

## Synthesis of ionic liquid-supported Schiff bases

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### Abstract

Some ionic liquid-supported Schiff bases **3** have been synthesized by condensation of aromatic aldehydes **2** with the ionic liquid 1-(2-aminoethyl)-3-methylimidazolium hexafluorophosphate **1** without solvent. The structure of **3a** has been proven by single crystal X-ray crystallography.

**Keywords:** Ionic liquid, Schiff base, synthesis, X-ray crystal structure

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### Introduction

In recent years, ionic liquids have received considerable attention as an attractive alternative to the traditional organic solvents.<sup>1-4</sup> The increased interest for their investigation is mainly due to their unique properties, such as chemical and thermal stability, high polarity, negligible vapor pressure, high electrical conductivity.<sup>5-8</sup> In addition, the miscibility of ionic liquids with organic solvents or water can be tuned by the choice of cations and anions. Owing to these properties, research has been focused on the synthesis of new ionic liquids with functional groups, so called “task-specific” or functionalized ionic liquids, and their applications.<sup>9-11</sup>

Schiff bases are usually formed by the condensation of a primary amine (or diamine) with an aldehyde.<sup>12-14</sup> Numerous reports on the preparation of Schiff bases and their applications have been published. Schiff bases are one of most prevalent mixed-donor ligands in coordination chemistry.<sup>15</sup> In addition, Schiff bases and their complexes are widely applied in biochemistry, material science, catalysis, encapsulation, activation, transport and separation phenomena, hydrometallurgy.<sup>16-19</sup>

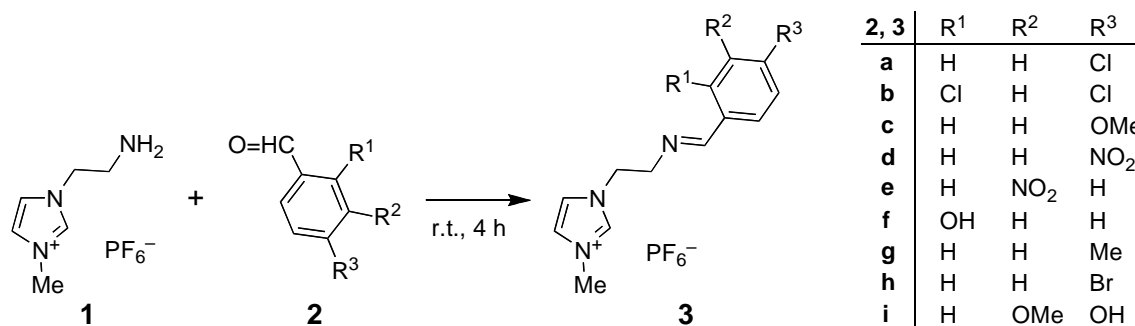
As part of our program aimed at developing a novel functionalized ionic liquid, we have synthesized a series of ionic liquid-supported Schiff bases.

## Results and Discussion

### Chemistry

Ionic liquid-supported Schiff bases **3a–i** were synthesized by condensation of the ionic liquid 1-(2-aminoethyl)-3-methylimidazolium hexafluorophosphate (**1**) with aromatic aldehydes **2a–i** at room temperature without both catalyst and solvent (Scheme 1).

A clear phase change was observed in all of the reactive systems investigated. The slurry of reactants eventually solidified after completion of the reaction forming the solid product.



**Scheme 1**

The reaction yields (between 21% and 54%) are low and/or moderate, which may be due to the reversible process of the condensation reaction. It should be mentioned that the nature of various substituents at the aromatic aldehydes has no obvious effect on yields.

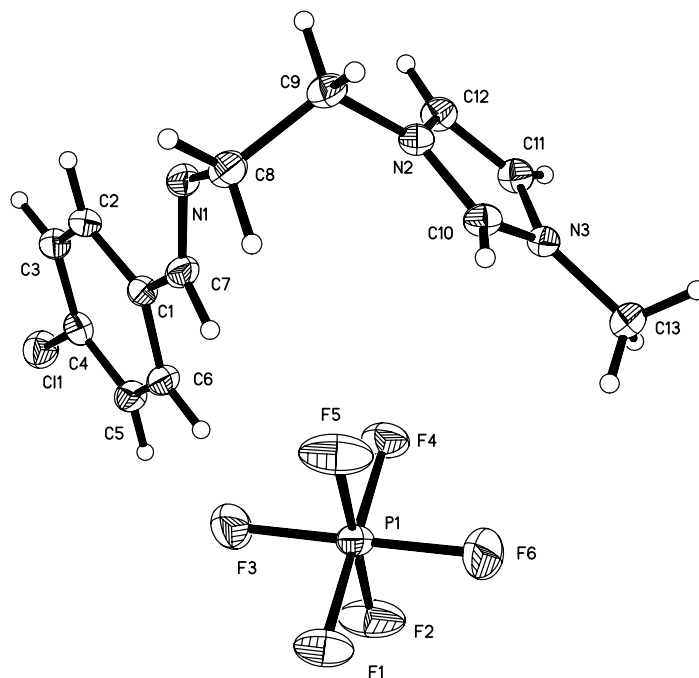
The structure of products was assigned on the basis of spectroscopic data. In IR spectra, compounds **3** exhibit absorption bands around 1640 cm<sup>-1</sup> for the C=N group. The stretching vibration of H-C(=N) appears in the region between 3100 and 3200 cm<sup>-1</sup>. In <sup>1</sup>H NMR spectra, the chemical shift of HC=N is displayed at δ 7.30–7.80; an exception is compound **3f** with δ 8.50 presumably due to the effect of the *ortho*-hydroxyl group in the aromatic ring.

### X-ray crystallography

An X-ray structure drawing of compound **3a** is shown in Figure 1. The crystal data structure refinement for compound **3a** is summarized in Table 1.

The single-crystal structure analysis reveals that complex contains one cation (C<sub>13</sub>H<sub>15</sub>ClN<sub>3</sub>)<sup>+</sup> and one PF<sub>6</sub><sup>-</sup> anion. The imidazole ring [N(2), C(10), N(3), C(11), C(12)] and aromatic ring [C(1), C(2), C(3), C(4), C(5), C(6)] are not coplanar with a dihedral angle of 52.84° between them. As expected, the molecular structure adopts a *trans* configuration about the C(7)=N(1) double bond. Within the imidazole fragments, the N(2)–C(10) and N(3)–C(10) are 1.328(2) and 1.323(2) Å, respectively, which is remarkably shorter than the normal C–N bond (1.47 Å) but longer than the typical C=N bond (1.28 Å).<sup>20</sup> The C(11)–C(12) bond length is 1.345(3) Å, remarkably shorter than the typical C–C single bond (1.478 Å)<sup>20</sup> due to the aromatic conjugated

system of the imidazole ring. In addition, as compared with normal C=N double bond values in other Schiff bases, the shorter C(7)=N(1) double bond distance of 1.272(3) Å may be attributable to the  $\pi$ -conjugated system of the aromatic ring and the C=N bond, too.



**Figure 1.** Crystal structure of compound **3a**.

**Table 1.** Crystal data structure refinement for compound **3a**

Empirical formula	C <sub>13</sub> H <sub>15</sub> ClF <sub>6</sub> N <sub>3</sub> P
Formula weight	393.70
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.2698(13) Å $\alpha$ = 112.286(2)° b = 9.8891(16) Å $\beta$ = 97.309(3)° c = 11.5980(19) Å $\gamma$ = 105.511(2)°
Volume	817.4(2) Å <sup>3</sup>
Z, Calculated density	2, 1.600 Mg/m <sup>3</sup>
Absorption coefficient	0.395 mm <sup>-1</sup>
F(000)	400
Crystal size	0.45 × 0.42 × 0.21 mm
Theta range for data collection	1.96 to 27.03°
Limiting indices	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14
Reflections collected/unique	6879 / 3507 [R(int) = 0.0182]
Completeness to theta = 27.03	97.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9216 and 0.8423
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3507 / 0 / 218
Goodness-of-fit on F <sup>2</sup>	1.079
Final R indices [I > 2sigma(I)]	R1 = 0.0380, wR2 = 0.1161
R indices (all data)	R1 = 0.0488, wR2 = 0.1321
Largest diff. peak and hole	0.405 and -0.355 e·Å <sup>-3</sup>

## Experimental Section

**General Procedures.** Melting points were measured on an Electrothermal X6 microscopy digital melting point apparatus. IR spectra were recorded on a Nicolet 6700 spectrometer using KBr pellets. <sup>1</sup>H NMR spectra were recorded in DMSO-*d*<sub>6</sub> on a Bruker AVANCE 300 (300 MHz) instrument with the TMS as an internal standard. Elemental analyses were carried out on a PE EA2400 CHN analyzer. The ionic liquid was prepared according to the method reported.<sup>21</sup>

**(E)-1-[2-(Arylideneamino)ethyl]-3-methyl-1*H*-imidazol-3-ium hexafluorophosphates (3).** A mixture of 1-(2-aminoethyl)-3-methylimidazolium hexafluorophosphate (**1**, 1.028 g, 4 mmol) and aromatic aldehydes (**2**, 3 mmol) without solvent was stirred at room temperature for 4 h. After completion of the reaction, ethanol (30 mL) was added to the reaction mixture, the solid

product formed was filtered off and washed with cold ethanol. The crude product was purified by recrystallization from ethanol/ethyl acetate (3:1 v/v).

**(E)-3-[2-(4-Chlorobenzylideneamino)ethyl]-1-methyl-1H-imidazol-3-ium hexafluorophosphate (3a).** White solid (0.25 g, 21.17%); mp 103–105 °C. IR (KBr),  $\text{cm}^{-1}$ : 1641 (C=N), 827 (P–F).  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  3.07 (s, 3H,  $\text{CH}_3$ ), 3.18 (t,  $J = 5.35$  Hz, 2H,  $\text{CH}_2$ ), 3.73 (t,  $J = 5.40$  Hz, 2H,  $\text{CH}_2$ ), 6.60, 6.64 (AA', 2H, Ar-H), 6.70 (s, 1H, NCH), 6.80 (s, 1H, NCH), 6.89, 6.92 (BB', 2H, Ar-H), 7.47 (s, 1H, N=CH). Anal. calcd. for  $\text{C}_{13}\text{H}_{15}\text{ClF}_6\text{N}_3\text{P}$ : C, 39.66; H, 3.84; N, 10.67. Found: C, 39.27; H, 3.51; N, 10.42.

X-ray single-crystal data for compound **3a** were collected at 173(2) K on a Bruker SMART CCD diffractometer equipped with a graphite-monochromatic MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) using an  $\omega$  scan technique. Crystal data absorption corrections were made with the SADABS program.<sup>22</sup> The structure was solved by direct methods and refined by full-matrix least-squares techniques using SHELXL-97.<sup>23</sup> The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were introduced geometrically.

Full crystallographic data for the structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC reference number 726047). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk; fax: +44 1223-336-033).

**1-[2-(2,4-Dichlorobenzylideneamino)ethyl]-3-methyl-3H-imidazol-3-ium hexafluorophosphate (3b).** White solid (0.53 g, 41.26%); mp 129–131 °C. IR (KBr): 1638 (C=N), 835  $\text{cm}^{-1}$  (P–F).  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  3.08 (s, 3H,  $\text{CH}_3$ ), 3.23 (t,  $J = 5.43$  Hz, 2H,  $\text{CH}_2$ ), 3.75 (t,  $J = 5.43$  Hz, 2H,  $\text{CH}_2$ ), 6.58 (d,  $J = 8.61$  Hz, 1H, Ar-H), 6.71 (s, 1H, NCH), 6.73 (s, 1H, NCH), 6.84 (s, 1H, Ar-H), 7.17 (d,  $J = 8.46$  Hz, 1H, Ar-H), 7.84 (s, 1H, N=CH). Anal. calcd. for  $\text{C}_{13}\text{H}_{14}\text{Cl}_2\text{F}_6\text{N}_3\text{P}$ : C, 36.47; H, 3.30; N, 9.81. Found: C, 36.41; H, 3.04; N, 9.71.

**1-[2-(4-Methoxybenzylideneamino)ethyl]-3-methyl-3H-imidazol-3-ium hexafluorophosphate (3c).** Yellow solid (0.43 g, 36.82%); mp 122–124 °C. IR (KBr): 1644 (C=N), 847  $\text{cm}^{-1}$  (P–F).  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  3.01 (s, 3H,  $\text{CH}_3$ ), 3.06 (s, 3H,  $\text{CH}_3$ ), 3.14 (t,  $J = 5.16$  Hz, 2H,  $\text{CH}_2$ ), 3.70 (t,  $J = 5.29$  Hz, 2H,  $\text{CH}_2$ ), 6.13, 6.16 (AA', 2H, Ar-H), 6.70 (s, 1H, NCH), 6.79 (s, 1H, NCH), 6.83, 6.86 (BB', 2H, Ar-H), 7.37 (s, 1H, N=CH). Anal. calcd. for  $\text{C}_{14}\text{H}_{18}\text{F}_6\text{N}_3\text{OP}$ : C, 43.20; H, 4.66; N, 10.79. Found: C, 42.29; H, 4.61; N, 10.55.

**1-[2-(4-Nitrobenzylideneamino)ethyl]-3-methyl-3H-imidazol-3-ium hexafluorophosphate (3d).** White solid (0.53 g, 43.70%); mp 180–182 °C. IR (KBr): 1641 (C=N), 829  $\text{cm}^{-1}$  (P–F).  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  3.83 (s, 3H,  $\text{CH}_3$ ), 4.01 (t,  $J = 5.33$  Hz, 2H,  $\text{CH}_2$ ), 4.52 (t,  $J = 5.27$  Hz, 2H,  $\text{CH}_2$ ), 7.67 (s, 1H, NCH), 7.76 (s, 1H, NCH), 7.97, 7.99 (AA', 2H, Ar-H), 8.28, 8.31 (BB', 2H, Ar-H), 8.48 (s, 1H, N=CH), 9.12 (s, 1H, N(H)CN). Anal. calcd. for  $\text{C}_{13}\text{H}_{15}\text{F}_6\text{N}_4\text{O}_2\text{P}$ : C, 38.63; H, 3.74; N, 13.86. Found: C, 38.48; H, 3.58; N, 13.62.

**1-[2-(3-Nitrobenzylideneamino)ethyl]-3-methyl-3H-imidazol-3-ium hexafluorophosphate (3e).** White solid (0.65 g, 53.60%); mp 133–135 °C. IR (KBr): 1645 (C=N), 838  $\text{cm}^{-1}$  (P–F).  $^1\text{H}$  NMR (300 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  3.09 (s, 3H,  $\text{CH}_3$ ), 3.25 (t,  $J = 5.20$  Hz, 2H,  $\text{CH}_2$ ), 3.78 (t,  $J = 5.32$  Hz, 2H,  $\text{CH}_2$ ), 6.73 (s, 1H, NCH), 6.85 (s, 1H, NCH), 6.88–7.62 (m, 4H, Ar-H), 7.78 (s, 1H,

N=CH). Anal. calcd. for  $C_{13}H_{15}F_6N_4O_2P$ : C, 38.63; H, 3.74; N, 13.86. Found: C, 38.05; H, 3.38; N, 13.62.

**1-[2-(2-Hydroxybenzylideneamino)ethyl]-3-methyl-3H-imidazol-3-ium hexafluorophosphate (3f).** Yellow solid (0.41 g, 36.42%); mp 132–134 °C. IR (KBr): 3422 (O–H), 1640 (C=N), 837  $cm^{-1}$  (P–F).  $^1H$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  3.82 (s, 3H, CH<sub>3</sub>), 3.99 (t,  $J$  = 5.49 Hz, 2H, CH<sub>2</sub>), 4.52 (t,  $J$  = 5.48 Hz, 2H, CH<sub>2</sub>), 6.85–7.42 (m, 4H, Ar-H), 7.67 (s, 1H, NCH), 7.73 (s, 1H, NCH), 8.50 (s, 1H, N=CH), 9.12 (s, 1H, OH). Anal. calcd. for  $C_{13}H_{16}F_6N_3OP$ : C, 41.61; H, 4.29; N, 11.20. Found: C, 40.81; H, 4.19; N, 10.99.

**1-[2-(4-Methylbenzylideneamino)ethyl]-3-methyl-3H-imidazol-3-ium hexafluorophosphate (3g).** Yellow solid (0.38 g, 33.93%); mp 131–133 °C. IR (KBr): 1647 (C=N), 833  $cm^{-1}$  (P–F).  $^1H$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  1.55 (s, 3H, CH<sub>3</sub>), 3.05 (s, 3H, CH<sub>3</sub>), 3.16 (t,  $J$  = 5.47 Hz, 2H, CH<sub>2</sub>), 3.72 (t,  $J$  = 5.47 Hz, 2H, CH<sub>2</sub>), 6.41 (s, 1H, NCH), 6.44 (s, 1H, NCH), 6.68–6.80 (m, 4H, Ar-H), 7.41 (s, 1H, N=CH). Anal. calcd. for  $C_{14}H_{18}F_6N_3P$ : C, 45.05; H, 4.86; N, 11.26. Found: C, 45.00; H, 5.36; N, 11.25.

**1-[2-(4-Bromobenzylideneamino)ethyl]-3-methyl-3H-imidazol-3-ium hexafluorophosphate (3h).** White solid (0.39 g, 29.67%); mp decomp. > 220 °C. IR (KBr): 1641 (C=N), 828  $cm^{-1}$  (P–F).  $^1H$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  3.07 (s, 3H, CH<sub>3</sub>), 3.18 (t,  $J$  = 5.46 Hz, 2H, CH<sub>2</sub>), 3.73 (t,  $J$  = 5.46 Hz, 2H, CH<sub>2</sub>), 6.69 (s, 1H, NCH), 6.76 (s, 1H, NCH), 6.79–6.85 (m, 4H, Ar-H), 7.45 (s, 1H, N=CH). Anal. calcd. for  $C_{13}H_{15}BrF_6N_3P$ : C, 35.64; H, 3.45; N, 9.59. Found: C, 35.17; H, 3.25; N, 9.48.

**1-[2-(4-Hydroxy-3-methoxybenzylideneamino)ethyl]-3-methyl-3H-imidazol-3-ium hexafluorophosphate (3i).** Yellow solid (0.52 g, 42.77%); mp 178–180 °C. IR (KBr): 1643 (C=N), 847  $cm^{-1}$  (P–F).  $^1H$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  3.06 (s, 3H, CH<sub>3</sub>), 3.07 (s, 3H, CH<sub>3</sub>), 3.15 (t,  $J$  = 5.59 Hz, 2H, CH<sub>2</sub>), 3.71 (t,  $J$  = 5.49 Hz, 2H, CH<sub>2</sub>), 5.98–6.31 (m, 3H, Ar-H), 6.70 (s, 1H, NCH), 6.80 (s, 1H, NCH), 7.30 (s, 1H, N=CH). Anal. calcd. for  $C_{14}H_{18}F_6N_3O_2P$ : C, 41.49; H, 4.48; N, 10.37. Found: C, 40.81; H, 4.47; N, 10.20.

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