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SYNTHESIS AND CHARACTERIZATION OF A SERIES OF ALKYL-OXADIAZOLYLPYRIDINIUM SALTS AS PERSPECTIVE IONIC LIQUIDS

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Abstract – The synthesis of a series of 1,2,4-oxadiazolyl-*N*-methylpyridinium salts differing in the length and the position of the alkyl chain in the heterocyclic ring and the counter ions is reported. Some features of this new family of salts as perspective ionic liquids are described and the influence of the varying moieties in the modulation of the properties is discussed.

INTRODUCTION

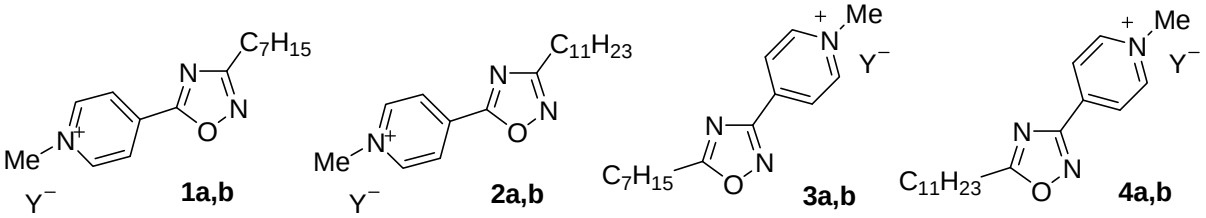
Ionic liquids are low temperature melting salts (mp usually below 100 °C) consisting in organic cations paired with a variety of anions. These compounds are of interest in different fields, such as green solvents for synthesis,[1] catalysts and new electrolytes in electrochemical systems.[2] Ionic liquids containing *N,N'*-dialkylimidazolium,[3] *N*-alkylpyridinium,[4] *N*-alkyl-*N'*-polyfluoroalkyl-imidazolium,[4] *N*(4)-polyfluoroalkyl-1,2,4-triazolium[5] and C(3)-perfluoroalkyl-1,2,4-triazolium as organic cations[6] have been reported. In the framework of our ongoing studies on heterocyclic compounds,[7] we became interested in the synthesis and characterization of organic salts containing an azole ring as a spacer between an azinium cation and an alkyl chain. These structures could be useful targets for different applications; in fact, it is our opinion that the possibility to specifically tune different parameters such as the heterocycle, the length of the chain and its position in the heterocyclic ring may allow the modification of physical and chemical properties.

Oxadiazolylpyridinium salts have been reported as oral hypoglycaemic agents.[8] Interesting examples on the combination of the oxadiazoles and pyridinium groups in modifying electronic properties of the resulting salts has been also emphasized in several studies.[9,10] In particular *N*-alkyl-pyridinium salts

containing the 1,3,4-oxadiazole heterocycle bearing an *S*-alkyl moiety have been reported as novel ionic liquid-crystalline compounds.[9] In this context we recently have reported the synthesis of a series of *N*-methyl-pyridinium salts bearing a perfluoroalkylated 1,2,4-oxadiazole or 1,2,4-triazole moiety, and pointed out some features of this new family of salts as prospective fluorous domains.[11]

RESULTS AND DISCUSSION

In this work, we considered a series of *N*-methyl pyridinium salts bearing at their C(4) an alkyl-1,2,4-oxadiazole moiety. Within the series, the salts differ: i) for the reciprocal position of the alkyl and the pyridinium moieties on the interspacing oxadiazole ring (see Chart 1); ii) for the length of the alkyl chain (C_7H_{15} for **1a,b** and **3a,b**; $C_{11}H_{23}$ for **2a,b** and **4a,b**); iii) for their anion (iodide for compounds (**1-4a**); trifluoromethanesulphonate for compounds (**1-4b**)).



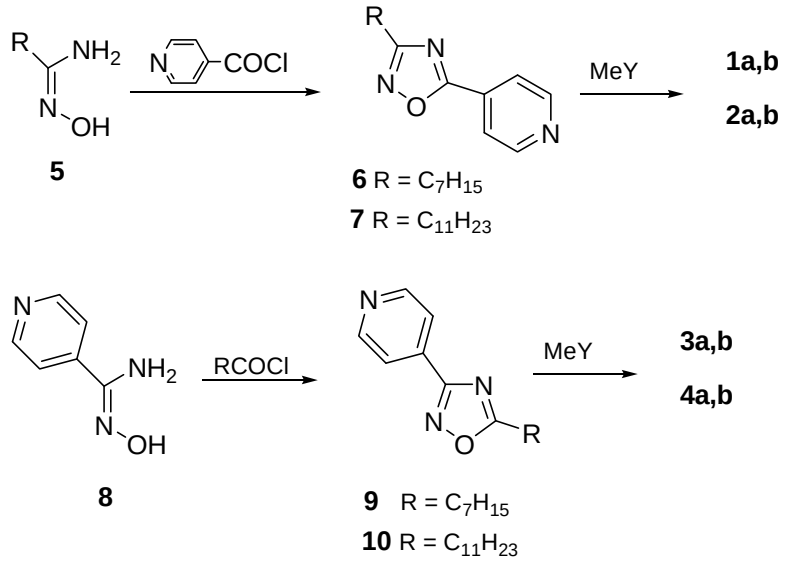
a: $Y^- = I^-$ **b**: $Y^- = TfO^-$

Chart 1

The 1,2,4-oxadiazoles, precursors of the above salts, have been prepared by exploiting the conventional amidoxime route (Scheme 1).[12] The subsequent quaternization reactions have been carried out by direct methylation of oxadiazolyl-pyridines, in acetonitrile, with suitable methylating reagents such as methyl iodide, or methyl trifluoromethanesulfonate. Both reagents furnished good yields of the desired products which were characterized by analytical and spectroscopic data. As expected on the basis of previous reports,[8,11] the methylation occurs at the pyridine nitrogen and was confirmed by NMR data, where a strong deshielding of pyridine hydrogens signals in going from starting compounds to the corresponding salts is observed (see experimental details, ^{1}H-NMR spectra).

A spectroscopic study, based on UV absorption and emission spectra (see Table 2), has been performed on the neutral compounds (**6**, **7, 9, 10**) as well as on their corresponding salts (**1-4a,b**). 5-Pyridyl-1,2,4-oxadiazoles (**6** and **7**) showed a single absorption band at 241 nm (with a shoulder at about 270 nm). On the other hand, 3-pyridyl- derivatives (**9,10**) presented two resolved absorption maxima, at 224 and 273 nm. This difference could be justified by the different extent of conjugation

between the pyridine and the oxadiazole chromophores when the two rings are linked through the C(5) or C(3) position of the azole ring.



Scheme 1

In the trifluoromethanesulphonate series, compounds (**1b** and **2b**) showed a red shifted maxima compared to the neutral precursors (**6** and **7**), while salts (**3b** and **4b**) showed a new band at 255 nm. Similar considerations were not possible for iodide salts as a strong band at 248 nm, typical of the iodide chromophore, overlaps the cation absorption bands.

As for photoluminescence spectra, for all salts a fluorescence emission has been observed and the corresponding singlet state energy calculated (see Table 2). Interestingly, no emission was observed in the case of neutral precursors (**6**, **7, 9**, **10**), likely because of some quenching effect of the pyridine nitrogen lone pair.[13] In fact, increasing emission was detected upon addition of increasing amounts of HCl to the sample solution.

Some interesting structural features have been also evidenced by MS data. The electrospray ionization (ESI) mass spectra[14] showed**,** besides the peaks due to cations M^+, peaks corresponding to ion aggregates formed by two cations and the related anion $[(M^+)_2 \cdot Y^-]$. Moreover, fragmentations corresponding to the loss of the alkyl chain have been recorded. This loss is affected by the substitution pattern on the oxadiazole ring and has been specifically observed for compounds with the alkyl chain in position 3. A specific study on this topic is currently under investigation.

The asymmetry of 1,2,4-oxadiazole, involving a distortion of the linearity of the molecule due to the bonding angles in the five-membered cycle, and an asymmetrical distribution of electronic density in the heterocycle, due to the presence of three heteroatoms with different electronegativity,[15] could justify the

different behaviour of compounds containing the alkyl chain linked to position 3 of the heterocycle (**1b** and **2b**), and compounds (**3b** and **4b**) presenting the alkyl chain in position 5.

The transition temperatures of compounds (**1-4a,b**) have been determined by Differential Scanning Calorimetry (DSC) (see Table 1). Thermodynamic data were collected in heating mode to obtain reproducible results. Apart the peaks relative to the melting transition which is quite evident in the series (see table 1), we observed small peaks prior to decomposition in the case of compounds (**1a** and **4a**) at T = 132 and T = 162 °C, respectively. These secondary processes are likely due to the loss of MeI through a retro S_{N2} mechanism, in analogy with what observed for imidazolium iodides.[16]

Table 1. Thermodynamic parameters for salts (**1-4**) measured by DSC

Compound	mp	ΔH_{fusion} (J g^{-1})	Decomposition temperature	Liquid range
1a	71 °C	68	155 °C	84 °C
1b	86 °C	69	218 °C	132 °C
2a	89 °C	101	157 °C	68 °C
2b	106 °C	87	222 °C	116 °C
3a	oil at rt; mp<-20°C	-	221 °C	>241 °C
3b	oil at rt; mp<-20°C	-	195 °C	>215 °C
4a	46 °C	66	208 °C	162 °C
4b	55 °C	69	202 °C	147 °C

The liquid range reported in Table 1 has been determined by difference between the decomposition and melting point temperatures. The substitution pattern affects the strength of intermolecular interactions as the 3-pyridinium salts all possess lower melting temperatures and wider liquid ranges than the corresponding 5-pyridinium derivatives. Another evidence is that increasing the length of the alkyl chain (from 7 to 11 carbon atoms units) we observed an increment of the melting points and a decrement of the liquid ranges. Moreover, the melting points are also affected by the nature of the counterion, in fact, all the trifluoromethansulfonate salts showed a higher melting point compared with their iodide analogues.

In conclusion, all the synthesized salts can be classified as ionic liquid, although on the whole **3a** and **3b**, because of their lower melting points and having a liquid range > 200 °C, could be considered as perspective room temperature ionic liquids.

Table 2. UV Absorption and Emission data of Compounds (**1-4a,b** and **7-10**)

Compound	$\lambda_{abs\ (nm)}$	logε	$\lambda_{em\ (nm)}$	ΔE (KJ/mol)
1a	248 270sh	4.34 4.21	351	399
1b	271	4.18	357	396
2a	248 270 sh	4.36 4.21	360	388
2b	269	4.04	363	404
3a	248 271sh	4.42 4.01	316	405
3b	232 sh 256 271 sh	3.75 3.89	311	420
4a	247 273sh	4.45 4.03	311	413
4b	233 255 270 sh	3.95 4.04	308	416
6	241 270 sh	4.56	348[a]	
7	241 270 sh	4.02	348[a]	
9	224 272	3.52 3.20	306[a]	
10	224 273	3.55 4.02	310[a]	

a) Emission observed after addition of HCl

EXPERIMENTAL

General. DSC parameters were determined on a 2920 CE, TA instruments, with aluminium cells, Indium calibration, in the range -20-300 °C with a rate of 10 °C/min and a N_2 flux of 60 cm^3/min. ^{1}H NMR spectra were recorded on a Bruker AC250 E spectrometer. GC/MS determinations were carried out on a VARIAN STAR 3400 CX/SATURN 2000 system and the electron spray ionization (ESI) mass spectra were performed on a Micromass Autospec Ultima instrument, samples were dissolved in MeOH/H_2O (1/1). UV absorption spectra were determined with a Jasco 7800 instrument, fluorescence emission spectra were

registered with a Jasco FP-777W Spectrofluorimeter. Flash chromatography was performed using silica gel (200-400 mesh) and mixtures of EtOAc and light petroleum (fraction boiling in the range 40-60°C) in various ratios and CH_3CN. Isonicotyl, nicotyl, [17] heptyl and undecyl amidoxime [18] were prepared as reported.

General procedure for the synthesis of compounds (6 and 7).

A mixture of the appropriate amidoxime (13.6 mmol), isonicotylchloride hydrochloride (2.40 g; 15 mmol) and pyridine (2.37 g, 30 mmol) in benzene (40 mL) was allowed to stir at rt overnight. After removal of the solvent, the residue was worked-up with water and filtered. The solid was melted at 70-100 °C and then purified by column chromatography with light petroleum/AcOEt (5/1 v/v) to give **6** (1.32 g; 40%) and **7** (1.51 g; 37%).

4-(3-Heptyl-1,2,4-oxadiazol-5-yl)pyridine (6) mp 40-42 °C (light petroleum). ^{1}H NMR (CD_3CN) δ 0.87 (t, *J* = 6.5 Hz, 3H, Me), 1.30 (m, 8H, CH_2), 1.76 (m, 2H), 2.79 (t, *J*= 7.4 Hz, 2H, CH_2), 7.93 (d, *J* = 5.8 Hz, 2H, Ar), 8.80 (d, *J* = 5.8 Hz, 2H, Ar); MS *m/z* (%) 247 (M+2, 100), 157 (14), 103 (58), 76 (12), 43 (13). Anal. Calcd for $C_{14}H_{19}N_3O$**:** C, 68.54; H, 7.81; N, 17.13. Found: C, 68.59; H, 7.89; N, 17.15.

4-(3-Undecyl-1,2,4-oxadiazol-5-yl)pyridine (7) mp 42-44 °C (light petroleum). ^{1}H NMR (CD_3CN) δ 0.85 (t, *J* = 6.1 Hz, 3H, Me), 1.24 (m, 16H, CH_2), 1.74 (m, 2H, CH_2), 2.78 (t, *J* = 7.3 Hz, 2H, CH_2), 7.93 (d, *J* = 5.8 Hz, 2H, Ar), 8.80 (d, *J* = 6.1 Hz, 2H, Ar); MS *m/z* (%) 303 (M+2, 100), 190 (12), 170 (18), 157 (35), 103 (74), 75 (36), 44 (26). Anal. Calcd for $C_{18}H_{27}N_3O$**:** C, 71.72; H, 9.03; N, 13.94. Found: C, 71.71; H, 9.10; N, 13.99.

General procedure for the synthesis of compounds (9 and 10).

A mixture of isonicotyl amidoxime (1.5 g; 10.9 mmol) and the appropriate acyl chloride (13.1 mmol) in pyridine (50 mL) was refluxed for 8 h. After removal of the solvent, the residue was worked-up with water neutralised with a saturated aq. $NaHCO_3$, filtered and purified by column chromatography with light petroleum/AcOEt (5/1 v/v) to give **9** (2.07 g; 78%) and **10** (2.51 g; 77%) respectively.

4-(5-Heptyl-1,2,4-oxadiazol-3-yl)pyridine (9) oil. ^{1}H NMR (CD_3CN) δ 0.87 (t, *J* = 6.7 Hz, 3H, Me), 1.27 (m, 8H, CH_2), 1.82 (m, 2H, CH_2), 2.96 (t, *J*= 7.4 Hz, 2H, CH_2), 7.89 (d, *J* = 5.9 Hz, 2H, Ar), 8.73 (d, *J* = 5.9 Hz, 2H, Ar); MS *m/z* (%) 246 (M+1, 100), 191 (5), 115 (6), 43 (5). Anal. Calcd for $C_{14}H_{19}N_3O$**:** C, 68.54; H, 7.81; N, 17.13. Found: C, 68.60; H, 7.87; N, 17.11.

4-(5-Undecyl-1,2,4-oxadiazol-3-yl)pyridine (10) had mp 34-35 °C (light petroleum). ^{1}H NMR (CD_3CN) δ 0.85 (t, *J* = 6.3 Hz, 3H, Me), 1.24 (m, 16H, CH_2), 1.81 (m, 2H, CH_2), 2.95 (t, *J* = 7.3 Hz, 2H, CH_2), 7.88 (d, *J* = 5.9 Hz, 2H, Ar), 8.73 (d, *J* = 5.7 Hz, 2H, Ar); MS *m/z* (%) 303 (M+2, 100), 272 (22), 257 (22), 241

(14), 222(22), 190 (38), 169 (98), 156 (97), 115 (85), 101 (35), 80 (33), 57 (34). Anal. Calcd for $C_{18}H_{27}N_3O$**:** C, 71.72; H, 9.03; N, 13.94. Found: C, 71.65; H, 9.07; N, 13.89.

General procedure for the synthesis of iodide salts.

To a solution of the oxadiazole (1.66 mmol) in anhydrous CH_3CN (20 mL), MeI (1.20 g; 8.5 mmol) was added and the mixture was refluxed for 4 h. After removal of the solvent under reduced pressure the residue was crystallised.

***N*-Methyl-4-(3-heptyl-1,2,4-oxadiazol-5-yl)pyridinium Iodide (1a)** (0.58 g; 73%). ^{1}H NMR (CD_3CN) δ 0.87 (t, *J* = 6.3 Hz, 3H, Me), 1.32 (m, 8H, CH_2), 1.78 (m, 2H, CH_2), 2.85 (t, *J* = 7.4 Hz, 2H, CH_2), 4.43 (s, 3H, Me), 8.57 (d, *J* = 5.9 Hz, 2H, Ar), 8.98 (d, *J* = 6.4 Hz, 2H, Ar); MS (ESI) *m/z* (%)647.20 ($M_2^+A^-$, 20), 260.27 (M^+, 100), 162.13 [(M-C_7H_{15})+1, 70]. Anal. Calcd for $C_{15}H_{22}N_3OI$**:** C, 46.52; H, 5.73; N, 10.85. Found: C, 46.50; H, 5.80; N, 10.82.

***N*-Methyl-4-(3-undecyl-1,2,4-oxadiazol-5-yl)pyridinium Iodide (2a.** (0.44 g; 58%). ^{1}H NMR (CD_3CN) δ 0.87 (t, *J* = 6.8 Hz, 3H, Me), 1.26 (m, 16H, CH_2), 1.77 (m, 2H, CH_2), 2.85 (t, *J* = 7.4 Hz, 2H, CH_2), 4.40 (s, 3H, Me), 8.55 (d, *J* = 6.3 Hz, 2H, Ar), 8.90 (d, *J* = 6.7 Hz, 2H, Ar); MS (ESI) *m/z* (%) 759.95 ($M_2^+A^-$, 5), 316.30 (M^+, 100), 162.11 [(M-$C_{11}H_{23}$)+1, 5]. Anal. Calcd for $C_{19}H_{30}N_3OI$**:** C, 51.47; H, 6.82; N, 9.48. Found: C, 51.50; H, 6.88; N, 9.52.

***N*-Methyl-4-(5-heptyl-1,2,4-oxadiazol-3-yl)pyridinium Iodide (3a)** (0.77 g; 97%). ^{1}H NMR (CD_3CN) δ 0.94 (t, *J* = 6.6 Hz, 3H, Me), 1.41 (m, 8H, CH_2), 1.92 (m, 2H, CH_2), 3.09 (t, *J* = 7.5 Hz, 2H, CH_2), 4.51 (s, 3H, Me), 8.61 (d, *J* = 6.1 Hz, 2H, Ar), 9.06 (d, *J* = 6.4 Hz, 2H, Ar); MS (ESI) *m/z* (%) 647.81 ($M_2^+A^-$, 20), 259.56 (M^+, 100). Anal. Calcd for $C_{15}H_{22}N_3OI$**:** C, 46.52; H, 5.73; N, 10.85. Found: C, 46.55; H, 5.70; N, 10.87.

***N*-Methyl-4-(5-undecyl-1,2,4-oxadiazol-3-yl)pyridinium Iodide (4a).** (0.73 g; 99%). ^{1}H NMR (CD_3CN) δ 0.93 (t, *J* = 6.6 Hz, 3H, Me), 1.39 (m, 16H, CH_2), 1.92 (m, 2H, CH_2), 3.10 (t, *J* = 7.6 Hz, 2H, CH_2), 4.49 (s, 3H, Me), 8.61 (d, *J* = 6.2 Hz, 2H, Ar), 8.98 (d, *J* = 6.3 Hz, 2H, Ar); MS (ESI) *m/z* (%)759.95 ($M_2^+A^-$, 2), 315.76 (M^+, 100). Anal. Calcd for $C_{19}H_{30}N_3OI$**:** C, 51.47; H, 6.82; N, 9.48. Found: C, 51.51; H, 6.80; N, 9.48.

General procedure for the synthesis of trifluoromethanesulfonate salts.

To a solution of the appropriate oxadiazole (1.66 mmol) in anhydrous CH_3CN (20 mL), methyltrifluoromethanesulfonate (CF_3SO_3Me; TfOMe) (0.41 g, 2.49 mmol) was added and the mixture was allowed to stir at rt overnight. After removal of the solvent under reduced pressure the residue was purified by column chromatography with AcOEt and then CH_3CN.

***N*-Methyl-4-(3-heptyl-1,2,4-oxadiazol-5-yl)pyridinium trifluoromethanesulfonate (1b)** (0.70 g; 84%). ^{1}H NMR (CD_3CN) δ 0.87 (t, *J* = 6.4 Hz, 3H, Me), 1.32 (m, 8H, CH_2), 1.78 (m, 2H, CH_2), 2.85 (t, *J* = 7.4 Hz,

2H, CH_2), 4.40 (s, 3H, Me), 8.55 (d, *J* = 6.2 Hz, 2H, Ar), 8.89 (d, *J* = 6.5 Hz, 2H, Ar); MS (ESI) *m/z* (%) 669.92 ($M_2^+A^-$, 100), 259.57 (M^+, 95), 161.25 (M-C_7H_{15}, 25). Anal. Calcd for $C_{16}H_{22}N_3O_4F_3S$**:** C, 46.94; H, 5.42; N, 10.26. Found: C, 46.90; H, 5.40; N, 10.22.

***N*-Methyl-4-(3-undecyl-1,2,4-oxadiazol-5-yl)pyridinium trifluoromethanesulfonate (2b)** (0.31 g; 40%). ^{1}H NMR (CD_3CN) δ 0.87 (t, *J* = 6.1 Hz, 3H, Me), 1.27 (m, 16H, CH_2), 1.78 (m, 2H, CH_2), 2.85 (t, *J* = 7.3 Hz, 2H, CH_2), 4.37 (s, 3H, Me), 8.54 (d, *J* = 6.3 Hz, 2H, Ar), 8.85 (d, *J* = 6.6 Hz, 2H, Ar); MS (ESI) *m/z* (%) 781.55 ($M_2^+A^-$, 2), 315.75 (M^+, 100), 161.24 (M-$C_{11}H_{23}$, 25). Anal. Calcd for $C_{20}H_{30}N_3O_4F_3S$**:** C, 51.60; H, 6.50; N, 9.03. Found: C, 51.50; H, 6.58; N, 9.02.

***N*-Methyl-4-(5-heptyl-1,2,4-oxadiazol-3-yl)pyridinium trifluoromethanesulfonate (3b)** (0.74 g, 89%). ^{1}H NMR (CD_3CN) δ 0.89 (t, *J* = 6.1 Hz, 3H, Me), 1.35 (m, 8H, CH_2), 1.85 (m, 2H, CH_2), 3.03 (t, *J* = 7.6 Hz, 2H, CH_2), 4.38 (s, 3H, Me), 8.52 (d, *J* = 6.1 Hz, 2H, Ar), 8.82 (d, *J* = 6.4 Hz, 2H, Ar); MS (ESI) *m/z* (%) 669.89 ($M_2^+A^-$, 12), 259.56 (M^+, 100). Anal. Calcd for $C_{16}H_{22}N_3O_4F_3S$**:** C, 46.94; H, 5.42; N, 10.26;. Found: C, 46.91; H, 5.40; N, 10.25.

***N*-Methyl-4-(5-undecyl-1,2,4-oxadiazol-3-yl)pyridinium trifluoromethanesulfonate (4b)** (0.55 g, 71%); ^{1}H NMR (CD_3CN) δ 0.86 (t, *J* = 6.2 Hz, 3H, Me), 1.31 (m, 16H, CH_2), 1.84 (m, 2H, CH_2), 3.02 (t, *J* = 7.5 Hz , 2H, CH_2), 4.36 (s, 3H, Me), 8.51 (d, *J* = 6.5 Hz, 2H, Ar), 8.80 (d, *J* = 6.7 Hz, 2H, Ar); MS (ESI) *m/z* (%) 315.76 (M^+, 100). Anal. Calcd for $C_{20}H_{30}N_3O_4F_3S$**:** C, 51.60; H, 6.50; N, 9.03. Found: C, 51.58; H, 6.52; N, 9.02.

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