New ionic liquid crystals based on imidazolium salts†

William Dobbs,[a] Laurent Douce,*[a] Lionel Allouche,[b] Alain Louati,[c]
François Malbosc[d] and Richard Welter[e]

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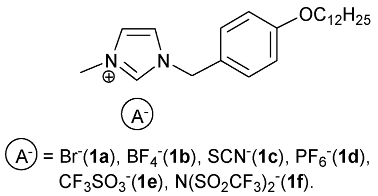
The new ionic liquid crystal 1-(4-dodecyloxybenzyl)-3-methyl-1*H*-imidazol-3-ium bromide has been synthesized and its X-ray structure obtained; various salts containing BF_4^-, SCN^-, PF_6^-, $CF_3SO_3^-$, $(CF_3SO_2)_2N^-$ have been prepared by anion metathesis in water from bromide species as starting materials, and finally, the mesomorphism and electrochemical behavior have been investigated.

Extensive studies of ionic liquids have revealed their many useful properties such as extremely low volatility, high thermal stability, non-flammability, high chemical stability, high ionic conductivity and a wide electrochemical window.[1,2] Ionic liquids based on imidazolium salts are particularly well known and have found application in dye-sensitized solar cells, electrochemical devices, wet double-layer capacitors and ion transport systems.[3] Certain ionic materials are known also to form amphitropic liquid crystals and such "ionic liquid crystals" have been widely studied.[4,5] They have especially great potential as ordered reaction media that can impart selectivity in reactions by organising reactants.[6] Full conjunction of the two fields of ionic liquid chemistry and liquid crystal chemistry could lead to a vast new range of materials for research and industry. Variation of the *N*,*N*′ substituents in imidazolium systems is a facile means of creating this range, one of the particularly interesting properties of these materials being their ease of deprotonation to give, formally, N-heterocyclic carbenes which are excellent ligands for transition-metal-based catalysts.[7]

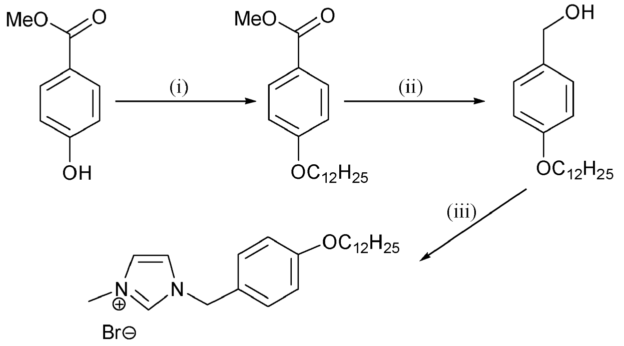
Despite growing interest in the properties of ionic liquids based on imidazolium compounds, very little is known of systems which form liquid crystals.[8] Only a few reports of thermotropic imidazolium compounds are available, one concerning our recent characterisation of a symmetrical dialkyl imidazolium derivative which shows a smectic-A phase between 119 and 172 °C.[9]

Herein, we report the synthesis of an unsymmetrical imidazolium species (Scheme 1) designed to give a lower mesophase transition temperature and to facilitate study of the influence of the counteranion on the mesomorphism, thermal stability and electrochemistry of imidazolium salts. Compound **1a**, 1-(4-dodecyloxybenzyl)-3-methyl-1*H*-imidazol-3-ium bromide, was obtained in a four-step procedure (Scheme 2). The last step is a nucleophilic substitution on 1-(bromomethyl)-4-(dodecyloxy)benzene by the methylimidazole which proceeds in 88% yield. The bromide salt **1a** is air stable and was purified by column chromatography on silica. Distinctive signals of the CH (1*H*-imidazolium) group appear in the ^{1}H and ^{13}C NMR spectra at 10.89 ppm and at 136.54 ppm, respectively.

To explore the occurrence of aggregation in solution, the ^{1}H NMR spectra were recorded as a function of concentration. Translational diffusion coefficients (*D*) were determined by Diffusion Ordered NMR Spectroscopy (DOSY) experiments in order to estimate the relative size of the molecular entities in solution.[10] The DOSY spectrum of **1a** at low concentration



Scheme 1 1-(4-Dodecyloxybenzyl)-3-methyl-1*H*-imidazol-3-ium salts.



1a (88%)

Scheme 2 Synthesis of the bromide **1a**. *Reaction conditions*: (i) DMF, K_2CO_3, $BrC_{12}H_{25}$, 60 °C, overnight; (ii) $LiAlH_4$, THF, 4 h; (iii) $SOBr_2$, DCM; dry THF, methylimidazole under inert atmosphere.

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[a] *Institut de Physique et Chimie des Matériaux de Strasbourg, Groupe des Matériaux Organiques, UMR 7504, CNRS-Université Louis Pasteur, BP 43, 23 rue du Loess, F-67034 Strasbourg Cedex 2, France. E-mail: laurent.douce@ipcms.u-strasbg.fr; Fax: +33 388 107 246; Tel: +33 388 107 107*
[b] *Service de R.M.N., Institut de Chimie de Strasbourg, CNRS-ULP, 1 rue Blaise Pascal, 67000 Strasbourg, France*
[c] *Laboratoire d'Electrochimie Analytique, Ecole Nationale Superieure de Chimie de Mulhouse, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France*
[d] *SOLVIONIC SA, Parc Technologique Delta Sud, 09340 Verniolle, France*
[e] *Laboratoire DECOMET, UMR CNRS 7177-LC003, Université Louis Pasteur, 4 rue Blaise Pascal, 67000 Strasbourg, France*

† Electronic Supplementary Information (ESI) available: Experimental data, DOSY spectra, DSC, TGA and XRD data and cyclic voltammograms. See DOI: 10.1039/b600279j.

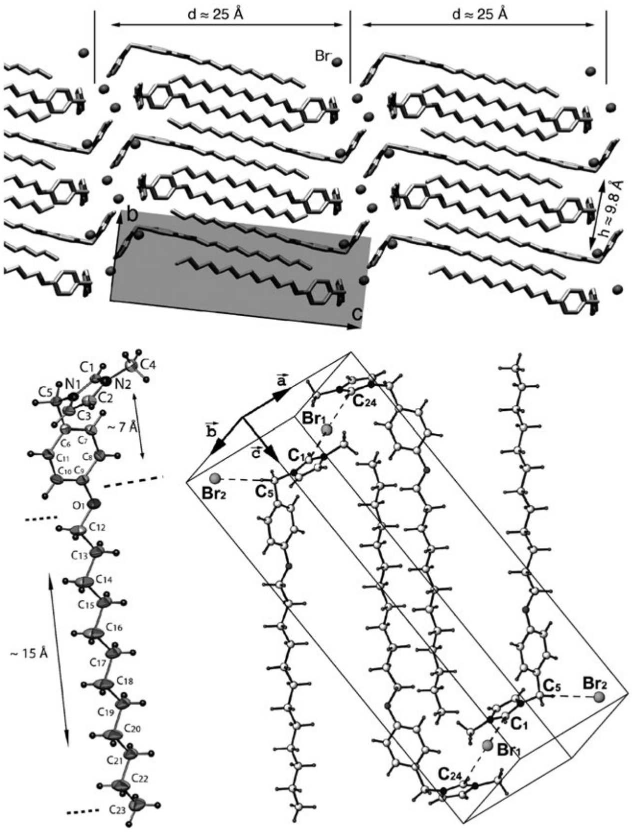

Fig. 1 Top: Partial crystal packing of the compound **1a** projected on to the (*bc*) plane. Bottom: ORTEP view of half asymmetric unit of compound **1a** with labelling scheme (left). Displacement ellipsoids are shown at the 50% probability level. The unit cell content of **1a** is shown on the right. Selected non-classical H-bonds are presented (dashed lines).

characterises the molecule in solution ($D = 700\ \mu m^2\ s^{-1}$); at high concentrations, the DOSY spectrum shows a characteristic polydisperse pattern ($450 < D < 700\ \mu m^2\ s^{-1}$), signalling the formation of aggregates in solution (see Fig. S1 and S2 in electronic supplementary information, ESI†).

Single crystals of **1a** suitable for X-ray diffraction were obtained by slow diffusion of ether into a CH_2Cl_2 solution. Both crystal and molecular structures are shown in Fig. 1. The *N*-alkyl chains and the phenyl groups are approximately orthogonal (82(1)°) to the imidazolium plane. The crystal structure packing, as shown in Fig. 1a, can be described as a pseudo-lamellar system perpendicular to the flexible (*N*-alkyl) chains (∼15 Å). Many non-classical hydrogen bonds have been detected in the crystal structure. This observation (partially reported in Fig. 1) is in good accordance with the segregation signaled above *i.e.* the Br^- anions are connected to the rigid part of the molecule by these weak interactions. Moreover, a CH–π interaction has been found between H10 (C10) and the C29–C34 phenyl group (distance of 2.92 Å between H10 and the centroid of the phenyl group). The layers are separated by $d \approx 25$ Å. Within the layer, the *N*-alkyl groups form another pseudo-lamellar network, with a characteristic distance of $h \approx 9.8$ Å. The rigid phenyl and imidazolium rings, forming a unit ∼7 Å long, are, along with the anions, completely segregated from the flexible chains. This is consistent with the amphiphilic character of the molecules and indicates that they could show liquid crystal behaviour at higher temperature.

In order to investigate the influence of the anion on the mesomorphism, we prepared compounds with BF_4^- (**1b**), SCN^- (**1c**), PF_6^- (**1d**) and $(CF_3SO_2)_2N^-$ (**1f**) anions in excellent yield by anion metathesis in water as solvent, except for $CF_3SO_3^-$ (**1e**) (see experimental details in ESI). All these compounds were characterized by ^1H NMR, C^{13} NMR $\{^1H\}$, FT-IR and elemental analysis. The IR spectra show typical anion vibrations at 1036 cm^{-1} (**1b** BF_4^-), 2063 cm^{-1} (**1c** SCN^-), 822 cm^{-1} (**1d** PF_6^-), 1260 and 1029 cm^{-1} (**1e** $CF_3SO_3^-$), 1353 and 1180 cm^{-1} (**1f** $(CF_3SO_2)_2N^-$). At low concentration (1 mg in 0.3 ml $CDCl_3$), the chemical shift for the CH proton is very dependent upon the anion, with δ 9.10 (**1b**), 9.63 (**1c**), 8.69 (**1d**), 9.40 (**1e**) and 8.93 ppm (**1f**).

The thermogravimetric analysis of compounds **1a–f** showed the general stability order to be $SCN^- \approx Br^- < BF_4^- \approx PF_6^- < CF_3SO_3^- \approx (CF_3SO_2)_2N^-$ (see Fig. S3 in ESI). For all the compounds, the mesomorphic behavior and phase transition temperatures were investigated by polarizing optical microscopy (POM), differential scanning calorimetry (DSC, see Fig. S5 in ESI), and X-ray powder diffractometry (XRD, see Fig. S4 in ESI). To avoid possible effects of hydration of the materials, all were dried under vacuum before X-ray and DSC analyses. The phase transition temperatures and the corresponding enthalpy changes derived for compounds **1a–f** are compiled in Table 1, while typical results are displayed in Fig. 2. Compounds **1e** and **1f**, not unexpectedly,[8d,e,f] do not show thermotropic behaviour, while the data for **1a–d** give an order of anion stabilisation of liquid crystal behaviour of $Br^- > BF_4^- > SCN^- > PF_6^-$ (see Fig. 2).

As described in the literature[4] and confirmed herein, it is difficult to observe good defect textures for the mesophase of an imidazolium salt by polarizing optical microscopy because of the tendency of the salts to form spontaneously a single homeotropic monodomain which gives a dark field between crossed polarizers. To avoid the homeotropic alignment, we observed the samples held between two microscope slides separated by a 100 μm spacer. The optical textures then observed upon slow cooling from the isotropic melt showed the emergence of a smectic A phase with appearance of batônnets, turning into focal conic structures co-existing with homeotropic areas. The structure of the liquid crystal phase

Table 1 Phase transition temperatures[a] and corresponding enthalpies ΔH determined from the 1st heating

Compound	T/°C Cr → I (ΔH/J g^{-1})	T/°C Cr → LC (ΔH/J g^{-1})	T/°C LC → I (ΔH/J g^{-1})
1a[b]		81 (101.4)	249 (1.1)
1b		65 (64.2)	203 (1.5)
1c		54 (114.2)	188 (1.2)
1d		77 (83.2)	148 (1.2)
1e	67 (92.2)		
1f	49 (98.2)		

[a] Abbreviations: Cr = crystalline phase, LC = smectic A phase, I = isotropic phase. [b] Decomposition is observed after clearing point.

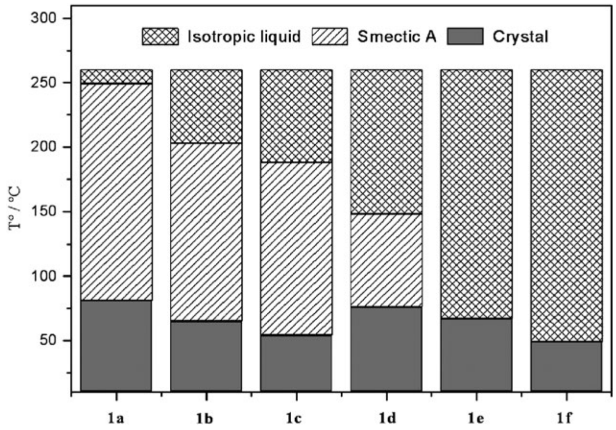

Fig. 2 Phase transition temperatures of compounds **1a–f**.

was established using XRD. The smectic A structure was characterized by patterns containing one to three sharp, equidistant reflections in the small angle region, related to the smectic layering, and a broad band in the wide angle region, related both to the disordered alkyl chains and the liquid-like lateral correlations of the aromatic cores within the layers. The *d*-spacing values obtained for the compounds at 80 °C were d_1 = 37.7 (**1a** Br^-), 37.2 (**1b** BF_4^-), 36.5 (**1c** SCN^-) and 35.8 Å (**1d** PF_6^-). Note that the *d*-spacings of the smectic layers of the compounds **1a–d** were less than two times the length of the molecules. This can be interpreted as indicative of the formation of an ionic double layer with interdigitated polar groups (Fig. 3). In our case, the *d*-spacing is not correlated with the anion size. The small differences in thickness (around 2 Å) originates from the fact that, owing to van der Waals and dipole interactions, the cationic centres adapt to allow the anions to penetrate to different extents within the aromatic layers.

Cyclic voltammetry was used to determine the electrochemical windows for the compounds **1a–f**, the voltammograms being recorded in CH_3CN solutions containing 0.1 M NBu_4PF_6 as supporting electrolyte at a platinum working electrode and with a SCE reference electrode (see Fig. S6 in ESI). The results are gathered in Table 2.

For all compounds, only an irreversible reduction process was observed at *ca.* −1.7 V. It is evident that this process corresponds to the reduction of the cationic imidazolium species. In the anodic scan, compound **1a** showed two oxidation steps, at 0.86 V and 1.15 V, while the compound **1c** exhibited one oxidation process at 0.85 V. We assume that the two oxidation processes in **1a** involve the formation of Br_2 and possibly then a higher-oxidation-state bromine species. For **1c**, the oxidation process can be attributed to the formation of thiocyanogen, $(NCS)_2$ (Fig. 4).[11] Thus, these preliminary results establish a cathodic limit of *ca.* −1.7 V for all compounds, while the anodic limit is related to the oxidation of the anionic species.

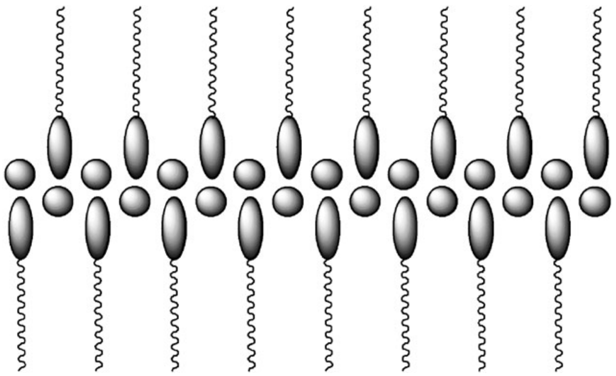

Fig. 3 Schematic drawing of the possible arrangement of the imidazolium species and anions in an ionic double layer.

Table 2 Main electrochemical peak potentials recorded in CH_3CN with NBu_4PF_6 (0.1 M)

Compound	Reduction processes/V	Oxidation processes/V	
1a	−1.74	0.86	1.15
1b	−1.71	—	—
1c	−1.67	0.85	—
1d	−1.73	—	—
1e	−1.76	—	—
1f	−1.73	—	—

In conclusion, we report the full characterisation of new mesomorphic compounds based on an imidazolium unit with different anions. NMR experiments have shown that these materials can form aggregates in solution. We are now investigating the ability of the conjugate base of the cation to form thermotropic carbene complexes with, for example, palladium(II). We are also attempting to introduce different length tails in order to obtain room temperature ionic liquid crystals.

Experimental

General

All commercially available chemicals were used without further purification. Dichloromethane (DCM) and tetrahydrofuran (THF) were carefully dried and distilled prior to use. Evaporation and concentration were done at water pressure and drying *in vacuo* at 10^{-2} torr. Column chromatography:

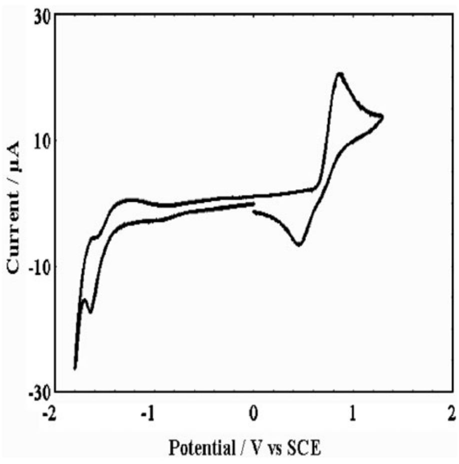

Fig. 4 Cyclic voltammogram of **1c** in CH_3CN (0.1 M NBu_4PF_6). Scan rate 100 mV s^{-1}.

silica gel 60 (230–400 mesh, 0.040–0.063 nm) was purchased from E. Merck.

Syntheses

1-(4-Dodecyloxybenzyl)-3-methyl-1*H*-imidazol-3-ium bromide, 1a. This reaction was carried out under argon atmosphere. 4-(Dodecyloxyphenyl)methanol (8.2 g, 28 mmol) and thionyl bromide (2.25 ml, 28 mmol) were dissolved in dry DCM. The progress of the reaction was monitored by TLC until no more alcohol was observed. After three hours, the solvent was removed under vacuum and the crude 1-bromomethyl-4-dodecyloxybenzene was used directly without further purification. This bromo derivative and 1-methylimidazole (2.3 ml, 28 mmol) were stirred in dry THF at room temperature overnight. After evaporation to dryness, the residue was purified by flash chromatography (silica gel column, elution DCM–MeOH, MeOH 2% to 8%). Yield: crystalline white solid, 10.8 g, 88% (Found: C, 62.7; H, 8.55; N, 6.45. $C_{23}H_{37}BrN_2O$ requires: C, 63.15; H, 8.5; N, 6.4%). ν_{max}/cm^{-1} 3133 (C–H aromatic), 2919 and 2850 (C–H aliphatic), 1513 (C=C aromatic), 1248 (aromatic ether). δ_H (300 MHz; $CDCl_3$): 0.88 (3 H, t, *J* 6.9, CH_3 aliphatic chain); 1.27 (16 H, br s, CH_2 aliphatic chain); 1.39–1.47 (2 H, m, CH_2 aliphatic chain); 1.78 (2 H, q, *J* 6.9, O–CH$_2$–CH_2); 3.95 (2 H, t, *J* 6.5, OCH_2); 4.08 (3 H, s, CH_3–N); 5.47 (2 H, s, N–CH_2-Ph); 6.91 (2 H, d, *J* 8.6, C*H* phenyl); 7.09 (1 H, m, C*H* imidazolium); 7.13 (1 H, m, C*H* imidazolium); 7.40 (2 H, d, *J* 8.6, C*H* phenyl); 10.89 (1 H, s, N–C*H*–N). δ_C (75 MHz; $CDCl_3$): 13.86 (CH$_3$ aliphatic chain); 22.42; 25.76; 28.92; 29.08; 29.15; 29.31; 29.34; 29.36; 29.40; 31.64 (CH$_2$ aliphatic chain); 36.52 (N–CH$_3$); 52.56 (N–CH$_2$–Ph); 67.90 (O–CH$_2$); 114.94 (*C*H phenyl); 121.58; 123.47 (*C*H imidazolium); 124.61 (*C* phenyl); 130.39 (*C*H phenyl); 136.54 (N–*C*H–N); 159.71 (*C* phenyl).

1-(4-Dodecyloxybenzyl)-3-methyl-1*H*-imidazol-3-ium tetrafluoroborate, 1b. The compound **1b** was obtained by anion metathesis in water as solvent (5 ml aqueous solution of sodium tetrafluoroborate (64 mg, 0.57 mmol) was added to 1-(4-dodecyloxybenzyl)-3-methyl-1*H*-imidazol-3-ium bromide (250 mg, 0.57 mmol) dissolved in 15 ml of water). A precipitate of 3-(4-dodecyloxybenzyl)-1-methyl-1*H*-imidazolium tetrafluoroborate occurred immediately. **1b** was filtered and washed with water and finally crystallized by slow diffusion of ether into a THF solution. Yield: crystalline white solid, 250 mg, 98% (Found C, 60.6; H, 8.25; N, 6.1. $C_{23}H_{37}BF_4N_2O \cdot 1/2H_2O$ requires C, 60.9; H, 8.4; N, 6.2%). ν_{max}/cm^{-1} 3154 (C–H aromatic), 2919 and 2848 (C–H aliphatic), 1515 (C=C aromatic), 1249 (aromatic ether), 1036 (BF_4^-). δ_H(300 MHz; $CDCl_3$): 0.89 (3 H, t, *J* 6.8, CH_3 aliphatic chain); 1.27 (16 H, br s, CH_2 aliphatic chain); 1.39–1.45 (2 H, m, CH_2 aliphatic chain); 1.76 (2 H, q, *J* 6.8, O–CH$_2$–CH_2); 3.94 (2 H, t, *J* 6.5, OCH_2); 3.98 (3 H, s, CH_3–N); 5.29 (2 H, s, N–CH_2–Ph); 6.91 (2 H, d, *J* 8.6, C*H* phenyl); 7.09 (1 H, m, C*H* imidazolium); 7.16 (1 H, m, C*H* imidazolium); 7.33 (2 H, d, *J* 8.6, C*H* phenyl); 9.1 (1 H, s, N–C*H*–N). δ_C (75 MHz; $CDCl_3$): 14.10 (CH$_3$ aliphatic chain); 22.67; 26.00; 29.16; 29.33; 29.39; 29.57; 29.59; 29.62; 29.65; 31.90 (CH$_2$ aliphatic chain); 36.37 (N–CH$_3$); 53.15 (N–CH$_2$–Ph); 67.18 (O–CH$_2$); 115.35 (*C*H phenyl); 121.57; 123.38 (*C*H imidazolium); 124.17 (*C* phenyl); 130.60 (*C*H phenyl); 136.56 (N–*C*H–N); 160.13 (*C* phenyl).

1-(4-Dodecyloxybenzyl)-3-methyl-1*H*-imidazol-3-ium trifluoromethanesulfonate, 1e. 1-(4-Dodecyloxybenzyl)-3-methyl-1*H*-imidazol-3-ium trifluoromethanesulfonate was obtained by mixing a solution of 1-(4-dodecyloxybenzyl)-3-methyl-1*H*-imidazol-3-ium bromide (250 mg, 0.57 mmol) in 10 ml of DCM and a solution of silver trifluoromethanesulfonate (147 mg, 0.57 mmol) in 5 ml of DCM. Silver bromide was removed by filtration over alumina and the solvent removed. The crude product was finally crystallized in good yield by slow diffusion of ether into a THF solution. Yield: crystalline white solid 260 mg, 90% (Found C, 56.8; H, 7.4; N, 5.6. $C_{25}H_{37}F_3N_2O_4S$ requires C, 56.9; H, 7.4; N, 5.5%). ν_{max}/cm^{-1} 3122 (C–H aromatic), 2918 and 2850 (C–H aliphatic), 1516 (C=C aromatic), 1260 and 1029 ($CF_3SO_3^-$). δ_H(300 MHz; $CDCl_3$): 0.89 (3 H, t, *J* 6.8, CH_3 aliphatic chain); 1.27 (16 H, br s, CH_2 aliphatic chain); 1.35–1.48 (2 H, m, CH_2 aliphatic chain); 1.78 (2 H, q, *J* 6.6, O–CH$_2$–CH_2); 3.95 (2 H, t, *J* 6.6, OCH_2); 3.99 (3 H, s, CH_3–N); 6.92 (2 H, d, *J* 8.6, C*H* phenyl); 7.10 (1 H, m, C*H* imidazolium); 7.16 (1 H, m, C*H* imidazolium); 7.32 (2H, d, *J* 8.6, C*H* phenyl); 9.40 (1 H, s, N–C*H*–N). δ_C (75 MHz; $CDCl_3$): 14.02 (CH$_3$ aliphatic chain); 22.60; 25.94; 29.10; 29.26; 29.26; 29.32; 29.50; 29.53; 29.58; 31.83 (CH$_2$ aliphatic chain); 36.26 (N–CH$_3$); 52.96 (N–CH$_2$-Ph); 68.10 (O–CH$_2$); 115.23 (*C*H phenyl); 120.6 (quadruplet, *J* = 320 Hz, CF_3); 121.76; 123.61 (*C*H imidazolium); 124.31 (*C* phenyl); 130.46 (*C*H phenyl); 136.34 (N–*C*H–N); 160.02 (*C* phenyl).

X-Ray crystallography

A suitable crystal of **1a** was mounted on a Nonius Kappa-CCD area detector diffractometer (MoKα, λ = 0.71073 Å). The complete conditions of data collection (Denzo software) and structure refinements are given below. The cell parameters were determined from reflections taken from one set of ten frames (1.0° steps in ϕ angle), each at 20 s exposure. The structures were solved using direct methods (SHELXS97) and refined against F^2 using the SHELXL97 software. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were generated according to stereochemistry and refined using a riding model in SHELXL97.‡ Colorless crystal; crystal dimension: 0.10 × 0.07 × 0.05 mm^3; $C_{23}H_{37}N_2O^+,Br^-$, M = 437.46 g mol^{-1}; monoclinic; space group $P\bar{1}$ (no. 2); a = 8.7610(2) Å; b = 9.7620(3) Å; c = 27.2570(5) Å; α = 93.675(1)°; β = 96.278(1)°; γ = 95.237(4)°; V = 2301.03(1) Å^3, Z = 4; D_c = 1.263 g cm^{-3}; μ(MoKα) = 1.801 mm^{-1}; a total of 16426 reflections; 1.51° < θ < 27.52°, 10512 independent reflections with 7277 having $I > 2\sigma(I)$; 487 parameters; Final results: R_1 = 0.0438; Rw_2 = 0.1147, Gof = 1.073, maximum residual electronic density = 0.541 e^- Å^{-3}.

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