Nitrile-Functionalized Pyridinium, Pyrrolidinium, and Piperidinium Ionic Liquids

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Supporting Information

ABSTRACT: Two series of 1-alkylpyridinium and *N*-alkyl-*N*-methylpiperidinium ionic liquids functionalized with a nitrile group at the end of the alkyl chain have been synthesized. Structural modifications include a change of the alkyl spacer length between the nitrile group and the heterocycle of the cationic core, as well as adding methyl or ethyl substituents on different positions of the pyridinium ring. The anions are the bromide and the bis(trifluoromethylsulfonyl)imide ion. All the bis(trifluoromethylsulfonyl)imide salts as well as the bromide salts with a long alkyl spacer were obtained as viscous liquids at



room temperature, but some turned out to be supercooled liquids. In addition, pyrrolidinium and piperidinium ionic liquids with two nitrile functions attached to the heterocyclic core have been prepared. The crystal structures of seven pyridinium bis-(trifluoromethylsulfonyl)imide salts are reported. Quantum chemical calculations have been performed on model cations and ion pairs with the bis(trifluoromethylsulfonyl)imide anion. A continuum model has been used to take solvation effects into account. These calculations show that the natural partial charge on the nitrogen atom of the nitrile group becomes more negative when the length of the alkyl spacer between the nitrile functional group and the heterocyclic core of the cation is increased. Methyl or methoxy substituents on the pyridinium ring slightly increase the negative charge on the nitrile nitrogen atom due to their electron-donating abilities. The position of the substituent (ortho, meta, or para) has only a very minor effect on the charge of the nitrogen atom. The ¹⁵N NMR spectra of the bis(trifluoromethylsulfonyl)imide ionic liquids were recorded with the nitrogen-15 nucleus at its natural abundance. The chemical shift of the ¹⁵N nucleus of the nitrile nitrogen atom could be correlated with the calculated negative partial charge on the nitrogen atom.

■ INTRODUCTION

Ionic liquids are solvents that are composed entirely of ions.^{1–3} They can possess properties that make them of interest for potential technological applications.⁴ For instance, many ionic liquids have an extremely low vapor pressure, a very large liquidus range, a very wide electrochemical window and an intrinsic ionic conductivity. Depending on their composition, they can be miscible or immiscible with organic solvents or water. Ionic liquids can be used as solvents for chemical reactions, including catalytic reactions.^{5–8} They can act as solvents for the synthesis of unusual inorganic compounds.^{9–13} Several ionic liquid exhibit liquid–crystalline behavior.¹⁴ They find use in electrochemical applications,¹⁵ for example as electrolytes in batteries,^{16,17} and in photovoltaic devices,^{18–20} but also as a medium for electrodeposition^{21–23} of metals. Many ionic liquids contain a 1-alkyl-3-methylimidazolium, 1-alkylpyridinium, *N*-alkyl-*N*-methylpyrrolidinium, quaternary ammonium, or a quaternary phosphonium group as the cation. Typical anions are chloride, bromide, acetate, diethylphosphate, triflate, dicyanamide, tetrafluoroborate, hexafluorophosphate, and the very important bis(trifluoromethylsulfonyl)imide (= bistriflimide) ion. However, a disadvantage of ionic liquids with weakly coordinating anions such as the bis(trifluoromethylsulfonyl)imide is their limited solubilizing ability for inorganic salts. This is a drawback for applications that require high concentrations of dissolved metal salts, e.g., the electrodeposition of reactive metals. A solution to this problem is to use ionic liquids with strongly coordinating anions, for instance chloride ions, but these ionic liquids have typically high melting points or there are stability issues as in the case of ionic liquids with β -diketonate anions.²⁴ Another possibility is to use functionalized ionic liquids, i.e., ionic liquids with functional, coordinating groups appended to the ionic liquid cation. A commonly used name for this type of ionic

Received:	March 24, 2011
Revised:	May 24, 2011
Published:	May 24, 2011



Figure 1. Overview of the nitrile-functionalized cations.

liquid is "task-specific ionic liquids", ^{25,26} but we prefer the term "functionalized ionic liquids". An example of such a functionalized ionic liquid is an imidazolium salt incorporating a thiourea moiety, which has been used for the extraction of mercury(II) and cadmium(II) from an aqueous phase.²⁷ Functionalized ionic liquids with appended tertiary phosphine groups have been used to immobilize rhodium(I) organometallic catalysts in [C4mim]- $[PF_6]$.^{28,29} During the last four years, we have developed ionic liquids functionalized with a carboxylic acid group.³⁰⁻³³ These ionic liquids are remarkable in their ability to dissolve large amounts of metal oxides or hydroxides, but they have unfortunately a poor stability against electrochemical reduction, so that they are of limited interest as solvents for electrodeposition of metals. Functionalized ionic liquids with a higher electrochemical stability are those containing a nitrile group. Nitrile-functionalized ionic liquids were first introduced by Dyson and co-workers.³⁴ The nitrile function is in general appended to the cationic core via

an alkyl spacer,^{35–40} although Hardacre et al. prepared ionic liquids with the nitrile group directly bonded to the heterocyclic ring of the cation.^{41–43} Nitrile-functionalized methimazolebased ionic liquids have been used for the extraction of Ag⁺ ions.⁴⁴ Ionic liquids with nitrile-functionalized anions have also been described.^{45,46} The dicyanamide anion is a well-known anion for obtaining low-viscous ionic liquids.⁴⁷ Recently we have reported on nitrile-functionalized pyrrolidinium ionic liquids, and we have found that the coordination chemistry of cobalt(II) in these ionic liquids strongly depends on the length of the alkyl spacer between the nitrile group and the nitrogen atom of the pyrrolidinium cation.⁴⁸ An important parameter determining the coordinating behavior of the nitrile function is the value of the negative partial charge on the nitrile nitrogen atom.

In order to investigate the influence of the structure of the ionic liquid cation on the charge distribution of the nitrile group and on the thermal properties, we synthesized a series of 50 nitrile-functionalized

Table 1.	Melting Points ($T_{\rm m}$) and	Decomposition	Tem
peratures	(T_d) of Ionic Lie	quids		

compound ^a	$T_{\rm m}$ (°C)	$T_{\rm d}$ (°C)
1-Br	160	210
2-Br	145	230
3-Br	83	255
6-Br	193	205
7-Br	183	220
8-Br	194	215
9-Br	160	220
10-Br	124	260
12-Br	139	250
13-Br	142	260
17-Br	120	220
18-Br	173	205
19-Br	152	260
21-Br	182	200
22-Br	192	220
23-Br	137	280
24-Br	142	205
25-Br	199	320
1-Tf ₂ N	44	390
8-Tf ₂ N	51	400
17-Tf ₂ N	48	380
24-Tf ₂ N	58	415
25-Tf ₂ N	62	415

^{*a*} Compounds not listed in this table are room-temperature ionic liquids. Their physicochemical properties are given in Table 2.

pyridinium, pyrrolidinium, and piperidinium ionic liquids with bromide and bis(trifluoromethylsulfonyl)imide anions. Pyrrolidinium and piperidinium ionic liquids with two nitrile functions attached to the heterocyclic core have been prepared as well. It should be noted that the piperidinium ring can be considered as the saturated analogue of the pyridinium ring. An overview of the cations considered in this study is given in Figure 1. The naming of the actual ionic liquids is a combination of the cation number and the bromide (Br) or bis(trifluoromethylsulfonyl)imide (Tf₂N) anion, for instance 1-Br or 1-Tf₂N. The crystal structure of several of the pyridinium ionic liquids has been determined in order to determine the cation-anion interactions in these functionalized ionic liquids. The charge distribution in the cation has been determined by density functional theory (DFT) calculations and was experimentally verified via the chemical shift of the nitrile group in the ¹⁵N NMR spectra.

EXPERIMENTAL SECTION

General Techniques. Elemental analyses (carbon, hydrogen, nitrogen) were conducted on a CE Instruments EA-1110 elemental analyzer. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance 300 spectrometer (operating at 300 MHz for ¹H and at 75.5 MHz for ¹³C). ¹⁵N NMR spectra were recorded on a Bruker 600 MHz Avance II spectrometer at 60.83 MHz frequency on a BBO 10 mm probe. Neat CH₃NO₂ was used as external standard for ¹⁵N chemical shift. The pulse program *zgig* was used with a pulse length of 28.3 μ s and a power level of -1.5 dB. The water content of the ionic liquids was determined by a coulometric Karl Fischer titrator (Mettler Toledo Coulometric

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Table 2.	Physicoc	hemical	Properties	of Re	oom-T	emperat	ure
Nitrile-F	unctionali	zed Ion	nic Liquids				

	$T_{\rm d}$	viscosity	ρ	water
compound ^a	$(^{\circ}C)^{b}$	$(cP)^c$	$(g \text{ cm}^{-3})^d$	content (ppm) ^e
4-Br	245	f	n.d. ^g	n.d.
5-Br	240	f	n.d.	n.d.
11-Br	270	f	n.d.	n.d.
14-Br	265	f	n.d.	n.d.
15-Br	255	f	n.d.	n.d.
16-Br	250	f	n.d.	n.d.
20-Br	250	f	n.d.	n.d.
$2 - Tf_2N$	360	326	1.50	60
$3-Tf_2N$	415	363	1.54	55
4-Tf ₂ N	410	150	1.45	73
5-Tf ₂ N	415	320	1.33	45
6-Tf ₂ N	390	280	1.56	30
$7-Tf_2N$	405	164	1.61	40
9-Tf ₂ N	410	578	1.53	40
$10-Tf_2N$	420	325	1.49	50
11-Tf ₂ N	430	168	1.43	29
12-Tf ₂ N	420	308	1.50	70
13-Tf ₂ N	440	165	1.43	90
14-Tf ₂ N	430	180	1.37	40
15-Tf ₂ N	420	167	1.40	80
16-Tf ₂ N	425	197	1.45	61
19-Tf ₂ N	430	297	1.45	30
20-Tf ₂ N	425	157	1.48	58
$21 - Tf_2N$	420	567	1.55	83
22-Tf ₂ N	410	481	1.53	67
23-Tf ₂ N	425	408	1.46	50

^{*a*} The compounds not listed in this table are solid at room temperature. ^{*b*} Onset of thermal decomposition. Determined by DSC. ^{*c*} The viscosities have been measured at 19 °C. ^{*d*} Mass density, measured at 19 °C. ^{*c*} The water content was measured by coulometric Karl Fischer titration. ^{*f*} The compounds were obtained as very viscous liquids. ^{*g*} n.d. = not determined.

Karl Fischer Titrator, model DL39). The viscosity of the ionic liquids was measured by the falling ball method (Gilmont Instruments). Differential scanning calorimetry (DSC) measurements were made on a Mettler-Toledo DSC822e module (scan rate of $10 \,^{\circ}$ C min⁻¹ under helium flow). DSC was used to determine the melting point and the onset temperature for thermal decomposition. The organic chemicals were purchased from Acros or from Sigma-Aldrich. Lithium bis(trifluoromethylsulfonyl)imide was obtained from IoLiTec (Denzlingen, Germany). All chemicals were used as received, without any additional purification step.

X-ray Crystallography. X-ray intensity data were collected at 100 K on a SMART 6000 diffractometer equipped with CCD detector using Cu–K α radiation ($\lambda = 1.54178$ Å). The images were interpreted and integrated with the program SAINT from Bruker.⁴⁹ All seven structures were solved by direct methods and refined by full-matrix least-squares on F² using the SHELXTL program package.^{50,51} Non-hydrogen atoms were anisotropically refined, and the hydrogen atoms in the riding mode and isotropic temperature factors were fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups). For the structure of compound 11-Tf₂N, the X-H distances could be left free to refine. CCDC-824765-824771 contains the supplementary crystallographic

Table 3. Crystallographic Data of Ionic Liquids 1-Tf₂N, 3-Tf₂N, 8-Tf₂N, 9-Tf₂N, 11-Tf₂N, 17-Tf₂N and 18-Tf₂N

	1-Tf ₂ N	3-Tf ₂ N	8-Tf ₂ N	9-Tf ₂ N	11-Tf ₂ N	17-Tf ₂ N	18-Tf ₂ N
molecular formula	$C_9H_7F_6N_3O_4S_2$	$C_{11}H_{11}F_6N_3O_4S_2$	$C_{10}H_9F_6N_3O_4S_2$	$C_{11}H_{11}F_6N_3O_4S_2$	$C_{12}H_{13}F_6N_3O_4S_2$	$C_{11}H_{11}F_6N_3O_4S_2$	$C_{11}H_{11}F_6N_3O_4S_2$
formula weight (g mol^{-1})	399.32	427.37	413.34	427.37	441.39	427.37	427.37
crystal dimensions (mm ³)	$0.4\times0.3\times0.3$	$0.4\times0.3\times0.25$	$0.25\times0.25\times0.2$	$0.4\times0.3\times0.25$	$0.4\times0.35\times0.2$	0.3 imes 0.15 imes 0.1	$0.3\times0.1\times0.05$
crystal system	triclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic	triclinic
space group	<i>P</i> 1 (No. 2)	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	<i>P</i> 1 (No. 2)	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)	<i>P</i> 1 (No. 2)
a (Å)	8.1408(1)	11.2891(2)	12.687(4)	8.2118(8)	11.5159(6)	8.255(3)	8.1340(6)
b (Å)	8.7005(1)	12.2491(2)	8.186(3)	8.6844(7)	12.2778(6)	13.880(3)	12.4922(9)
c (Å)	10.5820(2)	12.4087(2)	15.537(6)	12.621(1)	12.5068(6)	14.205(4)	17.291(1)
α (°)	80.863(1)			98.692(5)			72.707(4)
β (°)	76.270(1)	97.027(1)	106.36(2)	104.289(6)	96.726(2)	92.16(2)	80.807(5)
γ (°)	81.141(1)			104.167(5)			80.637(4)
$V(Å^3)$	713.55(2)	1703.00(5)	1548(1)	824.0(1)	1756.2(2)	1626.5(8)	1643.6(2)
Ζ	2	4	4	2	4	4	4
$ ho_{ m calc}~(m gcm^{-3})$	1.859	1.667	1.773	1.723	1.669	1.745	1.727
$2\theta_{\max}$ (°)	140.1	133.2	143.0	143.0	142.6	133.2	133.2
F(000)	400	864	832	432	896	864	864
measured reflections	14976	14505	25000	10750	17312	15061	26387
unique reflections	2608	2957	2981	3042	3352	2849	5697
obs. reflections $(I > 2\sigma(I))$	2588	2847	2655	2610	3231	2676	4549
parameters refined	218	235	227	237	253	236	471
R_1	0.0283	0.0282	0.0366	0.0382	0.0300	0.0291	0.0527
wR_2	0.0750	0.0721	0.0838	0.0941	0.0755	0.0741	0.1228
R1 (all data)	0.0285	0.0293	0.0422	0.0451	0.0311	0.0310	0.0675
wR ₂ (all data)	0.0752	0.0730	0.0872	0.0993	0.0764	0.0763	0.1328
goodness of fit	1.089	1.051	1.046	1.076	1.092	1.066	1.037
$\mu \ (\mathrm{mm}^{-1})$	4.338	3.678	4.022	3.801	3.587	3.851	3.811
CCDC-entry	CCDC-824765	CCDC-824766	CCDC-824767	CCDC-824769	CCDC-824768	CCDC-824771	CCDC-824770



Figure 2. Packing in the crystal structure of compound $1-Tf_2N$.

data for this paper and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge

Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or deposit@ccdc.cam.ac.uk).



Figure 3. Close contacts in the crystal structure of compound 1-Tf₂N.



Figure 4. Close contacts in the crystal structure of compound 3-Tf₂N.

Computational Details. The programs provided by the *Turbomole*-suite have been employed.⁵² Geometry optimizations were carried out using the BLYP-D density functional,^{53–55} with the resolution of identity (RI).^{56–58} The BLYP-D functional has proven to perform very well compared to MP2 for ionic liquid ion pairs.^{59,60} For these systems dispersion forces play an important

role for equilibrium structure and interaction energy.^{61,62} The TZVP basis set was applied for structure optimization.⁶³ Furthermore, the convergency criterion of the iteration cycle was increased to 10^{-8} Hartree for all calculations. Solvation was approximated by the continuum solvation model (COSMO) with the permittivity set to 15.^{64,65} Within continuum models such as



Figure 5. Packing in the crystal structure of compound 8-Tf₂N.



Figure 6. Close contacts in the crystal structure of compound 8-Tf₂N.

COSMO, it is not possible to consider microheterogeneity which may be important for ionic liquids with longer side chains.⁶⁶ However, COSMO was successfully applied in previous calculations to determine melting points of ionic liquids.^{67,68}

RESULTS AND DISCUSSION

Synthesis and Characterization of Compounds. The bromide salts were prepared by quaternization of the nitrogen

atom of the heterocycle with ω -bromoalkanenitrile. The bis-(trifluoromethylsulfonyl)imide salts were obtained from the corresponding bromide salts by a metathesis reaction with lithium bis(trifluoromethylsulfonyl)imide in water. Because the bromide ionic liquids are totally miscible with water and the bis(trifluoromethylsulfonyl)imide ionic liquids are immiscible, phase separation occurs during the metathesis reaction. The bis(trifluoromethylsulfonyl)imide ionic liquids were washed with plenty of water until the AgNO₃ test was negative for the washing water.



Figure 7. Close contacts in the crystal structure of compound 11-Tf₂N.



Figure 8. Packing in the crystal structure of compound 9-Tf₂N.

By drying of the ionic liquids in high vacuum $(10^{-2} \text{ to } 10^{-3} \text{ mbar})$ for several hours at 75 °C, the water content could be reduced to less than about 75 ppm (determined by coulometric Karl Fischer titration). The compounds were characterized by ¹H and ¹³C NMR spectroscopy, CHN analysis and electrospray ionization mass spectrometry (ESI-MS). For the compounds that were solid at room temperature, the melting point and the onset temperature of the thermal decomposition process was measured

(Table 1), and for the compounds that were liquid at room temperature, the viscosity, density, water content, and the onset temperature for thermal decomposition were determined (Table 2). The melting points of the bromide salts strongly depend on the alkyl spacer length between the cationic core and the nitrile function. Whereas the salts with only one CH₂ group in the spacer have high melting points (above 150 °C), the melting point decreases with increasing spacer lengths, so that compounds with a



Figure 9. Close contacts in the crystal structure of compound 9-Tf₂N.



Figure 10. Packing in the crystal structure of compound 18-Tf₂N.

 $(CH_2)_5$ or longer spacer are highly viscous liquids at room temperature. The presence of methyl or ethyl groups at different positions of the pyridinium ring are less efficient for lowering the melting point than a longer alkyl spacer. The bis(trifluoromethylsulfonyl)imide salts are liquid at room temperature, or they are low-melting solids. The room-temperature ionic liquids are quite viscous, with viscosities ranging between 150 cP and 580 cP at 19 °C. The pyrrolidinium and piperidinium bromide salts are high-melting solids, with melting points between 135 and 200 °C. The corresponding bis(trifluoromethylsulfonyl)-imide salts are low-melting solids or highly viscous liquids at room temperature. The ionic liquids with bis(trifluoromethylsulfonyl)-imide anions have a high thermal stability. The onset of thermal decomposition in an inert atmosphere (helium) was observed only at temperatures above 400 °C.

Crystal Structures. Although most of the nitrile-functionalized ionic liquids with bis(trifluoromethylsulfonyl)imide ionic liquids were obtained as viscous liquids at room temperature, some of the compounds showed a tendency to crystallize upon standing in a freezer. For seven compounds $(1-Tf_2N, 3-Tf_2N, 8-Tf_2N, 11-Tf_2N, 9-Tf_2N, 17-Tf_2N, and 18-Tf_2N)$, single crystals suitable for X-ray diffraction studies could be obtained. The crystal structures of these complexes give insight into the packing of cations and anions in the crystal structure and give information on the interactions between cation and anions. The crystal-lographic data are summarized in Table 3.

In the crystal structure of compound 1-Tf₂N one pyridinium cation and one bis(trifluoromethylsulfonyl)imide anion are found in the asymmetric unit. The nitrile-functionalized alkyl chain is almost perfectly planar with the pyridinium ring. (3.1° between the planes). Two symmetry equivalent (inversion center) pyridinium cations are contacting each other; their nitrile moieties are each pointing toward a C–H hydrogen atom of the symmetry equivalent pyridine ring (C–H···N distance of 2.67 Å),



Figure 11. Close contacts between the pyridinium rings and the first bis(trifluoromethylsulfonyl) imide anion in the crystal structure of compound 18-Tf₂N.



Figure 12. Close contacts between the pyridinium rings and the second bis(trifluormethylsulfonyl) inide anion in the crystal structure of compound 18-Tf₂N.

hence forming pyridinium dimers (Figure 2). $X-Y\cdots\pi$ interactions are found in the packing between the pyridine ring and two sulfonyl oxygen atoms of the bis(trifluoromethylsulfonyl)imide anion (both distances of 3.12 Å between the O-atom and the pyridine ring centroid). The bis(trifluoromethylsulfonyl)imide sulfonyl oxygen, CF₃ fluorine, and nitrogen atoms are involved in several C-H···O, C-H···N, and C-H···F interactions between the pyridinium cation and the bis(trifluoromethylsulfonyl)imide anion. In total, seven hydrogen contacts are observed with distances ranging from 2.43 to 2.62 Å (Figure 3). Structures containing the same pyridinium cation were not found in the CSD.⁶⁹ However, structures with similar pyridinium cations have been reported, containing short alkyl chains of one carbon atom and a COOH, CH₃, COH, CONH₂ or CSeH groups.⁷⁰⁻⁷⁹ In these structures, interactions have also been observed between the C-H pyridinium ring atoms and the respective anions, together with additional interactions between the functionalizing groups and the respective anions.

The asymmetric unit of compound 3-Tf₂N contains one pyridinium cation and one bis(trifluoromethylsulfonyl)imide anion. The nitrile-functionalized alkyl chain is almost perpendicular with respect to the pyridine ring (76.0° between planes through the respective atoms), and the nitrile moiety lies in the same plane as the alkyl chain (12.5°). $X-Y\cdots\pi$ interactions are found in the packing between the nitrile and the pyridine ring (distance of 3.37 Å between the nitrile N-atom and the ring centroid) and for a sulfonyl O-atom of the anion and the pyridine ring (distance of 3.35 Å). $C-H\cdotsO$, $C-H\cdotsN$, and



Figure 13. Packing in the crystal structure of compound 17-Tf₂N.



Figure 14. Close contacts in the crystal structure of compound $17-Tf_2N$.

C–H···F interactions are observed between the pyridinium cation and the bis(trifluoromethylsulfonyl)imide anion. In fact, eight hydrogen contacts (<3 Å), which originate from four different cations are observed and range between 2.47 and 2.73 Å (Figure 4). Such interactions between the C–H hydrogen atoms of the pyridinium cation and the anion have also been reported for structures of the same pyridinium cation, but with Cl⁻ and [PdCl₄]²⁻ anions.⁸⁰ Furthermore, structures with similar pyridinium cores have been reported, containing alkyl chains with the same number of carbon atoms, but with an end-standing methyl group, and show similar interactions between the C–H pyridine hydrogen atoms and the chloride⁸¹ and bromide⁸² anions, respectively.

The asymmetric unit of **8-Tf₂N** consists of one pyridinium cation and one bis(trifluoromethylsulfonyl)imide anion. Considering the pyridinium cation, the nitrile-functionalized alkyl is almost planar with the pyridine ring (2.3° between planes through the respective atoms). The nitrile group is pointing toward a C–H pyridine ring hydrogen atom (2.58 Å), linking the pyridinium cations together in chains, parallel with (010), running in the [101] direction (Figure 5). Three of the bis(trifluoromethylsulfonyl)-imide sulfonyl oxygen atoms are contacting the C–H hydrogen atoms of the methyl group, the nitrile-functionalized chain, as well as the pyridine ring, of several pyridinium cations. In total, 10 C–H···O/F contacts (in the range of 2.39–2.69 Å) are

Table 4. Natural Partial Charge (NPA) of the Nitrile Group for an Isolated Cation (q_{cation}) , for a Cation—Anion Pair with a Bis(trifluoromethylsulfonyl)imide Cation (q_{pair}) and for an Isolated Cation with a Solvation Approximated by the COS-MO Model $(q_{\text{COSMO}})^a$

cation	q_{cation} (a.u.)	$q_{\rm pair}$ (a.u)	$q_{\rm COSMO}$ (a.u.)			
I_1	-0.173	-0.243	-0.306			
I_2	-0.216	-0.283	-0.359			
I_3	-0.247	-0.293	-0.386			
I_4	-0.263	-0.304	-0.398			
I_5	-0.277	-0.303	-0.404			
I ₆	-0.285	-0.312	-0.407			
I_7	-0.292	-0.311	-0.408			
I_8	-0.296	-0.315	-0.410			
I ₉	-0.300	-0.314	-0.410			
II_1	-0.182		-0.299			
II_2	-0.221		-0.360			
II_3	-0.249		-0.386			
II_5	-0.278		-0.404			
\mathbf{II}_7	-0.292		-0.409			
II9	-0.301		-0.410			
III_1	-0.177		-0.281			
III_3	-0.247		-0.383			
IV_1	-0.185		-0.307			
IV ₃	-0.249		-0.386			
V_1	-0.179		-0.309			
V_3	-0.250		-0.387			
VI_1	-0.181		-0.311			
VI ₃	-0.251		-0.387			
VII ₁	-0.187		-0.315			
VII ₃	-0.253		-0.388			
The charges are expressed in atomic units (a.u.).						

involved in interactions between the bis(trifluoromethylsulfonyl)imide anion and four pyridinium cations (Figure 6). A structure with a similar pyridinium cation has been reported, containing a short hydroxymethyl chain, a propionic acid chain and a bromide as the anion.⁸³ The molecules are linked by bromide ions to form two intermolecular hydrogen bonds COOH····Br···HO yielding chains. An additional contact between the bromide and an alkyl chain C–H hydrogen atom exists.

The asymmetric unit of 11-Tf₂N consists of one pyridinium cation and one bis(trifluoromethylsulfonyl)imide anion. The molecular arrangement and packing environment is very similar to that of 3-Tf₂N, as the ring structure of 11-Tf₂N only differs in carrying an extra methyl group. The nitrile-functionalized alkyl chain is staggered and almost perpendicular with respect to the pyridine ring (82.3° between planes through the respective atoms). X- $Y \cdots \pi$ interactions are found in the packing between the nitrile group and the pyridine ring (distance of 3.39 Å between the nitrile nitrogen atom and the ring centroid) and for a sulfonyl oxygen atom of the anion and the pyridine ring (distance of 3.36 Å). $C-H\cdots O$, $C-H\cdots N$, and $C-H\cdots F$ interactions are observed between the pyridinium cation and the bis(trifluoromethylsulfonyl)imide sulfonyl oxygen and nitrogen atoms. In fact, nine hydrogen contacts, which originate from three different cations, are observed and range between 2.52 and 2.70 Å, including an additional contact with the extra methyl group on the cation (Figure 7).



Figure 15. Overview of the cations considered for the calculation of the charge distributions summarized in Table 4.

The asymmetric unit of 9-Tf₂N contains one pyridinium cation and one bis(trifluoromethylsulfonyl)imide anion. The pyridinium cation differs from the one in 8-Tf₂N by an extra methyl group in the meta-position. The nitrile function makes contact with a C-H pyridine ring and a methyl hydrogen atom (2.66 Å and 2.71 Å, respectively), in this way building up chains of pyridinium cations, parallel with (100), in the [010] direction (Figure 8). X–Y··· π interactions are observed in the crystal packing, between one bis(trifluoromethylsulfonyl)imide CF₃ fluorine and one sulfonyl oxygen atom, and a pyridine ring $(C-F\cdots)$ centroid S-O···centroid distance of 3.42 Å and 3.53 Å, respectively). The contacts between the pyridinium cation and the bis(trifluoromethylsulfonyl)imide anion resembles the observed contacts in 8-Tf₂N: four contacts with the nitrile-functionalized, one contact with the C-H pyridine ring and one contact with the meta-methyl (Figure 9). No contacts are observed with the orthomethyl group.

The asymmetric unit of 18-Tf₂N contains two pyridinium cations, each with a bis(trifluoromethylsulfonyl)imide counteranion. For both pyridinium cations, both the nitrile-functionalized alkyl chains $(0.8^{\circ}, 5.1^{\circ})$ and alkyl chains $(0.8^{\circ}, 3.4^{\circ})$ are almost planar with the pyridine ring. The nitrile group of the first pyridinium cation contacts a C-H hydrogen atom of the second pyridinium cation (C-H···N distance of 2.64 Å). The nitrile group of this second pyridinium cation contacts a C-H hydrogen atom of a symmetry equivalent molecule of the first pyridinium cation $(C-H \cdots N$ distance of 2.67 Å), in this way building up a tetrameric arrangement of pyridinium cations (Figure 10). An X-Y $\cdots \pi$ interaction is found in the packing between a bis(trifluoromethylsulfonyl)imide fluorine atom and a pyridine ring (distance of 3.19 Å between the fluorine atom and the pyridine ring centroid). Considering the first bis(trifluoromethylsulfonyl)imide anion, one of the sulfonyl oxygen atoms is contacting a C-H hydrogen atom of a pyridine ring. Two other sulfonyl oxygen atoms and the nitrogen atom make hydrogen contacts with C-H hydrogen atoms of the nitrile-functionalized alkyl chains. One CF₃ group is also involved in hydrogen contacts between the pyridine ring and the nitrile-functionalized alkyl chain. In total, nine $C-H\cdots O/N/F$ contacts (in the range of 2.21-2.64 Å) are involved in interactions between the bistriflimide anion and five pyridinium rings (Figure 11). Considering the second bis(trifluoromethylsulfonyl)imide anion in the



Figure 16. Electrostatic potential at the van der Waals surface (0.002 electrons/bohr³) for the 1-(3-cyanopropyl)pyridinium cation (left) and the 1-butylpyridinium cation (right). Solvation was taken into account via the COSMO model.

asymmetric unit, no contacts with pyridine ring C–H hydrogen atoms are observed. In fact, the bis(trifluoromethylsulfonyl)imide sulfonyl, nitrogen, and fluorine atoms make seven C–H···O/N/F contacts (in the range of 2.38-2.74 Å) with the hydrogen atoms of the nitrile-functionalized alkyl chains of three pyridinium ligands (Figure 12). Structures containing the same pyridinium cation were not found in the CSD.⁶⁹ A structure with a similar pyridinium cation has been reported, containing a short hydroxyethyl chain, a second propionic acid chain and a bromide as the anion.⁸³ The molecules form centrosymmetric dimers connected by a pair of hydrogen bonds between COOH and OH groups, and the OH group further interacts with the bromide ion. Several pyridine rings and one alkyl chain C–H hydrogen atom are contacting the bromide anion.

The asymmetric unit of 17-Tf₂N contains one pyridinium cation and one bis(trifluoromethylsulfonyl)imide anion. The pyridinium cation differs from the ring structure in 18-Tf₂N only in the paraposition of the ethyl chain. The nitrile function is hydrogen bonded to a C-H pyridine hydrogen atom of two symmetry equivalent (inversion center) pyridinium cations $(C-H\cdots N)$ distance of 2.56 Å and 2.51 Å, respectively). Because of the inversion center, the latter pyridinium cations contact the former one in exactly the same way, building up strands of cations, parallel with (001), running in the [100] direction (Figure 13). X–Y··· π interactions are observed in the crystal packing, especially for one bis(trifluoromethylsulfonyl)imide CF₃ group and a pyridine ring (C-F···centroid distances of 3.63, 3.46, and 3.86 Å, respectively) and one bis(trifluoromethylsulfonyl)imide sulfonyl oxygen atom and another pyridine ring $(S-O\cdots$ centroid distance of 3.18 Å). Contacts between the pyridinium cation and bis-(trifluoromethylsulfonyl)imide anion are observed: all bis-(trifluoromethylsulfonyl)imide sulfonyl oxygen atoms contact either C–H pyridine ring hydrogen atoms (two contacts), nitrilealkyl hydrogen atoms (three contacts), or an ethyl hydrogen atom (one contact) (Figure 14).

Quantum Chemical Calculations. Quantum chemical calculations have been performed on different nitrile-functionalized pyridinium and piperidinium ionic liquids to investigate the influence of the alkyl spacer on the charge located at the nitrogen atom of the nitrile function (Table 4). An overview of the investigated cations is given in Figure 15. Please note, that most investigated cations resemble those of the synthesized ionic liquids. Additional cations were added in the computational investigation to highlight trends and influences of substituents. For a given series of cations, it is found that the negative partial charge on the nitrogen atom of the nitrile function (N_{CN}) increases with an increase in length of the alkyl spacer between the nitrile function and the cationic heterocyclic ring. Significant differences between the negative partial charges on the N_{CN} atoms for the pyridinium series I and the piperidinium series II are only observed for the compounds with a short alkyl spacer. For a CH₂CH₂CH₂ spacer, the charges on the cations of the two series have already converged. It is worth mentioning that for alkyl nitriles, the negative partial charge on the nitrile nitrogen atom is virtually independent of the alkyl chain length.⁴⁸ However, the partial charge of N_{CN} for the pyrrolidinium cations with a long alkyl spacer are close to those observed for the alkyl nitriles.⁴⁸

For the pyridinium series I, calculations have been made for an ion pair consisting of a 1-(ω -cyanoalkyl)pyridinium cation and a bis(trifluoromethylsulfonyl)imide anion. It was observed that the negative partial charge on $N_{\rm CN}$ has been increased in comparison to the value obtained for one isolated cation in the gas phase. This shows that solvation affects the charge of N_{CN}. Unfortunately, an adequate quantum chemical description of solvation is unfeasible due to computational costs. One feasible solvation model is the continuum solvation model (COSMO).⁶⁴ Application of this model led to an additional increase of the negative partial charge at N_{CN} compared to the isolated ion pair calculations. Furthermore, the partial charges at N_{CN} for cations with long alkyl spacers converge toward -0.410 au. If the partial charges at the N_{CN} atoms of members of the pyridinium series I and the piperidinium series II with the same alkyl spacer length are compared, significant differences can be observed only for the shortest alkyl spacer lengths. As can be seen in Table 4, N_{CN} of cation III₁ possesses the smallest negative partial charge. A methyl or methoxy substituent on the pyridinium ring has an electron donation effect, but the increases of the negative partial charge of N_{CN} is negligible. The position of the methyl group (ortho, meta, or para) has also only a marginal effect on the negative partial charge of N_{CN}. In Figure 16, the electrostatic potentials at the van der Waals surface (0.002 electrons/bohr³) of the 1-(3-cyanopropyl)pyridinium cation (left) and the 1-butylpyridinium cation are compared.

¹⁵N NMR Measurements. Natural abundance nuclear magnetic resonance studies on the nitrogen-15 isotope (¹⁵N NMR) have been performed in order to gain additional insight into the structural and electronic properties of the synthesized ionic liquids. The electronic environment of the nitrogen atom is greatly influenced by changes in the molecular topology and intermolecular interactions. Those electronic changes are usually directly reflected



Figure 17. ¹⁵N NMR spectra of ionic liquids 2-Tf₂N (a), 4-Tf₂N (b), and 5-Tf₂N (c), recorded at room temperature and using CH₃NO₂ as external standard.



Figure 18. ¹⁵N NMR chemical shifts of ionic liquids $1-Tf_2N - 5-Tf_2N$ as a function of the number of carbon atoms in the aliphatic chain between nitrile and pyridine nitrogen atoms.

in the shielding and NMR chemical shift of the nitrogen nucleus.⁸⁴ ¹⁵N NMR spectra of compounds 2-Tf₂N, 4-Tf₂N, and 5-Tf₂N are shown in Figure 17. All three ionic liquids show three characteristic ¹⁵N resonances, corresponding to the three nitrogen atoms present in the structure. According to previously published ¹⁵N chemical shift tables,⁸⁵ the resonance at -242 ppm was assigned to the nitrogen atom in the bis(trifluoromethylsulfonyl)imide anion, while the resonances at around -175 ppm and -135 ppm were assigned to the pyridine and nitrile nitrogen atoms of the cationic part, respectively. Although at the first glance the spectra shown in Figure 17 look nearly identical, a careful analysis revealed that the chemical shifts of the pyridine and nitrile nitrogen atoms varied depending on the chemical structure. Since the only difference among these ionic liquids is the number of carbon atoms in the aliphatic spacer between the pyridine nitrogen and the nitrile function (2 carbon atoms in compound 2-Tf₂N, 5 in 4-Tf₂N, and 10 in 5-Tf₂N), the ¹⁵N NMR spectra of ionic liquids 1-Tf₂N and 3-Tf₂N, that contain one and three aliphatic carbon atoms, respectively, have been recorded in a next step. The data summarized in

Figure 18 show a systematic trend in the chemical shift of both the pyridine and nitrile nitrogen resonances. The simultaneous decrease of the nitrile and increase of the pyridine ¹⁵N chemical shifts is observed as the number of aliphatic carbons between them increases. This implies that the pyridine nitrogen is more deshielded, while the nitrile nitrogen $N_{\rm CN}$ is more shielded in compounds containing long aliphatic chains between them. This is in the agreement with the theoretical study that predicts that the quantity of the negative charge on $N_{\rm CN}$ becomes larger as the length of the spacer increases.

CONCLUSIONS

Within the scope of this work, a total of 50 nitrile-functionalized pyridinium and piperidinium ionic liquids with bromide or bis(trifluoromethylsulfonyl)imide anions have been prepared to investigate the influence of structural modifications on the properties of these ionic liquids. The most striking changes were observed upon an increase in the length of the alkyl spacer between the cationic core and the nitrile group. A longer alkyl spacer leads to lower melting points, but also to a more negative partial charge on the nitrogen atom of the nitrile group. The charge distribution in the pyridinium compounds was probed by ¹⁵N NMR spectroscopy, and the measurements were in agreement with DFT calculations. These results on the nitrogen partial charge are of importance for the use of these functionalized ionic liquids to form complexes with metal ions, as it was illustrated earlier by some of us for nitrile-functionalized pyrrolidinium ionic liquids.⁴⁸ The coordination chemistry of these ionic liquids is presently under investigation. Crystal structures of pyridinium compounds with bis(trifluoromethylsulfonyl)imide anions reveal the interactions between the cations and anions in the solid state.

ASSOCIATED CONTENT

Supporting Information. CIF-files of the crystal structures. Synthesis and characterization of ionic liquids. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

This project was supported by the K.U. Leuven (Projects IDO/05/005 and GOA 08/05, and a DBOF PhD grant to K.C.L.), by the IWT-Flanders (SBO-project "MAPIL") and by the FWO-Flanders (Research Community "Ionic Liquids"). The authors gratefully acknowledge the financial support of the DFG priority program SPP 1191 "Ionic Liquids" and the ERA Chemistry program, which allows collaboration under the project "A Modular Approach to Multi-responsive Surfactant/Peptide (SP) and Surfactant/Peptide/Nanoparticle (SPN) Hybrid Materials". The authors thank Ms. Kathleen Lava for assistance during the thermal analysis measurements and Mr. Dirk Henot for performing CHN analyses.

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