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Ionic Liquids on the Basis of 2,3,4,6,7,8,9,10-Octahydropyrimido-[1,2-*a*]azepine (1,8-Diazabicyclo[5.4.0]undec-7-ene)

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Abstract—New ionic liquids containing alkyl and polyfluoroalkyl substituents and various anions were synthesized from 2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]azepinium ion (1,8-diazabicyclo[5.4.0]undec-7-en-8-ium). Their NMR spectra and miscibility with water and organic solvents were studied.

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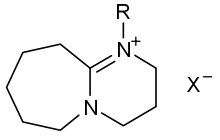
Ionic liquids are liquid or low-melting (with a melting point of lower than 100°C) organic salts which constitute a new class of solvents characterized by broad ranges of hydrophilicity, coordinating and dissolving capacity, and thermal stability [1]. The scope of application of first-generation ionic liquids, which include mainly quaternary ammonium salts and imidazolium or pyridinium chloroaluminates [2, 3], is limited owing to their high acidity and sensitivity to moisture. Second-generation ionic liquids are neutral substances, and they contain water-tolerant anions; due to their almost zero volatility and the possibility to be regenerated and used repeatedly, many processes performed in such solvents (including catalytic reactions) may be regarded as "green" [4]. An attractive property of ionic liquids is that the cation–anion couples may be varied over a wide range, thus controlling their miscibility with water and organic solvents of different polarity [5]. At present, the most widely used ionic liquids are those based on 1,3-dialkylimidazolium and pyridinium salts with various anions.

In the present article we describe the synthesis of a series of ionic liquids like **I** containing different substituents on the nitrogen atom from 2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]azepine (1,8-diazabicyclo[5.4.0]undec-7-ene, DBU). As anions we used chloride, bromide, *p*-toluenesulfonate, and trifluoromethanesulfonate. We found only one recent publication [6] on the synthesis of two salts on the basis of DBU (8-methyl- and 8-ethyl-1,8-diazabicyclo[5.4.0]-undec-7-en-8-ium trifluoromethanesulfonates) and their use as reaction medium [6, 7]; therefore, salts **I** may be regarded as a new class of ionic liquids.



I

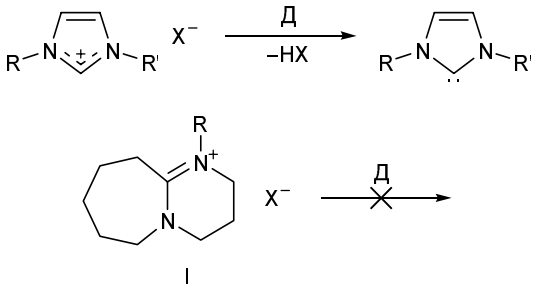
R = Me, Et, Bu, $PhCH_2$, $H(CF_2)_nCH_2$; X = Cl, Br, OTs, OTf.

The initial nitrogenous base (DBU) is readily available from caprolactam, and its synthetic and commercial accessibility is quite comparable with that of 1-alkylimidazoles which are initial compounds for the synthesis of most known ionic liquids. Salts **I** are characterized by a large size, low symmetry of the cationic moiety, and charge delocalization over the N–C=N triad; as a result, they have low melting points [8]. In addition, by varying combinations of hydrophobic substituents R and hydrophilic anion X, their solubility in water and organic solvents can be changed over a wide range. On the whole, the presence of saturated hydrocarbon bridges $(CH_2)_3$ and $(CH_2)_5$ should make salts **I** more hydrophobic than their imidazolium analogs; therefore, the choice of ionic liquids for particular processes could be extended considerably. Another difference between salts **I** and imidazole-based ionic liquids is that the former cannot lose HX with formation of carbenes; this shoud enhance their chemical and thermal stability as compared to imidazolium salts which are well known to produce carbene species [9] (Scheme 1).

Carbenes generated by proton abstraction from C^2 of the imidazole ring are capable of forming com-

plexes with metals [10]. Moreover, imidazolium salts themselves could give rise to hydride complexes via metal insertion into the C^2–H bond [11]. Therefore, the use of imidazolium salts in metal-complex catalysis is limited.

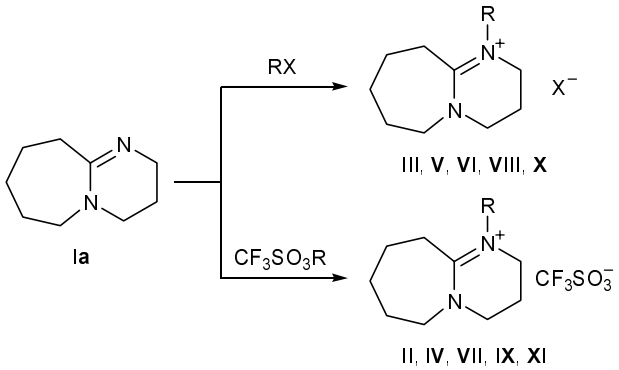
Scheme 1.



Insofar as ionic liquids are nonvolatile, they cannot be purified by distillation (which is a traditional method for solvent purification); impurities present therein can be removed only by washing with appropriate solvent and/or by heating under reduced pressure (for volatile impurities). Taking the above into account, high purity of the initial reactants is desirable for the synthesis of ionic liquids, and anion exchange reactions are widely used [1].

1-Alkyl-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]-azepin-1-ium halides **III**, **V**, and **VIII** were smoothly formed in quantitative yield by treatment of DBU with the corresponding alkyl halides using excess alkylating agent as solvent. *p*-Toluenesulfonate **VI** was obtained by anion exchange in **V** by the action of sodium *p*-toluenesulfonate, and *p*-toluenesulfonate **X**, by reaction of 2,2,3,3-tetrafluoropropyl *p*-toluenesulfonate with DBU. Trifluoromethanesulfonates **II**, **IV**, **VII**, **IX**, and **XI** were synthesized in two ways, by anion exchange between the corresponding halide and lithium trifluoromethanesulfonate and by alkylation of initial base **Ia** with trifluoromethanesulfonic acid esters (Scheme 2).

Scheme 2.

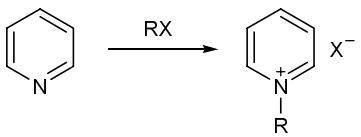


II, R = Me, X = OTf; **III**, R = Et, X = Br; **IV**, R = Et, X = OTf; **V**, R = Bu, X = Cl; **VI**, R = Bu, X = OTs; **VII**, R = Bu, X = OTf; **VIII**, R = $PhCH_2$, X = Cl; **IX**, R = $PhCH_2$, X = OTf; **X**, R = $H(CF_2)_2CH_2$, X = OTs; **XI**, R = $H(CF_2)_2CH_2$, X = OTf.

Alkyl perfluoroalkanesulfonates are very strong alkylating agents capable of reacting at both carbon and nitrogen, oxygen, or sulfur atom [12]. In fact, the reaction of **Ia** with methyl trifluoromethanesulfonate gave ionic liquid **II** in quantitative yield. On the other hand, such reactions are very sensitive to stereoelectronic effects of the polyfluoroalkyl group [13]; therefore, the alkylation of **Ia** with telomeric polyfluorinated alkyl trifluoromethanesulfonates of the general formula $CF_3SO_3CH_2(CF_2)_nH$ sharply slows down as the length of the fluoroalkyl chain increases. Thus the yield of compound **XI** (n = 2) is 75%, while in the reaction with octafluoropentyl trifluoromethanesulfonate (n = 4) the conversion does not exceed 35% (according to the ^{19}F NMR data), and dodecafluoroheptyl trifluoromethanesulfonate (n = 6) fails to react with compound **Ia** even on prolonged heating in boiling chloroform or without a solvent. The reaction is more facile when the reaction center is separated from the polyfluoroalkyl chain by a methylene group: 1-alkylimidazoles react with polyfluoroiodoalkanes of the general formula $R_FCH_2CH_2I$ (adducts of perfluoroiodoalkanes and ethylene) to give the corresponding imidazolium iodides in good yields [14, 15].

Steric factor is also important in the alkylation process; for example, no reaction occurs with 2-chloropropane under the conditions ensuring smooth formation of the corresponding ionic liquids from primary alkyl halides (such as ethyl bromide and *n*-butyl chloride). By contrast, the basicity of the substrate is less significant. Pyridine is much less basic than DBU (pK_{BH^+} 5.2 and 12, respectively), but it does react with $CF_3SO_3CH_2(CF_2)_nH$ (Scheme 3), though the yields of the N-alkylation products sharply decrease as the poly-

Scheme 3.

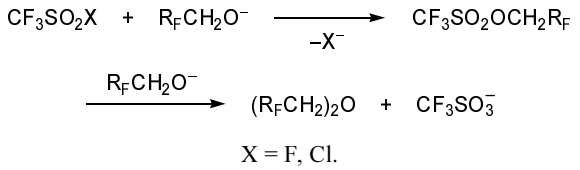


XII, R = Bu, X = Cl; **XIII**, R = Bu, X = Br; **XIV**, R = Bu, X = OTf; **XV**, R = $PhCH_2$, X = Cl; **XVI**, R = $PhCH_2$, X = OTf; **XVII**, R = $H(CF_2)_2CH_2$, X = OTf; **XVIII**, R = $H(CF_2)_4CH_2$, X = OTf.

fluorinated chain becomes longer: **XVII**: yield 73% (n = 2); **XVIII**, 37% (n = 4); 20% (n = 6) (according to the ^{19}F NMR data).

As noted in [12], the synthesis of trifluoromethanesulfonic acid esters from trifluoromethanesulfonyl halides and sodium salts $H(CF_2)_nCH_2ONa$ derived from polyfluoroalkanols may be accompanied by side formation of the corresponding ethers; therefore, the yields of the target products are often poor (Scheme 4). Taking these data into account, we synthesized esters $CF_3SO_3R_F$ from trifluoromethanesulfonic anhydride and polyfluorinated alcohols in the presence of pyridine according to the procedure described in [5].

Scheme 4.



The structure of the products was proved by the ^{1}H, ^{13}C, and ^{19}F NMR spectra. Unlike initial esters $CF_3SO_3R_F$, the ^{13}C NMR spectra of ionic liquids containing polyfluorinated substituents R_F displayed a triplet at δ_C ~50 ppm from the $\mathbf{C}H_2CF_2$ methylene group (the corresponding signal in the spectra of initial esters appeared at δ_C ~70 ppm). In the ^{19}F NMR spectra of trifluoromethanesulfonates **II**, **IV**, **VII**, **IX**, and **XI**, the signal of the CF_3SO_3 group (δ_F ~78 ppm) was located in a stronger field, as compared to esters $CF_3SO_3R_F$ (δ_F ~74 ppm). It should be noted that the ^{1}H NMR spectrum of compound **II** described in [6] is invalid (no singlet from the methyl group was given, and the overall number of protons did not correspond to the assumed structure). We assigned ^{1}H and ^{13}C signals on the basis of the two-dimensional ^{1}H–^{13}C NMR spectrum.

Table contains data on the solubility of 2,3,4,6,-7,8,9,10-octahydropyrimido[1,2-*a*]azepin-1-ium salts in water and various organic solvents. It is seen that the solubility of the obtained ionic liquids in organic solvents increases with rise in their polarity. Regardless of the substituent R and counterion X, compounds **II**–**XI** are soluble in acetonitrile, ethanol, acetone, and methylene chloride (ε = 8.91–36.2) and insoluble in hydrocarbons. The solubility in weakly polar media (such as ethyl acetate, chloroform, diethyl ether, benzene, and dioxane; ε = 2.2–6.0) depends on the solvent ability for specific solvation. All the examined ionic liquids are soluble in chloroform and insoluble in diethyl ether, despite almost similar polarities of these solvents. Obviously, the reason is that chloroform is capable of forming hydrogen bond with the anion, while no specific solvation occurs in diethyl ether. The solubility in benzene and dioxane depends upon both substituent R and counerion. Most ionic liquids are soluble in water; an exception is compound **XI** which contains a strongly hydrophobic $CHF_2(CF_2)_2CH_2$ group and trifluoromethanesulfonate ion.

Solubility of some ionic liquids based on 1,8-diazabicyclo[5.4.0]undec-7-ene in water and organic solvents

Compound no.	R, X	H_2O	MeCN	EtOH	Acetone	CH_2Cl_2	AcOEt	$CHCl_3$	Et_2O	C_6H_6	Dioxane	Hexane[a]
II	Me, OTf	+	+	+	+	+	+	+	–	–	+	–
III	Et, Br	+	+	+	+	+	+	+	–	–	–	–
IV	Et, OTf	+	+	+	+	+	+[b]	+	–	–	+	–
V	Bu, Cl	+	+	+	+	+	+	+	–	–	–	–
VI	Bu, OTs	+	+	+	+	+	+	+	–	+	–	–
VII	Bu, OTf	+	+	+	+	+	+	+	–	–	–	–
VIII	$PhCH_2$, Cl	+	+	+	+	+	+	+	–	–	–	–
IX	$PhCH_2$, OTf	+	+	+	+	+	+	+	–	–	+	–
X	$H(CF_2)_2CH_2$, OTs	+	+	+	+	+	+	+	–	+	+	–
XI	$H(CF_2)_2CH_2$, OTf	–	+	+	+	+	+	+	–	–	+	–

[a] The same is valid for petroleum ether.
[b] Poorly soluble.

EXPERIMENTAL

The ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker DPX-400 spectrometer at 400, 100, and 376 MHz, respectively; $CDCl_3$ and CD_3CN were used as solvent, and HMDS, as internal reference; the ^{19}F chemical shifts were referenced to trichlorofluoromethane.

Methyl trifluoromethanesulfonate was prepared by the procedure described in [16]. Yield 97%, bp 97–99°C; published data [16]: bp 98–99°C, n_D^{20} = 1.3260; ^1H NMR spectrum (CCl_4): δ 4.22 ppm, s. ^1H NMR spectrum ($CDCl_3$): δ 4.22 ppm, s (3H, CH_3). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 61.55 (CH_3), 118.71 q (CF_3, $^1J_{CF}$ = 319.6 Hz). ^{19}F NMR spectrum ($CDCl_3$): δ_F –74.14 ppm.

2,2,3,3-Tetrafluoropropyl *p*-toluenesulfonate was synthesized from sodium 2,2,3,3-tetrafluoropropan-1-olate and *p*-toluenesulfonyl chloride. Yield 97%, bp 108–113°C (0.05 mm; published data [17]: bp 124–126°C (2 mm). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.44 s (3H, CH_3), 4.32 t (2H, CH_2, J = 12.1 Hz), 5.84 t.t (1H, CHF_2, J = 52.9, 4.2 Hz), 7.37 d (2H, 3-H, 5-H), 7.78 d (2H, 2-H, 6-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.55 (CH_3), 64.09 t (CH_2, J = 30.6 Hz), 108.70 t.t (CHF_2, J = 250.3, 35.3 Hz), 113.20 t.t (CF_2, J = 251.4, 28.1 Hz), 128.01 (C^2, C^6), 130.13 (C^3, C^5), 131.58 (C^4), 145.98 (C^1). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –124.11 s (2F, CF_2), –138.14 d (2F, CF_2H, J = 53.1 Hz).

2,2,3,3-Tetrafluoropropyl trifluoromethanesulfonate was prepared by the procedure described in [5]. Yield 51%, bp 114–118°C, n_D^{24} = 1.3206; published data [18]: bp 122–125°C (737 mm), n_D^{25} = 1.3203. ^1H NMR spectrum (CD_3CN), δ, ppm: 4.74 t (2H, CH_2), 5.95 t.t (1H, CHF_2). ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 68.22 t (CH_2, J = 29.9 Hz), 108.95 t.t (CHF_2, J = 251.1, 37.1 Hz), 112.49 t.t (CF_2, J = 251.8, 29.5 Hz), 118.46 q (CF_3, J = 319.5 Hz). ^{19}F NMR spectrum (CD_3CN), δ_F, ppm: –74.48 s (3F, CF_3), –123.63 t (2F, CF_2, J = 11.9 Hz), –137.00 d (2F, CF_2H, J = 52.8 Hz).

2,2,3,3,4,4,5,5-Octafluoropentyl trifluoromethanesulfonate was prepared by the procedure described in [5]. Yield 36%, bp 146–148°C, n_D^{24} = 1.3190; published data [19]: bp 69–72°C (21 mm), n_D^{25} = 1.3191. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.80 t (2H, CH_2, J = 12.5 Hz), 6.04 t.t (1H, CHF_2, J = 51.8, 5.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 68.10 t (CHF_2, J = 27.8 Hz), 107.56 t.t (CF_2H, J = 254.8, 31.6 Hz), 112.90 t.t (CF_2, J = 254.8, 31.6 Hz), 118.48 q (CF_3, J = 319.2 Hz); weak signals of the other CF_2 groups could not be identified. ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –74.20 s (3F, CF_3), –120.12 m (2F, CH_2CF_2), –124.90 m (2F, $CH_2CF_2C\mathbf{F}_2$), –129.50 m (2F, $C\mathbf{F}_2CF_2H$), –137.25 d.m (2F, CHF_2, J = 51.9 Hz).

2,2,3,3,4,4,5,5,6,6,7,7-Dodecafluoroheptyl trifluoromethanesulfonate was prepared by the procedure described in [5]. Yield 40%, bp 186–190°C, n_D^{24} = 1.3190; published data [19]: bp 75–78°C (9 mm), n_D^{25} = 1.3194. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.80 t (2H, CH_2, J = 12.4 Hz), 6.03 t (1H, CHF_2, J = 51.9, 5.1 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 68.22 t (CH_2, J = 28.0 Hz), 107.70 t.t (CHF_2, J = 254.9, 31.7 Hz), 113.09 t.t ($CH_2\mathbf{C}F_2$, J = 254.9, 31.7 Hz), 118.56 q (CF_3, J = 318.9 Hz); signals of the other CF_2 groups were not identified due to their weak intensity and overlap. ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –74.95 s (CF_3), –120.48 s (CF_2), –122.55 s (CF_2), –123.58 s (CF_2), –123.92 s (CF_2), –130.05 s (CF_2), –137.97 d (CHF_2, J = 51.9 Hz).

1-Methyl-2,3,4,6,7,8,9,10-octahydropyrimido-[1,2-*a*]azepin-1-ium trifluoromethanesulfonate (II). Compound **Ia**, 0.304 g (2 mmol), was added to a solution of 0.33 g (2 mmol) of methyl trifluoromethanesulfonate in 1 ml of $CDCl_3$ or CH_2Cl_2, and the mixture was stirred for 40 min at room temperature and evaporated. Yield 0.58 g (100%), colorless liquid, n_D^{24} = 1.4681. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.48 m (6H, 7-H, 8-H, 9-H), 1.84 m (2H, 3-H), 2.57 m (2H, 10-H), 3.00 s (3H, CH_3), 3.25 m (4H, 4-H, 6-H), 3.37 m (2H, 2-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.03 (C^3), 21.27 (C^8), 25.32 (C^7), 27.76 (C^{10}), 27.82 (C^9), 40.29 (CH_3), 47.95 (C^4), 48.05 (C^6), 54.39 (C^2), 120.06 q (CF_3, J = 320.9), 165.95 (C=N). ^{19}F NMR spectrum ($CDCl_3$): δ_F –78.45 ppm.

1-Ethyl-2,3,4,6,7,8,9,10-octahydropyrimido-[1,2-*a*]azepin-1-ium bromide (III) was synthesized by the procedure described in [2]. A mixture of 3.04 g (0.02 mol) of compound **Ia** and 6.53 g (0.06 mol) of ethyl bromide was heated for 20 min under reflux and evaporated. Yield 5.22 g (100%), mp 97°C. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.18 t (3H, CH_3), 1.69 m (6H, 7-H, 8-H, 9-H), 2.07 m (2H, 3-H), 2.83 m (2H, 10-H), 3.53 t (2H, 4-H or 6-H, J = 5.3 Hz), 3.54 q (2H, $C\mathbf{H}_2CH_3$), 3.58 t (2H, 6-H or 4-H, J = 6.1 Hz), 3.64 m (2H, 2-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.67 (CH_3), 20.03 (C^3), 22.83 (C^8), 25.86 (C^7), 28.08 (C^9), 28.32 (C^{10}), 46.45 (C^4), 49.00 (C^6), 49.21 ($\mathbf{C}H_2CH_3$), 55.24 (C^2), 166.06 (C=N). Found, %:

C 50.40; H 8.83; Br 31.73; N 11.05. $C_{11}H_{21}BrN_2$. Calculated, %: C 50.58; H 8.10; Br 30.59; N 10.72.

1-Ethyl-2,3,4,6,7,8,9,10-octahydropyrimido-[1,2-*a*]azepin-1-ium trifluoromethanesulfonate (IV). A solution of 2.76 g (0.018 mol) of lithium trifluoromethanesulfonate in 10 ml of water was added to a solution of 4.62 g (0.018 mol) of salt **III** in 15 ml of water. The mixture was stirred for 40 min at room temperature and evaporated, methylene chloride was added to the residue, the precipitate was filtered off, and the filtrate was evaporated. Yield 5.84 g (100%), yellowish liquid. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.18 t (3H, CH_3), 1.70 m (6H, 7-H, 8-H, 9-H), 2.06 m (2H, 3-H), 2.80 m (2H, 10-H), 3.52 m (6H, C**H**$_2$CH$_3$, 4-H, 6-H), 3.62 m (2H, 2-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.42 (CH_3), 19.85 (C^3), 22.75 (C^8), 25.78 (C^7), 27.99 (C^9), 28.21 (C^{10}), 46.22 (C^4), 48.79 (C^6), 48.96 (**C**H$_2$CH$_3$), 54.99 (C^2), 120.32 q (CF_3, J_{CF} = 319.9 Hz), 166.08 (C=N). ^{19}F NMR spectrum ($CDCl_3$): δ_F –78.32 ppm. Found, %: C 44.01; H 6.69; F 16.28; N 8.74; S 9.71. $C_{12}H_{21}F_3N_2O_3S$. Calculated, %: C 43.63; H 6.41; F 17.25; N 8.48; S 9.71.

1-Butyl-2,3,4,6,7,8,9,10-octahydropyrimido-[1,2-*a*]azepin-1-ium chloride (V) was synthesized as described above for compound **III**; the reaction mixture was heated for 5 h at the boiling point. mp 42°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.87 t (3H, CH_3, J = 7.3 Hz), 1.28 m (2H, C**H**$_2$CH$_3$), 1.54 m (2H, C**H**$_2$-CH$_2$CH$_3$), 1.70 m (6H, 7-H, 8-H, 9-H), 2.10 m (2H, 3-H), 2.89 m (2H, 10-H), 3.47 m (2H, C**H**$_2$CH$_2$CH$_2$-CH$_3$), 3.57 t (2H, 4-H or 6-H, J = 5.7 Hz), 3.64 t (2H, 6-H or 4-H, J = 6.0 Hz), 3.72 m (2H, 2-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.52 (CH_3), 19.64 (C^3), 20.16 (**C**H$_2$CH$_3$), 23.08 (C^8), 25.98 (C^7), 28.17 (C^9), 28.40 (C^8), 30.66 (**C**H$_2$CH$_2$CH$_3$), 47.31 (C^4), 49.32 (C^6), 53.93 (**C**H$_2$CH$_2$CH$_2$CH$_3$), 55.33 (C^2), 166.36 (C=N). Found, %: C 63.46; H 10.70; Cl 14.76; N 11.80. $C_{13}H_{25}ClN_2$. Calculated, %: C 63.78; H 10.29; Cl 14.48; N 11.44.

1-Butyl-2,3,4,6,7,8,9,10-octahydropyrimido-[1,2-*a*]azepin-1-ium *p*-toluenesulfonate (VI) was synthesized from salt **V** and sodium *p*-toluenesulfonate; the reaction mixture was stirred for 4 h at 60°C. $n_D^{23.5}$ = 1.4355. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.74 t (3H, CH_3, J = 7.3 Hz), 1.13 m (2H, C**H**$_2$CH$_3$), 1.36 m (2H, C**H**$_2$CH$_2$CH$_3$), 1.52 m (6H, 7-H, 8-H, 9-H), 1.88 quint (2H, 3-H, J = 5.9 Hz), 2.14 s (3H, CH_3), 2.66 (2H, 10-H), 3.34 m (6H, 4-H, 6-H, C**H**$_2$-CH$_2$CH$_2$CH$_3$), 3.47 m (2H, 2-H), 6.93 d (2H, *m*-H, J = 7.9 Hz), 7.57 d (2H, *o*-H, J = 8.0 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.22 (CH_3), 19.25 (C^3), 19.64 (CH_3), 20.78 (**C**H$_2$CH$_3$), 22.48 (C^8), 22.58 (C^7), 25.53 (C^9), 27.82 (C^8), 30.20 (**C**H$_2$CH$_2$CH$_3$), 46.68 (C^4), 48.66 (C^6), 53.34 (**C**H$_2$CH$_2$CH$_2$CH$_3$), 54.67 (C^2), 125.52 (C^o), 127.89 (C^m), 138.21 (C^p), 144.20 (C^i), 165.93 (C=N).

1-Butyl-2,3,4,6,7,8,9,10-octahydropyrimido-[1,2-*a*]azepin-1-ium trifluoromethanesulfonate (VII) was synthesized as described above for salt **IV**. $n_D^{22.5}$ = 1.4455. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.76 t (3H, CH_3, J = 7.3 Hz), 1.17 m (2H, C**H**$_2$CH$_3$), 1.42 m (2H, C**H**$_2$CH$_2$CH$_3$), 1.58 m (6H, 7-H, 8-H, 9-H), 1.94 quint (2H, 3-H, J = 5.7 Hz), 2.65 m (2H, 10-H), 3.30 m (2H, C**H**$_2$CH$_2$CH$_2$CH$_3$), 3.34 t (2H, 4-H or 6-H, J = 5.7 Hz), 3.39 t (2H, 6-H or 4-H, J = 6.0 Hz), 3.48 m (2H, 2-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.12 (CH_3), 19.19 (C^3), 19.49 (**C**H$_2$CH$_3$), 22.48 (C^8), 25.44 (C^7), 27.74 (C^9), 27.94 (C^{10}), 30.08 (**C**H$_2$CH$_2$CH$_3$), 46.63 (C^4), 48.65 (C^6), 53.39 (**C**H$_2$CH$_2$CH$_2$CH$_3$), 54.69 (C^2), 120.36 q (CF_3, J_{CF} = 320.8 Hz), 165.93 (C=N). ^{19}F NMR spectrum ($CDCl_3$): δ_F –78.36 ppm. Found, %: C 46.83; H 7.90; F 15.81; N 7.78; S 8.73. $C_{14}H_{25}F_3N_2O_3S$. Calculated, %: C 46.91; H 7.03; F 15.90; N 7.82; S 8.95.

1-Benzyl-2,3,4,6,7,8,9,10-octahydropyrimido-[1,2-*a*]azepin-1-ium chloride (VIII) was synthesized as described above for salt **III**; the reaction mixture was heated for 4 h at the boiling point. Compound **VIII** was isolated as light brown transparent syrupy material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.64 s (2H, 8-H), 1.78 s (4H, 7-H, 9-H), 2.21 m (2H, 3-H), 2.95 m (2H, 10-H), 3.71 t (2H, 4-H or 6-H, J = 5.6 Hz), 3.77 t (2H, 6-H or 4-H, J = 5.6 Hz), 3.82 br.s (2H, 2-H), 4.89 s (2H, PhC**H**$_2$), 7.21 d (2H, *o*-H), 7.36 m (3H, *p*-H, *m*-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.99 (C^3), 22.34 (C^8), 25.78 (C^7), 28.03 (C^9), 28.97 (C^{10}), 47.61 (C^4), 49.30 (C^6), 55.44 (C^2), 56.73 (**C**H$_2$Ph), 126.10 (C^o), 128.15 (C^i), 129.06 (C^m), 133.97 (C^p), 167.14 (C=N).

1-Benzyl-2,3,4,6,7,8,9,10-octahydropyrimido-[1,2-*a*]azepin-1-ium trifluoromethanesulfonate (IX) was synthesized as described above for salt **IV**. Light brown syrupy material. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.53 s (2H, 8-H), 1.68 s (4H, 7-H, 9-H), 2.09 m (2H, 3-H), 2.77 m (2H, 10-H), 3.51 t (2H, 4-H or 6-H, J = 5.6 Hz), 3.57 t (2H, 6-H or 4-H, J = 5.7 Hz), 3.64 m (2H, 2-H), 4.70 s (2H, PhC**H**$_2$), 7.14 d (2H, *o*-H), 7.26 t (1H, *p*-H), 7.33 t (2H, *m*-H). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.77 (C^3), 22.39 (C^8),

25.69 (C^7), 28.29 (C^9), 28.77 (C^{10}), 47.48 (C^4), 49.13 (C^6), 55.29 (C^2), 56.51 (**C**H_2Ph), 120.16 q (CF_3, J = 319.1 Hz), 126.19 (C^o), 128.18 (C^i), 129.17 (C^m), 134.34 (C^p), 167.22 (C=N). ^{19}F NMR spectrum ($CDCl_3$): δ_F –78.33 ppm.

1-(2,2,3,3-Tetrafluoropropyl)-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]azepin-1-ium *p*-toluenesulfonate (X) was synthesized as described above for salt **II** from compound **Ia** and 2,2,3,3-tetrafluoropropyl *p*-toluenesulfonate; the reaction mixture was stirred for 45 min at 60°C. n_D^{20} = 1.5009. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.48 m (2H, 8-H), 1.55 m (4H, 7-H, 9-H), 1.71 quint (2H, 3-H), 2.36 s (3H, CH_3), 3.15 m (8H, 2-H, 4-H, 6-H, 10-H), 4.23 t.t (2H, CH_2CF_2, J = 12.2, 1.1 Hz), 5.77 t.t (1H, CHF_2, J = 52.9, 4.2 Hz), 7.28 d (2H, *m*-H, J = 8.3 Hz), 7.69 d (*o*-H, J = 8.3 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.42 (C^3), 21.87 (CH_3), 25.52 (C^8), 28.06 (C^7), 29.40 (C^9), 36.39 (C^{10}), 43.11 (C^4), 48.16 (C^6), 52.80 (C^2), 63.93 t (**C**H_2CF_2, J = 30.2 Hz), 108.53 t.t (CHF_2, J = 250.0, 35.3 Hz), 113.02 t.t (CH_2CF_2, J = 251.5, 28.1 Hz), 127.81 (C^o), 129.96 (C^m), 131.39 (C^p), 145.78 (C^i), 161.93 (C=N). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –124.37 s (2F, CH_2CF_2), –138.29 d (2F, CHF_2, J = 52.8 Hz). Found, %: C 51.81; H 5.75; S 7.89. $C_{19}H_{26}F_4N_2O_3S$. Calculated, %: C 52.04; H 5.98; S 7.31.

1-(2,2,3,3-Tetrafluoropropyl)-2,3,4,6,7,8,9,10-octahydropyrimido[1,2-*a*]azepin-1-ium trifluoromethanesulfonate (XI) was synthesized as described above for salt **II** from compound **Ia** and 2,2,3,3-tetrafluoropropyl trifluoromethanesulfonate. Yield 75%, mp 79–80°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.79 s (6H, 7-H, 8-H, 9-H), 2.19 m (2H, 3-H), 2.87 m (2H, 10-H), 3.63 t (2H, 2-H), 3.70 m (4H, 4-H, 6-H), 4.24 t (2H, CH_2CF_2, J = 15.1 Hz), 6.09 t.t (1H, CHF_2, J = 52.8, 3.6 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 19.67 (C^3), 22.31 (C^8), 22.41 (C^7), 25.30 (C^9), 28.30 (C^{10}), 49.44 (C^4), 49.57 (C^6), 51.66 t (**C**H_2CF_2, J = 21.2 Hz), 56.04 (C^2), 109.23 t.t (CHF_2, J = 250.1, 35.9 Hz), 115.09 t.t (CH_2CF_2, J = 250.7, 28.6 Hz), 120.60 q (CF_3, J = 320.2 Hz), 169.43 (C=N). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: –78.47 s (3F, CF_3), –120.31 s (2F, CH_2CF_2), –136.81 d (2F, CHF_2, J = 52.8 Hz). Found, %: C 37.37; H 4.84; N 6.86; S 7.52. $C_{13}H_{19}F_7N_2O_3S$. Calculated, %: C 37.50; H 4.60; N 6.73; S 7.70.

1-Butylpyridinium chloride (XII) was synthesized as described above for salt **III** from pyridine and 1-chlorobutane. Yield 20%, mp 103°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t (3H, CH_3, J = 7.3 Hz), 1.38 m (2H, C**H**$_2CH_3$), 2.01 m (2H, C**H**$_2CH_2CH_3$), 5.03 t (2H, NCH_2, J = 7.3 Hz), 8.12 t (2H, 3-H, 5-H, J = 6.6 Hz), 8.47 t (1H, 4-H, J = 7.7 Hz), 9.72 d (2H, 2-H, 6-H, J = 5.9 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 13.45 (CH_3), 19.28 (**C**H_2CH_3), 33.89 (**C**H_2CH_2-CH_3), 61.64 (NCH_2), 128.34 (C^3, C^5), 144.80 (C^4), 145.48 (C^2, C^6).

1-Butylpyridinium bromide (XIII) was synthesized as described above for salt **III** from pyridine and excess 1-boromobutane. Yield 94%, mp 99°C. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 0.93 t (3H, CH_3, J = 7.3 Hz), 1.35 m (2H, C**H**$_2CH_3$), 4.72 m (2H, NCH_2), 8.08 t (2H, 3-H, 5-H, J = 6.2 Hz), 8.55 t (1H, 4-H, J = 7.5 Hz), 9.14 m (2H, 2-H, 6-H); the C**H**$_2CH_2CH_3$ signal was obscured by the signal from the residual protons in the solvent. ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 13.60 (CH_3), 19.70 (**C**H_2CH_3), 33.86 (**C**$H_2CH_2CH_3$), 61.92 (NCH_2), 129.06 (C^3, C^5), 145.63 (C^2, C^6), 146.39 (C^4).

1-Butylpyridinium trifluoromethanesulfonate (XIV) was synthesized as described above for salt **IV**. Light brown liquid, n_D^{22} = 1.4606. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.94 t (3H, CH_3, J = 7.3 Hz), 1.36 m (2H, C**H**$_2CH_3$), 1.98 m (2H, C**H**$_2CH_2CH_3$), 4.68 t (2H, NCH_2, J = 7.5 Hz), 8.05 t (2H, 3-H, 5-H, J = 5.6 Hz), 8.47 t (1H, 4-H, J = 7.7 Hz), 8.98 d (2H, 2-H, 6-H, J = 5.5 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 12.74 (CH_3), 18.62 (**C**H_2CH_3), 32.84 (**C**$H_2CH_2CH_3$), 61.40 (NCH_2), 120.58 q (CF_3, J = 320.1 Hz), 128.08 (C^3, C^5), 144.12 (C^2, C^6), 145.08 (C^4). ^{19}F NMR spectrum ($CDCl_3$): δ_F –79.13 ppm. Found, %: C 42.22; H 4.96; F 19.44; N 4.94; S 10.80. $C_{10}H_{14}F_3NO_3S$. Calculated, %: C 42.10; H 4.95; F 19.98; N 4.91; S 11.24.

1-Benzylpyridinium chloride (XV) was synthesized as described above for salt **III** from pyridine and excess 1-chlorobutane. Yield 100%, mp 129°C. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 6.15 s (2H, NCH_2), 7.40 m (3H, *m*-H, *p*-H), 7.67 m (2H, *o*-H), 8.04 t (2H, 3-H, 5-H, J = 6.8 Hz), 8.50 t (1H, 4-H, J = 7.8 Hz), 9.53 d (2H, 2-H, 6-H, J = 5.8 Hz). ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 64.23 (CH_2), 129.27 (C^p), 130.17 (C^o), 130.23 (C^m), 130.45 (C^3, C^5), 135.04 (C^i), 146.02 (C^2, C^6), 146.75 (C^4).

1-Benzylpyridinium trifluoromethanesulfonate (XVI) was synthesized as described above for salt **IV**. mp 61°C. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 5.77 s (2H, NCH_2), 7.46 m (5H, C_6H_5), 8.04 t (2H, 3-H, 5-H, J = 7.0 Hz), 8.52 t.t (1H, 4-H, J = 1.0, 7.8 Hz), 8.86 d

(2H, 2-H, 6-H, J = 5.6 Hz). ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 65.24 (CH_2), 121.93 q (CF_3, J = 320.1 Hz), 129.51 (C^p), 130.11 (C^o), 130.38 (C^m), 130.75 (C^3, C^5), 134.03 (C^i), 145.46 (C^2, C^6), 147.08 (C^4). ^{19}F NMR spectrum (CD_3CN): δ_F –79.045 ppm.

1-(2,2,3,3-Tetrafluoropropyl)pyridinium trifluoromethanesulfonate (XVII) was synthesized as described above for salt **II** from pyridine and 2,2,3,3-tetrafluoropropyl trifluoromethanesulfonate. Light brown liquid. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 5.35 t (2H, CH_2CF_2, J = 15.0 Hz), 6.41 t.t (1H, CHF_2, J = 52.0, 4.0 Hz), 8.19 t (2H, 3-H, 5-H, J = 7.2 Hz), 8.72 t.t (1H, 4-H, J = 1.1, 7.8 Hz), 8.87 d (2H, 2-H, 6-H, J = 5.9 Hz). ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 59.36 t (**C**H_2CF_2, J = 21.7 Hz), 110.30 t.t (CHF_2, J = 249.2, 34.2 Hz), 114.69 t.t (CH_2**C**F_2, J = 252.9, 28.7 Hz), 121.97 q (CF_3, J = 320.1 Hz), 129.90 (C^3, C^5), 147.69 (C^2, C^6), 149.30 (C^4). ^{19}F NMR spectrum (CD_3CN), δ_F, ppm: –79.25 s (3F, CF_3), –122.23 s (2F, CH_2CF_2), –137.70 d.t (2F, CHF_2, J = 52.2, 3.1 Hz).

1-(2,2,3,3,4,4,5,5-Octafluoropentyl)pyridinium trifluoromethanesulfonate (XVIII) was synthesized as described above for salt **II** from pyridine and 2,2,3,3,4,4,5,5-octafluoropentyl trifluoromethanesulfonate. Light brown liquid. ^{1}H NMR spectrum (CD_3CN), δ, ppm: 5.58 t (2H, CH_2CF_2, J = 15.4 Hz), 6.55 t.t (1H, CHF_2, J = 51.0, 5.3 Hz), 8.22 t (2H, 3-H, 5-H, J = 7.2 Hz), 8.75 t (1H, 4-H, J = 7.9 Hz), 8.97 d (2H, 2-H, 6-H, J = 6.0 Hz). ^{13}C NMR spectrum (CD_3CN), δ_C, ppm: 59.23 t (**C**H_2CF_2, J = 20.5 Hz), 109.08 t.t (CHF_2, J = 253.5, 31.6 Hz), 119.48 q (CF_3, J = 319.6 Hz), 130.15 (C^3, C^5), 148.09 (C^2, C^6), 149.77 (C^4); signals from carbons atoms in the other CF_2 groups were not identified. ^{19}F NMR spectrum (CD_3CN), δ_F, ppm: –79.41 s (3F, CF_3), –118.08 quint (2F, CH_2CF_2, J = 13.6 Hz), –124.78 m (2F, CH_2CF_2C**F**$_2$), –130.04 m (2F, C**F**$_2CF_2H$), –139.00 d.m (2F, CHF_2, J = 51.0 Hz).

REFERENCES

1. Wasserscheid, P. and Keim, W., *Angew. Chem., Int. Ed. Engl*., 2000, vol. 39, p. 3772.
2. Wilkes, J.S., Levisky, J.A., Wilson, R.A., and Hyssey, C.L., *Inorg. Chem*., 1982, vol. 21, p. 1263.
3. Green, L., Hemeon, I., and Singer, R.D., *Tetrahedron Lett*., 2000, vol. 41, p. 1343.
4. Hardacre, Ch., Holbrey, J.D., Katdare, S.P., and Seddon, R.R., *Green Chem*., 2002, vol. 4, p. 143.
5. Bonhote, P., Dias, A-P., Papageorgiou, N., Kalyanasundaram, K., and Gratzel, M., *Inorg. Chem*., 1996, vol. 35, p. 1168.
6. Kitazume, T., Zulfiqar, F., and Tanaka, G., *Green Chem*., 2000, vol. 2, p. 133.
7. Zulfiqar, F. and Kitazume, T., *Green Chem*., 2000, vol. 2, p. 137.
8. McFarlane, D.R., Sun, J., Golding, J., Meakin, P., and Forsyth, M., *Electrochim. Acta*, 2000, vol. 45, p. 1271.
9. Arduengo, A.J., III, *Acc. Chem. Res*., 1999, vol. 32, p. 913.
10. Xu, L., Chen, W., and Xiao, J., *Organometallics*, 2000, vol. 19, p. 1123.
11. Clement, N.D., Cavell, K.J., Jones, K., and Elsevier, C.J., *Angew. Chem., Int. Ed*., 2004, vol. 43, p. 1277.
12. Stang, P.J., Hanack, M., and Subramanian, L.R., *Synthesis*, 1982, p. 85.
13. McBee, E.T., Battershell, R.D., and Braendlin, H.P., *J. Am. Chem. Soc*., 1962, vol. 84, p. 3157.
14. Merrigan, T.L., Bates, E.D., Dorman, S.C., and Davis, J.H., Jr., *Chem. Commun*., 2000, p. 2051.
15. Singh, R.P., Manandhar, S., and Shreeve, J.M., *Tetrahedron Lett*., 2002, vol. 43, p. 9497.
16. Beard, C.D., Baum, K., and Grakauskas, V., *J. Org. Chem*., 1973, vol. 38, p. 3673.
17. Cohen, W.V., *J. Org. Chem*., 1961, vol. 26, p. 4021.
18. Hansen, R.L., *J. Org. Chem*., 1965, vol. 30, p. 322.
19. Hansen, R.L., Fr. Patent no. 1470669, 1967; *Chem. Abstr*., 1967, vol. 67, p. 63788.