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2-BROMO-1,3-DI(METHOXY)IMIDAZOLIUM TRIBROMIDE AS STARTING SALT FOR 2-ARYL- AND 2-HETEROARYLMERCAPTO DERIVATIVES

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Abstract – A one-pot alkylation/bromination sequence of 1-hydroxyimidazole 3-oxide led to the simple isolation of new 2-bromo-1,3-di(methoxy)imidazolium tribromide **1** by spontaneous precipitation from the aqueous reaction mixture. The related bromide **2**, quantitatively and cleanly derived from the tribromide **1** via sacrificial bromination of cyclohexene, as well as the hexafluorophosphate **3**, easily accessible through anion metathesis, represent valuable congeners for a rich follow-up chemistry. The reactivity of the 2-bromo substituent towards nucleophilic substitution by different *S*-nucleophiles was chosen as a starting point. Thus, a series of 2-arylmercapto- and 2-hetarylmercaptoimidazolium salts, which are otherwise only elaborately to access, could be isolated with minimal effort. In addition to routine spectroscopic characterization, eleven selected compounds have been determined using single-crystal X-ray diffraction.

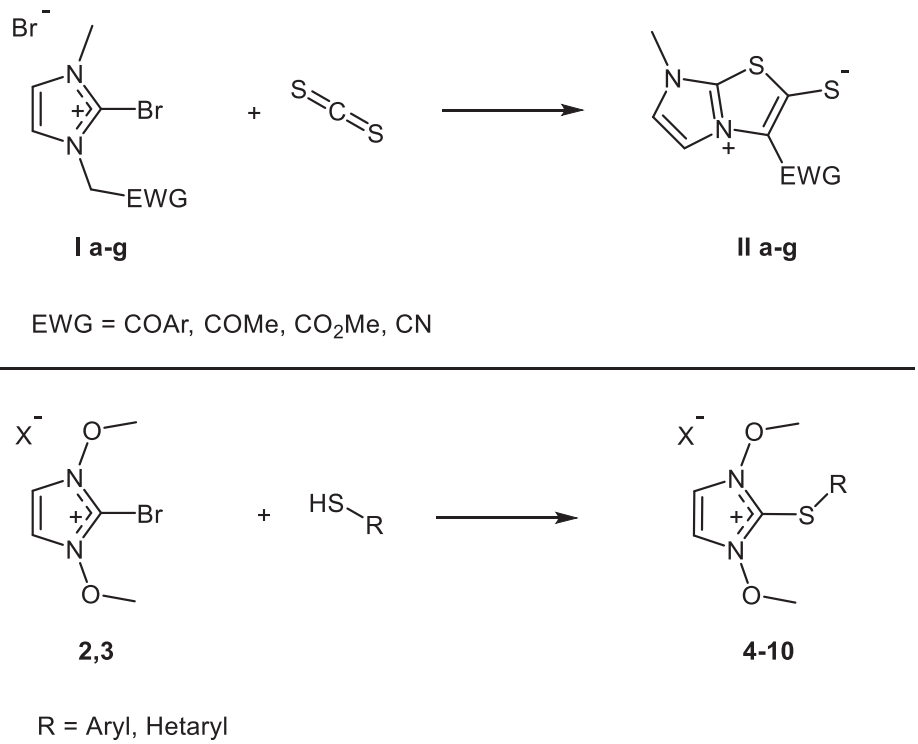
INTRODUCTION

In comparison to their more common dialkylated quaternary parent compounds, the incorporation of an N-O moiety into imidazolium-based ionic liquids and related salts leads to a diverging electronic situation in such "*N*-alkoxylated" nitrogen heterocyclic cationic cores. Most notably, this structural motif induces a remarkably high kinetic acidity.[1] Therefore, *N*,*N*′-di(alkoxy)imidazolium salts[2-4] represent useful precursors for catalytically active[1] N-heterocyclic carbene (NHC) complexes. A further functionalization of the 2-position can be achieved by simple bromination to yield 2-bromo-1,3-di(alkyloxy)imidazolium

salts, which in turn may serve as convenient intermediates for the oxidative insertion of zero-valent metals into the C–Br bond.[2] Moreover, their weak, yet stable heteroelement N-O bonds offer a proven concept for degradability by design.[5] For example, demethoxylation by hydrogenolysis of 1-methoxy-3-methylimidazolium salts leads to the destruction of the quaternary character of the heterocyclic moiety.[3]

Another notable aspect in terms of structural comparison is the fact that 2-halogenations of the parent 1,3-dimethylimidazolium systems[6] require more elaborate synthetic approaches than the analogous conversions of related 1,3-di(alkoxy)imidazolium salts, yet both topics of research have already been advanced. In the precedent literature concerning azole halogenations, 2-brominations have been described predominantly. In the case of dialkoxyimidazolium, this also allows for easy subsequent substitutions, for example, and most temptingly, by N_3^-. Consequently, well-established types of organic azide chemistry have eventually been applied to 2-azido-1,3-di(alkoxy)imidazolium salts, chiefly by cycloadditions with norbornene and norbornadiene, as well as with triphenylphosphine.[7] The latter reaction sequence yields the expected Staudinger intermediates and final products. With the aim of further exploring the substitutability of 2-bromo-1,3-di(alkoxy)imidazolium salts within the scope of the present contribution, we envisaged several different *S*-nucleophiles as reactants.

Interestingly, even in the field of the more extensively investigated 2-halo-dialkylimidazolium and 2-halo-diarylimidazolium salts, the reports concerning the reactivity towards *S*-nucleophiles are very scarce. To the best of our knowledge, only a multi-step synthesis of mesoionic thiazolo[3,2-*a*]imidazoles under insertion of carbon disulfide (see Scheme 1),[8] as well as the substitution by chlorosulfite anion leading to the formation of a formal carbene sulfur trioxide adduct have been described so far.[9]



Scheme 1. Previously described multi-step reaction to form mesoionic thiazolo[3,2-*a*]imidazoles (**II a-g**) starting from 2-bromo-dialkylimidazolium bromides (**I a-g**) under substitution of the 2-bromo moiety through CS_2,[8] in contrast to the substitution of 2-bromo-di(methoxy)imidazolioum salts (**2,3**) to form the 2-aryl- or 2-hetarylmercapto derivatives (**4-10**) presented in this publication

RESULTS AND DISCUSSION

For the preparation of *N*,*N*′-dialkoxylated imidazolium derivatives,[10] aqueous media are inevitable because of the solubility/polarity profile of the starting reactant 1-hydroxyimidazole 3-oxide which can be obtained via known or improved procedures, see experimental part.[11-16] This qualifies dialkyl sulfates as the alkylation reagents of choice, but, independently of the actual quarternization method, the final work-up of *N*,*N*′-dialkoxylated imidazolium salts relies on ion metathesis by means of weakly coordinating anions (WCA) such as triflimide, hexafluorophosphate or tetrachloroferrate.[10] In contrast to the polar monoalkyl sulfate counter ions stemming from the quarternization step, WCA effect low solubility of the organic cations in water and concurrently a higher phase affinity towards organic extractants. However, as is generally known, there are some disadvantages to WCA such as considerably high costs or inherent handling drawbacks. Therefore, newly modified synthetic routes and improvements concerning the isolation and further possibility of derivatizing the highly polar heterocyclic cations remain desirable.

When our established bromination procedures for the preparation of 2-bromo-1,3-di(methoxy)imidazolium hexafluorophosphate (**3**, [951020-90-9])[2] were now and then

followed inaccurately, some remaining orange coloration of the precipitate attracted our attention. Apparently, this incidental observation was suggesting the formation/occlusion of polybromide species.
A single crystal X-ray structure determination has shown that the deliberate superstoichiometric usage of bromine has in fact yielded a mixed Br_3^-/PF_6^- salt with an anion/anion ratio of 1:2, henceforth denoted as **1**·**3** (1/2).

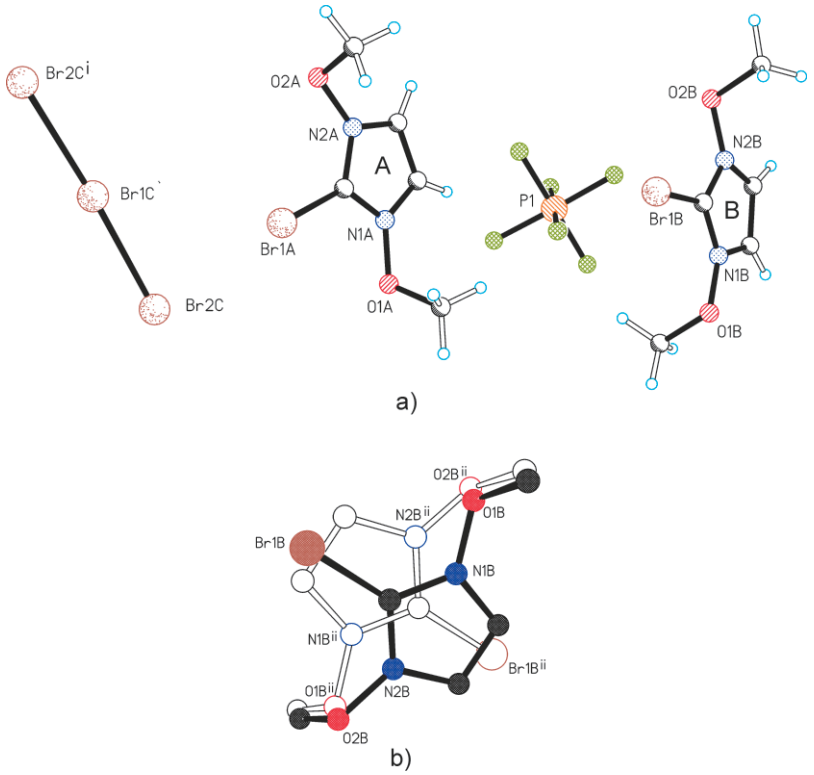
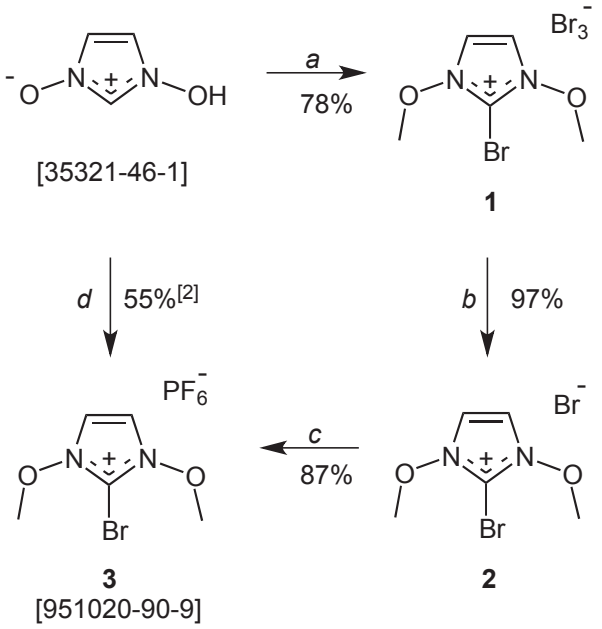


Figure 1. a) Molecular structure of the 2-bromo-1,3-di(methoxy)imidazolium tribromide/hexafluorophosphate(1:2) mixed salt [**1**·**3** (1/2)], obtained in an attempt to synthesize **3**.[2] Cation B is disordered over an inversion centre, whilst the central Br atom of the tribromide ion lies on a two-fold axis. Consequently, both these moieties have an occupancy of 0.5, and this diagram does not reflect the actual stoichiometry of the compound. b) Relative arrangement of the two disorder components of cation B. Symmetry transformations (i) –*x*+1, *y*, –*z*+1/2 (ii) –*x*+1/2, –*y*+3/2, –*z*+1.

Based on these findings, we were prompted to qualify tribromide as a moderately coordinating anion for the direct preparation[17] of the 2-bromo-1,3-di(methoxy)imidazolium cations as a sole precipitant from the aqueous reaction mixture. Fortunately, this undertaking was met with success (see experimental section). However, the easily isolable tribromide **1** has to be phlegmatized, because of the inherent hazards, as well as unwanted side reactions and solvent incompatibilities, caused by the large positive redox potential of the tribromide anion.[18] In particular, the direct use of **1**, would not allow for a clean substitution with the mercapto nucleophiles due to the competing oxidative disulfide formation. Thus, a subsequent clean and almost quantitative conversion to the monobromide **2** was expediently achieved by bromine trapping with cyclohexene.[19] Due to its high solubility in H_2O, the isolation of compound **2** gives the synthetic

opportunity for a wide diversity of further anion metathesis with WCA. As a first proof, the constituent bromide was effortlessly exchanged in aqueous solution with NH_4^+ PF_6^- to obtain the respective hexafluorophosphate **3**. In comparison to the established two step reaction[2] giving **3** in 55% overall yield, this novel three step reaction route allows for the isolation of **3** in 66% overall yield (see Scheme 2).



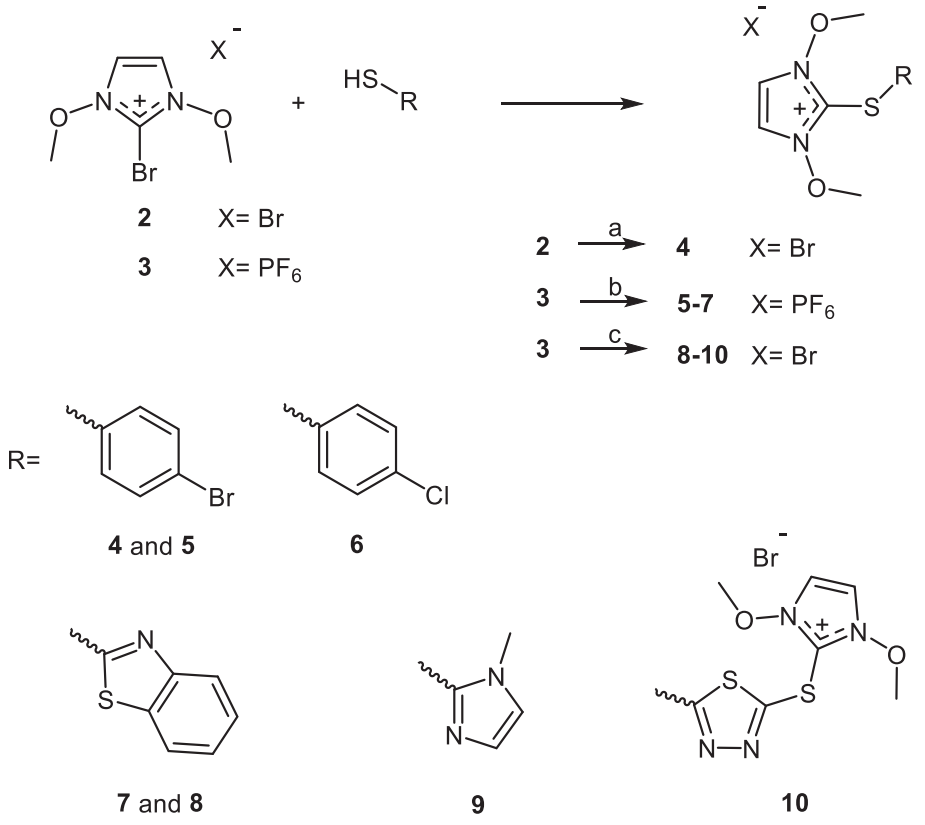
a) Me_2SO_4 in H_2O, then $CaCO_3$, Br_2 in H_2O/MeOH; b) cyclohexene in CH_2Cl_2; c) NH_4PF_6 in H_2O, d) 2 steps: Me_2SO_4 neat, then $NaHCO_3$ in H_2O then NH_4PF_6; Br_2 in MeOH/H_2O then Na_2CO_3

Scheme 2. Preparation of 2-bromo-1,3-di(methoxy)imidazolium hexafluorophosphate (**3**) according to the published two step procedure[2] (route d), in comparison to the novel three step reaction (routes a-c)

In order to determine appropriate conditions for the nucleophilic substitution of the 2-bromo substituent, experiments were undertaken to react the monobromide salt **2** with 4-bromothiophenol. Different attempts varying the bases from K_2CO_3 to NEt_3 or *N*,*N*-diisopropyl-*N*-ethylamine (Hünig's base) in the solvents MeCN, MeOH, acetone or mixtures thereof were explored. However, these only led – if at all – to a partial formation of the targeted compound, as evidenced by ^{1}H-NMR spectra of the raw products. At refluxing temperatures, dissociation predominantly occurred, and at lower temperatures, no conversion was observed. Only by adapting a reported procedure,[20] using Ag_2CO_3 in a $CHCl_3$/MeOH mixture, the desired product **4** could be isolated in traces (see Table 1, entry 1).

The experienced difficulties seemed to be ascribable to the low solubility of **2** in aprotic-nonpolar solvents, and the instability of the 1,3-di(methoxy)imidazolium entity at elevated temperatures, which were needed to obtain any conversion at all. Therefore, the hexafluorophosphate salt **3** was chosen as

starting material, due to its good solubility in $CHCl_3$, acetone, and MeCN, thus allowing for milder reaction conditions. Surprisingly, when starting from compound **3**, the seemingly most promising reaction procedure[20] did not lead to any appreciable results. However, product **5** could be obtained by stirring of **3** with 4-bromothiophenol and NEt_3 in acetone (see Table 1, entry 2). It is evident that the driving force of the reaction was a shifted equilibrium attributable to the precipitation of triethylammonium bromide from the reaction mixture. The quite apolar aromatic thiols, such as 4-chlorothiophenol or benzo[*d*]thiazole-2-thiol, could also be reacted by using this procedure, yielding **6** and **7** (see Table 1, entries 3 and 4). For more polar thiol species, such as 1-methyl-1*H*-imidazole-2-thiol or 1,3-dithiothiadiazole, modified reaction conditions had to be applied, as the bromide salts of the reaction products also precipitated from solution and their separation from triethylammonium bromide proved to be tedious.



a) Ag_2CO_3 in $CHCl_3$/MeOH (5:1); b) NEt_3 in acetone; c) *N,N*-diisopropyl-*N*-ethylamine in MeCN

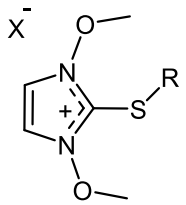
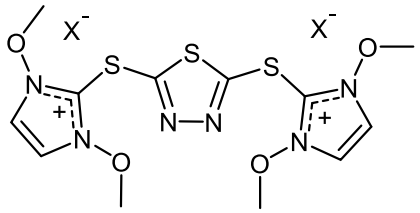
Scheme 3. Starting compounds and conditions for the formation of products **4-10**

By applying Hünig's base in MeCN, the desired bromides **9** and **10** as well as the bromide of the benzo[*d*]thiazole-2-thiol adduct **8** were easily formed and could be isolated in acceptable yields without issues by precipitation with Et_2O (see Table 1, entries 5-7), owing to the high solubility of

N,*N*-diisopropyl-*N*-ethylammonium hexafluorophosphate in the MeCN/Et_2O solvent mixture and, conversely, the insolubility of the target products therein.

The constitution of compounds **1, 2** and **4 – 9** was complementarily confirmed by single crystal structure determinations which will be discussed below. Various attempts to establish the structure of the dibromide salt **10** resulted in a highly disordered structure model, which could provide only the basic information of a successful conversion. An anion metathesis applying NH_4PF_6 in H_2O was therefore carried out, which yielded the corresponding bis(hexafluorophosphate) salt **11** (see Table 1, entry 8).

Table 1. Overview of synthesized 2-aryl and 2-hetaryl-1,3-di(methoxy)imidazolium compounds **4-11**

Entry		X^-	R	isolated yield (%)	molecular structure
1	**4**	Br^-	C_6H_4Br	9	
2	**5**	PF_6^-	C_6H_4Br	52	
3	**6**	PF_6^-	C_6H_4Cl	51	
4	**7**	PF_6^-	C_7H_4NS	38	
5	**8**	Br^-	C_7H_4NS	55*	
6	**9**	Br^-	$C_4H_5N_2$	57	
7	**10**	Br^-	–	58	
8	**11**	PF_6^-	–	N/A	

***Note**: Isolated as hemihydrate **8·0.5 H_2O**

In addition, preliminary tests with ethanethiol were conducted to determine the reactivity towards aliphatic thiols. Again, the precipitation of triethylammonium bromide indicated successful conversion. However, the isolation of the product has turned out to be difficult. Taking the toxicity and malodorousness of alkyl thiols into account, it would be preferable to follow a complementary synthetic strategy in any case. *S*-Alkylation of cyclic thioureas,[21] and especially of 1,3-di(alkoxy)imidazoline-2-thiones would likewise, but more satisfactorily, form the corresponding 2-alkylmercaptoimidazolium derivatives. This, in contrast to arylthiolation requirements, appears to be highly favorable for the introduction of alkylthio substituents in position 2.

CRYSTAL STRUCTURES AND DISCUSSION

The crystallographic data for the structure determinations are collected in Tables 2 and 3. Molecular structures are depicted in Figures 1 – 4. The investigated crystal structures contain 1,3-di(methoxy)imidazolium fragments displaying the following essential bond parameters: N–O 1.36 to 1.38 Å, C1–N 1.32 to 1.33 Å, C2–N 1.36 to 1.37 Å, C2–C3 1.35 Å and N–C–N 105°. These values are in good agreement with the known geometries of related compounds.[2,4] The out-of-plane twist of the two methoxy groups gives rise to two fundamental conformations in that, with reference to the imidazolium ring plane, they either point towards the same side (*syn* conformer) or different sides (*anti* conformer). The C1–Br bond lengths of 1.82 and 1.85 Å present in the bromoimidazolium derivatives **1**, **2**, **2·0.5 H_2O** and **1·3** (1/2), are in concert with those in the corresponding hexafluorophosphate and bis(trifluoromethanesulfonyl)imide analogues.[2] The asymmetric unit of **1·3** (1/2) consists of one cation (denoted as A) and one PF_6^- ion as well as one half of each a cation (denoted as B) and a Br_3^- unit. Cation B is disordered over an inversion centre (see Figure 1b), and the central Br atom of the Br_3^- ion is located on a two-fold axis. The cations of **1**, **2**, **2·0.5 H_2O** and cation A of **1·3** (1/2) adopt the *syn* conformation (see Figures 1 and 2), whilst cation B of **1·3** (1/2) and the cations of the hexafluorophosphate and bis(trifluoromethanesulfonyl)imide analogues represent *anti* conformers.[2] In the hemihydrate **2·0.5 H_2O**, the water molecule is located on a two-fold axis and serves as an Br···H–O–H···Br bonded bridge between two bromide ions. As expected, the cations of compounds **4** – **9** (see Figure 3) show C1–S bond lengths between 1.72 to 1.73 Å, which are significantly shorter than the corresponding (**R**)C–S distances between 1.76 and 1.79 Å. The hexafluorophosphate salts **5** and **6** differ only in the type of halogen substituent (Br *vs.* Cl) at the phenyl group, and their crystal structures were found to be isostructural. The asymmetric unit of each of the two benzo[*d*]thiazole-2-thiol derivatives **7** and **8·0.5 H_2O** contains one cation/anion pair. Additionally, the hemihydrate displays a water molecule located on a two-fold axis which is H-bonded to two Br^- moieties *via* Br···H–O–H···Br interactions. The asymmetric unit of the solvent structure **9·0.25 MeOH** contains two cation/anion pairs and additionally one half of a MeOH molecule which is disordered over an inversion center. The crystallisation of compound **11** resulted in the hexane hemisolvate **11·0.25 (C_6H_{14})** whose asymmetric unit contains two formula units. The first cation in the asymmetric units displays an *anti*/*anti* conformation of its 1,3-di(methoxy)imidazolium fragments, whilst the disordered second cation moiety represents a 60:40 mixture of *anti*/*anti* and *anti*/*syn* conformers (see Figure 4). Additionally, the 1,3,4-thiadiazole ring of the first cation is disordered over two orientations which are related by an approximate 180° rotation about to S5–C···C–S6 axis (occupancy ratio 77:23; see Figure 4, top) disorder.

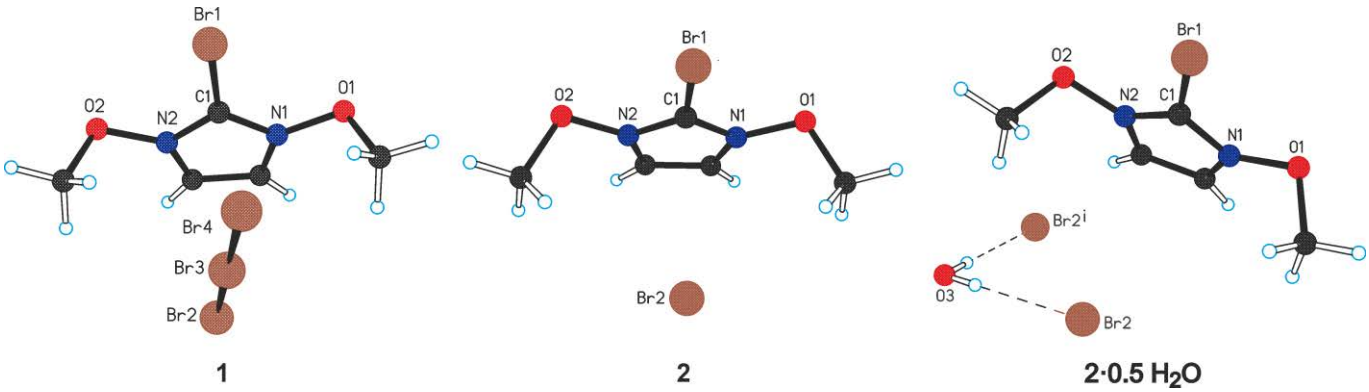


Figure 2. Molecular structures of compounds **1**, **2** and **2·0.5 H_2O**. Symmetry transformation (i) 1 – *x*, *y*, 1.5 - *z*.

Table 2. Crystal data and structure refinement for 2-bromo-1,3-di(methoxy)imidazolium salts **1**, **2**, **2·0.5 H_2O** and **1·3** (1/2).

Compound	**1**	**2**	**2·0.5 H_2O**	**1 · 3** (1/2)
Moiety formula	$(C_5H_8BrN_2O_2)^+ Br_3^-$	$(C_5H_8BrN_2O_2)^+ Br^-$	$(C_5H_8BrN_2O_2)^+ Br^- \cdot 0.5(H_2O)$	$3(C_5H_8BrN_2O_2)^+Br_3^- 2PF_6^-$
Empirical formula	$C_5H_8Br_4N_2O_2$	$C_5H_8Br_2N_2O_2$	$C_5H_9Br_2N_2O_{2.5}$	$C_{15}H_{24}Br_6F_{12}N_6O_6P_2$
Formula weight	447.77	287.95	296.96	1153.80
Temperature (K)	173	193	183	193
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	*P*2$_1$/*n*	*Pccn*	*C*2/*c*	*C*2/*c*
a (Å)	8.7030(8)	7.9878(7)	12.7757(16)	22.207(4)
b (Å)	12.4606(10)	17.2084(13)	7.6374(8)	12.758(3)
c (Å)	11.0182(9)	13.5475(12)	20.999(3)	13.767(3)
α (°)	90	90	90	90
β (°)	91.235(7)	90	109.150(15)	115.73(3)
γ (°)	90	90	90	90
Unit cell volume (Å^3)	1194.59(18)	1862.2(3)	1935.5(4)	3513.8(15)
Z / *Z*'	4 / 1	8 / 1	8 / 1	4 / 0.5
Reflections collected / R_{int}	7502 / 0.0454	11295 / 0.0481	5756 / 0.0416	11730 / 0.0589
Data / restraints / parameters	2398 / 0 / 121	1899 / 0 / 102	1763 / 2 / 109	3545 / 79 / 263
Goodness-of-fit on F^2	1.024	1.066	1.013	1.000
*R*1 [$I > 2\ \sigma(I)$]	0.0289	0.0317	0.0286	0.0400
*wR*2 (all data)	0.0543	0.0752	0.0515	0.0696
Largest diff. peak and hole (e · Å^{-3})	0.464 and -0.521	0.581and -0.760	0.551 and -0.498	0.562 and -0.518
CCDC no.	1969810	1969807	1969804	1969811

Table 3. Crystal data and structure refinement for 2-arylmercapto-1,3-di(methoxy)imidazolium salts **4-6** and 2-hetarylmercapto-1,3-di(methoxy)imidazolium salts **7**, **8·0.5 H_2O**, **9·0.25 MeOH** and **11·0.5 (C_6H_{14})**

Compound	**4**	**5**	**6**	**7**	**8·0.5 H_2O**	**9·0.25 MeOH**	**11·0.5 (C_6H_{14})**
Moiety formula	$(C_{11}H_{12}BrN_2O_2S)^+$ Br^-	$(C_{11}H_{12}BrN_2O_2S)^+$ PF_6^-	$(C_{11}H_{12}ClN_2O_2S)^+$ PF_6^-	$(C_{12}H_{12}N_3O_2S_2)^+$ PF_6^-	$(C_{12}H_{12}N_3O_2S_2)^+$ $Br^- \cdot 0.5(H_2O)$	$(C_9H_{13}N_4O_2S)^+$ $Br^- \cdot 0.25(CH_4O)$	$(C_{12}H_{16}N_6O_4S_3)^{2+}$ $2PF_6^- \cdot 0.5(C_6H_{14})$
Empirical formula	$C_{11}H_{12}Br_2N_2O_2S$	$C_{11}H_{12}BrF_6N_2O_2PS$	$C_{11}H_{12}ClF_6N_2O_2PS$	$C_{12}H_{12}F_6N_3O_2PS_2$	$C_{12}H_{13}BrN_3O_{2.5}S_2$	$C_{9.25}H_{14}BrN_4O_{2.25}S$	$C_{15}H_{23}F_{12}N_6O_4P_2S_3$
Formula weight	396.11	461.17	416.71	383.28	383.28	329.21	737.51
Temperature (K)	183	183	183	183	183	173	183
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	$P2_1/c$	*C*2/*c*	$P\bar{1}$	$P\bar{1}$
a (Å)	29.2880(15)	28.419(2)	28.3333(10)	15.198(3)	30.469(4)	10.6166(6)	12.7782(10)
b (Å)	7.8574(4)	8.3920(6)	8.3027(2)	8.8501(16)	7.0683(8)	12.6955(7)	14.4022(12)
c (Å)	13.3836(6)	13.9845(10)	14.0580(5)	13.670(2)	15.278(2)	12.8013(7)	15.9550(13)
α (°)	90	90	90	90	90	110.532(2)	80.306(3)
β (°)	114.567(2)	94.131(2)	94.1334(15)	108.611(5)	112.289(4)	110.402(2)	84.903(2)
γ (°)	90	90	90	90	90	101.752(2)	74.764(2)
Unit cell volume ($Å^3$)	2801.1(2)	3326.6(4)	3298.44(18)	1742.6(6)	3044.6(6)	1406.14(14)	2789.5(4)
Z / *Z*'	8 / 1	8 / 1	8 / 1	4 / 1	8 / 1	4 / 2	4 / 2
Reflections collected / R_{int}	24975 / 0.0319	20845 / 0.0292	23401 / 0.0231	3061 / –	2806 / –	45061 / 0.0349	80606 / 0.0282
Data / restraints / parameters	2874 / 0 / 164	3090 / 0 /294	3066 / 0 / 254	3061 / 0 / 274	2806 / 1 / 2806	4936 / 3 / 332	10195 / 745 / 942
Goodness-of-fit on F^2	1.109	1.063	1.051	1.112	1.141	1.029	1.021
*R*1 [$I > 2\ \sigma(I)$]	0.0212	0.0295	0.0312	0.0490	0.0470	0.0268	0.0466
*wR*2 (all data)	0.0489	0.0714	0.0807	0.1102	0.0930	0.0716	0.1324
Largest diff. peak and hole (e · $Å^{-3}$)	0.354 and -0.291	0.540 and -0.535	0.287 and -0.350	0.337 and -0.524	0.609 and -0.480	0.757 and -0.502	0.906 and 0.906
CCDC no.	1969806	1969814	1969812	1969805	1969808	1969809	1969813

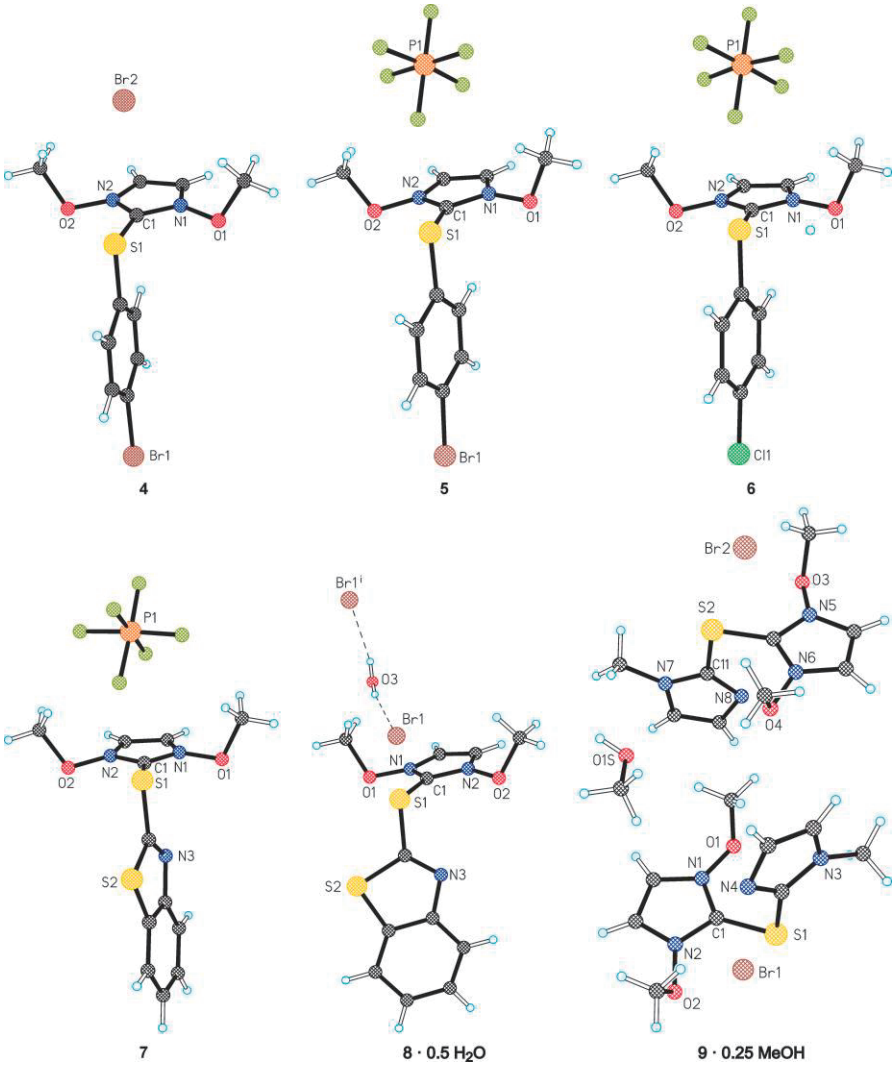


Figure 3. Molecular structures of compounds **4** – **7**, **8·0.5 H_2O** and **9·0.25 MeOH**. Minor disorder of PF_6^- ions (**5** – **7**) and solvent molecules omitted for clarity. Symmetry transformation (i) $1 - x$, y, $0.5 - z$.

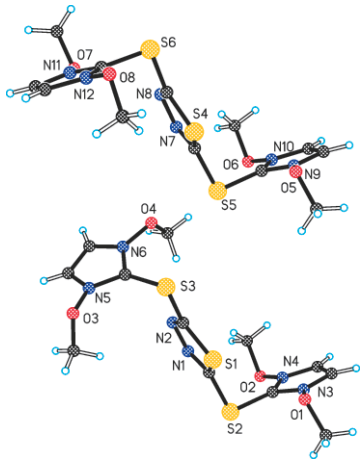


Figure 4. The structures of two independent cations in **11·0.5 (C_6H_{14})**, displaying an *anti*/*anti* conformation (top) and an *anti*/*syn* conformation (bottom; the disorder fragment shown represents a 40% occupancy *vs.* 60% for *anti*/*anti*).

CONCLUSIONS AND OUTLOOK

As mere onlookers to the pioneering[22] and continual contributions[23] to the chemistry of imidazole *N*-oxides by the group of Prof. Mlostoń and other distinguished colleagues, we are nonetheless enthusiastic about the unique chemical features and peculiarities of N-alkoxylated heterocycles. We still intend to continue the exploration of respective substitution patterns in position 2 along with ion metathesis, which is now facilitated by the new synthetically advantageous tribromide and bromide salts.

EXPERIMENTAL

Reagents and solvents were purchased from Sigma-Aldrich and used as received unless stated otherwise. 1-Hydroxymidazole 3-oxide **[35321-46-1]**, as well as 1,3-di(methoxy)imidazolium PF_6^- **[951020-81-8]**, a one-step precursor[2] of 2-bromo-1,3-di(methoxy)imidazolium PF_6^- (**3**), are commercially available, e.g. from Merck-Sigma-Aldrich.

NMR spectra were recorded with a Bruker Avance DPX 300 spectrometer. IR spectra were obtained with a Bruker ALPHA Platinum FT-ATR instrument. The X-ray powder diffraction (XRPD) patterns were obtained with a *X'Pert PRO* diffractometer (PANalytical, Almelo, The Netherlands) equipped with a theta/theta coupled goniometer in transmission geometry, programmable XYZ stage with well plate holder, Cu-$K\alpha_{1,2}$ radiation source (λ = 1.5419 Å) with a focussing mirror, a 0.5° divergence slit, a 0.02° soller slit collimator and a 0.5° anti-scattering slit on the incident-beam side, a 2 mm anti-scattering slit, a 0.02° soller slit collimator, a Ni-filter and a solid state PIXcel detector on the diffracted-beam side. The patterns were recorded at a tube voltage and current of 40 kV and 40 mA, respectively, using a stepsize of $2\theta = 0.013°$ in the angular range of $2° \leq 2\theta \leq 40°$ with 40 s per step.

Diffraction intensity data for the single crystal structure determinations of **1**, **2**, **2·0.5 H_2O**, **and 1·3** $(1/2)$, were recorded with a Nonius KappaCCD Gemini Ultra diffractometer and those for **4** – **7**, **8·0.5 H_2O** **9·0.25 MeOH** and **11·0.5 (C_6H_{14})** were recorded with a Bruker D8 Quest Photon 100 diffractometer, in each case using Mo$K\alpha$ radiation (λ = 0.7107 Å). The crystal structures were solved by Direct Methods with SHELXT[24] or SIR 2002[25] and were refined by full-matrix least-squares techniques using SHELXL.[26] The structures of **7** and **8·0.5 H_2O** were refined as non-merohedral twins with two components in a ratio of 0.52:0.48 and 0.73:0.37, respectively. The hexane molecule of **11·0.5 (C_6H_{14})** was found to be severely disordered over multiple orientations, and the structure refinement did not result in a geometrically sensible model of the disordered solvent molecule. Therefore, a *PLATON* SQUEEZE procedure was applied on the data before the final refinement was carried out.[27] CCDC 1969804–14 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/structures.

1-Hydroxyimidazole 3-oxide ([35321-46-1], improved procedure for large scale)

Note and warning: As already mentioned above, 1-hydroxyimidazole 3-oxide is commercially available, but only at overly inflated prices - notwithstanding the fact that it is accessible by minimum synthetic effort. Strangely, the unmodified original procedure has been republished countless times.[11-16] No any additional helpful procedural details have been supplemented therein. In particular, instead of stating a final pH, it would be advantageous to specify the required molar amount of NaOH in order to achieve maximum precipitation. The compound readily crystallizes from the aqueous mother liquor as anhydrate.[3] It was reported to undergo exothermic decomposition at 200 – 250 °C, and is considered a sensitive detonating and deflagrating explosive.[28]

A solution of glyoxal (40 wt% in H_2O, 3.1 mol, 437 g) was added to a solution of formaldehyde (35 wt% in H_2O/ MeOH 9:1, 3.6 mol, 309 g) and diluted with MeOH (700 mL). The reaction mixture was cooled to 2 °C by means of an ice-bath and stirred for 1 h, before a solution of hydroxylamine hydrochloride in H_2O (6.13 mol, 500 mL) was slowly added via dropping funnel over a time period of 2 h. Precautions were taken to keep the reaction temperature below 20 °C. After completion of the addition, the ice bath was removed and concentrated hydrochloric acid (37 wt% in H_2O, 0.77 mol, 64 mL) was added drop-wise. After the addition was completed, the solution was stirred for 20 h at room temperature. Subsequently, the reaction mixture was cooled again by means of an ice-bath before a solution of NaOH (50 wt% in H_2O, 6.65 mol, 350 mL) was slowly added via a dropping funnel, resulting in copious amounts of white precipitate. The reaction mixture was kept at -24 °C for 18 h, followed by filtration of the precipitate (sintered glass suction filter G4). The product was triturated and washed twice with cold H_2O (4 °C, 150 mL), cold MeOH (4 °C, 70 mL) and Et_2O (100 mL) each and dried under reduced pressure (over P_4O_{10}) to yield 243 g (78%) of a white powder. Recrystallization from H_2O yields an analytically pure product. Mp 188 – 190 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.64 (t, J = 2.2 Hz, 1H), 7.29 (d, J = 2.0 Hz, 2H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6) δ 124.49, 116.53 (2C) ppm. IR (neat): ν 3165 (w), 3137 (m), 3104 (m), 1508 (w), 1363 (m), 1247 (m), 1185 (s), 1109 (m), 1058 (m), 1020 (m), 965 (s), 914 (s), 886 (s), 778 (vs), 748 (s), 725 (vs), 659 (m), 616 (s), 594 (vs), 492 (s), 435 (m) cm^{-1}. According to XRPD, the bulk material is a crystallographically pure form and corresponds to the calculated pattern according to published CCDC no. 673922[3] (see Electronic Supporting Information (ESI) Figure S1).

2-Bromo-1,3-di(methoxy)imidazolium tribromide (1)

1-Hydroxyimidazole 3-oxide (**[35321-46-1]**, 90 mmol, 9.0 g) was suspended in H_2O (22 mL) before dimethyl sulfate (202 mmol, 19.2 mL) was slowly added by means of a dropping funnel under stirring. After completion of the addition, the suspension was stirred for another 30 min at room temperature

before carefully adding $CaCO_3$ (100 mmol, 10.0 g) and stirring the reaction mixture for another 16 h. Thereafter, the mixture was diluted with MeOH (6.0 mL), and bromine (200 mmol, 32.0 g) was carefully added. After stirring for another 48 h at room temperature, an orange precipitate had formed, which was filtered off, washed with cold MeOH (4 °C, 10 mL) and dried under reduced pressure to yield 31.4 g (78%) of an orange, crystalline solid. Single-crystals were obtained by recrystallization of **1** from MeOH. Mp 81 °C (decomp.). ^{1}H NMR (300 MHz, DMSO-d_6-slight dissociation) δ 8.51 (s, 2H), 4.23 (s, 6H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6-slight dissociation) δ 118.24 (2C), 117.31, 69.12 (2C) ppm. IR (neat): ν 3106 (w), 3045 (s), 3017 (m), 2964 (m), 2943 (m), 2895 (w), 2823 (w), 1605 (w), 1552 (w), 1458 (m), 1355 (w), 1318 (w), 1186 (w), 1156 (m), 1133 (m), 1101 (w), 1049 (s), 937 (vs), 863 (w), 744 (s), 720 (m), 664 (m), 593 (s), 540 (w) cm^{-1}. According to XRPD, the bulk material is a crystallographically pure form and corresponds to the calculated pattern according to CCDC no. 1969810 (see ESI Figure S2).

2-Bromo-1,3-di(methoxy)imidazolium bromide (2)

2-Bromo-1,3-di(methoxy)imidazolium tribromide (**1**, 22.3 mmol, 10.0 g) was dissolved in CH_2Cl_2 (100 mL) before cyclohexene (112 mmol, 9.20 g) was added very slowly in order to blunt the ensuing exothermic reaction. The solution was stirred at room temperature for 16 h, leading to the precipitation of the product as a white solid amidst the yellow reaction solution. The product was filtered off, washed with CH_2Cl_2 (50 mL) and dried under reduced pressure, yielding 6.20 g (97%) of a white solid. Single-crystals were obtained by diffusion of Et_2O into a methanolic solution of **2** at 4 °C or by slow evaporation of a solution of **2** in H_2O at 4 °C (**2·0.5 H_2O**). Mp 137 – 139 °C. ^{1}H NMR (300 MHz, MeOH-d_4) δ 8.32 (s, 2H), 4.34 (s, 6H) ppm. ^{13}C NMR (75 MHz, MeOH-d_4) δ 119.91 (2C), 118.24, 70.14 (2C) ppm. IR (neat): ν 3106 (w), 3045 (s), 3017 (m), 2964 (m), 2943 (m), 2895 (w), 2823 (w), 1605 (w), 1552 (w), 1458 (m), 1355 (w), 1318 (w), 1186 (w), 1156 (m), 1133 (m), 1101 (w), 1049 (s), 937 (vs), 863 (w), 744 (s), 720 (m), 664 (m), 593 (s), 540 (w) cm^{-1}. According to XRPD, the bulk material is a crystallographically pure form and corresponds to the calculated pattern according to structure CCDC no. 1969807 (see ESI Figure S3).

2-Bromo-1,3-di(methoxy)imidazolium hexafluorophosphate (**3**, [951020-90-9])

2-Bromo-1,3-di(methoxy)imidazolium bromide (**2**, 17.4 mmol, 5.00 g) was suspended in H_2O (20 mL) and ultrasonicated for 15 min, forming a colorless solution. Thereafter, a solution of ammonium hexafluorophosphate (19.1 mmol, 3.10 g) in H_2O (10 mL) was quickly added, resulting in the precipitation of the product. The reaction mixture was ultrasonicated for another 15 min and kept at 4 °C for 2 h. The precipitate was filtered off, washed with cold H_2O (4 °C, 15 mL) and dried under reduced pressure, yielding 5.30 g (87%) of a white solid. Mp 146 – 148 °C. ^{1}H NMR (300 MHz, acetone-d_6) δ

8.30 (s, 2H), 4.38 (s, 6H) ppm. ^{13}C NMR (75 MHz, acetone-d_6) δ 119.66 (2C), 117.09, 70.05 (2C) ppm. IR (neat): ν 3170 (w), 3150 (w), 1557 (w), 1458 (w), 1441 (w), 1049 (m), 940 (m), 826 (vs), 732 (m), 650 (m), 556 (s) cm^{-1}.

2-((4-Bromophenyl)thio)-1,3-di(methoxy)imidazolium bromide (4, adapted from a previously reported procedure[20])

2-Bromo-1,3-di(methoxy)imidazolium bromide (**2**, 0.87 mmol, 0.25 g), 4-bromothiophenol (1.04 mmol, 0.20 g) and Ag_2CO_3 (0.54 mmol, 0.15 g) were suspended in a mixture of $CHCl_3$ and MeOH (5:1, 12 mL). The reaction mixture was heated to 60 °C for 1 h, before cooling to room temperature and stirring for another 2 h. The formed brown deposit was separated from the slightly yellow solution by filtration and washed with MeOH (20 mL). After removal of the solvent under reduced pressure, the off-white residue was redissolved in MeOH (5 mL), treated with Et_2O (100 mL) and kept at -32 °C for 16 h. The resulting off-white precipitate was filtered off and washed with Et_2O (30 mL). The raw product was dissolved in MeOH (2 mL), purified by syringe filtration and crystallized through diffusion of Et_2O at 4 °C for 72 h. The resulting colorless crystals were filtered off, washed with acetone (10 mL) and dried under reduced pressure, yielding 30.0 mg (9%) of a white crystalline solid. Single-crystals were obtained by diffusion of Et_2O into a methanolic solution of **4** at 4 °C. Mp 118 – 121 °C (decomp.). ^{1}H NMR (300 MHz, MeOH-d_4) δ 8.31 (s, 2H), 7.74 – 7.45 (m, 4H), 4.27 (s, 6H) ppm. ^{13}C NMR (75 MHz, MeOH-d_4) δ 136.05 (2C), 134.77 (2C), 127.17, 126.35, 120.28 (2C), 120.17, 70.31ppm. IR (neat): ν 3091 (w), 3026 (s), 2993 (m), 2913 (w), 1546 (m), 1470 (s), 1457 (s), 1443 (m), 1383 (m), 1155 (w), 1116 (w), 1078 (s), 1069 (m), 1046 (s), 1000 (s), 952 (s), 933 (vs), 801 (vs), 777 (s), 721 (m), 688 (w), 619 (m), 551 (w), 478 (s) cm^{-1}.

2-((4-Bromophenyl)thio)-1,3-di(methoxy)imidazolium hexafluorophosphate (5)

2-Bromo-1,3-di(methoxy)imidazolium hexafluorophosphate (**3**, 0.71 mmol, 0.25 g) and 4-bromothiophenol (0.78 mmol, 0.15 g) were dissolved in acetone (10 mL). NEt_3 (1.07 mmol, 0.11 g) was added, quickly giving a white precipitate of triethylammonium bromide. The suspension was stirred at room temperature for 1 h, before the precipitate was filtered off and washed with Et_2O (10 mL). The solvent was removed under reduced pressure and the off-white residue was recrystallized from boiling MeOH (5 mL). The resulting white crystals were filtered off, washed with cold MeOH (-24 °C, 5 mL) and Et_2O (15 mL) and dried under reduced pressure, yielding 0.17 g (52%) of a white crystalline solid. Single-crystals were obtained by recrystallization of **5** from MeOH. Mp 166 – 168 °C. ^{1}H NMR (300 MHz, acetone-d_6) δ 8.34 (s, 2H), 7.75 – 7.66 (m, 4H), 4.36 (s, 6H) ppm. ^{13}C NMR (75 MHz, acetone-d_6) δ 135.96 (2C), 134.26 (2C), 126.88, 125.53, 120.12 (2C), 105.39, 70.30 (2C) ppm. IR (neat): ν 3170 (w),

3152 (w), 3088 (w), 1549 (w), 1473 (w), 1458 (w), 1444 (w), 1386 (w), 1082 (w), 1042 (m), 1004 (m), 939 (w), 825 (vs), 801 (s), 741 (s), 690 (w), 620 (w), 555 (s), 475 (m) cm^{-1}.

2-((4-Chlorophenyl)thio)-1,3-di(methoxy)imidazolium hexafluorophosphate (6)

2-Bromo-1,3-di(methoxy)imidazolium hexafluorophosphate (**3**, 0.71 mmol, 0.25 g) and 4-chlorothiophenol (0.78 mmol, 0.11 g) were dissolved in acetone (10 mL). Triethylamine (1.07 mmol, 0.11 g) was added, resulting in the formation of a white precipitate of triethylammonium bromide. The suspension was stirred at room temperature for 1 h, before the precipitate was filtered off and washed with Et_2O (10 mL). The solvent was removed under reduced pressure and the off-white residue was recrystallized from boiling MeOH (5 mL). The resulting white crystals were filtered off, washed with cold MeOH (-24 °C, 5 mL) and Et_2O (15 mL) and dried under reduced pressure, yielding 0.15 g (51%) of a white crystalline solid. Single-crystals were obtained by recrystallization of **6** from MeOH. Mp 154 – 156 °C. ^{1}H NMR (300 MHz, acetone-d_6) δ 8.34 (s, 2H), 7.79 (d, J = 8.6 Hz, 2H), 7.55 (d, J = 8.7 Hz, 2H), 4.36 (s, 6H) ppm. ^{13}C NMR (75 MHz, acetone-d_6) δ 137.37, 135.91 (2C), 134.39, 131.25 (2C), 126.20, 120.09 (2C), 70.28 (2C) ppm. IR (neat): ν 3170 (w), 3153 (w), 3088 (w), 1549 (w), 1476 (m), 1457 (w), 1444 (w), 1390 (w), 1093 (w), 1042 (m), 948 (w), 826 (vs), 806 (s), 743 (s), 690 (w), 620 (w), 555 (s), 481 (m) cm^{-1}.

2-(Benzo[*d*]thiazol-2-ylthio)-1,3-di(methoxy)imidazolium hexafluorophosphate (**7**)

2-Bromo-1,3-di(methoxy)imidazolium hexafluorophosphate (**3**, 0.71 mmol, 0.25 g) and benzo[*d*]thiazole-2-thiol (0.78 mmol, 0.13 g) were dissolved in acetone (10 mL). Triethylamine (1.07 mmol, 0.11 g) was added, resulting in the formation of a white precipitate of triethylammonium bromide. The suspension was stirred at room temperature for 2 h and afterwards kept at -32 °C for 2 h before the precipitate was filtered off and washed with Et_2O (10 mL). The solvent was removed under reduced pressure and the off-white residue was recrystallized from boiling MeOH (5 mL) and kept at -32 °C for 16 h. The resulting white crystals were filtered off, washed with cold MeOH (-24 °C, 5 mL) and Et_2O (15 mL) and dried under reduced pressure, yielding 0.12 g (38%) of a white crystalline solid. Single-crystals were obtained by recrystallization of **7** from MeOH. Mp 158 – 160 °C. ^{1}H NMR (300 MHz, acetone-d_6) δ 8.62 (s, 2H), 8.17 – 8.09 (m, 1H), 7.96 – 7.90 (m, 1H), 7.63 – 7.49 (m, 2H), 4.47 (s, 6H) ppm. ^{1}H NMR (300 MHz, DMSO-d_6-slight dissociation) δ 8.79 (s, 2H), 8.17 – 8.10 (m, 1H), 7.91 – 7.84 (m, 1H), 7.55 – 7.44 (m, 2H), 4.30 (s, 6H) ppm.^{13}C NMR (75 MHz, DMSO-d_6-slight dissociation) δ 158.81, 151.50, 136.10, 130.50, 126.94, 125.95, 122.42, 122.21, 119.67 (2C), 69.78 (2C) ppm. IR (neat): ν 3170 (w), 3149 (w), 1549 (w), 1468 (w), 1447 (w), 1427 (w), 1394 (w), 1309 (w), 1236 (w), 1044 (w), 1005 (w), 950 (w), 860 (m), 826 (vs), 755 (s), 741 (m), 725 (m), 705 (w), 672 (w), 617 (w), 555 (s) cm^{-1}.

2-(Benzo[*d*]thiazol-2-ylthio)-1,3-di(methoxy)imidazolium bromide (8)

2-Bromo-1,3-di(methoxy)imidazolium hexafluorophosphate (**3**, 0.71 mmol, 0.25 g) and benzo[*d*]thiazole-2-thiol (0.71 mmol, 0.12 g) were dissolved in MeCN (10 mL). *N*,*N*-diisopropyl-*N*-ethylamine (0.78 mmol, 0.10 g) was added and the solution was stirred at room temperature for 2 h. After addition of Et_2O (40 mL) the mixture was kept at -32 °C for 16 h, resulting in the formation of white crystals. The precipitate was filtered off, washed with Et_2O (15 mL) and dried under reduced pressure, yielding 0.15 g of a white crystalline solid. IR-data indicated the presence of H_2O (see ESI Figure S32). A thermogravimetric analysis (TGA) of the bulk material showed a mass loss of 2.3%, which is consistent with a molecular ratio of 0.5 mol H_2O (theoretical value 2.35% for a hemihydrate, see ESI Figure S5). Thus, the isolated 0.15 g of the hemihydrate **8·0.5 H_2O** correspond to a yield of 55%. Single-crystals were obtained by diffusion of Et_2O into a methanolic solution of **8·0.5 H_2O** at 4 °C. Mp 118 – 120 °C (decomp.). ^{1}H NMR (300 MHz, MeOH-d_4) δ 8.57 (s, 2H), 8.03 – 7.97 (m, 1H), 7.89 – 7.83 (m, 1H), 7.58 – 7.43 (m, 2H), 4.37 (s, 6H) ppm. ^{13}C NMR (75 MHz, MeOH-d_4) δ 158.91, 153.63, 137.92, 132.39, 128.41, 127.59, 123.79, 123.17, 121.26 (2C), 70.92 (2C) ppm. IR (neat): ν 3389 (broad; H_2O), 3108 (w), 3077 (w), 3026 (m), 3026 (m), 2941 (w), 1543 (w), 1454 (m), 1416 (m), 1397 (w), 1311 (m), 1234 (w), 1040 (m), 987 (s), 931 (vs), 888 (w), 847 (w), 779 (m), 762 (vs), 724 (s), 705 (w), 675 (m), 636 (w), 618 (m), 592 (m), 540 (m), 504 (w), 437 (w), 408 (m) cm^{-1}. According to XRPD, the bulk material is a crystallographically pure form and corresponds to the calculated pattern according to CCDC no. 1969808 (see ESI Figure S4).

1,3-Dimethoxy-2-((1-methyl-1*H*-imidazol-2-yl)thio)imidazolium bromide (9)

2-Bromo-1,3-di(methoxy)imidazolium hexafluorophosphate (**3**, 0.71 mmol, 0.25 g) and 1-methyl-1*H*-imidazole-2-thiol (0.71 mmol, 0.08 g) were dissolved in MeCN (5 mL). *N*,*N*-diisopropyl-*N*-ethylamine (0.78 mmol, 0.10 g) was added and the solution was stirred at room temperature for 1 h. After addition of Et_2O (25 mL) the mixture was kept at -32 °C for 16 h, resulting in the formation of white crystals. The precipitate was filtered off, washed with Et_2O (15 mL) and dried under reduced pressure, yielding 0.13 g (57%) of a white crystalline solid. Single-crystals were obtained by diffusion of Et_2O into a methanolic solution of **9** at 4 °C, resulting in the formation of the MeOH solvate **9·0.25 MeOH**. Mp 123 – 125 °C (decomp.). ^{1}H NMR (300 MHz, MeOH-d_4) δ 8.33 (s, 2H), 7.46 (d, J = 1.3 Hz, 1H), 7.15 (d, J = 1.3 Hz, 1H), 4.30 (s, 6H), 3.97 (s, 3H) ppm. ^{13}C NMR (75 MHz, MeOH-d_4) δ 133.82, 131.96, 131.32, 127.88, 120.16 (2C), 70.66 (2C), 35.33 ppm. IR (neat): ν 3090 (w), 3016 (m), 2942 (w), 1543 (m), 1506 (w), 1457 (m), 1406 (w), 1364 (w), 1280 (m), 1124 (m), 1086 (w), 1039 (s), 934 (vs), 914 (s), 849 (w), 780 (s), 766 (s), 749 (s), 729 (m), 696 (w), 681 (m), 657 (m), 618 (m), 480 (w), 428 (m), 416 (w) cm^{-1}.

2,2'-((1,3,4-Thiadiazole-2,5-diyl)bis(sulfanediyl))bis(1,3-di(methoxy)imidazolium) bromide (10)

2-Bromo-1,3-di(methoxy)imidazolium hexafluorophosphate (**3**, 1.42 mmol, 0.50 g) and 1,3,4-thiadiazole-2,5-dithiol (0.64 mmol, 0.096 g) were suspended in MeCN (15 mL) and shortly heated to boiling temperature to obtain a yellow solution. *N*,*N*-diisopropyl-*N*-ethylamine (1.70 mmol, 0.22 g) was added and the solution was stirred at room temperature for 1 h, resulting in the formation of a white precipitate. Then Et_2O (40 mL) was added and the mixture was kept at -32 °C for further 16 h. The precipitate was filtered off, washed with Et_2O (15 mL) and dried under reduced pressure, yielding 0.21 g (58%) of an off-white solid. Mp 111 – 113 °C (decomp.). ^{1}H NMR (300 MHz, MeOH-d_4 –slight dissociation) δ 8.49 (s, 4H), 4.35 (s, 12H) ppm. ^{13}C NMR (75 MHz, MeOH-d_4 –slight dissociation) δ 163.62 (2C), 131.81 (2C), 121.21 (4C), 70.93 (4C) ppm. IR (neat): ν 3035 (w), 2994 (w), 1544 (w), 1440 (m), 1378 (m), 1306 (m), 1204 (w), 1146 (w), 1035 (vs), 933 (s), 880 (w), 837 (s), 757 (s), 728 (s), 647 (m), 617 (w), 602 (w), 557 (m), 497 (m), 433 (w) cm^{-1}.

2,2'-((1,3,4-Thiadiazole-2,5-diyl)bis(sulfanediyl))bis(1,3-di(methoxy)imidazolium) hexafluorophosphate (11)

2,2'-((1,3,4-Thiadiazole-2,5-diyl)bis(sulfanediyl))bis(1,3-di(methoxy)imidazolium) bromide (**10**, 0.05 mmol, 30 mg) was dissolved in H_2O (3 mL) before a solution of NH_4PF_6 (0.07 mmol, 30 mg) in H_2O (4 mL) was added. The mixture was ultrasonicated by means of an ultrasonication bath for 5 min. The insoluble matter was filtered off by syringe filtration and the filtrate was kept at 4 °C for 3 h, whereas a white precipitate formed. The precipitate was filtered off and immediately redissolved in MeOH. Single crystals of **11** were obtained by slow evaporation of the methanolic solution at ambient temperature. No additional analytical measurements were performed.

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REFERENCES

1. S. Bartz, B. Blumenröder, A. Kern, J. Fleckenstein, S. Frohnapfel, J. Schatz, and A. Wagner, *Z. Naturforsch. B*, 2009, **64**, 629.
2. G. Laus, A. Schwärzler, P. Schuster, G. Bentivoglio, M. Hummel, K. Wurst, V. Kahlenberg, T. Lörting, J. Schütz, P. Peringer, G. Nauer, and H. Schottenberger, *Z. Naturforsch. B*, 2007, **62**, 295.
3. G. Laus, A. Schwärzler, G. Bentivoglio, M. Hummel, V. Kahlenberg, K. Wurst, E. Kristeva, J. Schütz, H. Kopacka, C. Kreutz, G. Bonn, Y. Andriyko, G. Nauer, and H. Schottenberger, *Z. Naturforsch. B*, 2008, **63**, 447.

4. G. Laus, K. Wurst, V. Kahlenberg, H. Kopacka, C. Kreutz, and H. Schottenberger, *Z. Naturforsch. B*, 2010, **65**, 776.
5. R. Salchner, G. Laus, S. Haslinger, V. Kahlenberg, K. Wurst, D. E. Braun, S. Vergeiner, H. Kopacka, H. Schottenberger, A. Puckowski, M. Markiewicz, S. Stolte, and S. Nerdinger, *Heterocycles*, 2015, **90**, 1018.
6. M. Lampl, G. Laus, K. Wurst, V. Kahlenberg, T. Gelbrich, S. Nerdinger, H. Huppertz, and H. Schottenberger, *Heterocycles*, 2018, **97**, 1116.
7. G. Laus, M. E. Kostner, V. Kahlenberg, and H. Schottenberger, *Z. Naturforsch. B*, 2016, **71**, 997.
8. S. Zama, A. Bouraiou, S. Bouacida, T. Roisnel, and A. Belfaitah, *Tetrahedron Lett.*, 2013, **54**, 5605.
9. N. Kuhn, K. Eichele, and M. Walker, *Z. anorg. allg. Chem.*, 2001, **627**, 2565.
10. C. Froschauer, R. Salchner, G. Laus, H. K. Weber, R. Tessadri, U. Griesser, K. Wurst, V. Kahlenberg, and H. Schottenberger, *Aust. J. Chem.*, 2013, **66**, 391.
11. P. Franchetti, M. Grifantini, C. Lucarelli, and M. L. Stein, *Farmaco Sci.*, 1972, **27**, 46.
12. K. Hayes, *J. Heterocycl. Chem.*, 1974, **11**, 615.
13. G. Laus, J. Stadlwieser, and W. Klötzer, *Synthesis*, 1989, 773.
14. B. L. Eriksen, P. Vedsø, S. Morel, and M. Begtrup, *J. Org. Chem.*, 1998, **63**, 12.
15. I. Erdelmeier, I. Pelisson, I. Suzuki, and J.-C. Yadan, *WO Pat.-appl.*, WO2008006824.
16. F. Meischl, M. Harder, C. G. Kirchler, J. Kremser, C. W. Huck, G. K. Bonn, and M. Rainer, *J. Mol. Liq.*, 2019, **289**, 111157.
17. J. A. Shropshire and D. J. Eustace, *US Pat.-appl.*, US4124693.
18. P. K. Adanuvor, *J. Electrochem. Soc.*, 1987, **134**, 1450.
19. B. Alimenla, B. Kuotsu, and U. B. Sinha, *Chem. Sci. Trans.*, 2014, **3**, 826.
20. C. N. Neumann, J. M. Hooker, and T. Ritter, *Nature*, 2016, **534**, 369.
21. N. Taccardi, I. Niedermaier, F. Maier, H.-P. Steinrück, and P. Wasserscheid, *Chemistry*, 2012, **18**, 8288.
22. G. Mloston, M. Jasinski, A. Wróblewska, and H. Heimgartner, *Curr. Org. Chem.*, 2016, **20**, 1359.
23. G. Mlostoń, M. Celeda, K. Urbaniak, M. Jasiński, V. Bakhonsky, P. R. Schreiner, and H. Heimgartner, *Beilstein J. Org. Chem.*, 2019, **15**, 497.
24. G. Sheldrick, *Acta Cryst. A*, 2015, **71**, 3.
25. M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidori, and R. Spagna. *J. Appl. Cryst*., 2003, **36**, 1103.
26. G. Sheldrick. *Acta Cryst. C*, 2015, **71**, 3.
27. A. L. Spek, *Acta Cryst. C*, 2015, **71**, 9.
28. A. P. Flynn, *Chem. Brit.*, 1984, **20**, 30.