Ionic Liquids

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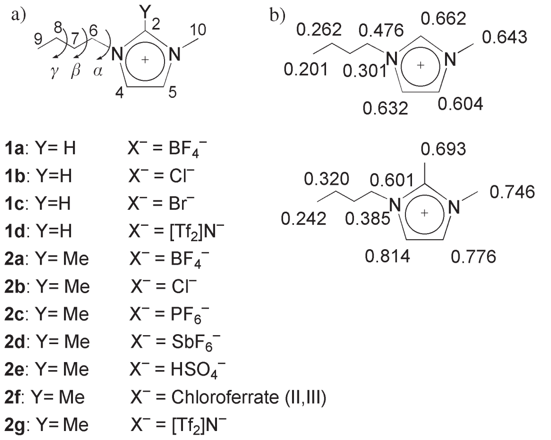
The Local Structure of Ionic Liquids: Cation–Cation NOE Interactions and Internuclear Distances in Neat [BMIM][BF$_4$] and [BDMIM]-[BF$_4$]**

Andrea Mele, Greta Romanò, Matteo Giannone, Enzio Ragg, Giovanni Fronza, Guido Raos, and Valentina Marcon*

The increasing interest in room-temperature ionic liquids (RTILs) is related to their possible exploitation as environmentally friendly neoteric solvents because of their vanishing vapor pressure, thermal and chemical stability, air and moisture stability, wide liquidus range, solvent capability. Suitable applications of RTILs in synthesis, catalysis, biocatalysis, material science, and chemical engineering have been reported.[1] The rapidly increasing number and relevance of applications stimulated deeper understanding of the structure of RTILs in terms of intermolecular interactions that take place in the bulk liquid at the atomic level.[2] In such a context, the nuclear overhauser effect (NOE) is a powerful investigative tool, as it originates from dipolar interaction between pairs of nuclei and thus provides information on the molecular sites involved in the interactions. A pioneering study by Osteryoung and co-workers[3] demonstrated the existence of intermolecular NOE interactions between ring protons in 1-ethyl-2-methylimidazolium [EMIM]Cl·AlCl$_3$. The cation–cation contacts suggested a local or short-range structure of the liquid. The concept of a local structure in liquid methylimidazolium salts that resembles those found in the solid state has been stressed by some authors on the basis of X-ray diffraction,[4] neutron scattering,[5] and NMR spectroscopy.[6]

Herein, we present the first attempt to provide cation–cation distances in neat liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]$^+$[BF$_4$]$^-$ (**1a**)) and 1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([BDMIM]$^+$[BF$_4$]$^-$ (**2a**); Scheme 1) by NMR spectroscopy. Two-dimensional NOE experiments (NOESY) on neat **1a** and **2a** showed both intra- and intermolecular contacts. Interestingly, no intermolecular contacts were detected in neat BMIM bis(trifluoromethylsulfonylimide) ([BMIM]$^+$[Tf$_2$N]$^-$ (**1d**)) and [BDMIM]$^+$[Tf$_2$N]$^-$ (**2g**), which bear a bulky and non-coordinating anion, possibly because of the effect of increased intercation distance rather than unfavorable correlation times. The methodology for the assessment of distances in the liquid relies upon the distance dependence of the cross-relaxation rate σ obtained by intermolecular NOE build-up rates.[7]



Scheme 1. a) chemical structure and atom numbering of [BMIM]$^+$[X]$^-$ (**1**) and [BDMIM]$^+$[X]$^-$ (**2**). Curved arrows and Greek letters refer to the torsion angles of the butyl chain. b) Effective correlation times $\tau_{\rm eff}$ (ns) at 305 K for **1a** and 315 K for **2a**. Tf = triflate.

The cations **1a** and **2a** can be depicted as a polar head (the charged imidazolium ring) and an apolar tail (the *n*-butyl chain). NOESY spectra showed both head-to-head and head-to-tail cation–cation contacts. Herein, we assume that a) the tumbling of the system is isotropic and can be described by a single correlation time and b) the contact time of the cation–cation association is long enough to contribute to dipolar relaxation. These are reasonable hypotheses for head-to-head contacts and could be verified if individual correlation times

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[*] Prof. A. Mele, G. Romanò, M. Giannone, Dr. G. Raos, V. Marcon
Dipartimento di Chimica
Materiali e Ingegneria Chimica "Giulio Natta" Politecnico di Milano
Via L. Mancinelli, 7, 20131 Milano (Italy)
Fax: (+39) 022-399-3080
E-mail: andrea.mele@polimi.it
Prof. E. Ragg
Dipartimento di Scienze Molecolari Agroalimentari
Università di Milano
Via Celoria, 2, 20133 Milano (Italy)
Prof. G. Fronza
CNR—Istituto di Chimica del Riconoscimento Molecolare
Via L. Mancinelli, 7
20131 Milano (Italy)

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of the component of the noncovalent association could be experimentally assessed, as in the case of cation–anion association.[8] In the present case, such an approach cannot be applied as the individual components are chemically identical cations and therefore cannot be distinguished.

Quantitative NOE interaction data and average internuclear distances of the head-to-head interactions are presented in Tables 1 and 2. The rather short distances H5–H10, H2–H4, and H2–H5 are consistent with the presence of some type of aromatic-ring association, either stacking, as previously postulated for structurally related [EMIM] halides,[9] or perpendicular T-shaped assembly. Moreover, the short distances of H6–H4 and H6–H10 rule out the aggregation of imidazolium rings with parallel and eclipsed butyl chains as a dominant aggregation motif. Simple sketches of the aggregation motives of cations in **1a** and **2a** are depicted in Scheme 2.

Table 1: Corrected[17] cross-relaxation rate constant σ_{ij} (s^{-1}, absolute value) and average internuclear distances $\langle r_{ij} \rangle$ (Å) in **1a** (liquid) and **1b** and **1c** (single crystal).

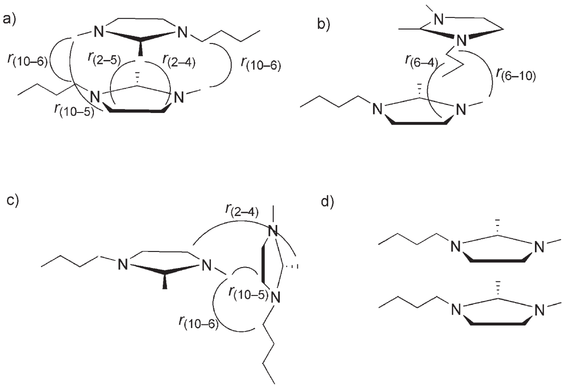
Distance (type)	σ_{ij} [s^{-1}]	R^2 [a]	**1a**[b]	**1b**[c]	**1b**[d]	**1c**[e]
H2–H10 (H–Me)	0.2880	0.997	3.03[f]	2.82[g]	2.91[g]	2.75[g]
H5–H10 (H–Me)	0.1055	0.998	3.5(8)	3.47	–	3.44
H6–H4 (CH_2–H)	0.0545	0.914	4.0(0)	3.27	–	3.22

[a] Correlation coefficient for linear regression of NOE interaction intensity versus mixing time τ_m; only the regressions that afford $R^2 \geq 0.900$ are reported. [b] Average intermolecular distance (Å) of a given H-atom pair in liquid **1a** from NOE interactions (this work). [c] Average intermolecular distance (Å) of a given H-atom pair in single crystal of orthorhombic $[BMIM]^+Cl^-$; atomic coordinates taken from ref. [21]. [d] As in [c] but for monoclinic $[BMIM]^+Cl^-$, from ref. [4c]. [e] As in [c] but for monoclinic $[BMIM]^+Br^-$; from ref. [22]. [f] Reference proton–proton distance (intramolecular) calculated ab initio [average value from Equation (3)]; the distance is in good agreement with the equivalent in 1-methyl-3-ethylimidazolum tetrafluoroborate, as calculated from atomic coordinates of ab initio calculations reported by Tsuzuki et al.[23] [g] Intramolecular distance reported for the sake of comparison with [f].

Table 2: Corrected[17] cross-relaxation rate constant σ_{ij} (s^{-1}, absolute value) and average internuclear distances $\langle r_{ij} \rangle$ (Å) in **2a** (liquid) and **2a**–**2f** (single crystal).

Distance (type)	σ_{ij} [s^{-1}]	R^2 [a]	**2a** (liquid)[b]	**2a**[c]	**2b**[d]	**2c**[c]	**2d**[c]	**2e**[d]	**2f**[d]
H4–H10 (H–Me)	0.2627	0.987	3.00[e]	2.97[f]	3.03[f]	2.99[f]	3.02[f]	3.00[f]	2.99[f]
H5–H10 (H–Me)	0.1807	0.999	3.1(9)	–	3.33	3.10	–	–	–
H5–H2 (H–Me)	0.1888	0.995	3.1(7)	–	⟨3.14⟩ 3.14 2.89 3.48 3.31 3.00	3.59	3.24	–	3.17
H4–H2 (H–Me)	0.1435	0.967	3.3(2)	–	3.37	3.04	⟨3.19⟩ 3.23 3.15	⟨3.41⟩ 3.50 3.34	⟨3.35⟩ 3.27 3.44
H6–H4 (CH_2–H)	0.1518	0.951	3.2(9)	⟨2.90⟩ 2.56 3.04 3.60 2.78	⟨3.09⟩ 2.98 3.56	–	–	⟨2.84⟩ 3.26 2.58	–
H6–H10 (CH_2–Me)	0.2218	0.977	3.0(9)	–	⟨3.19⟩ 3.52 3.22 3.13 2.90 3.31	⟨3.14⟩ 3.44 3.05 3.48 2.55 3.55 3.29	⟨3.30⟩ 3.13 3.51	–	⟨3.02⟩ 2.71 3.54 3.04

[a] As in note [a] in Table 1. [b] As in note [b] in Table 1. [c] As in note [c] in Table 1; atomic coordinates taken from ref. [11]]. [d] As in note [c]; from ref. [24]. [e] Reference proton–proton distance (intramolecular) calculated ab initio (this work) [average calculated by using Equation (3)]. [f] Intramolecular distance reported for the sake of comparison with [e].



Scheme 2. Sketch of the head-to-head aggregation motives of $[BMIM]^+$ and $[BDMIM]^+$ which are consistent with the displayed experimental intermolecular distances r_{ij}: a), b) sandwich, c) T-shaped, d) arrangement is not consistent with experimental data; for the sake of simplicity only $[BDMIM]^+$ ions are depicted.

Distance restraints alone, however, do not allow a conclusion about the parallelism of the imidazolium rings or the existence of π–π interactions to be drawn. It is interesting to note that a similar sketch for molecular arrangements have been recently reported for $[BMIM]^+[PF_6]^-$ by X-ray reflectivity study.[10] The distance values corresponding to head-to-head aggregation in liquids **1a** and **2a** can be compared to the values of the corresponding contacts in the solid state. To this end, the full set of intermolecular contacts of the type reported in the first column of Tables 1 and 2 was generated from the atomic coordinates of various $[BMIM]^+[X]^-$ ionic liquids taken from the literature, and the distances in the range for detectable NOE interactions ($r_{ij} \leq 4$ Å) were selected along with the average value (see the Experimental Section). The results are reported in the right-hand side of Tables 1 and 2. The comparison between the data obtained from the liquid and the solid state points out that the cation–cation distances obtained in this investigation are in the range of the homologous short contacts observed in the crystals of $[BMIM]^+$ and $[BDMIM]^+$ with miscellaneous anions. Indeed, the imidazolium cations in the liquid are close in space despite coulombic repulsion, and show, at short range, the same attitude to “close packing” demonstrated in all the quoted single crystal structures, with the unique exception of the bulky $[SbF_6]^-$ ion. In particular, the close packing of **2a** observed in the solid state is described as the result of “maximizing non-directional interactions”.[11] It seems that also for liquid **1a** and **2a** the same principle could be invoked to provide a rationale for the observed short intermolecular contacts. These findings provide quantitative foundation to the general idea of local structure in ionic liquids, direct evidence of the existence of polar domains in the pure liquid (in close analogy to that reported for the single crystal), and quantitative distance parameters to characterize such domains.

NOE interaction data at a mixing time of 50 ms for the head-to-tail contacts are reported in Table 3. The assessment of distances in this case is hampered by the internal motion and conformational flexibility of the butyl chain (Scheme 1, right) and will not be attempted herein.[12] Nevertheless, the data of Table 3 show that the butyl chain points toward the polar head of adjacent cations, as evidenced by NOE interactions H10–H9 and H5–H9 for both **1a** and **2a** and H2–H9 for **2a**. The NOE interactions that involve H8 and the polar head groups H2, H5, and H4 suggest that the apolar chain significantly penetrates the polar domain of surrounding cations. Consequently, the possibility of micellar aggregates is ruled out. In a similar way, the formation of extended nonpolar domains because of aggregation of the alkyl chains seems not to be consistent with the observed NOE interactions (the direct observation of intermolecular tail-to-tail contacts is not possible due to difficulty in separating intra- and intermolecular contributions to cross relaxation). However, the issue of alkyl-chain aggregation in $[BMIM]^+$ ions is still open to debate, as opposite conclusions have been reported by experimental[10] and theoretical methods.[13]

Table 3: Head-to-tail intermolecular NOE interactions [a] in liquid **1a** and **2a**.

NOE interactions [%]	H4–H7	H5–H7	H2–H7	H10–H7	H4–H8	H5–H8	H2–H8	H10–H8	H4–H9	H5–H9	H2–H9	H10–H9
1a	[b]	[b]	0.62	[b]	0.27	0.41	0.40	[b]	[b]	0.66	[b]	0.84
2a	0.48	0.79	0.99	[b]	[b]	0.49	[b]	0.64	[b]	0.57	0.86	0.73

[a] NOE (%) interactions are scaled to the number of equivalent spins and are thus directly comparable; only the NOE interactions that belong to linear regression with $R^2 \geq 0.900$ are reported. [b] Data not fulfilling the criterion reported above.

In conclusion, we have reported our attempt to use quantitative intermolecular NOE interaction studies for the assessment of the polar domains within bulk model RTILs. Cation–cation distances and sites of interaction thus obtained show significant correlation with data taken from X-ray diffraction studies of similar compounds. Moreover, semi-quantitative intermolecular NOE interactions point out significant interactions of the butyl chains with the polar domains. A detailed knowledge of the structural features of polar domains in RTILs is a requisite for a rational understanding of solute–solvent interactions. Indeed, recent neutron-scattering studies on a RTIL–benzene mixture demonstrated that the cation–cation first shell plays a key role in the mechanism of dissolution of benzene in 1,3-dimethylimidazolium hexafluorophosphate.[14] From this viewpoint, NOE interaction data can be complementary to partial radial distribution functions obtained from neutron scattering and contribute to a deeper understanding of the structure of the liquid.

Experimental Section

Compounds **1a**, **1d**, **2a**, and **2g** were synthesized as reported previously,[15] dried under vacuum at 70 °C overnight, and kept either under nitrogen or in a vacuum desiccator.

Routine NMR experiments and sample preparations were carried out on a Bruker Avance 500 instrument as previously described.[6a] Gradient-selected NOESY experiments were carried out using standard library sequences with mixing times τ_m of 10, 20, 30, 40, and 50 ms; longer mixing times gave spectra affected by spin diffusion.[16] All NOE interactions (intra- and intermolecular) were negative. The volumes of intermolecular cross peaks plotted versus τ_m provided the NOE interaction build-up curve; all the experimental points fell in the linear region. The cross-relaxation rates σ_{ij} were extracted from the slope of the linear fitting of the experimental points (initial rate approximation). Spin equivalence was accounted for.[17] Distances r_{ij} were calculated from Equation (1):

$$r_{ij} = r_{\text{ref}} \left[\frac{\sigma_{\text{ref}}\, \zeta_{\text{ref}}}{\sigma_{ij}\, \zeta_{ij}} \right]^{1/6} \tag{1}$$

where r_{ref} is a “reference distance” (e.g., from X-ray diffraction, ab initio calculations, etc.) and ζ_{ij} is defined as:

$$\zeta_{ij} = K\, \tau_c \left(\frac{6}{1 + 4\omega^2\, \tau_c^2} \right) \tag{2}$$

Overall (effective) correlation times τ_{eff} (Scheme 1) were estimated through $^{13}C\{^1H\}$ NOE factors η measured at the same temperature of NOESY experiments, assuming only dipole–dipole relaxation. The values thus obtained should be considered as a first approximation as other mechanisms can be effective.[18] The measurements were carried out in quintuplicate.

Crystallographic data were processed using SHELXL-97.[19] Average distance values reported in Table 1 are calculated as in Equation (3):

$$\langle r_{ij} \rangle = \left(\frac{1}{n} \sum_{k=1}^{n} \frac{1}{r_{ij,k}^3} \right)^{-1/3} \tag{3}$$

Ab initio calculations on **1a** and **2a** were based on hybrid density functional theory (DFT). The geometries were optimized at the B3LYP/6-31G** level, with the GAMESS-USA program.[20] NOESY spectra of **1a** and **2a** are available in the Supporting Information.

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[12] The effective correlation times of nonquaternary carbon atoms displayed in Scheme 1 clearly show that the butyl chain undergoes unrestricted motion. The conformational flexibility of the chain is documented by the analysis of the J(H6,H7) and J(H7,H8) coupling constants and is in turn connected to the β and γ torsion angles (see Scheme 1). Indeed, the *trans t* population for β and γ is 49 and 59% for **1a** and 54 and 59% for **2a** (both liquid, this work). Conversely, in the solid state the β angle assumes either a pure $\pm g$ (orthorombic: **1b**, **1c**, **2b**, **2c**, **2e**) or pure *t* conformation (monoclinic: **1b**, **2a**). The dihedral angle corresponding to the γ torsion angle is reported as *t* in all the reported X-ray structures. Only **2f** showed disordered butyl chains.

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