Synthesis of 3-substituted pyridinium salts

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Abstract

A novel class of 3-substituted pyridinium salts have been synthesised in high yield by a convenient two-step procedure. A new synthetic pathway to 1-substituted benzimidazolium salts has been developed and the effects of the anionic component of the salts have been studied.

Keywords: Alkylations, Mannich bases, condensations, pyridinium salts, benzimidazolium salts

Introduction

Compounds containing a pyridinium moiety attached to a heterocyclic system are important in natural product chemistry[1] and in organic synthesis[2, 3]. Pyridinium salts have found use as acylating agents[4], phase transfer catalysts[5], biocides with a wide range of antimicrobial activity[6], dyes[7] and cationic surfactants. The 1-alkylpyridinium salts, which are liquid at rt., so-called ionic liquids, are potential new solvents for synthesis and catalysis[8]. Several synthetic routes to pyridinium salts are known, but the most commonly used method is the Menschutkin reaction, the SN2 reaction of a pyridine derivative with an organic halide. Chloromethylalkyl ethers or sulphides are also reagents for the quaternization of the pyridine nitrogen. In these cases the reactions proceed via the SN1 mechanism[9-11].

The present paper reports on a general and convenient route for the preparation of 3-substituted pyridinium salts such as shown in Figure 1 by utilization of N-Mannich bases as starting materials.

The *N*-(1*H*-benzimidazolalkyl)-3-pyridinecarboxamides (**1a** and **1b**) are new compounds which were obtained in a one-pot condensation reaction of benzimidazole-aldehyde-nicotinamide (Scheme 1).

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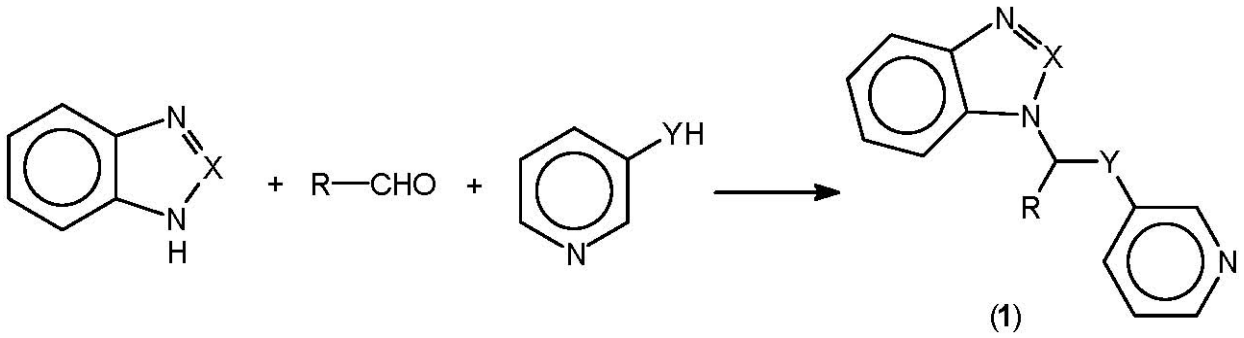
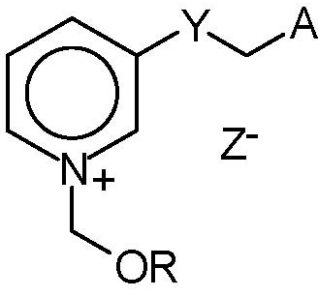


Scheme 1

The chemotypes which have been prepared along with reaction times, yields and melting points are tabulated in Table 1.

The limitation of this procedure is that only two aldehydes, formaldehyde and benzaldehyde undergo reaction with benzimidazole and nicotinamide.



Y = CONH or NH; A = azole

Figure 1

The compounds were characterised by their 1H and 13C NMR spectra and by elemental analyses. The NH proton for **1a** resonated at δ = 9.93 - 9.89 as a triplet with a coupling constant in the range 5.6 Hz. The methine protons appeared in the spectrum as a doublet at δ = 5.83 - 5.81 (*J* = 6 Hz). The chemical shift of the carbonyl carbon appeared at δ = 165.3. As expected, the absorption peak for the characteristic α carbon between the benzimidazole ring and the amide fall in the region of δ = 53 - 48. Analogue **1c** was prepared by treatment of 3-aminopyridine with formaldehyde and benzimidazole.

Table 1. Condensation Products 1

Product	R	X	Y	Time(h)	Yield(%)	m.p.[a] (°C)
1a	H	CH	CONH	48	90	218-220
1b	C_6H_5	CH	CONH	48	45	230-232
1c	H	CH	NH	5	80[b]	160-162[c]
1d	H	N	CONH	48	86	177-178[d]
1e	C_6H_5	N	CONH	48	75	184-186[e]
1f	H	N	NH	5	80b	153-154f

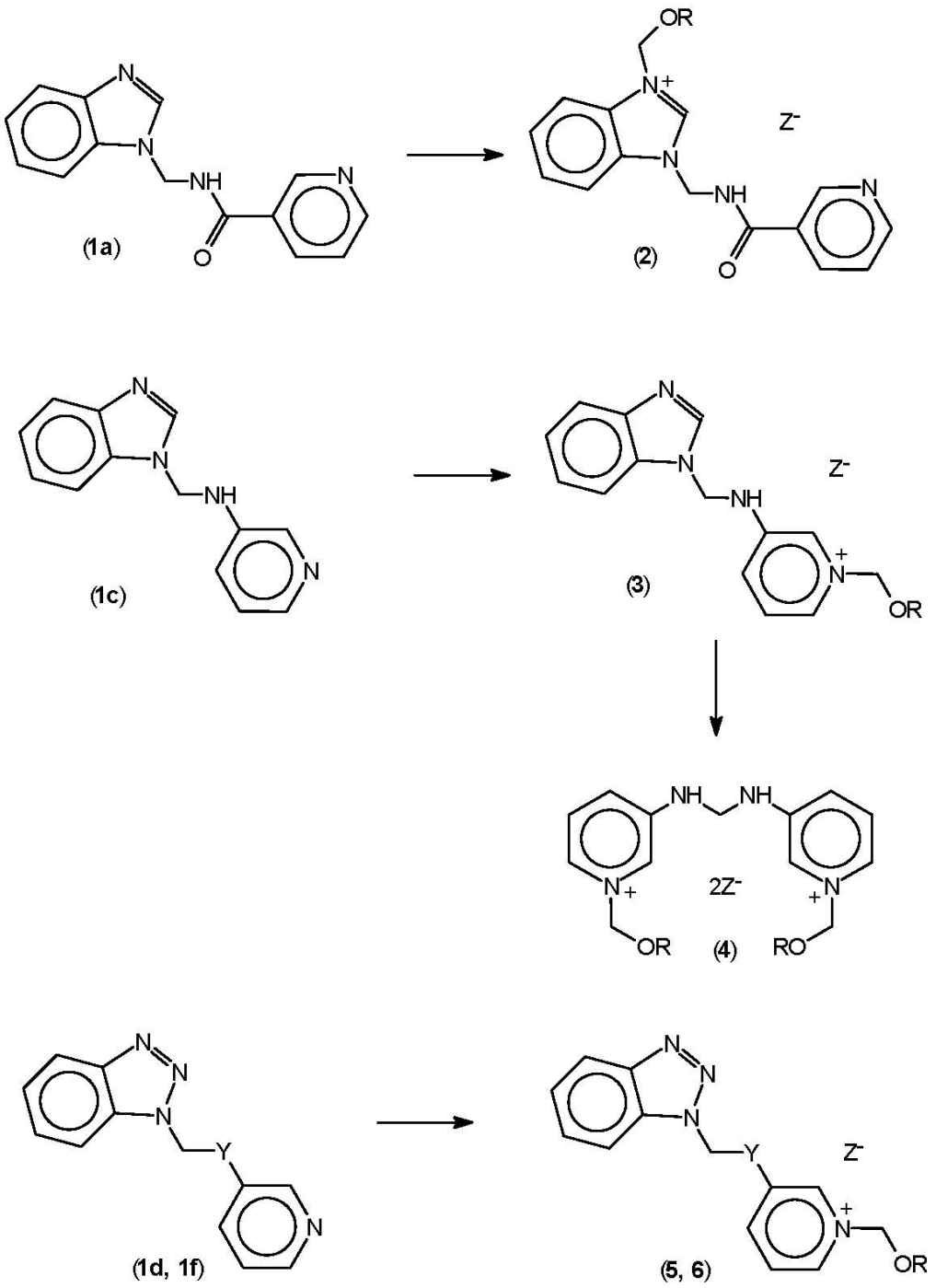
[a] Solvent for recrystallization: MeOH (**1a, b**), EtOH/H_2O (**1c-f**), [b] The same yield in microwave reactor (time 10 min., 200°C, 850W), [c] Lit.[12] m.p. 163-164°C, [d] Lit.[13] m.p. 177-178°C, [e] Now is available in Aldrich, [f] Lit.[12] m.p. 150-151°C

The N-Mannich reagents, N-(1 *H*-benzotriazol-1-ylmethyl)-3-pyridinecarboxamide (**1d)** and 3-(benzotriazol-1-ylmethylamino)pyridine (**1f)**, were easily prepared by the condensation of benzotriazole-formaldehyde with the appropriate amide or amine[14,15]. The 3-aminopyridine reacts with formaldehyde and benzotriazole at rt to give monosubstituted product **1f**, previously prepared by the condensation of 3-aminopyridine with 1-(hydroxymethyl)benzotriazole[14].

When the condensed product **1d** was prepared directly from nicotinamide, formaldehyde and benzotriazole, the reaction conditions required were more vigorous due to the lower nucleophilicity of nicotinamide compared to 3-aminopyridine.

Analogue **1e** was prepared from pyridine-3-carboxamide-benzaldehyde-benzotriazole.The reactions of benzotriazole was carried out in high yield with the regioselective formation of the N-1 isomer. In this condensation, azoles other than benzotriazole have been utilized (imidazole[16], triazole[13]).

The quaternization of a N-Mannich bases such as benzimidazoles 1a and 1c by chloromethylalkyl ether afforded two products 2 and 3 (Scheme 2).



Scheme 2

The structure of the quaternazation product depends on the Y group in compounds 1a and 1c. The strong electron-withdrawing group (CONH) in the 3-position of the pyridine ring deactivates the nitrogen atom in pyridine. Chloromethylalkyl ether quaternarizes the N-3 of 1-substituted benzimidazole giving benzimidazolium chlorides 2 (Table 2). This study has shown that N-3 is nucleophilic enough to react with electrophiles.

Table 2. 1-Alkoxymethyl-3-[N-methyl-(3-pyridinecarbonyl)] benzimidazolium Salts 2

Salt	R	Z	Yield (%)	m.p.[a] (°C)
2a	C_4H_9	Cl	85	133-137[b]
2b	$C_{12}H_{25}$	Cl	70	119-123[b]
2c	Cyclo$C_{12}H_{25}$	Cl	70	163-165[b]
2d	C_3H_7	BF_4	78	128-130
2e	C_8H_{17}	BF_4	75	125-128
2f	$C_{12}H_{25}$	I	80	111-112
2g	$C_{12}H_{25}$	BF_4	83	127-128
2h	$C_{12}H_{25}$	ClO_4	81	133-134
2i	Cyclo$C_{12}H_{25}$	ClO_4	80	175-176
2j	Cyclo$C_{12}H_{25}$	Br	80	164-166
2k	Cyclo$C_{12}H_{25}$	I	78	154-156
2l	Cyclo$C_{12}H_{25}$	NO_3	70	138-143
2m	Cyclo$C_{12}H_{25}$	BF_4	70	138-140

[a] Solvent for recrystallization: $CHCl_3$:$CH_3CO_2C_2H_5$ - **2a-2c**; $CH_3CO_2C_2H_5$ – **2d-2m**; bHygroscopic

The pyridinium salts 3-6 were prepared by the reaction of N-Mannich bases 1c, 1d and 1f with chloromethylalkyl ethers. The reactions and the results are shown in Scheme 2 and Tables 3 and 4.

Table 3. 1-Alkoxymethyl-3-(1-benzimidazolmethylamino)- pyridinium Salts 3 And Bis(1-Alkoxymethyl- pyridinium) Salts 4

Salt	R	Z	Yield (%)	m.p.[a] (°C)
3a	C_3H_7	Cl	82	143-145
3b	C_8H_{17}	Cl	70	141-143
3c	$C_{11}H_{23}$	Cl	70	146-147
3d	C_3H_7	Br	70	143-144
3e	C_8H_{17}	NO_3	70	118-120
3f	C_8H_{17}	I	70	121-122
3g	C_8H_{17}	BF_4	70	115-117
3h	C_8H_{17}	PF_6	75	109-112
3i	C_8H_{17}	ClO_4	73	108-110
3j	$C_{12}H_{25}$	I	70	107-109
3k	$C_{12}H_{25}$	PF_6	70	111-114
3l	$C_{12}H_{25}$	ClO_4	80	114-116
4a	C_9H_{19}	Cl	85	68-71
4b	$C_{11}H_{23}$	Cl	84	72-73
4c	C_8H_{17}	ClO_4	87	125-127
4d	C_8H_{17}	BrO_3	85	129-130
4e	C_8H_{17}	I	85	130-132
4f	C_8H_{17}	Br	80	126-128
4g	$C_{12}H_{25}$	PF_6	76	129-132
4h	$C_{12}H_{25}$	SbF_6	73	92-94
4i	$C_{12}H_{25}$	I	70	144-146

[a] Solvent for recrystallization: MeOH/Me2CO (1:10) for 3a, 3b, H2O for 3c, MeOH/H2O (1:1) for 3c, 3d, H2O-4a, 4b, MeOH 4c-4i

Symmetrically substituted bis(1-alkoxymethyl)pyridinium chlorides **4** were synthesised by trea-ting 1-alkoxymethyl-3-(1-benzimidazolmethylamino)pyridinium chloride **3** with chloromethyl-alkyl ether (Scheme 2). The formation of bispyridinium chloride is probably the result of the attack of chloromethylalkyl ether on the N-3 of benzimidazole ring to give an intermediate shown is Figure 2 which is unstable and quickly converted to bispyridinium chloride to replace the benzimidazole moiety.

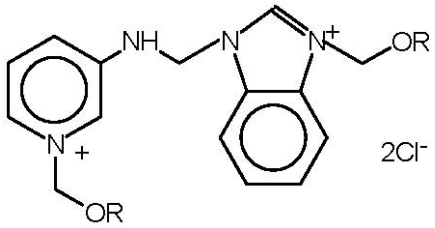


Figure 2

The substrate **3** was converted into the same derivative **4** by heating with hydrochloric acid.

Benzimidazole is a good leaving group in N-(1 *H*-benzimidazolmethyl)-3-pyridinecarboxamide **1a** in basic and acidic solutions (Scheme 3). Hydrolysis is generally effected by heating with dilute hydrochloric acid. Treatment of compound **1a** with alkoxides at rt, displaces the benzimidazole anion giving a symmetrical diamide.

All of the salts 2-6 were prepared via metathesis of pyridinium or benzimidazolium chlorides with the appropriate inorganic salt in water solution (Tables 2, 3 and 4). In general, the chlorides were very hygroscopic.

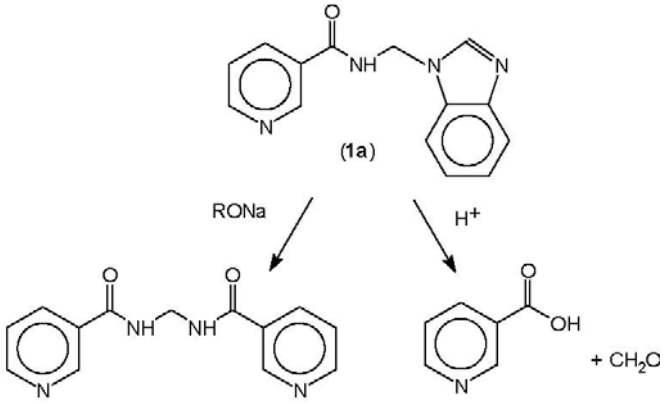
Table 4. Pyridinium Salts 5,6

Salt	R	Y	Z	Yield(%)	m.p.[a] (°C)
5a	C_6H_{13}	CONH	I	80	138-140
5b	C_8H_{17}	CONH	Br	80	159-161
6a	C_3H_7	NH	Cl	80	132-134
6b	C_4H_9	NH	Cl	80	139-140
6c	C_5H_{11}	NH	Cl	82	139-141
6d	C_6H_{13}	NH	Cl	81	146-148
6e	C_7H_{15}	NH	Cl	78	133-135
6f	C_8H_{17}	NH	Cl	80	132-134
6g	C_9H_{19}	NH	Cl	80	134-136
6h	$C_{10}H_{21}$	NH	Cl	78	138-140
6i	$C_{11}H_{23}$	NH	Cl	77	135-136
6j	$C_{12}H_{25}$	NH	Cl	78	134-136
6k	C_3H_7	NH	I	70	140-141
6l	C_3H_7	NH	SbF_6	70	136-138
6m	C_4H_9	NH	ClO_4	73	138-140
6n	C_4H_9	NH	NO_3	70	134-136
6o	C_4H_9	NH	PF_6	70	141-143
6p	C_4H_9	NH	BF_4	72	144-145
6q	C_4H_9	NH	I	73	145-147

[a] Solvent for recrystallization: H_2O (**5a, 5b** and **6a-j**), MeOH-H_2O -(**6k-6q**).

The conversions of the chlorides to the Br, I, NO3, BrO3, ClO4, BF4, PF6 and SbF6 salts led to some which were hydrophobic. The larger -size anions changed the character of the salt.

In conclusion, a procedure has been developed for the preparation of 3-substituted pyridinium and 1-substituted benzimidazolium salts. The work-up procedures are very simple, the products are easily purified and the yields are high.



Scheme 3

Experimental Section

General Procedures. Melting points were determined on a Kofter hot stage apparatus and are uncorrected. The 1H NMR spectra were recorded with a Varian Model XL 300 Spectrometer at 300 MHz with TMS as the standard. The 13C NMR spectra were recorded on the same instrument at 75 MHz. Elemental analyses was performed at the A. Mickiewicz University, Poznań. For all compounds **1-6** satisfactory microanalyses were obtained C ± 0.31, H ± 0.30 and N ± 0.28. Chloromethylalkyl ethers were prepared via the procedures, which were reported earlier[17].

The salts obtained were characterised by their 1H and 13C NMR spectra and by elemental analyses. The 1H and 13C NMR chemical shifts are summarised in Tables 5-10. The chemical shifts of the protons are anion-dependent in equivalent concentrations. This effect is strong for protons in the Y group (H-N) and weaker for the benzimidazole or benzotriazole ring protons. The H-N chemical shift decreases in the following order Cl > NO3 > I, ClO4, PF6 > BF4. This phenomenon has been noticed previously in the imidazole ring protons in 1,3 dialkylimidazolium salts[18].

General Procedure for the condensation of nicotinamide

Nicotinamide (12.2 g, 0.1 mol), formaldehyde (3 g, 0.1 mol, paraformaldehyde - powder) and benzimidazole or benzotriazole (0.1 mol) were refluxed in toluene (200 mL) to which two drops of concd. sulphuric acid had been added. The water formed during the reaction was removed azeotropically by a Dean-Stark apparatus. The toluene was then removed under reduced pressure

(60 oC/30 Torr) and the resulting solids were recrystallized.

3-(Benzimidazolmethylamino)pyridine (1c): A mixture of 3-aminopyridine (9.4 g, 0.1 mol), formaldehyde (3 g, 0.1 mol, paraformaldehyde - powder) and benzimidazole (11.8 g, 0.1 mol) was refluxed in EtOH (100 mL). After cooling to r.t. H2O (50 mL) was added, the product was collected by filtration and recrystallized.

Pyridinium salts 3, 5 and 6. General procedure

The 3-(Benzimidazolmethylamino)pyridine (**1c)** or 3-(benzotriazol-1-yl-methylamino)pyridine (**1f)** or N-(1 *H*-benzotriazol-1-ylmethyl)-3-pyridinecarboxamide (**1d)** (0.01 mol) was dissolved in anhydrous acetone and the corresponding chloromethylalkyl ether (0.01 mol) was added. The mixture was stirred at rt for 5-10 min. The precipitated solid was collected by filtration and recrystallised. A solution of the 1-alkoxymethylpyridinium chloride (0.005 mol) in 40 mL of H2O and the appropriate inorganic salt (0.02 mol, MZ) in 20 mL of H2O were mixed at rt by stirring. The solid was collected by filtration and recrystallized.

Benzimidazolium salts 2; General procedure

The corresponding chloromethylalkyl ether (0.01 mol) was added to N-(1 *H*-benzimidazolmethyl)-3-pyridinecarboxamide (2.52 g, 0.01 mol, **1a**) in dry DMF (30 mL) by stirring for 1h at r.t. The solvent was removed under reduced pressure. The crude product was washed with hexane and acetone and recrystallized. A sample of the benzimidazolium chloride (0.01 mol) in 40 mL of H2O and the appropriate inorganic salt (0.01 mol, MZ) in 20 mL was mixed at r.t. The solution was extracted by 50 mL of ethyl acetate, the extract was dried over Na2SO4 and concentrated *in vacuum*. The resultant residue was recrystallized.

Bispyridinium Salts 4; General procedure

To 1-alkoxymethylpyridinium chloride (0.01 mol, **3**) in dry CHCl3 (40 mL), chloromethylalkyl ether (0.01 mol) was added with stirring for 10 min at r.t. The solvent was removed under reduced pressure. The crude product was washed with hexane and recrystallized. A solution of prepared bispyridinuim chloride (0.01 mol) in 80 mL of H_20 and a solution of inorganic salt (0.02 mol, MZ) in 20 mL was mixed with stirring. The resulting product was collected by filtration and recrystallized.

Table 5. ^{1}H NMR Spectral Data (δ, J in Hz)[a] Benzimidazolium Salts **2**

Salt	NH	Pyridine	NCH_2N	Benzimidazole	NCH_2O	R
2b	11.25 (t, *J*=6.0)	9.22(s, 1H), 8.80(d, *J*=4.2, 1H), 8.52(d, *J*=6.7, 1H), 7.60(t, *J*=7.7, 1H)	6.08 (d, *J*=7.4)	10.38(s, 1H), 8.58(d, *J*=6.2, 1H), 8.08(d, *J*=5.8, 1H), 7.74(m, 2H)	6.06(s)	3.57(t, *J*=6.3, 2H), 1.45(m, 2H), 1.13(m, 18H), 0.85(t, *J*=6.6, 3H)
2d	10.10 (t, *J*=6.0)	9.07(s, 1H), 8.78(d, *J*=4.8, 1H), 8.23(m, 1H), 7.58(t, *J*=8.0, 1H)	6.08 (d, *J*=6.0)	10.10(s, 1H), 8.23(m, 1H), 8.09(d, *J*=7.0, 1H), 7.77(m, 2H)	6.01(s)	3.55(t, *J*=6.3, 2H), 1.53(m, 2H), 0.81(t, *J*=6.7, 3H)
2e	10.08 (t, *J*=6.0)	9.05(s, 1H), 8.77(d, *J*=4.8, 1H), 8.23(m, 1H), 7.56(t, *J*=7.8, 1H)	6.05 (d, *J*=6.3)	10.08(s, 1H), 8.23(m, 1H), 8.10(d, *J*=7.4, 1H), 7.75(m, 2H)	6.00(s)	3.56(t, *J*=6.3, 2H), 1.47(m, 2H), 1.14(m, 10H), 0.81(t, *J*=6.7, 3H)
2f	10.16 (t, *J*=6.0)	9.07(s, 1H), 8.78(d, *J*=5.0, 1H), 8.25(m, 1H), 7.58(t, *J*=7.8, 1H)	6.08 (d, *J*=6.0)	10.16(s, 1H), 8.25(m, 1H), 8.08(d, *J*=6.0, 1H), 7.77(m, 2H)	6.01(s)	3.56(t, *J*=6.3, 2H), 1.47(m, 2H), 1.14(m, 18H), 0.86(t, *J*=6.7, 3H)
2g	10.21 (t, *J*=6.0)	9.07(s, 1H), 8.78(d, *J*=3.6, 1H), 8.25(m, 1H), 7.58(t, *J*=7.8, 1H)	6.08 (d, *J*=6.0)	10.16(s, 1H), 8.25(m, 1H), 8.08(d, *J*=7.1, 1H), 7.77(m, 2H)	6.01(s)	3.56(t, *J*=6.3, 2H), 1.47(m, 2H), 1.14(m, 18H), 0.86(t, *J*=6.7, 3H)
2h	10.21 (t, *J*=6.0)	9.07(s, 1H), 8.78(d, *J*=3.6, 1H), 8.25(m, 1H), 7.58(t, *J*=7.7, 1H)	6.08 (d, *J*=6.0)	10.16(s, 1H), 8.25(m, 1H), 8.08(d, *J*=7.1, 1H), 7.77(m, 2H)	6.01(s)	3.56(t, *J*=6.3, 2H), 1.47(m, 2H), 1.14(m, 18H), 0.86(t, *J*=6.7, 3H)
2m	10.23 (t, *J*=6.0)	9.06(s, 1H), 8.78(d, *J*=4.8, 1H), 8.25(m, 1H), 7.58(t, *J*=8.0, 1H)	6.08 (d, *J*=6.0)	10.21(s, 1H), 8.25(m, 1H), 8.07(d, *J*=7.8, 1H), 7.78(m, 2H)	6.03(s)	3.63(m, 1H), 1.54(m, 2H), 1.40(m, 2H), 1.14(m, 18H)

[a] Solvent DMSO-d_6

Table 6. ^{13}C NMR Spectral Data Benzimidazolium Salts **2**[a]

Salt	C=O	Pyridine	NCH_2N	Benzimidazole	NCH_2O	R
2b	165.8	152.2, 148.3, 136.2, 128.2, 123.9	51.81	143.9, 130.6, 130.5, 127.0, 114.6, 114.2	76.76	69.0, 31.3, 29.0, 28.98, 28.92, 28.89, 28.7, 28.5, 28.0, 25.2, 22.1, 14.0
2d	166.2	152.7, 148.4,135.2, 128.1, 123.5	51.76	143.3, 130.5, 130.4, 127.0, 126.9, 114.0, 113.9	76.78	70.79, 21.83, 9.99
2e	166.2	152.7, 148.4, 135.1, 128.1, 123.5	51.76	143.3, 130.5, 130.4, 126.9, 114.1, 113.9	76.76	69.1, 30.9, 28.4, 28.3, 28.2, 25.1, 21.8, 13.7
2f	166.2	152.9, 148.6, 135.3, 128.0, 123.6	51.84	143.6, 130.5, 130.4, 127.0, 114.2, 114.1	76.82	69.0, 31.3, 29.0, 28.9, 28.86, 28.85, 28.7, 28.6, 28.5, 25.2, 22.1, 13.9
2g	166.3	152.8, 148.6, 135.3, 128.1, 123.7	51.86	143.6, 130.6, 130.5, 127.1, 114.2, 114.1	76.85	69.1, 31.3, 29.0, 28.98, 28.93, 28.91, 28.7, 28.6, 28.5, 25.3, 22.1, 13.9
2h	166.3	152.9, 148.6, 135.3, 128.1, 123.7	51.86	143.6, 130.6, 130.5, 127.1, 114.2, 114.1	76.84	69.1, 31.3, 29.0, 28.98, 28.92, 28.89, .28.7, 28.6, 28.5, 25.3, 22.1, 13.9
2m	166.3	152.9, 148.6, 135.2, 128.1, 123.7	51.73	143.2, 130.6, 130.4, 127.1, 114.3, 114.1	76.49	75.2, 28.5, 23.6, 23.4, 22.6, 20.3

[a] Solvent DMSO-d_6

Table 7. ^{1}H NMR Spectral Data (δ, J in Hz)[a] of Pyridinium Salts **3** and Bispyridinium Salts **4**

Salt	NH	Pyridine	NCH_2N	Benzimidazole	NCH_2O	R
3a	-	8.53(s, 1H), 8.30(d, *J*=6.0, 1H), 8.05(d, *J*=8.8, 1H), 7.84(m, 1H)	5.95(s)	8.51(s, 1H), 7.65(d, *J*=7.7, 1H), 7.84(m, 1H), 7.32(m, 2H)	5.81(s)	3.46(t, *J*=6.6, 2H), 1.55(m, 2H), 0.85(t, *J*=7.4, 3H)
3b	8.98 (t, *J*=6.9)	8.75(s, 1H), 8.36(d, *J*=5.8, 1H), 8.08(d, *J*=8.7, 1H), 7.87(t, *J*=8.5, 1H)	5.91 (d, *J*=6.9)	8.69(s, 1H), 7.94(d, *J*=7.4, 1H), 7.64(d, *J*=7.7, 1H), 7.25(m, 2H)	5.82(s)	3.45(t, *J*=6.4, 2H), 1.45(m, 2H), 1.22(m, 10H), 0.84(t, *J*=6.8, 3H)
3c	9.09 (t, *J*=6.9)	8.81(s, 1H), 8.36(d, *J*=5.5, 1H), 8.10(d, *J*=8.6, 1H), 7.86(t, *J*=8.6, 1H)	5.91 (d, *J*=6.9)	8.71(s, 1H), 7.96(d, *J*=7.4, 1H), 7.62(d, *J*=7.4, 1H), 7.23(m, 2H)	5.83(s)	3.48(t, *J*=6.5, 2H), 1.46(m, 2H), 1.21(m, 16H), 0.85(t, *J*=6.7, 3H)

Table 7. Continued

3f	8.52 (t, *J*=6.7)	8.60(s, 1H), 8.41(d, *J*=5.8, 1H), 8.09(d, *J*=8.7, 1H), 7.93(t, *J*=8.5, 1H)	5.94 (d, *J*=6.7)	8.62(s, 1H), 7.87(d, *J*=7.9, 1H), 7.67(d, *J*=7.6, 1H), 7.28(m, 2H)	5.84(s)	3.50(t, *J*=6.4, 2H), 1.46(m, 2H), 1.23(m, 10H), 0.85(t, *J*=6.7, 3H)
3g	8.49 (t, *J*=6.6)	8.56(s, 1H), 8.36(d, 1H, *J*=5.8), 8.05(d, 1H, *J*=8.8), 7.90(t, *J*=8.8, 1H)	5.91 (d, *J*=6.9)	8.52(s, 1H), 7.84(d, *J*=7.7, 1H), 7.67(d, *J*=7.4, 1H), 7.27(m, 2H)	5.79(s)	3.49(t, *J*=6.3, 2H), 1.48(m, 2H), 1.22(m, 10H), 0.85(t, *J*=6.4, 3H)
3h	8.49 (t, *J*=6.9)	8.55(s, 1H), 8.35(d, *J*=5.8, 1H), 8.03(d, *J*=8.7, 1H), 7.89(t, *J*=8.7, 1H)	5.90 (d, *J*=6.6)	8.52(s, 1H), 7.83(d, *J*=8.0, 1H), 7.66(d, *J*=7.7, 1H), 7.23(m, 2H)	5.78(s)	3.48(t, *J*=6.6, 2H), 1.48(m, 2H), 1.22(m, 10H), 0.85(t, *J*=6.7, 3H)
4b	9.51 (t, *J*=6.0, 2H)	9.38(s, 2H), 8.16(d, *J*=8.5, 2H), 7.97(d, *J*=6.0, 2H), 7.65(t, *J*=8.5, 2H)	4.87 (t, *J*=5.5, 2H)	_	6.07 (s, 4H)	3.68(t, *J*=6.4, 4H), 1.61(m, 4H), 1.32(m, 32H), 0.88(t, *J*=6.6, 6H)
4c	8.01 (t, *J*=5.5, 2H)	8.35(m, 4H), 7.89(m, 4H)	4.84 (t, *J*=5.4, 2H)	_	5.79 (s, 4H)	3.56(t, *J*=6.6, 4H), 1.52(m, 4H), 1.25(m, 20H), 0.85(t, *J*=6.7, 6H)
4e	8.58 (t, *J*=6.0, 2H)	9.17(s, 2H), 8.33(d, *J*=8.6, 2H), 8.12(d, *J*=5.8, 2H), 7.69(t, *J*=8.8, 2H)	4.87 (t, *J*=5.9, 2H)	_	6.18 (s, 4H)	3.74(t, *J*=6.5, 4H), 1.64(m, 4H), 1.31(m, 20H), 0.87(t, *J*=6.7, 6H)
4i	8.02 (t, *J*=5.5, 2H)	8.35(m, 4H), 7.89(m, 4H)	4.83 (t, *J*=5.5, 2H)	_	5.78 (s, 4H)	3.54(t, *J*=6.5, 4H), 1.51(m, 4H), 1.24(m, 36H), 0.86(t, *J*=6.7, 6H)

[a] Solvent: CD_3OD – **3a;** $CDCl_3$ – **4b, 4e;** DMSO-d_6 – **3b, 3c, 3f, 3g, 3h, 4c, 4i**

Table 8. ^{13}C NMR Spectral Data[a] of Pyridinium Salts **3** and Bispyridinium Salts **4**

Salt	Pyridine	NCH_2N	Benzimidazole	NCH_2O	R
3a	147.8, 133.0, 130.1, 129.3, 127.5	53.94	144.5, 144.3, 134.2, 124.9, 124.2, 120.4, 112.1	90.73	73.9, 23.5, 10.6
3b	146.0, 131.8, 128.5, 128.0, 126.6	51.89	144.0, 143.5, 133.0, 122.6, 122.1, 119.4, 111.4	88.62	70.1, 31.2, 28.6, 25.2, 22.1, 14.0
3c	146.0, 131.8, 128.4, 128.0, 126.6	51.88	143.9, 122.6, 122.0, 119.5, 111.3	88.62	70.1, 31.3, 28.9, 28.6, 28.6, 25.1, 22.1, 13.9
3f	146.0, 132.0, 128.6, 128.2, 126.5	52.00	144.0, 143.7, 133.2, 122.7, 122.1, 119.6, 111.2	88.68	70.2, 31.1, 28.5, 28.45, 25.1, 22.0, 13.8
3g	145.9, 131.9, 128.4, 128.1, 126.5	51.96	122.7, 122.1, 119.6, 111.1	88.01	70.2, 31.2, 28.6, 25.2, 22.1, 14.0
3h	145.9, 131.9, 128.4, 128.1, 126.5	51.95	122.7, 122.1, 119.6, 111.1	88.78	70.2, 31.2, 28.6, 25.2, 22.1, 14.0
4b	146.7, 130.7, 127.5, 127.0, 125.8	50.00	_	88.83	71.7, 31.7, 29.4, 29.3, 29.1, 29.0, 25.6, 22.5, 13.9
4c	146.1, 130.8, 128.3, 127.5, 126.0	50.70	_	88.61	70.1, 31.1, 28.6, 28.5, 25.2, 22.0, 13.9
4e	145.8, 130.4, 128.4, 127.0, 124.6,	49.01	_	88.31	71.6, 31.4, 29.0, 28.9, 28.8, 25.5, 22.3, 13.8
4i	146.3, 131.4, 128.5, 127.8, 126.3	50.66	_	88.74	70.2, 31.3, 29.1, 29.0, 29.0, 28.8, 28.7, 28.65, 25.3, 22.1, 14.0

[a] Solvent: CD_3OD – **3a;** $CDCl_3$ – **4b, 4e;** DMSO-d_6 – **3b, 3c, 3f, 3g, 3h, 4c, 4i**

Table 9. ^{1}H NMR Spectral Data (δ, J in Hz)[a] of Pyridinium Salts **5,6**

Salt	NH	Pyridine	NCH_2N	Benzotriazole	NCH_2O	R
5a	10.61 (t, *J*=6)	9.53(s, 1H), 9.26(d, *J*=6, 1H), 9.07(d, *J*=7, 1H), 8.37(t, *J*=7, 1H)	6.34 (d, *J*=6)	8.09(d, *J*=9, 2H), 7.65(t, *J*=8, 1H), 7.47(t, *J*=8, 1H)	5.97(s)	3.60(t, *J*=7, 2H), 1.54(m, 2H), 1.24(m, 6H), 0.84(t, *J*=7, 3H)
5b	10.78 (t, *J*=6)	9.59(s, 1H), 9.29(d, *J*=6, 1H), 9.15(d, *J*=7, 1H), 8.37(t, *J*=7, 1H)	6.33 (d, *J*=6)	8.15(d, *J*=8, 1H), 8.08(d, *J*=8, 1H), 7.64(t, *J*=8, 1H), 7.46(t, *J*=8, 1H)	5.98(s)	3.60(t, *J*=7, 2H), 1.54(m, 2H), 1.24(m, 8H), 0.86(t, *J*=7, 3H)

Table 9. Continued

6b	9.55 (t, *J*=7.0)	8.70(s, 1H), *J*=5.8, 1H), *J*=8.7, 1H), *J*=8.5, 1H)	8.44(d, 8.17(d, 7.92(t,	6.38 (d, *J*=6.9)	8.27(d, *J*=8.2, 1H), 8.04(d, *J*=8.5, 1H), 7.58(t, *J*=7.7, 1H), 7.41(t, *J*=7.6, 1H)	5.84(s)	3.47(t, *J*=6.5, 2H), 1.45(m, 2H), 1.20(m, 2H), 0.75(m, *J*=7.3, 3H)
6h	9.47 (t, *J*=6.6)	8.70(s, 1H), *J*=5.8, 1H), *J*=8.7, 1H), *J*=8.5, 1H)	8.43(d, 8.14(d, 7.92(t,	6.37 (d, *J*=6.9)	8.26(d, *J*=8.2, 1H), 8.02(d, *J*=8.5, 1H), 7.58(t, *J*=7.6, 1H), 7.41(t, *J*=7.7, 1H)	5.84(s)	3.48(t, *J*=6.6, 2H), 1.46(m, 2H), 1.16(m, 14H), 0.83(t, *J*=6.7, 3H)
6i	10.31 (t, *J*=6.6)	8.97(s, 1H), *J*=5.8, 1H), *J*=8.7, 1H), *J*=8.5, 1H)	8.36(d, 8.23(d, 7.7(t,	6.24 (d, *J*=6.6)	8.32(d, *J*=8.5, 1H), 7.95(d, *J*=8.2, 1H), 7.47(t, *J*=7.3, 1H), 7.33(t, *J*=8.0, 1H)	5.92(s)	3.56(t, *J*=6.6, 2H), 1.58(m, 2H), 1.23(m, 16H), 0.87(t, *J*=6.7, 3H)
6m	8.67 (t, *J*=7.0)	8.59(s, 1H), *J*=5.8, 1H), *J*=8.7, 1H), *J*=8.6, 1H)	8.41(d, 8.15(d, 7.97(t,	6.43 (d, *J*=7.0)	8.10(d, 2H), 7.68(t, *J*=7.9, 1H), 7.47(t, *J*=8.1, 1H)	5.84(s)	3.53(t, *J*=6.6, 2H), 1.51(m, 2H), 1.26(m, 2H), 0.81(t, *J*=7.3, 3H)
6n	8.78 (t, *J*=6.9)	8.62(s, 1H), *J*=6.1, 1H), *J*=8.5, 1H), *J*=8.5, 1H)	8.44(d, 8.15(d, 7.98(t,	6.44 (d, *J*=7.0)	8.10(d, 2H), 7.66(t, *J*=8.2, 1H), 7.47(t, *J*=8.1, 1H)	5.85(s)	3.52(t, *J*=6.6, 2H), 1.50(m, 2H), 1.25(m, 2H), 0.80(t, *J*=7.3, 3H)
6o	8.67 (t, *J*=7.0)	8.59(s, 1H), *J*=5.5, 1H), *J*=8.9, 1H), *J*=8.9, 1H)	8.41(d, 8.14(d, 7.96(t,	6.42 (d, *J*=7.0)	8.09(d, 2H), 7.67(t, *J*=7.9, 1H), 7.47(t, *J*=7.8, 1H)	5.82(s)	3.52(t, *J*=6.6, 2H), 1.50(m, 2H), 1.25(m, 2H), 0.81(t, *J*=7.3, 3H)
6p	8.66 (t, *J*=7.0)	8.59(s, 1H), *J*=5.8, 1H), *J*=8.7, 1H), *J*=8.9, 1H)	8.41(d, 8.14(d, 7.97(t,	6.42 (d, *J*=7.0)	8.10(d, 2H), 7.67(t, *J*=8.2, 1H), 7.47(t, *J*=8.1, 1H)	5.83(s)	3.53(t, *J*=6.6, 2H), 1.50(m, 2H), 1.25(m, 2H), 0.81(t, *J*=7.3, 3H)
6q	8.67 (t, *J*=7.0)	8.61(s, 1H), *J*=5.8, 1H), 8.12(m, 1H), 7.98(t, *J*=8.6, 1H)	8.44(d,	6.44 (d, *J*=7.0)	8.12(m, 1H), 8.07(d, *J*=8.4, 1H), 7.65(t, *J*=7.5, 1H), 7.45(t, *J*=7.7, 1H)	5.86(s)	3.52(t, *J*=6.6, 2H), 1.49(m, 2H), 1.24(m, 2H), 0.79(t, *J*=7.5, 3H)

[a] Solvent: DMSO-d_6 for **5a, 5b, 6b, 6m-6q** and in $CDCl_3$ for **6i, 6h**

Table 10. ^{13}C NMR Spectral Data[a] of Pyridinium Salts **5,6**

Salt	C=O	Pyridine	NCH_2N	Benzotriazole	NCH_2O	R
5a	162.0	144.9, 143.3, 127.9, 127.4, 124.1	51.4	145.1, 145.0, 132.2, 132.0, 118.9, 111.2	88.8	70.4, 30.8, 28.6, 24.8, 21.6, 13.9
5b	162.0	145.2, 143.6, 128.0, 127.7, 124.3	51.4	145.3, 145.1, 132.4, 132.3, 119.1, 111.2	88.9	70.4, 31.2, 28.6, 25.2, 22.1, 14.0
6b	-	145.5, 132.1, 128.6, 128.0, 126.7	54.8	146.2, 132.3, 127.7, 124.5, 119.3, 111.5	88.6	69.9, 30.6, 18.3, 13.4
6h	-	145.2, 131.8, 128.4, 127.7, 126.4	54.7	145.8, 132.0, 127.4, 124.2, 119.0, 111.2	88.5	70.2, 31.3, 28.9, 28.7, 28.6, 25.2, 22.2, 14.0
6i	-	146.1, 129.7, 128.5, 128.1, 126.7	55.1	147.1, 132.2, 127.7, 124.4, 119.3, 111.1	89.3	71.8, 31.6, 29.3, 29.2, 29.2, 29.0, 28.9, 28.8, 25.4, 22.3, 13.8
6m	-	145.5, 132.3, 128.9, 128.1, 126.8	54.8	146.1, 132.3, 127.9, 124.6, 119.4, 111.0	88.8	70.0, 30.6, 18.3, 13.4
6n	-	145.5, 132.3, 128.9, 128.1, 126.8	54.8	146.1, 132.3, 127.9, 124.5, 119.4, 111.0	88.8	69.8, 30.6, 18.3, 13.4
6o	-	145.5, 132.3, 128.9, 128.1, 126.8	54.8	146.1, 132.2, 127.9, 124.6, 119.4, 111.0	88.8	70.0, 30.6, 18.4, 13.4
6p	-	145.5, 132.3, 128.9, 128.1, 126.8	54.8	146.1, 132.3, 127.9, 124.6, 119.4, 111.0	88.8	70.0, 30.6, 18.4, 13.4
6q	-	145.2, 132.0, 128.7, 127.8, 126.5	54.8	145.7, 132.0, 127.6, 124.3, 119.1, 110.9	88.5	69.9, 30.5, 18.3, 13.4

[a] Solvent: DMSO-d_6 for **5a, 5b, 6b, 6m-6q** and $CDCl_3$ for **6i, 6h**

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