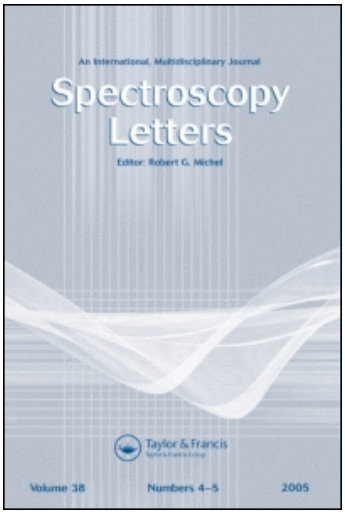

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Yousif Z. Yousif[a]; Fadhil S. Kamounah[a]; Mahir K. Ali[a]; Jasim M. A. Al-rawi[b]
[a] Chemistry Department, College of Education, Basrah University, Basrah, IRAQ [b] Chemistry Department, College of Science, Mosul University, Mosul, IRAQ

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^{1}H AND ^{13}CNMR STUDY OF A NEW CLASS OF BIPYRIDINIUM LIQUID CRYSTALS

Yousif Z. Yousif*, Fadhil S. Kamounah and Mahir K. Ali
Chemistry Department , College of Education , Basrah University , Basrah , IRAQ.

Jasim M. A. Al-Rawi
Chemistry Department, College of Science, Mosul University , Mosul , IRAQ.

ABSTRACT:

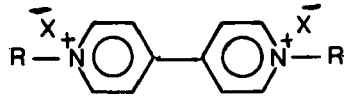
^{1}H and ^{13}C NMR , as well as UV and IR , spectra of a new class of bipyridinium salts made by double quaternization of trans-1,2-bis(4-pyridyl) ethene unit with n-alkyl salts are reported. The effect of quaternization on the ^{1}H and ^{13}C NMR spectra of the salts is discussed.

INTRODUCTION

There has been many references in the literature on pyridinium salts and more relevant to this work ,

* Author to whom correspondance should be addressed.

bipyridinium salts (1,1'-dialkyl-4,4'-bipyridinium salts;I) known as violagens.



(I)

Type (I) violagens (R= n-alkyl and X= halogen) have been previously investigated in dilute aqueous solutions for electrcchromic display applications[1,2]. The relevant phenomena is based on the reversible colour change that accompanys the oxidation - reduction reaction[3].

It has been known that certain amphiphilic molecules (ion pairs) exhibit thermotropic mesophases, e.g., neat soaps and pyridinium salts[4]. In a recent study[5] on type(I) violagens it was revealed for the first time that these molecules (•X = $MeSO_3$ or 4-$MeC_6H_4SO_3$) exhibit liquid-crystalline phases of both types.

In this study we report some of the properties (UV,IR,^1H, and ^{13}C NMR spectra) of a new class of bipyridinium salts type II (R= n-alkyl chain and X= $MeSO_3$ or 4-$MeC_6H_4SO_3$) made by double quaternization of the trans-1,2-bis(4-pyridyl)ethene unit.

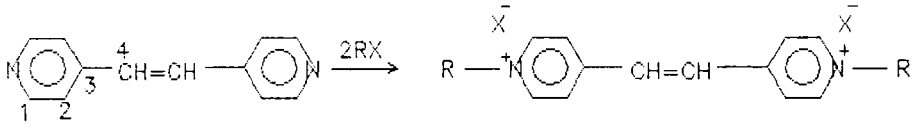
RESULTS AND DISCUSSION

All of the bipyridinium salts exhibited intense i.r. absorptions at ca. 1200 cm^{-1} ($-CH_2-N$)[6], 1630 cm^{-1} (C=C stretch)[7] and 1160 cm^{-1}(S=O stertch). A Medium absorption was also recorded at 3050 cm^{-1}(C=C-H unsat ,

stretch) , 2930 cm^{-1}(C-CH sat , stretch), 1370 cm^{-1} (C-C stretch) and 820-850 cm^{-1} (P-substituted aromatic ring).

The U.V. absorption spectra in methanol of all the salts were identical and contained three bands (due to double bond conjugation) with λ_{max} at 310, 322 and 336 nm (logE=5.53,5.60 and 5.42 respectivelly, where E is the molar extinction coefficient). Three other bands (due to II-II*) transitions in the pyridyl rings with max at 252,258 and 264 nm (log E= 5.23, 5.26 and 5.23 respectively).

The ^1H-n.m.r. spectral data for the compounds (scheme 1) are given in Table 1. The trans-1,2-bis(4-pyridyl) ethene (PE) unit showed two double - doublets (1J = 7.8 and 2J = 2.2) at 8.6 and 7.8 ppm for H-2 and H-3 respectively , while the ethene protons, H-5, appeared as a singlet at 7.3 ppm. The n-dialkyl salts, PEDMn and PEDTn (M=$MeSO_3$, T= 4-$C_6H_4SO_3$ and n=number of carbon atoms in the normal alkyl chain) also showed two broad doublets at 8.99 - 0.05 and 8.38 - 0.05 ppm for H-2 and H-3, respectively as well as a singlet at 8.06 $\mp$ 0.04 ppm for H-5 in addition to the expected singals for the alkyl chain and the anion M or T. It is clear from above data that protons α-to the pyridine nitrogen (H-2) suffer deshielding of (0.5 ppm) while β - and γ - protons (H-3 and H-5) are deshielded to a larger extent than expected (0.79 and 0.8 ppm respectively). The positive charge on the quaternary nitrogen is expected to deshield



PE (II)

$PEDM_3$, $R=-CH_2CH_2CH_3$, $X=CH_3SO_3$

$PEDM_4$, $R=-CH_2CH_2CH_2CH_3$, $X=CH_3SO_3$

$PEDM_6$, $R=-CH_2CH_2CH_2CH_2CH_2CH_3$, $X=CH_3SO_3$

$PEDM_7$, $R=-CH_2CH_2CH_2CH_2CH_2CH_2CH_3$, $X=CH_3SO_3$

$PEDT_3$, $R=-CH_2CH_2CH_3$, $X=CH_3$-C6H4-SO_3

$PEDT_4$, $R=-CH_2CH_2CH_2CH_3$, $X=CH_3$-C6H4-SO_3

$PEDT_6$, $R=-CH_2CH_2CH_2CH_2CH_2CH_3$, $X=CH_3$-C6H4-SO_3

$PEDT_7$, $R=-CH_2CH_2CH_2CH_2CH_2CH_2CH_3$, $X=CH_3$-C6H4-SO_3

$PEDT_{18}$ $R=-CH_2CH_2CH_2CH_2CH_2CH_3(CH_2)_9CH_2CH_2CH_3$, $X=CH_3$-C6H4-SO_3

Figure 1. Sequence used for labelling the compounds synthesized in this work.

in the order : α - > β- > γ-. However , the positively - charged nitrogen also causes cross polarization at the adjacent CH_2-group (hyperconjugation) which results in partial shielding of the α- protons, while β - and γ - protons are deshielded by resonance.

Table 1. ^{1}H n.m.r. chemical shifts of the dialkyl bipyridinium salts in CD_3OD (TMS internal standard).

	R					X			
Compound	H-1 (d,d)	H-2 (d,d)	H-4 (s)	2xH-5 (t)	CH_3 (t)		CH_3 (15)	H-16 (AB)	H-17 (AB)
PE	8.60 (7.8,2.2)	7.60 (7.8,2.2)	7.3	-	-	-	-	-	-
$PEDM_3$	9.03 (7.9,u*)	8.40 (7.9,u)	8.10	4.82 (7)	1.04 (7)	2.08(h,J=7.0,2H-6)	2.71	-	-
$PEDM_4$	9.01 (7.9,u)	8.40 (7.9,u)	8.10	4.80 (7)	1.02 (7)	1.2-2.2(m,4XH6,7)	2.71	-	-
$PEDM_8$	9.0 (7.9,u)	8.41 (7.9,u)	8.10	4.71 (7)	0.90 (7)	1.2-2.2(m,8XH6-9)	2.71	-	-
$PEDM_7$	9.0 (7.9,u)	8.38 (7.9,u)	8.10	4.71 (7.2)	0.89 (7.2)	1.2-2.2(m,12XH6-11)	2.70	-	-
$PEDT_3$	8.95 (7.8,u)	8.33 (7.8,u)	8.04	4.53 (7.2)	1.0 (7.2)	2.01(h,J=7.2,2H-6)	2.36	7.71 (8.0)	7.2 (8.0)
$PEDT_4$	8.98 (7.7,u)	8.33 (7.7,u)	8.04	4.53 (7.2)	1.0 (7.2)	1.2-2.2(m,4XH6,7)	2.33	7.71 (8.0)	7.2 (8.0)
$PEDT_8$	8.97 (7.8,u)	8.33 (7.8,u)	8.02	4.55 (7.2)	0.9 (7.2)	1.2-2.2(m,8XH6-9)	2.33	7.7 (8.0)	7.2 (8.0)
$PEDT_7$	8.98 (7.8,u)	8.33 (7.8,u)	8.04	4.50 (7.0)	0.9 (7.0)	1.2-2.2(m,12XH6-11)	2.34	7.72 (8.0)	7.2 (8.0)
$PEDT_{12}$	8.98 (7.9,u)	8.33 (7.9,u)	8.02	4.52 (7.0)	0.84 (7.0)	1.2-2.2(m,32XH6-13)	2.33	7.71 (8.0)	7.2 (8.0)

* u indicates unresolved coupling.

Proton - decoupled , off - resonance and gated decoupled spectra were recorded and used to aid the assignment of carbon-13 chemical shifts in the compounds under study. Furthermore, systematic comparison within the series was used to confirm the assignments (Table 2). Carbon-13 spectrum of PE revealed only four singals at 150.1, 122.4, 144.4 and 131.4 ppm. The quaternary carbon at 144.4 ppm is assigned to C-γ (C-3)and the most deshielded carbon to C-α (C-1); while the most shielded carbon (δ 122.4 ppm) is assigned to C-β (C-2) by analogy with pyridine or the 4-methyl pyridines[8]. The remaining protonated carbon is assigned to C-δ (C-4).

The n-dialkyl salts PEDMn and PEDTn showed the expected signals for the alkyl chain and anion moieties. For example $PEDM_6$ showed the expected signals for R at 62.5, 32.2, 26.8 and 23.4 ppm for C-5,6,7,8 and 9 respectively. The $MeSO_3$ anion exhibited a signal at 39.5 ppm. The PE portion of the compound exhibits four carbon-13 signals. The non-protonated carbon (C-γ) showed the most deshielded signal at 152.3 ppm, while C-α , C-β and C-δ exhibited signals at 145.8, and 135.0 ppm respectively. The analogous carbon-13 chemical shift assignments for the remaining compounds are given in Table 2. Quaternization of the nitrogen caused shielding at C-1 by 4.3 ppm and deshielding at C-2, C-3 and C-4 by 4.4 , 7.9 and 3.6 ppm respectively. The results are in agreement with those found for the quaternization of pyridine[9] .

Table 2. ^{13}C n.m.r. chemical shifts of the dialkyl bipyridinium salts in CD_3OD (TMS internal standard).

Comp.	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	C-13	C-14	C-15	C-16	C-17	C-18	C-19
PE	150.1	122.4	144.4	131.4	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
$PEDM_3$	145.7	126.8	152.2	134.9	63.6	25.6	10.8	-	-	-	-	-	-	-	39.5	-	-	-	-
$PEDM_4$	145.7	126.8	152.2	134.9	62.4	33.8	21.2	13.6	-	-	-	-	-	-	39.5	-	-	-	-
$PEDM_6$	145.8	126.9	152.3	135.0	62.5	32.2	32.2	26.8	23.4	14.2	-	-	-	-	39.5	-	-	-	-
$PEDM_7$	145.8	126.9	152.3	135.0	62.5	32.2	32.2	29.2	27.0	33.5	14.3	-	-	-	39.5	-	-	-	-
$PEDT_3$	145.6	126.5	152.2	134.9	63.7	25.6	10.8	-	-	-	-	-	-	-	143.5	126.5	129.5	141.2	21.3
$PEDT_4$	145.5	126.8	152.1	134.9	62.2	33.9	21.2	13.6	-	-	-	-	-	-	143.9	126.5	129.4	140.4	20.2
$PEDT_6$	145.6	126.7	152.2	134.9	62.1	32.1	32.1	26.7	23.3	14.2	-	-	-	-	143.5	126.6	129.4	141.2	21.3
$PEDT_7$	145.6	126.8	152.2	134.9	62.4	32.6	32.2	29.2	27.0	33.5	14.3	-	-	-	143.3	126.3	129.5	141.1	21.3
$PEDT_{18}$	145.7	126.9	152.3	135.0	62.4	32.3	32.3	30.4	30.4	30.7	30.7	27.1	23.1	14.3	143.3	126.6	129.4	141.3	21.3

Differential scanning calorimetry, polarized optical microscopy and X-ray studies revealed that these bipyridinium salts are liquid crystalline and their mesomorphic behavior shall be reported elsewhere.

EXPERIMENTAL

n-alkyl alcohols, 4-$MeC_6H_4SO_2Cl$, $MeSO_2Cl$, trans-1,2-bis (4-pyridyl) ethene, 3-pentanone and pyridine were purchased from Fluka Chemicals.

(1) Preparation of n-alkyl Salts , RX :

The appropriate alcohol, ROH, (0.1 mol) was dissolved in dry pyridine (50 cm^3) and cooled in an ice-bath. A solution of 4-$MeC_6H_4SO_2Cl$ (0.11 mol) or $MeSO_2Cl$ (0.11 mol) in dry pyridine (50 cm^3) was added dropwise with stirring under N_2, and the temperature was maintained between 0-10 C range. Stirring was continued for a further 2 hours at this temperature. The reaction mixture was then poured into ice-water (400 cm^3) with stirring and the resulting precipitate was removed by filtration. The crude product was dissolved in benzene, washed successively with 3N HCl (2x100 cm^3) and saturated $NaHCO_3$ (100 cm^3); the benzene extract was dried over anhydrous Na_2SO_4 and the solvent was removed on a rotary evaporator. The concentrate was applied to a silicon gel column and the pure tosylates (or methane sulfonates) were eluted with a 1:1 mixture of benzene/ether.

(2) preparation of n-dialky salts of trans-1, 2-bis(4-pyridyl) ethene :

The alkyl salt , RX, (0.03 mol) was added to a solution of trans-1,2-bis(4-pyridyl) ethene (0.01 mol) in 3-pentanone (20 cm^3). After refluxing (150 C, 4h), the light-brown solid was filtered from the solution mixture while hot, washed with Me_2CO and recrystallized from MeOH or 1:9 H_2O/Me_2CO. The detailed syntheses of the studied compounds will be reported elsewhere.

All of the new compounds has satisfactory spectral properties and elemental analyses. I.r. spectra (KBr) were recorded on a Pye Unicam SP3-300 spectrometer. U.V. spectra were recorded on a Pye Unicam SP8-100 UV Spectrophotometer.

^1H and ^{13}C NMR spectra were obtained on a Bruker WH90 DS spectrometer. The ^{13}C n.m.r. were obtained using the pulsed FT method at 22.63 MHz. The free-induction decays were stored in an Aspect 2000 computer and were transformed after accumulation of a sufficient number , using 8K data points and a spectral width of 6024 Hz. The acquisition time was 0.75,i.e., the resolution limit did not exceed 1.47 Hz. The spectra were recorded in 10 mm n.m.r tubes using CD_3OD as solvent and traces of TMS as reference.

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