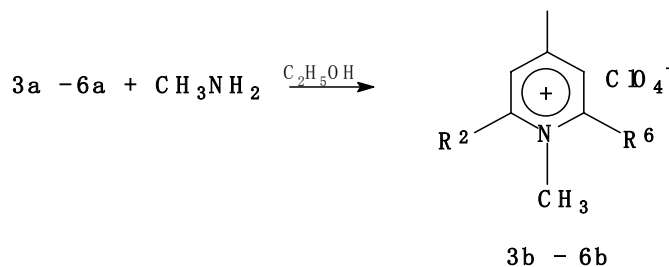
The atom numbering for NMR assignments is given in Figure 1 (ring atoms are not numbered).

The assignment of the proton signal is in all cases straightforward. When the signals were ascertained, 2D techniques were used.

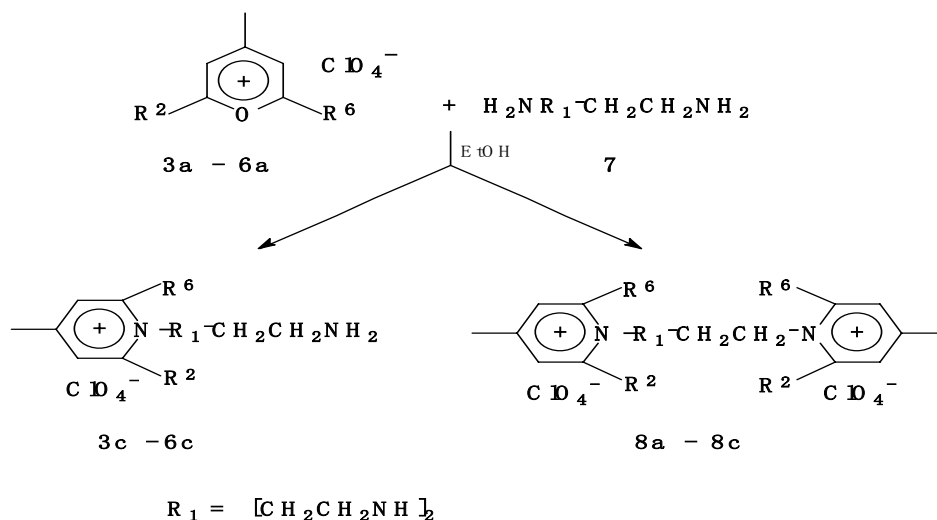
The 2,4,6-trialkylpyridinium salt moiety is a very useful probe for measuring the ring current of aromatics as an internal reference. For carbon spectra, unambiguous assignments for all new compounds were accomplished using two-dimensional correlation spectroscopy (COSY, HMQC and HMBC).



Scheme 1 – Conversion of pyrylium salts into pyridinium salts **3a–6a**.



Scheme 2 – Conversion of pyrylium salts into pyridinium salts **3b–6b**.



Scheme 3 – Conversion of pyrylium salts **3a-6a** into pyridinium salts **3c-6c**.

Table 1

¹H-NMR chemical shifts (δ, ppm) at 400 MHz of compound **3c**, **5a-c**, **6a-c** in CDCl₃

Comp. Protons	O ⁺		N ⁺ -CH ₃		N ⁺ -TETA			
	5a	6a	5b	6b	3c	4c	5c	6c
3-H	7.70	7.72	7.40	7.40	7.45	7.49	7.49	7.49
5-H	-	-	-	-	7.55	-	-	-
4-CH ₃	2.79	2.79	2.56	2.54	2.56	2.57	2.50	2.50
6-CH ₃	-	-	-	-	2.73	-	-	-
1'-CH ₂	3.14	3.15	3.04	3.04	3.14	3.17	3.09	3.03
2'-CH ₂	1.84	1.85	1.75	1.75	1.73	1.76	1.75	1.75
3'-CH ₂	1.37	1.39	1.46	1.46	1.46	1.48	1.47	1.48
n'-CH ₃	0.88	0.88	0.88	0.88	0.88	0.88	0.89	0.89
1''-CH ₂	-	-	4.13	4.12	4.96	4.99	4.92	4.93
2''-CH ₂	-	-	-	-	4.85	4.73	4.70	4.70
3''-CH ₂	-	-	-	-	3.75	3.73	3.65	3.64
n''-CH ₂	-	-	-	-	3.60	3.60	3.61	3.55

Table 2

¹³C-NMR chemical shifts (δ, ppm) at 100 MHz of compound **3c**, **5a-c**, **6a-c** in CDCl₃

Comp. Carbon	O ⁺		N ⁺ -CH ₃		N ⁺ -TETA			
	5a	6a	5b	6b	3c	4c	5c	6c
C-2	180.80	180.20	157.31	157.36	157.28	157.43	152.21	152.28
C-4	171.52	174.85	158.52	158.47	162.49	158.50	158.77	158.92
C-6	-	-	-	-	153.04	-	-	-
C-5	-	-	-	-	125.20	-	-	-

Table 1 (continued)

C-3	122.98	123.30	126.57	126.50	123.89	124.23	123.16	123.85
4-CH ₃	21.93	22.74	21.84	21.90	22.51	22.66	22.47	22.75
6-CH ₃	-	-	-	-	21.99	-	-	-
1'-CH ₂	34.92	35.00	34.20	34.17	32.93	33.76	33.64	32.99
2'-CH ₂	26.83	27.09	27.72	27.72	28.77	28.80	28.80	28.87
(n-2)'-CH ₂	32.02	31.96	31.92	31.70	29.52	30.46	29.90	29.42
(n-1)'-CH ₂	22.67	21.96	21.93	22.70	20.72	22.30	21.48	21.70
n'-CH ₃	-	-	14.20	14.03	13.96	14.08	14.07	14.11
1''-CH ₂	-	-	38.85	38.84	36.71	36.55	36.01	36.77
2''-CH ₂	-	-	-	-	33.47	35.82	35.44	35.64
3''-CH ₂	-	-	-	-	31.73	32.09	31.88	30.41
n''-CH ₂	-	-	-	-	31.28	31.91	30.91	29.76

*assignment based by H-C spectra

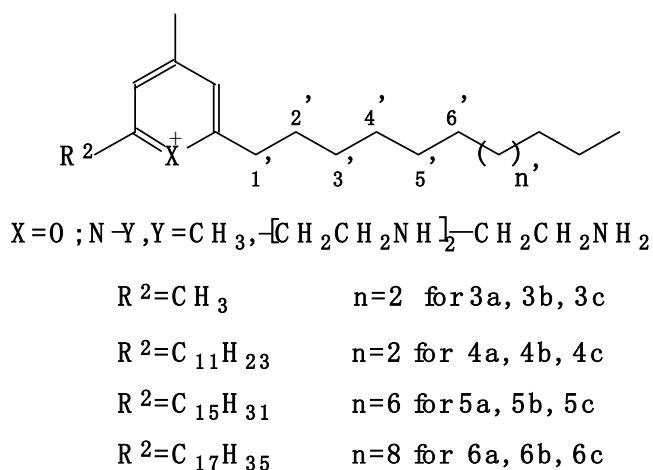


Fig. 1 – The atom numbering for NMR assignments.

Surfactant properties

It was shown that many pyridinium salts with long alkyl substituents have or are expected to have surfactant properties.^{19,20}

The first example of determination of critical micellar concentration (CMC) for pyridinium salts with different long chain substituents using spectrophotometry methods in the UV-Vis region of the spectrum at 20 °C was reported recently.¹ Similar procedure was useful for compounds **3c-6c**, which have a free amino group.

UV-Vis spectra for **3c-6c** in range 200-400 nm are characterized by two bands whose intensities and positions are solvent dependent. UV-Vis spectra of these compounds ethanolic solution are presented in the Experimental part.

In order to obtain the diagrams absorbances vs concentration for CMC determination, the mixtures **3c-6c** / ethanol were prepared and let to stand at 20 °C for one day and by measuring absorbance as a function of amphiphiles concentration, one can estimate its CMC from intercept of two straight lines. By using of such methods the CMC values for **3c-6c** are estimated to be: 95.6 (λ, nm = 396.30), 35.7 (λ, nm = 366.02), 20.20 (λ, nm = 347.26) and 11.70 (λ, nm = 347.26) mMx10⁻³.

Relatively short N-ethyleneamino-chain substituent leads to smaller CMC values for all compounds irrespective of the number and position side chain of the pyridinium ring. A new substituent at N-atom which contain a higher long chain with four amino group increases significantly the hydrophilicity and

CMC values. A similar effect was noticed for surfactants with long chain with different number of amino group. So, for these compounds when NH group was displaced by center to the terminal side chain the increase of CMC values was observed.²¹

It is found that CMC decreases with increasing length of the hydrophobic alkyl group.²² **Figure 2** shows the diagram CMC vs number of carbon atoms of alkyl side chains for compounds **3c** – **6c** and according to the well-known data, a drastic decrease of CMC was observed.

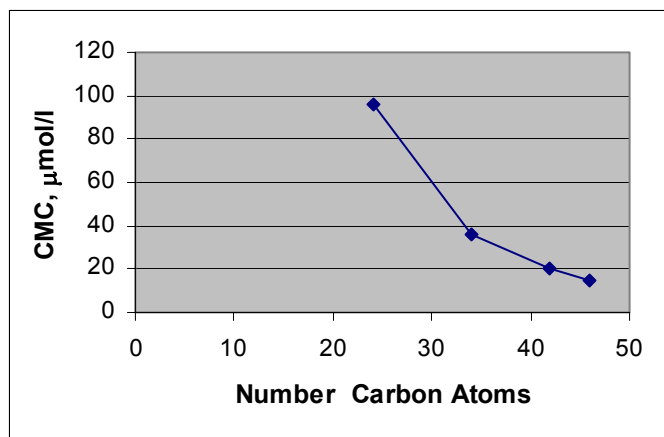


Fig. 2 – Plot of CMC as a function of length of the hydrophobic alkyl side chains.

EXPERIMENTAL PART

The NMR spectra have been recorded with a BRUKER AVANCE 400 DRX instrument, equipped with a 5 mm inverse detection multinuclear probe head and field gradients on the z axis, operating at 400 MHz for ^1H and at 100 MHz for ^{13}C nuclei. The COSY45, HMQC and HMBC spectra have been recorded with standard Bruker parameters in the versions employing pulsed field gradients. All spectra have been recorded in deuterated chloroform, and the chemical shifts have been reported as δ values referenced to TMS as internal standard. Infrared spectra were run on a BRUKER VERTEX 70 instrument equipped with a Golden Gate diamond ATR. The UV-VIS spectra were recorded with a GBC type 918 instrument in 1 cm cuvettes. Melting points were measured in open capillary tubes (for the low melting compounds) or on a hot-stage melting points apparatus (equipped with a polarizator to check for nematic properties).

2,6-Dipalmitoyl-4-methylpyrylium perchlorate **5a** and 2,6-distearoyl-4-methylpyrylium perchlorate **6a**

In a four-necked flask equipped with mechanical stirrer, immersed thermometer, reflux condenser, dropping funnel and outlet protected by a CaCl_2 tube, SnCl_4 (57.4 g, 0.22 moles), were added under external cooling (ice and water bath) to palmitoyl chloride 98% (61.80 g, 0.22 moles) or stearoyl chloride 99% (66.45 g, 0.22 moles b.p.=174-178 °C/12mm). The t-butyl-chloride (11.72 g, 0.11 moles) was added dropwise maintaining the temperature between 22° and 25 °C.

The stirring was continued at room temperature for 72 hours. The evolution of hydrogen chloride ceases after additional stirring for 3 hours at 35-40 °C.

The reaction mixture was decomposed and separated by the method developed in our laboratory. In the order to examine the generality of this method, we extended the study to the title compounds. For related observation see.^{7, 10-14}

So, the reaction mixture was then placed on a column chromatography (silica gel type extra pure Merck, ratio silica/oil = 2/1). The intermediates and the by-products of the

acylation reaction were eluted in the forerun, as previously described.^{7, 10, 14}

Pyrylium perchlorate **5a** and **6a** were lastly eluted with a mixture of ethyl acetate : methanol = 9:1, respectively ethyl acetate:methanol:water = 8:1:1. From this fraction, after drying (over MgSO_4) and concentration, the pyrylium perchlorate **5a** and **6a** crystallised as colourless crystals with m.p.= 81-82 °C (43.63 g, 7.1 mmole), in 6.45% yield (**5a**) and with 83-84 °C (34.87g, 5.2 mmole), in 4.72% yield (**6a**).

The IR and UV-Vis spectra for compounds **5a** were:
IR ν, cm^{-1} : 622.86, , 1081.76, 1552.22, 1639.70, 2852.76, 2921.24.

UV ($\text{C}_2\text{H}_5\text{OH}$), λ_{nm} (max): 246.9.

The IR and UV-Vis spectra for perchlorate **6a** was in full agreement with the data presented for compounds **5a**.

Elemental analyses for compounds **5a** and **6a**:

5a $\text{C}_{36}\text{H}_{67}\text{ClO}_5$ Calcd.: C 70.30% H 10.90% Cl 5.78%.

Found: C 70.11 % H 11.11% Cl 5.75%.

6a $\text{C}_{40}\text{H}_{75}\text{ClO}_5$ Calcd.: C 71.59% H 11.18% Cl 5.29%

Found: C 71.58 % H 11.21% Cl 5.32%.

Conversion of pyrylium salts into N-methyl -pyridinium salts **5b** and **6b**

Pyridinium salts **5b** and **6b** were prepared according to the following general procedure: to the solution of pyrylium salt **5a** (for **5b**), or to the solution of pyrylium salt **6a** (for **6b**) in ethanol, an excess of amine (solution 40% wt. in ethanol were added (molar ratio 1:5 for **5b**, or 1:8 for **6b**); a deep-red colour developed instantly. The mixture was heated at a gentle reflux of the solvent, for two hours when the colour of the solution turned into cognac. The pyridinium salts **5b** and **6b** crystallized spontaneously; after setting for one hour in the refrigerator; the crystals were collected on a sintered glass filter and washed twice with diethyl ether; recrystallization from i-propanol gave colourless crystals with m.p.=91-93 °C (**5b**) and with m.p.=94-96 °C (**6b**) respectively.

The yields in **5b** and **6b** were 72% and 70% respectively.

The IR and UV-Vis spectra for compound **5b** were:

IR ν, cm^{-1} : 622.99, 1081.67, 1685.78, 2858.56, 2924.43;

UV (C₂H₅OH), λ_{nm} (max): 222.2; 273.9.

The IR and UV-Vis spectra for perchlorate **6b** was in full agreement with the data presented for compounds **5b**.

Elemental analyses for compounds **5b** and **6b**:

5b C₃₇H₇₀NCIO₄ Calcd.: N 2.23%
Found: N 2.23%

6b C₄₁H₇₈NCIO₄ Calcd.: N 2.05%,
Found: N 2.08%.

Conversion of pyrylium salts into N-triethyltri-amino - pyridinium salts **3c-6c**

To the solution of pyrylium salt in ethanol an excess of TETA was added (1:5 –1:10 molar ratio); a deep - red colour developed instantly. The mixture was heated at a gentle reflux of the solvent for 5 hours when the colour of the solution turned into cognac. The reaction mixture contains pyridinium and bis-pyridinium salts. After cooling the pyridinium salts are separated by thin layer chromatography (silica gel Merck type 60G, solvents hexane : acetic acid : ethyl acetate = 2 : 5 : 3). After solvents evaporation waxy oils which crystallized in refrigerator were obtained (m.p.=20-22°C for **3c** and m.p.=24-25 °C for **4c**). The pyridinium salts **5c** and **6c** crystallized spontaneously after storing for one hour in the refrigerator. Recrystallization from *t*-propanol gave colorless crystals with m.p.=70-70.5°C (**5c**) and with m.p.= 115-116°C (**6c**).

The yields in **3c-6c** were 55%, 46%, 48% and 44% respectively.

IR $\nu_{\text{cm}^{-1}}$: 1081.45, 1249.45, 1482.33, 1574.22, 1638.43, 2383.11, 2852.22, 2927.67, 3581.78, for **3c**.

IR $\nu_{\text{cm}^{-1}}$: 1081.97, 1255.69, 1489.34, 1574.70 1642.23, 2384.09, 2852.96, 2930.01, 3581.56, for **4c**.

The IR spectra for perchlorates **5c** and **6c** was in full agreement with the data presented for compound **4c**.

Elemental analyses for compounds **3c-6c**:

3c C₂₄H₄₇N₄ClO₄ Calcd.:N 11.42%
Found: N 11.51%

4c C₃₄H₆₇N₄ClO₄ Calcd.: N 8.88%,
Found: N 8.86%.

5c C₄₂H₈₃N₄ClO₄ Calcd.:N 7.54%
Found: N 7.53%

6c C₄₆H₉₁N₄ClO₄ Calcd.: N 7.01%,
Found: N 7.03%.

Surfactant properties

In order to obtain the diagrams absorbances vs concentration for CMC determination, the mixtures **3a-3d** / ethanol were prepared and let to stand at 20 °C for one day. The UV-Vis spectra were recorded with a GBC type 918 instrument in a 1 cm cuvettes.

As evaluation of absorption at a fixed wavelength and temperature and various concentrations of amphiphiles shown that lie on two lines experimental points which intersect at CMC value.

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