

Synthesis and Structural Characterization of 1-Butyl-2,3-dimethylimidazolium Bromide and Iodide

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1-Butyl-2,3-dimethylimidazolium bromide {(bdmim)Br} (**1**) and iodide {(bdmim)I} (**2**) were prepared conveniently by the reaction of 1,2-dimethylimidazole and the corresponding 1-halobutane. The compounds were characterized by ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy as well as by X-ray single crystal crystallography. **1** crystallizes in the monoclinic crystal system, space group $P2_1/n$, with $Z = 4$, and unit cell dimensions $a = 8.588(2)$, $b = 11.789(1)$, $c = 10.737(2)$ Å, $\beta = 91.62(3)^\circ$. Compound **2** crystallizes in the monoclinic crystal system, space group $P2_1/c$, with $Z = 8$, and unit cell dimensions $a = 10.821(2)$, $b = 14.221(3)$, $c = 15.079(2)$ Å, $\beta = 90.01(3)^\circ$. The lattices of the salts are built up of 1-butyl-2,3-dimethylimidazolium cations and halide anions. The cations of **1** form a double layer with the imidazolium rings stacked together due to π interactions. The Br^- anions lie approximately in the plane of the imidazolium ring, and the closest interionic $\text{Br}\cdots\text{H}$ contacts span a range of 2.733(1)–2.903(1) Å. Compound **2** shows no π stacking interactions. The closest interionic $\text{I}\cdots\text{H}$ contacts are 2.914(1)–3.196(1) Å.

Key words: 1-Butyl-2,3-dimethylimidazolium Bromide,
1-Butyl-2,3-dimethylimidazolium Iodide,
X-Ray Crystal Structure

Introduction

Ionic liquids, especially those based on imidazolium cations, have seen an intense research activity and have attracted interest because of their use in synthetic applications [1, 2]. However, the solid state structural information of the ionic liquids based on 1,2,3-trialkylimidazolium cations is still rather scattered. In this paper, we report the crystal structures of two 1-butyl-2,3-dimethylimidazolium (bdmim) salts, namely of (bdmim)Br (**1**) and (bdmim)I (**2**). Crys-

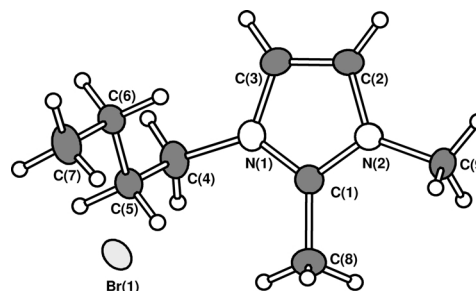


Fig. 1. The crystal structure of (bdmim)Br (**1**) indicating the numbering of atoms (displacement ellipsoids at the 50 % probability level).

tal structures have been reported for (bdmim)Cl [3], (bdmim)[HSO_4] [3], (bdmim) $_4[\text{Fe}^{\text{II}}\text{Cl}_4][\text{Fe}^{\text{III}}\text{Cl}_4]_2$ [3], (bdmim)[BF_4] [4], (bdmim)[PF_6] [4], [bdmim][SbF_6] [4], and (bdmim) [$\text{CH}_6\text{B}_{11}\text{Cl}_6$] [5].

Experimental Section

The NMR spectra were recorded on a Bruker DPX200 spectrometer operating at 200.13 and 50.32 MHz for ^1H and $^{13}\text{C}\{^1\text{H}\}$, respectively. Tetramethylsilane (TMS) was used as an internal standard. All spectra were recorded in CDCl_3 that served as an internal ^2H lock. Chemical shifts (ppm) of ^1H and ^{13}C are reported relative to TMS.

Synthesis

(bdmim)Br (**1**): 19.8 mL (21 mmol) of 1,2-dimethylimidazole and 36 mL (33 mmol) of 1-bromobutane were mixed at 88 °C over a period of 72 h under dinitrogen. The product was washed twice with ethyl acetate (15 mL) and then crystallized at 5 °C from an ethyl acetate/acetonitrile mixture (1 : 1). The crystals obtained were recrystallized from CH_3CN , washed with small amounts of cold EtOAc, and dried. Yield: 42 g (86 %). – Anal. calcd. for $\text{C}_9\text{H}_{17}\text{N}_2\text{Br}$: C 46.36, H 7.35, N 12.02; found: C 46.37, H 7.17, N 11.98. – ^1H NMR: $\delta = 0.95$ (t, $J = 7.0$ Hz, 3H, 7- CH_3), 1.39 (m, $J = 7.1$ Hz, 2H, 6- CH_2), 1.82 (m, $J = 7.6$ Hz, 2H, 5- CH_2), 2.84 (s, 3H, 8- CH_3), 4.05 (s, 3H, 9- CH_3), 4.24 (t, $J = 7.5$ Hz, 2H, 4- CH_2), 7.56 (d, $J = 2.1$ Hz, 1H, 3-CH), 7.78 (d, $J = 2.1$ Hz, 1H, 2-CH). – ^{13}C NMR: $\delta = 10.75$ (C8), 13.37 (C7), 19.55 (C6), 31.83 (C5), 36.00 (C9), 48.63 (C4), 121.30 (C2), 123.00 (C3), 143.74 (C1); for numbering of atoms, see Fig. 1.

(bdmim)I (**2**): Compound **2** was synthesized with the same procedure as **1** using 19.4 mL (21 mmol) of 1,2-dimethylimidazole and 33 mL (29 mmol) of 1-iodobutane. The reaction time was 20 h. Yield: 49 g (85 %). – Anal. calcd. for $\text{C}_9\text{H}_{17}\text{N}_2\text{I}$: C 38.59, H 6.12, N 10.00; found: C 38.55, H 6.16, N 9.91. – ^1H NMR: $\delta = 0.98$ (t, $J = 7.3$ Hz,

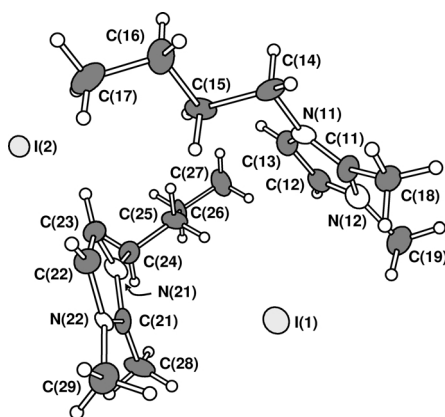


Fig. 2. The crystal structure of (bdmim)I (**2**) indicating the numbering of atoms (displacement ellipsoids at the 50 % probability level).

3H, 7-CH₃), 1.42 (m, J = 7.6 Hz, 2H, 6-CH₂), 1.82 (m, J = 7.7 Hz, 2H, 5-CH₂), 2.84 (s, 3H, 8-CH₃), 4.01 (s, 3H, 9-CH₃), 4.20 (t, J = 7.5 Hz, 2H, 4-CH₂), 7.46 (d, J = 2.1 Hz, 1H, 3-CH), 7.62 (d, J = 2.1 Hz, 1H, 2-CH). – ¹³C NMR: δ = 11.44 (C8), 13.39 (C7), 19.62 (C6), 31.77 (C5), 36.52 (C9), 48.89 (C4), 121.24 (C2), 122.86 (C3), 143.85 (C1); for numbering of atoms, see Fig. 2.

X-Ray crystallography

Diffraction data for **1** and **2** were collected on a Nonius Kappa CCD diffractometer using graphite monochromated MoK α radiation (λ = 0.71073 Å). Crystal data and details of the structure determinations are given in Table 1. The structures were solved by Direct Methods using SIR-92 [6] and refined using SHELXL-97 [7]. After full-matrix least-squares refinement of the non-hydrogen atoms with anisotropic thermal parameters, the hydrogen atoms were placed in calculated positions (C–H = 0.95, 0.99, and 0.98 Å in the case of arene hydrogen atoms, methylene hydrogen atoms, and methyl hydrogen atoms, respectively). In the final refinement the calculated hydrogen atoms were riding with the carbon atoms to which they are bonded. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2 (arene and methylene hydrogens) or 1.5 (methyl hydrogens) times that of the corresponding carbon atom. The scattering factors for the neutral atoms were those incorporated in the programs.

Results and Discussion

(Bdmim)X [X = Br (**1**), I (**2**)] can conveniently be synthesized by the reaction of 1,2-dimethylimidazole and the corresponding 1-halobutane. The crystal structures of **1** and **2** together with the numbering scheme of the atoms are shown in Figs. 1 and 2, respectively. The bond lengths and angles are within the normal ranges (see Table 2) and they can be com-

Table 1. Crystal data and details of the crystal structure determinations of **1** and **2**.

	1	2
Empirical formula	C ₉ H ₁₇ N ₂ Br	C ₉ H ₁₇ N ₂ I
Relative molecular mass	233.16	280.15
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a [Å]	8.588(2)	10.821(2)
b [Å]	11.789(2)	14.221(3)
c [Å]	10.737(2)	15.079(3)
β [deg]	91.62(3)	90.01(3)
V [Å ³]	1086.7(4)	2320.5(8)
Z	4	8
$F(000)$ [e]	480	1104
D_c [g cm ⁻³]	1.425	1.604
μ (MoK α) [mm ⁻¹]	3.737	2.718
Crystal size [mm]	0.20×0.15×0.15	0.15×0.12×0.10
T [K]	120(2)	120(2)
θ Range [deg]	2.80–26.00	3.29–25.00
Reflections collected	7632	4057
Unique reflections	2115	4057
Observed reflections ^a	1877	3321
Parameters / restraints	113/0	218/0
R_{int}	0.0827	0.0830
R_1 ^{a, b}	0.0399	0.0506
wR_2 ^{a, b}	0.0994	0.1482
R_1 (all data) ^b	0.0465	0.0617
wR_2 (all data) ^b	0.1046	0.1542
GOOF	1.1061	1.401
Max. and min. heights in final diff. synthesis [e Å ⁻³]	0.484, –0.410	0.816, –0.905

^a $I \geq 2\sigma(I)$; ^b $R_1 = [\sum ||F_o| - |F_c||] / [\sum |F_o|]$, $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]\}^{1/2}$.

pared to the values of the analogous chloride salt [3] which is in fact isomorphous with **1**. The asymmetric unit of **1** consists of one cation and anion whereas the asymmetric unit of **2** contains two independent cations and anions. The differences in the packing of **1** and **2** are shown in Figs. 3(a) and 3(b), respectively.

In the crystals of **1** the cations form a double layer with the imidazolium rings stacked together due to π interactions. The closest distance between the centroids of two imidazolium rings (the second ring is generated by the symmetry operation $1 - x, 1 - y, 1 - z$) is 3.445(1) Å, which is similar to that described recently for the chloride analogue [3]. The Br[–] anions lie approximately in the plane of the imidazolium ring. The closest interionic Br \cdots H contacts in this plane span a range of 2.733(1)–2.903(1) Å [Br \cdots C 3.653(3)–3.827(3) Å].

The packing of the compounds in crystals of **2** differs from that observed in **1** and in its chloride analogue by showing no π stacking interactions between the imidazolium rings [see Fig. 3(b)]. The closest interionic I \cdots H contacts involving I(1) are 3.136(1)–3.196(1) Å [I(1) \cdots C 3.874(7)–3.927(8) Å], and those involving I(2) are 2.914(1)–3.118(1) Å [I(2) \cdots C 3.884(1)–4.073(1) Å].

Table 2. Selected bond lengths (Å) and angles (deg) of **1** and **2**.

1	2				1	2			
			<i>n</i> = 1	<i>n</i> = 2				<i>n</i> = 1	<i>n</i> = 2
N(1)–C(1)	1.332(4)	N(<i>n</i> 1)–C(<i>n</i> 1)	1.33(1)	1.37(1)	N(1)–C(1)–N(2)	108.2(3)	N(<i>n</i> 1)–C(<i>n</i> 1)–N(<i>n</i> 2)	108.7(7)	107.1(7)
N(1)–C(3)	1.388(4)	N(<i>n</i> 1)–C(<i>n</i> 3)	1.38(1)	1.37(1)	N(1)–C(1)–C(8)	127.2(3)	N(<i>n</i> 1)–C(<i>n</i> 1)–C(<i>n</i> 8)	127.2(7)	126.7(8)
N(1)–C(4)	1.475(4)	N(<i>n</i> 1)–C(<i>n</i> 4)	1.457(9)	1.50(1)	N(1)–C(4)–C(5)	111.4(3)	N(<i>n</i> 1)–C(<i>n</i> 4)–C(<i>n</i> 5)	112.6(7)	110.9(6)
N(2)–C(1)	1.336(4)	N(<i>n</i> 2)–C(<i>n</i> 1)	1.34(1)	1.32(1)	N(2)–C(1)–C(8)	124.5(3)	N(<i>n</i> 2)–C(<i>n</i> 1)–C(<i>n</i> 8)	124.6(8)	126.0(8)
N(2)–C(2)	1.387(4)	N(<i>n</i> 2)–C(<i>n</i> 2)	1.37(1)	1.36(1)	C(1)–N(1)–C(3)	108.4(3)	C(<i>n</i> 1)–N(<i>n</i> 1)–C(<i>n</i> 3)	108.9(7)	106.9(7)
N(2)–C(9)	1.465(4)	N(<i>n</i> 2)–C(<i>n</i> 9)	1.43(1)	1.51(1)	C(1)–N(1)–C(4)	126.2(3)	C(<i>n</i> 1)–N(<i>n</i> 1)–C(<i>n</i> 4)	127.7(7)	128.0(6)
C(1)–C(8)	1.484(4)	C(<i>n</i> 1)–C(<i>n</i> 8)	1.49(1)	1.49(1)	C(1)–N(2)–C(2)	108.7(3)	C(<i>n</i> 1)–N(<i>n</i> 2)–C(<i>n</i> 2)	108.6(7)	109.8(7)
C(2)–C(3)	1.335(4)	C(<i>n</i> 2)–C(<i>n</i> 3)	1.36(1)	1.31(1)	C(1)–N(2)–C(9)	125.2(2)	C(<i>n</i> 1)–N(<i>n</i> 2)–C(<i>n</i> 9)	124.9(7)	125.4(8)
C(4)–C(5)	1.521(4)	C(<i>n</i> 4)–C(<i>n</i> 5)	1.53(1)	1.50(1)	C(2)–N(2)–C(9)	126.0(3)	C(<i>n</i> 2)–N(<i>n</i> 2)–C(<i>n</i> 9)	126.5(7)	124.2(7)
C(5)–C(6)	1.523(4)	C(<i>n</i> 5)–C(<i>n</i> 6)	1.51(1)	1.55(1)	C(2)–C(3)–N(1)	107.6(3)	C(<i>n</i> 2)–C(<i>n</i> 3)–N(<i>n</i> 1)	106.5(7)	108.7(7)
C(6)–C(7)	1.504(5)	C(<i>n</i> 6)–C(<i>n</i> 7)	1.49(1)	1.55(1)	C(3)–N(1)–C(4)	125.3(3)	C(<i>n</i> 3)–N(<i>n</i> 1)–C(<i>n</i> 4)	123.3(6)	125.1(6)
					C(3)–C(2)–N(2)	107.1(3)	C(<i>n</i> 3)–C(<i>n</i> 2)–N(<i>n</i> 2)	107.7(7)	107.5(7)
					C(4)–C(5)–C(6)	113.4(3)	C(<i>n</i> 4)–C(<i>n</i> 5)–C(<i>n</i> 6)	113.6(7)	108.7(6)
					C(5)–C(6)–C(7)	112.2(3)	C(<i>n</i> 5)–C(<i>n</i> 6)–C(<i>n</i> 7)	114.9(7)	111.6(6)

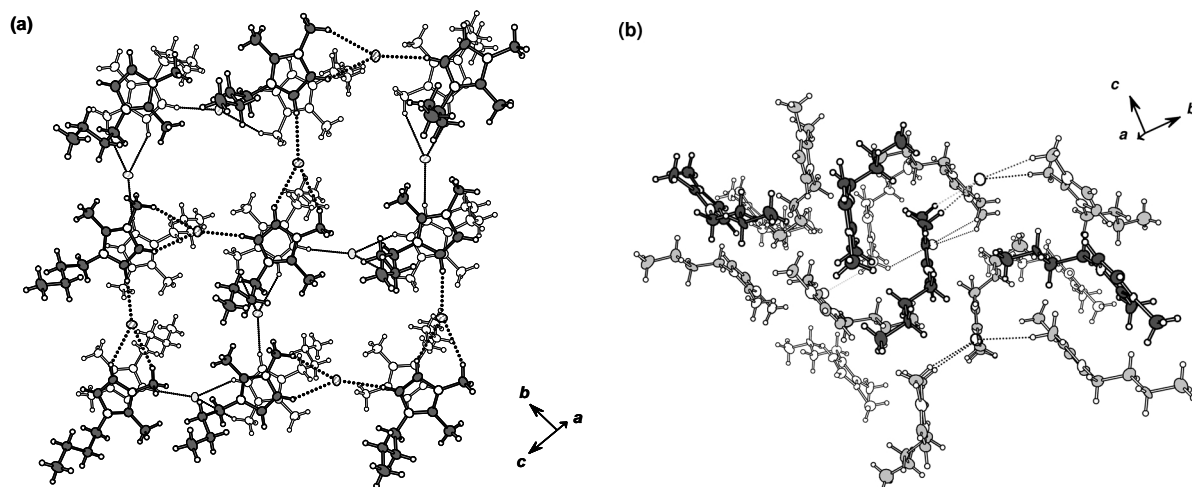


Fig. 3. (a) The cation-anion interactions in **1**. The cations and anions form layers showing π stacking interactions. The anions lie approximately in the plane of the imidazolium rings. (b) The cation-anion interactions in **2**. No π stacking interactions are discernible.

Supplementary material

CCDC 634383 and 634384 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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