Markus Jochriem, Christian G. Kirchler, Gerhard Laus*, Klaus Wurst, Holger Kopacka, Thomas Müller and Herwig Schottenberger

Synthesis and crystal structures of non-symmetric 1,3-di(alkyloxy)imidazolium salts

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Abstract: A series of non-symmetric 1,3-di(alkyloxy)imidazolium salts were synthesized by stepwise alkylation of 1-hydroxyimidazole-3-oxide. The quaternary salts were subsequently functionalized by bromination in 2-position. A 2-azidoimidazolium salt and an imidazoline-2-thione were prepared exemplarily. Crystal structures of two 2-bromo-1-alkyloxy-3-methyloxyimidazolium tribromides and a mercury(II)-thione complex have been determined by X-ray diffraction.

Keywords: imidazolium salt; ionic liquid; mercury; thione; tribromide.

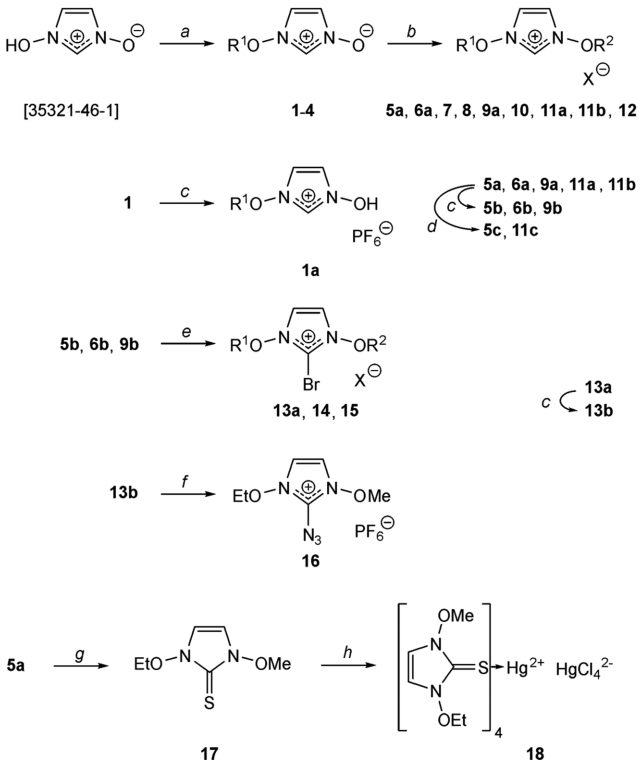
1 Introduction

In continuation of our interest in *N*-(alkyloxy)imidazolium salts [1–3], a series of new non-symmetric 1,3-di(alkyloxy)imidazolium salts were synthesized. Beside the additional synthetic challenge, the primary motivation for this endeavor was the high likelihood of such compounds, due to their non-symmetric substitution patterns, to exhibit lower melting points than their symmetric congeners and therefore qualify as true Ionic Liquids (ILs), even at room temperature. In addition, the quaternary salts and their 2-bromo derivatives would be valuable intermediates for further synthetic modification. The preparation and structural characterization of a transition metal complex with 1,3-di(alkyloxy)imidazoline-2-thione ligands was also conceived and could be successfully accomplished.

***Corresponding author: Gerhard Laus,** Faculty of Chemistry and Pharmacy, University of Innsbruck, 6020 Innsbruck, Austria, Fax: +43 512 507 57099, E-mail: gerhard.laus@uibk.ac.at
Markus Jochriem, Christian G. Kirchler, Klaus Wurst, Holger Kopacka, Thomas Müller and Herwig Schottenberger: Faculty of Chemistry and Pharmacy, University of Innsbruck, 6020 Innsbruck, Austria

2 Results and discussion

In order to obtain non-symmetric 1,3-di(alkyloxy)imidazolium salts, a modified strategy was required in contrast to symmetric 1,3-di(alkyloxy)imidazolium salts [1], namely a stepwise alkylation. The key step was monoalkylation of 1-hydroxyimidazole-3-oxide by an alkyl halide (ethyl, allyl, butyl, and benzyl). Thus, one equivalent of ethyl bromide converted 1-hydroxyimidazole-3-oxide to 1-ethyloxyimidazole-3-oxide (**1**). Treatment of the resulting zwitterionic liquid **1** with NH_4PF_6 yielded the solid 1-hydroxyimidazolium salt **1a**. So far, 1,3-dihydroxyimidazolium salts [3, 4] and 1-alkyl-3-hydroxyimidazolium [3] have been described. Salt **1a** is therefore a representative of the new class of 1-alkyloxy-3-hydroxyimidazolium salts. In the same manner the new liquid *N*-oxides **2** and **3** were prepared. The intermediate 1-benzyloxyimidazole-3-oxide (**4**) was mentioned in an earlier paper but not isolated [5]. The 1-alkyloxyimidazole-3-oxides **1**–**4** were subsequently alkylated to yield the non-symmetric 1,3-di(alkyloxy)imidazolium salts (Scheme 1). Employing dialkyl sulfates or alkyl halides for the second alkylation step, the imidazolium alkyl sulfates **5a**, **7**, **8**, **9a**, **10**, and **11a** or halides **6a** and **12** were obtained. According to NMR the quaternary salts tend to tenaciously retain water and residual solvents even after prolonged treatment in vacuum. In fact, this hygroscopic nature of the ILs prevented the aquisition of meaningful elemental analyses. In several cases, isolation and purification was accomplished by ion metathesis of the crude primary product to the corresponding crystalline hexafluoridophosphates **5b**, **6b** and **9b**. This anion was chosen because the salts crystallize more readily and are less hygroscopic than the halides or alkyl sulfates. The hexafluoridophosphate **11b** was obtained directly when the respective Meerwein's reagent was used. Ion metathesis also yielded the hydrophobic ILs **5c** and **11c** containing the weakly coordinating bis(trifluoromethanesulfonyl)amide ('triflimide') anion. Allyl substituents, as in **7**, **8**, **12**, evoke the scenario of presumable polymerization. However, the reactivity of *N*-allyl-functionalized ILs has not yet been explored to any degree of satisfaction. It seems obvious to continue the investigation of *N*-allylimidazolium salts [6] before



	R^1	R^2	X
1	Et	O	
1a	Et	OH	PF_6
2	All	O	
3	Bu	O	
4	Bn	O	
5a	Et	Me	$MeOSO_3$
5b	Et	Me	PF_6
5c	Et	Me	Tf_2N
6a	Et	Bu	I
6b	Et	Bu	PF_6
7	All	Me	$MeOSO_3$
8	All	Et	$EtOSO_3$
9a	Bu	Me	$MeOSO_3$
9b	Bu	Me	PF_6
10	Bn	Me	$MeOSO_3$
11a	Bn	Et	$EtOSO_3$
11b	Bn	Et	PF_6
11c	Bn	Et	Tf_2N
12	Bn	All	Br
13a	Et	Me	Br_3
13b	Et	Me	PF_6
14	Et	Bu	PF_6
15	Bu	Me	Br_3

Scheme 1: (a) KOH, MeOH, R^1X; (b) R^2X; (c) NH_4PF_6, H_2O; (d) $LiTf_2N$, H_2O-CH_2Cl_2; (e) Br_2, MeOH-H_2O, Na_2CO_3; (f) NaN_3, acetone; (g) S_8, pyridine, Et_3N; (h) $HgCl_2$, MeOH.

tackling the more challenging *N*-allyloxyimidazolium salts. This topic therefore will be deferred to a subsequent scientific discourse. The quaternary salts described here are *N*-heterocyclic carbene precursors and are readily converted to imidazoline-2-thiones [7]. Bromination of the hexafluoridophosphates **5b** and **9b** in aqueous methanol gave 2-bromo derivatives as before [1, 2], but the products bear two different alkyloxy groups and appear as crystalline tribromides **13a** and **15**. It is noteworthy that **6b** remained a hexafluoridophosphate after conversion to the 2-bromo compound **14**, presumably due to lower solubility. Exemplarily, the 2-azido derivative **16**, the imidazoline-2-thione **17**, and the mercury(II) complex **18** were prepared.

The crystal structures of three representative derivatives have been determined by single-crystal X-ray diffraction. Crystallographic data and refinement details are summarized in Table 1. In the crystal structures of 2-bromo-1-ethyloxy-3-methyloxyimidazolium tribromide (**13a**, Fig. 1) and 2-bromo-1-butyloxy-3-methyloxyimidazolium tribromide (**15**, Fig. 2), the two independent ion pairs exhibit typical Br···Br contacts which involve negative ring domains and positive end cap domains ('σ holes') of Br atoms (Fig. 3a) due to their polarizability [8, 9]. The direction of a Br···Br contact can then be judged from the pertinent C–Br···Br and Br···Br–C angles which are summarized in Table 2. In addition, other red areas of the Hirshfeld surface [10] indicate C–H···Br contacts which according to Hirshfeld analysis account for 81% of the total surface of one of the two tribromide anions in compound **13a** (Fig. 3b), 63% in the second. In **15**, C–H···Br contacts amount to 77 and 78% of the total surface of the anions. A fingerprint plot shows the characteristic Br···Br, Br···C and Br···H intermolecular contacts (Fig. 3c). These electrostatic interactions are not obvious from a conventional inspection of short contacts. The tribromide ions deviate only slightly from linearity with Br3–Br4–Br5 and Br6–Br7–Br8 angles of 179.3 and 175.2° in **13a**, and 176.7 and 178.6° in **15**, respectively. The Br–Br bonds are unsymmetrical, their lengths ranging from 2.479 to 2.622 Å. Whereas there are numerous crystal structures of networks of polybromides [11], including tribromides, in the Cambridge Structural Database [12], only a limited number of structures display interactions between tribromides and carbon-bound bromine [13–21]. As expected, the geometry of these Br···Br contacts is determined by the anisotropic distribution of the electron density.

Conformational *syn* and *anti* isomers of 1,3-di(alkyloxy)imidazolium cations have been

Table 1: Crystallographic data and structure refinement details.

Compound	13a	15	18
Formula	$C_6H_{10}BrN_2O_2 \cdot Br_3$	$C_8H_{14}BrN_2O_2 \cdot Br_3$	$C_{24}H_{40}N_8O_8S_4 \cdot Cl_4Hg_2$
M_r	461.80	489.85	1239.86
Crystal size, mm³	0.16×0.15×0.14	0.31×0.15×0.03	0.15×0.11×0.07
Crystal system	Triclinic	Monoclinic	Tetragonal
Space group	$P\bar{1}$	$P2_1/n$	$I\bar{4}$
a, Å	6.9153(2)	16.1386(7)	13.1046(4)
b, Å	14.1795(5)	10.7917(3)	
c, Å	14.5134(7)	19.6146(8)	23.719(1)
α, °	98.580(2)	90	90
β, °	103.747(2)	113.803(2)	90
γ, °	100.950(2)	90	90
V, Å³	1328.71(9)	3125.6(2)	4073.3(3)
Z	4	8	4
D_{calcd}, g cm^{-3}	2.31	2.08	2.02
μ(MoK_α), mm^{-1}	12.1	10.3	8.1
F(000), e	864	1856	2384
hkl range	$-8 \le h \le 8$	$-18 \le h \le 19$	$-15 \le h \le 15$
	$-17 \le k \le 17$	$-12 \le k \le 12$	$-15 \le k \le 15$
	$-17 \le l \le 17$	$-23 \le l \le 23$	$-27 \le l \le 28$
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.62	0.59	0.60
Reflections collected	8925	17 081	47 932
Independent reflections/R_{int}	5172/0.043	5482/0.078	3718/0.034
Reflections [$I > 2\sigma(I)$]	3922	3903	2851
Parameters	255	318	228
R_1/wR_2 indices [$I > 2\sigma(I)$]	0.045/0.101	0.056/0.131	0.029/0.052
R_1/wR_2 indices (all data)	0.067/0.111	0.084/0.144	0.043/0.055
Goodness-of-fit on F^2	1.04	1.06	1.13
$\Delta\rho_{max/min}$, e Å^{-3}	0.71/−0.76	0.70/−1.14	0.29/−0.71
CCDC No.	1473135	1473136	1473137

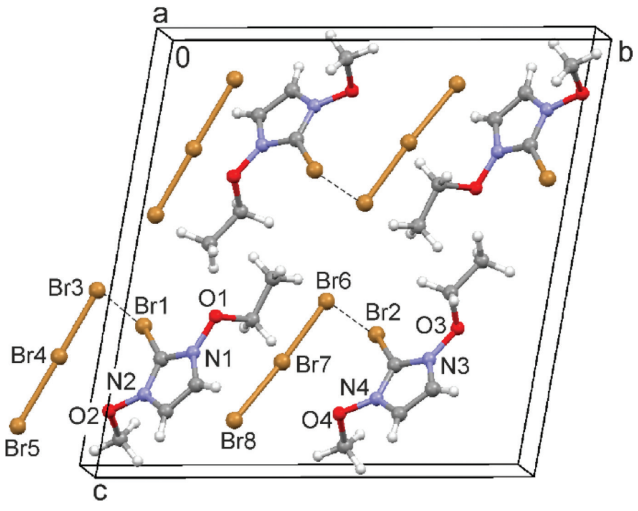


Fig. 1: Crystal structure of 2-bromo-1-ethyloxy-3-methyloxyimidazolium tribromide (**13a**). Dashed lines indicate Br···Br interactions.

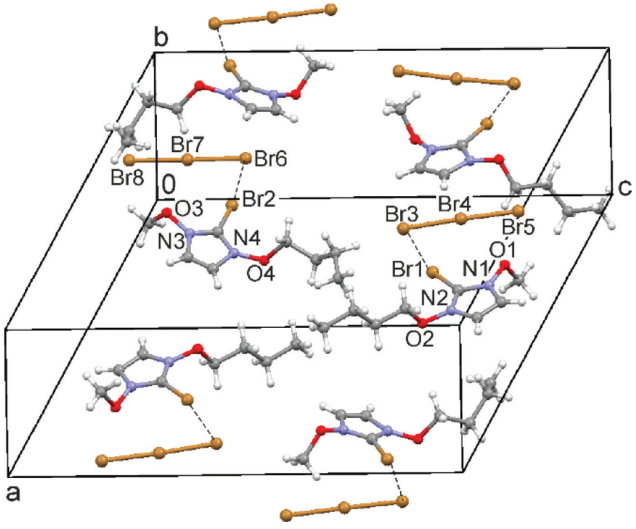


Fig. 2: Crystal structure of 2-bromo-1-butyloxy-3-methyloxyimidazolium tribromide (**15**). Dashed lines indicate Br···Br interactions.

described previously [2] and corroborated by theoretical calculations [22]. Interestingly, the alkyloxy substituents of the two independent cations in the crystal structure of **13a** adopt both *syn* and *anti* conformations. The C–O···O–C dihedral angle in the *syn* conformer is 1°, whereas in the *anti* conformer it is 172° (Fig. 4). In

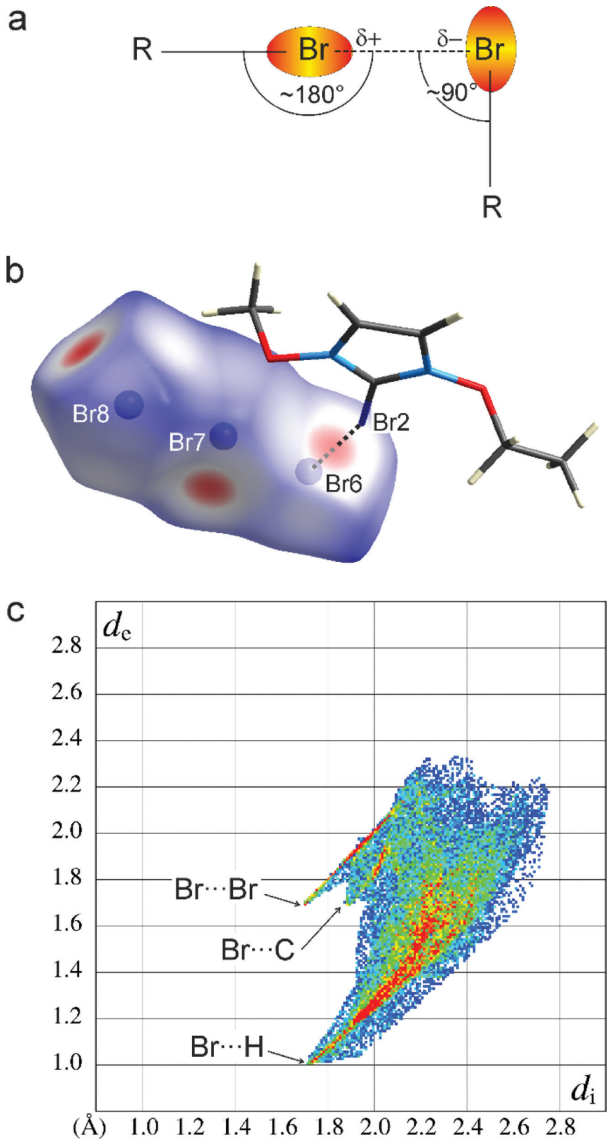


Fig. 3: (a) Preferred geometry for Br · · · Br interactions. (b) Hirshfeld surface of one of the tribromide ions in **13a**. (c) Hirshfeld fingerprint plot showing characteristic intermolecular contacts.

Table 2: Geometric parameters of the Br · · · Br contacts (Å, deg).

Compound	13a	15
Br1 · · · Br3	3.387(1)	3.304(1)
Br2 · · · Br6	3.388(1)	3.327(1)
C1–Br1 · · · Br3	163.4(2)	164.1(2)
Br1 · · · Br3–Br4	78.8(1)	80.6(1)
C8[a](9)[b]–Br2 · · · Br6	164.2(2)	170.1(2)
Br2 · · · Br6–Br7	77.8(1)	83.4(1)

[a]For **13a**; [b]for **15**.

contrast, the cations of **15** adopt two different *anti* conformations in the crystal structure with torsion angles of 157 and 176°.

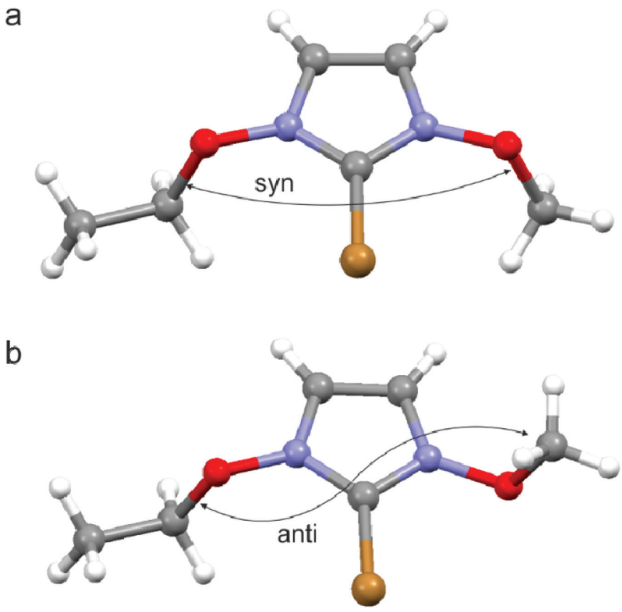


Fig. 4: Conformational isomers identified in the crystal structure of **13a**, exhibiting (a) a *syn* dihedral angle of 1° and (b) an *anti* dihedral angle of 172°.

The crystal structure of complex **18** was refined as a 2-component inversion twin. There were two independent quarter molecules in the asymmetric unit. Mercury atoms were located at fourfold rotoinversion axes in the *c* direction and exhibited distorted tetrahedral coordination geometries. Four thione groups surround each mercury(II) ion with Hg1–S1 and Hg2–S2 bond lengths of 2.563 and 2.576 Å, respectively. To our knowledge, this is the first crystal structure of a mercury-thione complex with a 1:4 metal-to-thione ratio. The distorted geometry is reflected by S1–Hg1–S1 angles of 107.1 and 114.3°, and S2–Hg2–S2 angles of 103.8 and 112.4°. The thione ligand at Hg1 exhibits a slight positional disorder (not solved) and shows increased anisotropic displacement parameters for non-H atoms. The other ligand at Hg2 shows a 3:2 positional disorder for all atoms, where O, N and C atoms were refined isotropically. Only the major component is shown in Fig. 5. The alkyloxy substituents adopt *anti* conformations with torsion angles of 170 and 172°. The $HgCl_4^{2-}$ counter ions are well ordered, exhibiting interatomic distances of Hg3–Cl1 and Hg4–Cl2 of 2.461 and 2.499 Å, respectively. The distorted tetrahedral anions display Cl1–Hg3–Cl1 angles of 107.1 and 114.3°, and Cl2–Hg4–Cl2 angles of 106.6 and 115.4°. Crystal structures of other Hg–imidazolinethione complexes have been reported previously [23–25], they typically involve a 1:2 metal-to-thione ratio and additional ligands such as chloride, triflimide or acetate.

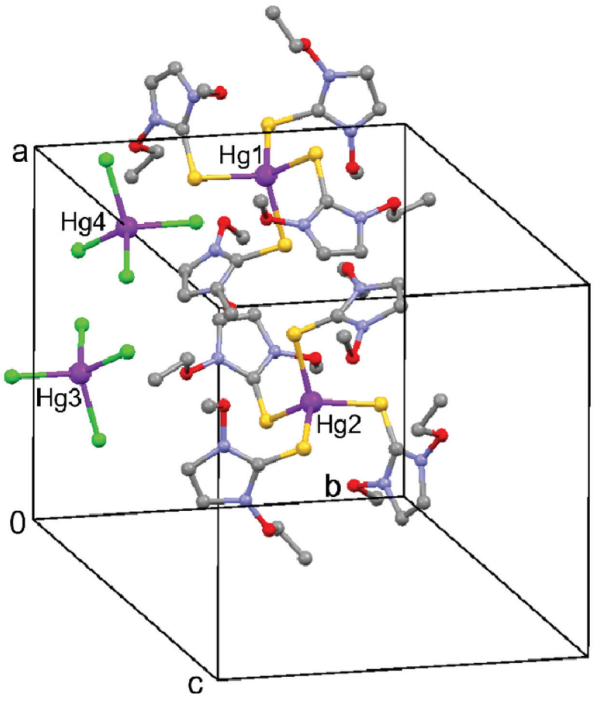


Fig. 5: Crystal structure of Hg(II)-thione complex **18**.

3 Experimental section

1-Hydroxyimidazole-3-oxide [CAS-RN 35321-46-1] was prepared as previously described [26]. NMR spectra were recorded with a Bruker AC 300 spectrometer. IR spectra were obtained using a Nicolet 5700 FT spectrometer in ATR mode. High-resolution mass spectra were measured with a Finnigan MAT 95 spectrometer. Commercial chemicals were used as received.

3.1 1-Ethyloxyimidazole-3-oxide (1)

Potassium hydroxide (85%, 4.3 g, 65 mmol) was added to an ice-cooled solution of 1-hydroxyimidazole-3-oxide (5.0 g, 50 mmol) in MeOH (50 mL), and EtBr (5.5 g, 50 mmol) was added during 2 min. The reaction mixture was refluxed for 48 h. The solution was filtered, and the filter cake was washed with MeOH (2×40 mL). The solvent was evaporated, and the residue was resuspended in CH_2Cl_2. Removal of precipitate, evaporation of solvent and drying yielded 1-ethyloxyimidazole-3-oxide as orange-brown oil. Yield: 4.0 g (63%). – ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 1.23 (t, J = 7.1 Hz, 3H), 4.29 (q, J = 7.0 Hz, 2H), 7.13 (t, J = 2.0 Hz, 1H), 7.62 (t, J = 2.0 Hz, 1H), 8.84 (t, J = 1.9 Hz, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6] DMSO): δ = 12.9, 76.8, 115.0, 118.3, 124.0 ppm. – IR (neat): ν = 3071 (m), 2982 (m), 1683 (m), 1538 (s), 1479 (m), 1386 (m), 1361 (m), 1301 (s), 1148 (s), 1117 (m), 1085 (m), 1007 (s), 855 (m), 776 (m), 741 (s), 722 (s), 666 (m), 633 (m), 582 (s), 500 (m) cm^{-1}. – HRMS ((+)-ESI): m/z = 129.0665 (calcd. 129.0659 for $C_5H_9N_2O_2$, $[M+H]^+$).

3.2 1-Butyloxyimidazole-3-oxide (2)

1-Hydroxyimidazole-3-oxide (5.0 g, 50 mmol) was suspended in MeOH (50 mL) and cooled to 0°C. KOH (4.3 g, 65 mmol) was added slowly. The resulting solution was allowed to warm to room temperature, and BuI (5.7 mL, 50 mmol) was added. The solution was refluxed for 20 h and turned red-brown. The white precipitate was filtered off, the solvent evaporated and the residue suspended in CH_2Cl_2. The mixture was filtered again and then evaporated, and the residue was dried in vacuum to yield orange-brown liquid 1-butyloxyimidazole-3-oxide. Yield: 6.7 g (86%). – ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 0.91 (t, J = 7.3 Hz, 3H), 1.40 (m, 2H), 1.61 (m, 2H), 4.25 (t, J = 6.5 Hz, 2H), 7.08 (t, J = 2 Hz, 1H), 7.58 (t, J = 2 Hz, 1H), 8.74 (t, J = 2 Hz, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6] DMSO): δ = 14.4, 19.1, 29.9, 81.3, 115.1, 119.2, 123.5 ppm. – HRMS (ESI): m/z = 157.0983 (calcd. 157.0972 for $C_7H_{13}N_2O_2$, $[M+H]^+$).

3.3 1-Allyloxyimidazole-3-oxide (3)

Potassium hydroxide (85%, 4.3 g, 65 mmol) was added to an ice-cooled solution of 1-hydroxyimidazole-3-oxide (5.0 g, 50 mmol) in MeOH (50 mL). The ice-bath was removed when the solution was clear, and allyl bromide (97%, 6.2 g, 50 mmol) was added during 2 min. The reaction mixture was refluxed for 23 h. The solution was filtered, and the filter cake was washed with MeOH (2×40 mL). The solvent was evaporated, and the residue was resuspended in CH_3CN. Removal of precipitate, evaporation of solvent and drying yielded 1-allyloxyimidazole-3-oxide as a brown liquid. Yield: 5.4 g (86%). – ^{1}H NMR (300 MHz, [D_4]methanol): δ = 4.74 (d, J = 6.6 Hz, 2H), 5.33–5.40 (m, 2H), 5.95–6.08 (m, 1H), 7.06 (t, J = 2.0 Hz, 1H), 7.54 (t, J = 2.0 Hz, 1H), 8.70 (t, J = 2.0 Hz, 1H) ppm. – IR (neat): ν = 3090 (m), 3016 (m), 2981 (m), 2941 (m), 2882 (m), 1681 (m), 1564 (m), 1539 (s), 1497 (m), 1451 (m), 1422 (m), 1352 (m), 1301 (s), 1195 (w), 1142 (s), 1077 (m), 1003 (s), 934 (s), 895 (s), 754 (s), 726 (s), 679 (m), 627 (m), 581 (m), 505 (w) cm^{-1}. – HRMS (ESI): m/z = 141.0668 (calcd. 141.0659 for $C_6H_9N_2O_2$, $[M+H]^+$).

3.4 1-Benzyloxyimidazole-3-oxide (4)

Potassium hydroxide (85%, 4.3 g, 65 mmol) was added to an ice-cooled solution of 1-hydroxyimidazole-3-oxide (5.0 g, 50 mmol) in MeOH (50 mL). The ice-bath was removed when the solution was clear, and benzyl bromide (6.0 mL, 50 mmol) was added during 2 min. The reaction mixture was refluxed for 1 h. The solution was filtered, and the filter cake was washed with MeOH (2×40 mL). The solvent was evaporated, and the residue was redissolved in CH_3CN. Removal of precipitate, evaporation of solvent and drying yielded 1-benzyloxyimidazole-3-oxide as a brown liquid. Yield: 7.9 g (83%) – ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 5.28 (s, 2H), 7.04 (t, J = 1.9 Hz, 1H), 7.37–7.43 (m, 5H), 7.45 (t, J = 1.9 Hz, 1H), 8.64 (t, J = 1.9 Hz, 2H) ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 81.9, 114.4, 118.3, 122.9, 128.6 (2C), 129.5, 129.8 (2C), 133.1 ppm. – IR (neat): ν = 3149 (m), 3064 (m), 3031 (m), 1681 (w), 1565 (m), 1540 (m), 1496 (m), 1454 (m), 1374 (m), 1300 (m), 1212 (w), 1141 (m), 1082 (w), 1005 (m), 952 (w), 907 (m), 845 (w), 735 (s), 696 (s), 628 (m), 582 (m), 557 (w), 496 (w) cm^{-1}. – HRMS (ESI): m/z = 191.0831 (calcd. 191.0815 for $C_{10}H_{11}N_2O_2$, $[M+H]^+$).

3.5 1-Ethyloxy-3-hydroxyimidazolium hexafluoridophosphate (1a)

1-Ethyloxyimidazole-3-oxide (**1**; 0.33 g, 2.6 mmol) was added to a saturated aqueous solution of NH_4PF_6 (0.42 g, 2.6 mmol) and stirred for 3 h. The precipitate was collected by filtration and dried in vacuum to yield 1-ethyloxy-3-hydroxyimidazolium hexafluoridophosphate (0.69 g, 98%), mp. >240°C. ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 1.26 (t, J = 7.1 Hz, 3H), 4.33 (q, J = 7.0 Hz, 2H), 7.17 (br s, 1H), 7.26 (s, 1H), 7.71 (s, 1H), 8.99 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 12.9, 77.0, 115.2, 118.3, 124.2 ppm. – ^{31}P NMR (121 MHz, [D_6]DMSO): δ = –143.6 (sept, J = 711 Hz) ppm. – IR (neat): ν = 3334 (w), 3170 (w), 2991 (w), 1550 (w), 1445 (m), 1319 (w), 1143 (w), 1011 (m), 816 (s), 740 (s), 723 (m), 671 (m), 627 (m), 590 (m), 553 (s) cm^{-1}.

3.6 1-Ethyloxy-3-methyloxyimidazolium methyl sulfate (5a)

1-Ethyloxyimidazole-3-oxide (**1**; 0.65 g, 5.1 mmol) was stirred with dimethyl sulfate (0.77 g, 6.1 mmol) overnight at ambient conditions. Removal of volatiles yielded 1-ethyloxy-3-methyloxyimidazolium methyl sulfate as brown liquid. Yield: 1.1 g (87%). – ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 1.32 (t, J = 6.9 Hz, 3H), 3.38 (s, 3H), 4.26 (s, 3H), 4.50 (q, J = 6.9 Hz, 2H), 8.26 (t, J = 2.3 Hz, 1H), 8.31 (t, J = 2.3 Hz, 1H), 10.27 (t, J = 2.0 Hz, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 12.9, 52.9, 69.5, 78.3, 117.1, 117.8, 129.9 ppm. – IR (neat): ν = 3116 (m), 3085 (m), 2995 (m), 2952 (m), 1725 (m), 1651 (m), 1553 (m), 1448 (m), 1390 (w), 1251 (s), 1174 (s), 1044 (m), 1001 (s), 947 (m), 859 (m), 759 (m), 611 (m), 580 (s), 436 (m) cm^{-1}.

3.7 1-Ethyloxy-3-methyloxyimidazolium hexafluoridophosphate (5b)

To a solution of 1-ethyloxy-3-methyloxyimidazolium methyl sulfate (**5a**; 0.27 g, 1.1 mmol) H_2O (1 mL) and NH_4PF_6 (0.18 g, 1.1 mmol) were added. Two layers were formed. After drying in high vacuum the brown oily residue was redissolved in acetone. Removal of precipitate and evaporation of solvent yielded 1-ethyloxy-3-methyloxyimidazolium hexafluoridophosphate as brown oily liquid (0.23 g, 74%). ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 1.33 (t, J = 7.1 Hz, 3H), 4.26 (s, 3H), 4.50 (q, J = 6.9 Hz, 2H), 8.26 (t, J = 2.3 Hz, 1H), 8.30 (t, J = 2.3 Hz, 1H), 10.28 (t, J = 2.0 Hz, 1H) ppm. – ^{31}P NMR (121 MHz, [D_6]DMSO): δ = –143.1 (sept, J = 711 Hz) ppm.

3.8 1-Ethyloxy-3-methyloxyimidazolium bis(trifluoromethanesulfonyl)amide (5c)

1-Ethyloxy-3-methyloxyimidazolium methyl sulfate (**5a**; 1.0 g, 3.9 mmol) was dissolved in H_2O (10 mL) and CH_2Cl_2 (10 mL) was added. To this mixture Li Tf_2N (1.8 g, 6.3 mmol) was added while stirring. After 5 min the organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (10 mL). The combined organic fractions were evaporated and the liquid residue dried in vacuum. Yield: 1.2 g (72%). – ^{1}H NMR (300 MHz, [D_4]methanol): δ = 1.43 (t, J = 6.9 Hz, 3H), 4.32 (s, 3H), 4.55 (q, J = 6.9 Hz, 2H), 7.99 (t, J = 2.0 Hz, 1H), 8.02 (t, J = 2.0 Hz, 1H), 9.93 (t, J = 2.0 Hz, 1H) ppm. – ^{13}C NMR (75 MHz, [D_4]methanol): δ = 13.4, 70.6, 80.5, 118.6, 119.3, 123.5, 131.0 ppm.

3.9 1-Butyloxy-3-ethyloxyimidazolium iodide (6a)

1-Ethyloxyimidazole-3-oxide (**1**; 1.0 g, 7.8 mmol) was stirred with BuI (0.89 mL, 7.8 mmol) for 24 h at ambient conditions. Removal of volatiles yielded 1-butyloxy-3-ethyloxyimidazolium iodide as a brown viscous liquid. Yield: 2.4 g (99%). – ^{1}H NMR (300 MHz, [D_4]methanol):

δ = 1.01 (m, 3H), 1.44 (m, 3H), 1.53 (m, 2H), 1.78 (m, 2H), 4.59 (m, 4H), 8.07 (s, 2H) ppm. – ^{13}C NMR (75 MHz, [D_4] methanol): δ = 13.6, 14.1, 19.8, 30.7, 80.6, 84.5, 119.2, 119.4 ppm. – HRMS (ESI): *m/z* = 185.1300 (calcd. 185.1285 for $C_9H_{17}N_2O_2$, $[M]^+$).

3.10 1-Butyloxy-3-ethyloxyimidazolium hexafluoridophosphate (6b)

To 1-butyloxy-3-ethyloxyimidazolium iodide (**6a**; 2.4 g, 7.9 mmol) was added a solution of NH_4PF_6 (1.5 g, 9.4 mmol) in H_2O (4 mL). After stirring overnight the solution was extracted with CH_2Cl_2. Evaporation of the organic phase and drying in vacuum yielded 1-butyloxy-3-ethyloxyimidazolium hexafluoridophosphate. Yield: 1.8 g (69%). – ^{1}H NMR (300 MHz, [D_4]methanol): δ = 1.00 (m, 3H), 1.43 (m, 3H) 1.52 (m, 2H), 1.79 (m, 2H), 4.54 (m, 4H), 7.98 (s, 2H) ppm.

3.11 1-Allyloxy-3-methyloxyimidazolium methyl sulfate (7)

1-Allyloxyimidazol-3-oxide (**2**; 0.60 g, 4.3 mmol) was stirred with dimethyl sulfate (0.65 g, 5.2 mmol) for 3 d at ambient conditions. Removal of volatiles yielded 1-allyloxy-3-methyloxyimidazolium methyl sulfate as brown oily liquid (1.1 g, 99%). ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 3.39 (s, 3H), 4.25 (s, 3H), 4.96 (d, *J* = 6.6 Hz, 2H), 5.44–5.50 (m, 2H), 5.99–6.12 (m, 1H), 8.23 (t, *J* = 2.3 Hz, 1H), 8.31 (t, *J* = 2.2 Hz, 1H), 10.26 (t, *J* = 2.0 Hz, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 53.0, 69.6, 82.3, 117.1, 118.1, 124.7, 129.8, 130.1 ppm. – IR (neat): ν = 3114 (m), 3085 (m), 3008 (m), 2951 (m), 1717 (m), 1647 (m), 1553 (m), 1454 (m), 1427 (m), 1371 (w), 1247 (s), 1202 (s), 1056 (m), 1001 (s), 945 (m), 884 (m), 757 (s), 611 (m), 581 (s), 435 (m) cm^{-1}.

3.12 1-Allyloxy-3-ethyloxyimidazolium ethyl sulfate (8)

1-Allyloxyimidazole-3-oxide (**2**; 0.49 g, 3.5 mmol) was stirred with diethyl sulfate (0.55 g, 3.5 mmol) overnight at ambient conditions. Removal of volatiles yielded 1-allyloxy-3-ethyloxyimidazolium ethyl sulfate as brown oil (1.0 g, 99%). ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 1.10 (t, *J* = 7.1 Hz, 3H), 1.31 (t, *J* = 7.1, 3H), 3.74 (q, *J* = 7.1 Hz, 2H), 4.50 (q, *J* = 6.9 Hz, 2H), 4.96 (d, *J* = 6.9 Hz, 2H), 5.43–5.49 (m, 2H), 6.00–6.13 (m, 1H), 8.26 (t, *J* = 2.3 Hz, 1H), 8.29 (t, *J* = 2.3 Hz, 1H), 10.27 (t, *J* = 2.0 Hz, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6] DMSO): δ = 12.8, 15.1, 61.2, 78.3, 82.2, 117.8, 118.0, 124.7, 129.7, 130.5 ppm. – IR (neat): ν = 3307 (w), 3137 (w), 2983 (w), 1651 (m), 1445 (w), 1391 (w), 1150 (m), 1031 (s), 997 (s), 920 (m), 864 (m), 792 (m), 653 (m), 621 (m), 581 (m), 444 (m) cm^{-1}.

3.13 1-Butyloxy-3-methyloxyimidazolium methyl sulfate (9a)

1-Butyloxyimidazole-3-oxide (**3**; 5.2 g, 33 mmol) was cooled to 0°C and dimethyl sulfate (3.8 mL, 40 mmol) was added. Stirring for 20 h and removal of volatiles yielded 1-butyloxy-3-methyloxyimidazolium methyl sulfate as brown liquid. Yield: 9.3 g (99%). – ^{1}H NMR (300 MHz, [D_4] methanol): δ = 1.01 (m, 3H), 1.52 (m, 2H), 1.79 (m, 2H), 3.67 (m, 3H), 4.32 (m, 3H), 4.52 (m, 2H), 7.08 (m, 2H), 9.99 (m, 1H) ppm. – ^{13}C NMR (75 MHz, [D_4]methanol): δ = 14.1, 19. 8, 30.7, 55.2, 70.7, 84.5, 118.6, 119.2, 131.0 ppm.

3.14 1-Butyloxy-3-methyloxyimidazolium hexafluoridophosphate (9b)

1-Butyloxy-3-methyloxyimidazolium methyl sulfate (**9a**; 5 g, 17.7 mmol) and a solution of NH_4PF_6 (3.5 g, 21.3 mmol) in H_2O (9 mL) were stirred overnight. Then the heavier phase was separated and dried in vacuum to yield 1-butyloxy-3-methyloxyimidazolium hexafluoridophosphate (4.03 g, 72%). ^{1}H NMR (300 MHz, [D_4]methanol): δ = 1.00 (m, 3H), 1.51 (m, 2H), 1.78 (m, 2H), 4.32 (s, 3H), 4.51 (m, 2H), 7.96 (m, 2H), 9.84 (m, 1H) ppm. – ^{13}C NMR (75 MHz, [D_4]methanol): δ = 14.0, 19.7, 30.6, 70.6, 84.5, 118.5, 119.1, 130.8 ppm.

3.15 1-Benzyloxy-3-methyloxyimidazolium methyl sulfate (10)

1-Benzyloxyimidazole-3-oxide (**4**; 0.71 g, 3.8 mmol) was stirred with dimethyl sulfate (0.47 g, 3.8 mmol) overnight at ambient conditions. Removal of volatiles yielded 1-benzyloxy-3-methyloxyimidazolium methyl sulfate as brown oil (1.2 g, 99%). ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 4.22 (s, 3H), 4.26 (s, 3H), 5.49 (s, 2H), 7.32–7.48 (m, 5H), 8.20 (t, *J* = 2.3 Hz, 1H), 8.29 (t, *J* = 2.3 Hz, 1H), 10.20 (t, *J* = 2.0 Hz, 1H) ppm. – IR (neat): ν = 3087 (m), 2951 (w), 1722 (m), 1552 (w), 1497 (w), 1455 (m), 1212 (s), 1056 (m), 1001 (s), 946 (m), 909 (w), 869 (w), 845 (m), 754 (m), 698 (m), 652 (m), 618 (m), 576 (m), 551 (m), 496 (w), 464 (w), 438 (m) cm^{-1}.

3.16 1-Benzyloxy-3-ethyloxyimidazolium ethyl sulfate (11a)

1-Benzyloxyimidazole-3-oxide (**4**; 0.50 g, 2.6 mmol) was stirred with diethyl sulfate (0.42 g, 2.6 mmol) for 4 h at ambient conditions. Removal of volatiles yielded 1-benzyloxy-3-ethyloxyimidazolium ethyl sulfate as brown liquid (0.88 g, 99%). ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 1.10 (t, J = 7.1 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H), 3.74 (q, J = 7.1 Hz, 2H), 4.44 (q, J = 7.1 Hz, 2H), 5.51 (s, 2H), 7.38–7.49 (m, 5H), 8.23–8.29 (m, 2H), 10.15 (t, J = 2.0 Hz, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 12.7, 15.1, 61.2, 78.2, 83.3, 117.8, 117.9, 128.9 (2C), 130.1, 130.2 (2C), 130.4, 131.9 ppm. – IR (neat): ν = 3068 (m), 2980 (m), 2901 (m), 1683 (m), 1551 (m), 1497 (w), 1455 (m), 1387 (m), 1213 (s), 1111 (m), 1059 (m), 1016 (s), 915 (s), 847 (m), 762 (s), 702 (m), 621 (m), 579 (m), 419 (w) cm^{-1}.

3.17 1-Benzyloxy-3-ethyloxyimidazolium hexafluoridophosphate (11b)

1-Benzyloxyimidazol-3-oxide (**4**; 0.05 g, 0.3 mmol) was added to a solution of triethyloxonium hexafluoridophosphate (0.07 g 0.3 mmol) in CH_2Cl_2. The precipitate was collected by filtration and dried in vacuum to yield 1-benzyloxy-3-ethyloxyimidazolium hexafluoridophosphate as liquid (0.10 g, 99%). ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 1.25 (t, J = 7.1 Hz, 3H), 4.44 (q, J = 6.9 Hz, 2H), 5.50 (s, 2H), 7.39–7.47 (m, 5H), 8.22 (t, J = 2.2 Hz, 1H), 8.25 (t, J = 2.3 Hz, 1H), 10.15 (t, J = 2.0 Hz, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 12.7, 78.3, 83.4, 117.8, 117.9, 128.9 (2C), 130.1, 130.2 (2C), 130.4, 132.9 ppm. – ^{31}P NMR (121 MHz, [D_6]DMSO): δ = –146,5 (sept, J = 711 Hz) ppm. – IR (neat): ν = 3153 (m), 1554 (w), 1457 (w), 1390 (w), 1087 (w), 1012 (m), 825 (s), 756 (m), 701 (m), 598 (m), 555 (s), 497 (m) cm^{-1}.

3.18 1-Benzyloxy-3-ethyloxyimidazolium bis(trifluoromethanesulfonyl)amide (11c)

HCl (37%, 0.06 g, 1.7 mmol) and Li Tf_2N (0.48 g, 1.7 mmol) was added to 1-benzyloxy-3-ethyloxyimidazolium ethyl sulfate (**11a**; 0.56 g, 1.7 mmol). The product was partitioned between H_2O (5 mL) and CH_2Cl_2 (5 mL) by stirring the mixture for 3 h. After separation of the organic layer the solvent was evaporated. Drying in vacuum yielded 1-benzyloxy-3-ethyloxyimidazolium bis(trifluoromethanesulfonyl)amide as brown liquid (0.77 g, 91%). ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 1.26 (t, J = 6.9 Hz, 3H), 4.44 (q, J = 6.9 Hz, 2H), 5.50 (s, 2H), 7.47 (s, 5H), 8.22 (t, J = 2.3 Hz, 1H), 8.25 (t, J = 2.3 Hz, 1H), 10.15 (t, J = 2.0 Hz, 1H) ppm. – ^{13}C NMR (75 MHz, [D_6]DMSO): δ = 12.6, 78.3, 83.4, 117.8, 117.9, 119.5 (q, J = 321 Hz, 2C), 128.9 (2C), 130.1, 130.2 (2C), 130.4, 131.9 ppm.

3.19 1-Allyloxy-3-benzyloxyimidazolium bromide (12)

A solution of allyl bromide (97%, 0.14 g, 1.1 mmol) in CH_2Cl_2 (5 mL) was added dropwise to 1-benzyloxyimidazole-3-oxide (**4**; 0.21 g, 1.1 mmol). The reaction mixture was stirred at 50°C for 1 h to obtain 1-allyloxy-3-benzyloxyimidazolium bromide as brown oil which was freed from volatiles under reduced pressure (0.35 g, 99%). ^{1}H NMR (300 MHz, [D_6]DMSO): δ = 4.92 (d, J = 6.9 Hz, 2H), 5.33 (s, 2H), 5.38–5.44 (m, 2H), 5.88–6.11 (m, 1H), 7.47 (s, 5H), 8.25 (s, 1H), 8.26 (s, 1H), 10.27 (t, J = 2.0 Hz, 1H) ppm. – IR (neat): ν = 3326 (w), 3153 (m), 3034 (m), 1677 (m), 1548 (w), 1496 (w), 1424 (m), 1401 (m), 1314 (w), 1214 (w), 1141 (w), 1083 (m), 1012 (m), 939 (m), 825 (s), 741 (s), 699 (s), 626 (w), 554 (s) cm^{-1}.

3.20 2-Bromo-1-ethyloxy-3-methyloxyimidazolium tribromide (13a)

1-Ethyloxy-3-methyloxyimidazolium hexafluoridophosphate (**5b**; 1.0 g, 3.5 mmol) was suspended in MeOH (1.5 mL) and H_2O (3.0 mL). Then bromine (0.18 mL, 3.5 mmol) was added and the mixture was stirred for 24 h. After this time Na_2CO_3 (369 mg, 3.5 mmol) and again bromine (0.18 mL, 3.5 mmol) were added. After stirring again for 24 h the orange precipitate was filtered off, dissolved in hot MeOH (5 mL) and precipitated again by addition of Et_2O (60 mL) and cooling to –20°C. Filtration and drying in air yielded 2-bromo-1-ethyloxy-3-methyloxyimidazolium tribromide as bright orange crystals. Yield: 0.7 g (45%). – ^{1}H NMR (300 MHz, [D_4]methanol): δ = 1.49 (t, J = 6.9 Hz, 3H), 4.33 (s, 3H), 4.58 (q, J = 6.9 Hz, 2H), 8.27 (d, J = 3.0 Hz, 1H), 8.29 (d, J = 3.0 Hz, 1H) ppm. – ^{13}C NMR (75 MHz, [D_4]methanol): δ = 13.7, 70.1, 80.3, 119.8, 120.7, 161.0 ppm. – IR (neat): ν = 3129 (m), 3098 (m), 3078 (m), 2997 (m), 2940 (m), 1683 (w), 1547 (m), 1446 (m), 1391 (m), 1352 (w), 1319 (w), 1263 (w), 1192 (w), 1152 (w), 1111 (m), 1040 (s), 1003 (s), 933 (s), 843 (s), 754 (w), 723 (s), 678 (w), 633 (s), 604 (s), 558 (m), 527 (w), 463 (m), 428 (w) cm^{-1}.

3.21 2-Bromo-1-ethyloxy-3-methyloxyimidazolium hexafluoridophosphate (13b)

2-Bromo-1-ethyloxy-3-methyloxyimidazolium tribromide (**13a**; 300 mg, 0.65 mmol) was suspended in H_2O

and NH_4PF_6 (127 mg, 7.8 mmol) was added. After stirring for 24 h the white precipitate was filtered off and washed with H_2O. Drying in vacuum yielded 2-bromo-1-ethyloxy-3-methyloxyimidazolium hexafluoridophosphate as yellowish powder, mp. 101°C. Yield: 220 mg (92%). – IR (neat): ν = 3169 (w), 3149 (w), 1704 (w), 1557 (w), 1458 (w), 1397 (w), 1357 (w), 1064 (m), 1001 (w), 994 (w), 821 (s), 726 (m), 680 (w), 645 (w), 619 (w), 555 (s), 456 (w) cm^{-1}.

3.22 2-Bromo-1-butyloxy-3-ethyloxyimidazolium hexafluoridophosphate (14)

1-Butyloxy-3-ethyloxyimidazolium hexafluoridophosphate (**6b**; 1.77 g, 5.4 mmol) was dissolved in MeOH (2.3 mL) and H_2O (4.6 mL) and bromine (0.28 mL, 5.4 mmol) was added slowly. The solution was stirred for 66 h and then Na_2CO_3 (570 mg, 5.4 mmol) and bromine (0.28 mL, 5.4 mmol) were added. The solution was stirred again overnight, the resulting red oil was separated from the yellow solution and dried in vacuum (1.06 g, 48%). ^{1}H NMR (300 MHz, [D_4]methanol): δ = 1.01 (m, 3H), 1.46 (m, 3H) 1.58 (m, 2H), 1.83 (m, 2H), 4.59 (m, 4H), 8.21 (s, 2H) ppm. – ^{13}C NMR (75 MHz, [D_4]methanol): δ = 13.8, 14.2, 19.9, 30.9, 80.4, 84.2, 120.5, 120.7 ppm. – IR (neat): ν = 3121 (w), 2960 (w), 2873 (w), 1745 (w), 1551 (w), 1456 (w), 1387 (w), 1115 (w), 1042 (m), 1003 (m), 929 (w), 836 (s), 713 (w), 636 (w), 631 (w), 557 (m), 453 (w) cm^{-1}.

3.23 2-Bromo-1-butyloxy-3-methyloxyimidazolium tribromide (15)

1-Butyloxy-3-methyloxyimidazolium hexafluoridophosphate (**9b**; 3.5 g, 10.9 mmol) was dissolved in MeOH (4.6 mL) and H_2O (9.2 mL) and bromine (0.56 mL, 10.9 mmol) was added slowly. The solution was stirred for 66 h and then Na_2CO_3 (1.2 g, 10.9 mmol) and bromine (0.56 mL, 10.9 mmol) were added. The solution was stirred again overnight, and the resulting red oil separated from the yellow solution and dried in vacuum (2.94 g, 55%). ^{1}H NMR (300 MHz, [D_4]methanol): δ = 1.03 (t, J = 7.4 Hz, 3H), 1.58 (sext, 2H), 1.86 (m, 2H), 4.35 (s, 3H), 4.56 (t, J = 6.6 Hz, 2H), 8.21 (d, J = 2.6 Hz, 1H), 8.23 (d, J = 2.6 Hz, 1H) ppm. – ^{13}C NMR (75 MHz, [D_4]methanol): δ = 14.1, 19.9, 30.9, 70.2, 84.3, 119.9, 120.6 ppm. – IR (neat): ν = 3151 (w), 2960 (w), 2873 (w), 1553 (w), 1453 (w), 1383 (w), 1123 (w), 1044 (m), 937 (m), 832 (s), 714 (w), 675 (w), 639 (w), 611 (w), 557 (m) cm^{-1}.

3.24 2-Azido-1-ethyloxy-3-methyloxyimidazolium hexafluoridophosphate (16)

2-Bromo-1-ethyloxy-3-methyloxyimidazolium hexafluoridophosphate (**13b**; 110 mg, 0.3 mmol) and sodium azide (20 mg, 0.3 mmol) were suspended in acetone (2 mL) and stirred for 71 h. The precipitate was filtered off and the solvent evaporated. Drying of the residue in vacuum yielded 2-azido-1-ethyloxy-3-methyloxyimidazolium hexafluoridophosphate as slightly brownish powder, mp. 160°C (decomposition). Yield: 26 mg (26%). – IR (neat): ν = 3171 (w), 2164 (w), 1684 (w), 1604 (w), 1481 (w), 1434 (w), 1261 (w), 1095 (w), 1070 (w), 1026 (m), 999 (w), 952 (w), 834 (s), 742 (m), 692 (m), 660 (w), 609 (w), 556 (m), 529 (w), 509 (w), 494 (m) cm^{-1}.

3.25 1-Ethyloxy-3-methyloxyimidazoline-2-thione (17)

1-Ethyloxy-3-methyloxyimidazolium methylsulfate (**5a**; 1.0 g, 3.9 mmol) was dissolved in pyridine and sulfur (127 mg, 3.9 mmol) and triethylamine (0.6 mL, 4.3 mmol) were added. After heating to 70°C for 2 h the solvent was evaporated. The residue was dissolved in EtOAc and washed with H_2O (2×100 mL) and HCl (1 M, 2×25 mL). Evaporation of solvent and drying yielded 1-ethyloxy-3-methyloxymidazoline-2-thione as oil that solidified at room temperature after shock-cooling with liquid N_2, mp. 63°C. Yield: 189 mg (28%). – ^{1}H NMR (300 MHz, [D_4]methanol): δ = 1.35 (t, J = 6.9 Hz, 3H), 4.06 (s, 3H), 4.36 (q, J = 6.9 Hz, 2H), 7.22 (m, 2H) ppm. – ^{13}C NMR (75 MHz, [D_4]methanol): δ = 13.6, 66.0, 75.1, 112.9, 114.2, 155.1 ppm. – HRMS (ESI): m/z = 175.0551 (calcd. 175.0536 for $C_6H_{11}N_2O_2S$, $[M+H]^+$).

3.26 Tetrakis(1-ethyloxy-3-methyloxyimidazoline-2-thione)mercury(II) tetrachloridomercurate(II) (18)

1-Ethyloxy-3-methyloxymidazoline-2-thione (**17**; 75 mg, 0.43 mmol) was dissolved in MeOH and mercury(II) chloride (58.4 mg, 0.215 mmol) was added. After stirring for 30 min the solvent was evaporated and the resulting brownish powder was dried in vacuum. Single crystals suitable for X-ray characterization were grown from MeOH, mp. 139°C. Yield: 132 mg (99%). – IR (neat): ν = 3116 (m), 3062 (w), 2941 (w), 1721 (w), 1541 (s), 1439 (m), 1406 (s), 1388 (s), 1261 (w), 1151 (w), 1123 (m), 1028 (s), 1007 (s), 943 (s), 857 (s), 762 (m), 727 (s), 676 (m), 655 (s), 594 (m), 530 (s), 439 (w) cm^{-1}.

3.27 X-ray structure determinations

Single crystal diffraction intensity data were recorded by ϕ and ω scans with a Nonius KappaCCD diffractometer using Mo$K\alpha$ radiation at 233(2) K. The crystal structures were solved by Direct Methods and refined by full-matrix least-squares techniques [27, 28]. All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement.

CCDC 1473135–1473137 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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Graphical synopsis

Markus Jochriem, Christian G. Kirchler, Gerhard Laus, Klaus Wurst, Holger Kopacka, Thomas Müller and Herwig Schottenberger

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