Synthesis and Crystal Structures of New 1,3-Disubstituted Imidazoline-2-thiones

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Two methods ($MeOH/K_2CO_3$, pyridine/Et_3N) were assessed for the introduction of sulfur into the 2-position of 1,3-disubstituted quaternary imidazolium salts **1**–**9** (Cl, I, BF_4, PF_6, CH_3OSO_3 were used as anions) to yield nine 1,3-disubstituted imidazoline-2-thiones **10**–**18** (**1**, **10**: $R^1 = CH_3$, $R^2 = CH_3$; **2**, **11**: $R^1 = OCH_2Ph$, $R^2 = CH_3$; **3**, **12**: $R^1 = OCH_3$, $R^2 = CH_3$; **4**, **13**: $R^1 = OCH_3$, $R^2 = OCH_3$; **5**, **14**: $R^1 = NH_2$, $R^2 = CH_2Ph$; **6**, **15**: $R^1 = NCHPh$, $R^2 = CH_3$; **7**, **16**: $R^1 = NH_2$, $R^2 = CH_3$; **8**, **17**: $R^1 = NCHPh$, $R^2 = NCHPh$; **9**, **18**: $R^1 = NH_2$, $R^2 = OCH_3$). Compounds **11**–**18** represent *N*-alkyloxy and *N*-amino imidazoline-2-thiones, whereas **10** served as reference compound. The first method was advantageous for the conversion **1** → **10** due to faster reaction, whereas in the reaction **2** → **11** considerable amounts of by-products were formed. Pure thiones **11**, **14**, **16**, **17**, and **18** were obtained only by the second method. Both methods worked for the synthesis of the methoxy derivatives **12** and **13** from **3** and **4**, and the benzylideneamino derivative **15** from **6**. 1-Amino-3-methylimidazoline-2-thione (**16**) was also prepared by hydrolysis of the benzylideneamino derivative **15**. Crystal structures of seven 1,3-disubstituted imidazoline-2-thiones were determined by single-crystal X-ray diffraction. Intermolecular C–H···S contacts were identified and, additionally, N–H···S interactions in aminothiones **14** and **16**. The ^{1}H NMR shifts of **10** and **13** were satisfactorily correlated with the Kamlet-Abboud-Taft π^* and β parameters in ten solvents. From the lack of correlation with the α parameter and from the C=S bond length (average 1.68 Å) a significant contribution of a mesoionic imidazolium-2-thiolate resonance structure seems unlikely.

Key words: Crystal Structure, Hydrogen Bond, Imidazole, Thione

Introduction

Imidazole is one of the most important heterocycles, and the respective imidazoline-2-thiones are valuable intermediates for many purposes, as discussed below. Historically, heterocyclic thiones were obtained by cleavage of 'carbene dimers' by fused sulfur [1] or sulfur in pyridine solution [2, 3]. Imidazoline-2-thiones were also synthesized by cyclization of linear precursor molecules [4 – 6]. The thione function was most conveniently introduced by reaction of heterocyclic quaternary salts with sulfur in $MeOH/K_2CO_3$ [7 – 9], or MeOH/pyridine/DBU [10, 11]. Recently, the use of CH_2Cl_2/Et_3N [12] and THF/KO*t*Bu [13] was reported. Pyridine is known to be an effective solvent for this reaction in the triazole and thiazole series, often in the presence of triethylamine [14 – 16]. The popular '$MeOH/K_2CO_3$ method' has been used for the synthesis of 1,3-dimethylimidazoline-2-thione [8, 9], bridged bis(imidazoline-2-thiones) [17 – 22], and also for multidentate ligands [23]. Very recently, mixed-donor bidentate ligands based on carbene and thione functions have been reported [24]. The 'pyridine/Et_3N method' was successfully employed for the preparation in high yields of 1-benzyloxy-3-methylimidazoline-2-thione [25], 1,3-bis(benzylideneamino)imidazoline-2-thione [26, 27], and 1,3-di(benzyloxy)imidazoline-2-thione [28]. Alternative thionations were performed with potassium thioacetate or thiocyanate as sulfur source using microwave conditions [29]. Imidazolin-2-ylidenes (carbenes) formed by deprotonation of the respective imidazolium cations were presumed to be intermediates in these reactions. In fact, some imidazoline-2-thiones were prepared from isolated carbenes [30], from electrolytically generated carbenes [31], and

the imidazolium ion was designated as 'protocarbene' [32]. Some 1,3-dialkylimidazoline-2-thiones were reportedly prepared by alkylation of 2-mercapto-1-methylimidazole [33] and by thermal isomerization of *S*-alkyl compounds [21].

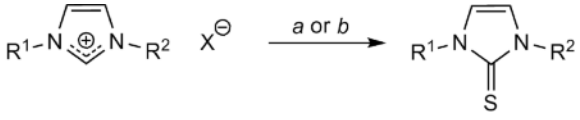
Typical reactions of these imidazoline-2-thiones include *S*-alkylation [34–36], addition of halogen [37, 38], oxidative desulfurization [4, 10, 39, 40], reduction to the carbene [41, 42], and formation of metal complexes [43–45]. Numerous crystal structures of 1,3-disubstituted imidazoline-2-thione complexes with Al, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Ru, Rh, Ag, Cd, In, Sb, Te, W, Re, Ir, Au, Hg, Pb, and Bi were found in the Cambridge Structural Database (version 5.33, August 2012). The crystal structure of 1,3-dimethylimidazoline-2-thione (**10**) [46, 47] at room temperature is known, but was now re-determined at 173 K to get comparable data.

In continuation of our studies in azole chemistry, we report the synthesis of 1,3-disubstituted imidazoline-2-thiones containing *N*-heteroatom substituents (N or O), preferably small ones, which have not yet been described although several quaternary precursor salts are known, and the tools for the synthesis of other ones are available. To our knowledge, the first representative of this class of compounds was 1-benzyloxy-3-methylimidazoline-2-thione (**11**) [25], and the second one was 1,3-bis(benzylideneamino)imidazoline-2-thione (**17**) without spectroscopic data [26]. 1-Methoxy-3-methylimidazoline-2-thione (**12**) was described in a patent [12]. Recently, we reported the first crystal structure of a fourth example, 1,3-di(benzyloxy)imidazoline-2-thione [28]. No other crystal structure of these *N*-heteroatom-substituted thiones has been disclosed so far. Here, we report the synthesis of nine 1,3-disubstituted imidazole-2-thiones and crystal structures of three new and four known thiones.

Results and Discussion

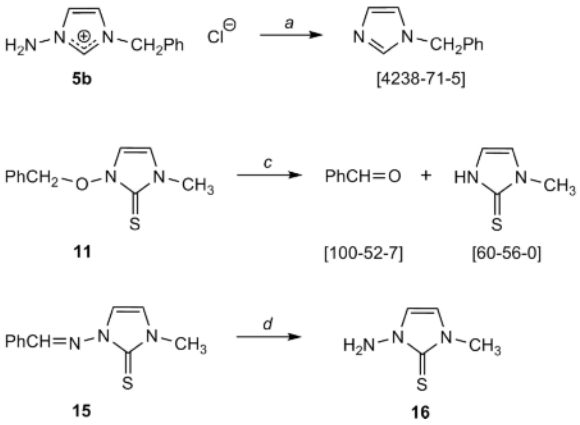
Synthetic considerations

Two methods ($MeOH/K_2CO_3$ or $pyridine/Et_3N$, Scheme 1) for the transformation of quaternary salts **1–9** to the thiones **10–18** were investigated. Different precursor salts (chloride, hexafluorophosphate, iodide, methylsulfate, tetrafluoroborate) were tested. The synthesis of 1,3-dimethylimidazoline-2-thione (**10**) was studied in more detail. Thionation of 1,3-dimethylimidazolium iodide (**1a**) in $MeOH/K_2CO_3$ is long known, but the reported yields are inexplicably modest (58–62 % after 40 hours at room temperature [9]). We found that the reaction stopped at 60 percent conversion at 20 °C in accordance with the reported yield, but 75 percent conversion was achieved at 65 °C after one hour (increasing only slightly to 80 % after 20 hours), as judged by ^{1}H NMR. In $pyridine/Et_3N$, the iodide reacted very slowly (45 % conversion after 28 hours at 20 °C; 40 % after one hour at 65 °C). More sulfur or more Et_3N did not increase the rate of reaction. We also tried the precursor hexafluorophosphate **1b** and found that it did not react at all in pyridine at 20 °C (less than 1 % after 28 hours) and gave only 25 % conversion after one hour at 65 °C. In MeOH, conversion of **1b** was 75 % at 20 °C after 3 days, 80 % at 65 °C after one hour, where the reaction stopped. However, the presence of KPF_6 interfered with the crystallization of the thione from water, thus compromising the yield. Surprisingly, under otherwise identical conditions the reaction slowed significantly when Na_2CO_3 was used instead of K_2CO_3 (iodide gave 30 %, hexafluorophosphate 15 % conversion after one hour at 65 °C). We confirmed that the use of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) inexplicably resulted in high conversion (90 %) only when two equivalents were employed [10]. Triethylamine in MeOH was not effective either. Pure pyridine has been observed to allow only slow thionation [28]. Use of either precipitated ('lac sulfuris') or sublimed sulfur did not make a significant difference. Colloidal sulfur sometimes caused problems during work-up. We observed that in the presence of 10 % water (by volume) the reaction at 65 °C stopped at 15 % conversion. It has been reported that the introduction of sulfur failed when ethanol or water were used as solvents [9]. Therefore, we reasoned that small amounts of water liberated by neutralization of the carbonate could explain this strange behavior. To our disappointment, addition of molecular sieves to trap water did not promote the reaction, but gave lower conversion. Attempted azeotropic removal of water using *tert*-butylmethylether did not improve the yield, either. The use of the crude methylsulfate **1c** unexpectedly but fortunately resulted in 90 % conversion in MeOH at 65 °C after one hour, where the reaction again halted (in pyridine only 40 % conversion was obtained). In summary, use of methylsulfate as preferred anion, methanol as



1–9 **10–18**

Salt	R^1	R^2	X	Thione
1a	CH_3	CH_3	I	
1b	CH_3	CH_3	PF_6	
1c	CH_3	CH_3	CH_3OSO_3	**10**
2	OCH_2Ph	CH_3	PF_6	**11**
3	OCH_3	CH_3	I	**12**
4	OCH_3	OCH_3	PF_6	**13**
5a	NH_2	CH_2Ph	DNP	
5b	NH_2	CH_2Ph	Cl	**14**
6	N=CHPh	CH_3	BF_4	**15**
7a	NH_2	CH_3	DNP	
7b	NH_2	CH_3	Cl	**16**
8	N=CHPh	N=CHPh	Cl	**17**
9a	NH_2	OCH_3	DNP	
9b	NH_2	OCH_3	Cl	**18**



5b **11** **15** **16**

Scheme 1. a) $^1/_8$ S_8, K_2CO_3/MeOH; b) $^1/_8$ S_8, Et_3N/pyridine; c) 130 °C; d) HCl/H_2O.

preferred solvent, K_2CO_3 as preferred base, and heating in the absence of water gave the best result for the synthesis of **10**. The situation was found to be completely different, however, for the thionations of other quaternary salts.

Thus, 1-benzyloxy-3-methylimidazolium hexafluorophosphate (**2**) gave complete conversion to the respective thione **11** in pyridine/Et_3N after one hour at 65 °C, whereas in MeOH/K_2CO_3 numerous unidentified by-products were encountered. Thermal *N*-alkyl/*S*-alkyl rearrangements of imidazoline-2-thiones have been reported [48]. However, when thione **11** was heated at 130 °C, the molecule was cleaved into benzaldehyde and 1-methylimidazoline-2-thione (Scheme 1), according to ^{1}H and ^{13}C NMR spectra and mass spectrometry. TLC and characteristic odor were confirmative. In contrast, 1-methoxy-3-methylimidazolium iodide (**3**) and 1,3-dimethoxyimidazolium hexafluorophosphate (**4**) gave complete conversion after two hours at 65 °C in either pyridine or methanol, yielding the thiones **12** and **13**, respectively. 1,3-Dimethoxyimidazolium salts are known to undergo degradation in alkaline aqueous solution involving carbene formation and ring opening [49]. It is interesting enough that the desired thione was formed at all, but surprisingly no degradation occurred in methanol as judged by the absence of the tell-tale methyl NMR signals of the degradation product. In pyridine again a clean reaction was observed. On the other hand, the *N*-amino imidazolium chlorides **5b** and **7b** did not tolerate the MeOH/K_2CO_3 conditions. Thus, attempted thionation of **5b** gave a surprising 70% isolated yield of 1-benzylimidazole (Scheme 1). Deamination was also observed by NMR in the case of 1-amino-3-methylimidazolium chloride (**7b**). In pyridine, the thiones **14** and **16** were readily obtained in satisfactory yields. 1-Benzylideneamino-3-methylimidazoline-2-thione (**15**) was best prepared from the tetrafluoroborate **6** in pyridine. Although conversion was also high in MeOH/K_2CO_3, insoluble KBF_4 complicated work-up. However, we found that, in this case, Na_2CO_3 also gave full conversion. This compound was intended as an alternative approach to the initially elusive 1-amino-3-methylimidazoline-2-thione (**16**). Hydrolysis of **15** in dilute hydrochloric acid proceeded smoothly at 60 °C to compound **16** with a free amino group (Scheme 1), whereas at 100 °C only decomposition was observed. Thus, we ended up with two synthetic pathways to **16**. The previously described 1,3-bis(benzylideneamino)imidazoline-2-thione (**17**) could be prepared only in pyridine. In methanol complete decomposition of the corresponding quaternary chloride **8** occurred at room temperature, whereas the thione **17** was stable under the conditions. No spectroscopic data of **17** have been reported so far, and they are therefore disclosed here. Preliminary attempts to remove the benzylidene groups from **17** (which is insoluble even in concentrated hydrochloric acid) were not successful. Finally, 1-amino-3-methoxyimidazoline-2-thione (**18**), a mixed *N*/*O*-substituted imidazoline-2-thione, was prepared by the pyridine method from chloride **9** in

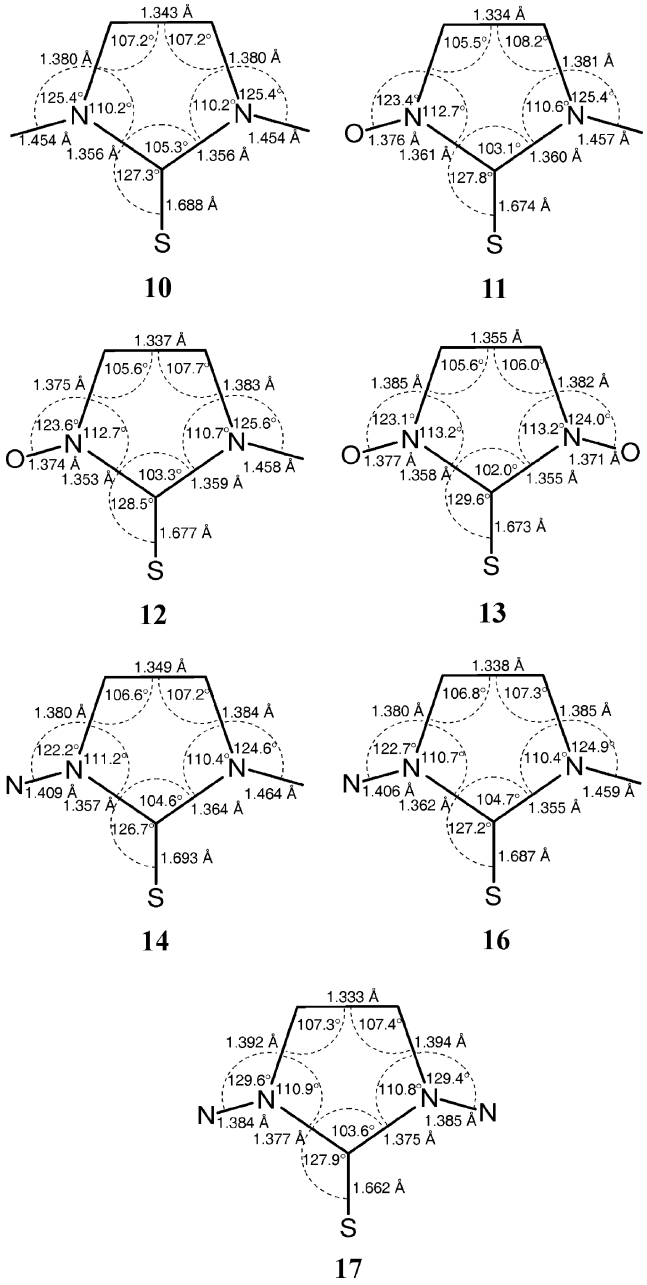


Fig. 1. Interatomic distances (Å) and angles (deg) in imidazoline-2-thiones.

modest yield. In general, work-up comprised evaporation of the solvent and extraction of the residue. In some cases (**11**, **15** and **17**) the products could be precipitated by addition of water to the reaction mixture.

Crystallography

The imidazoline-2-thiones crystallized readily from various solvents (ranging in polarity from H_2O to CCl_4) or could be purified by sublimation. The crystal-

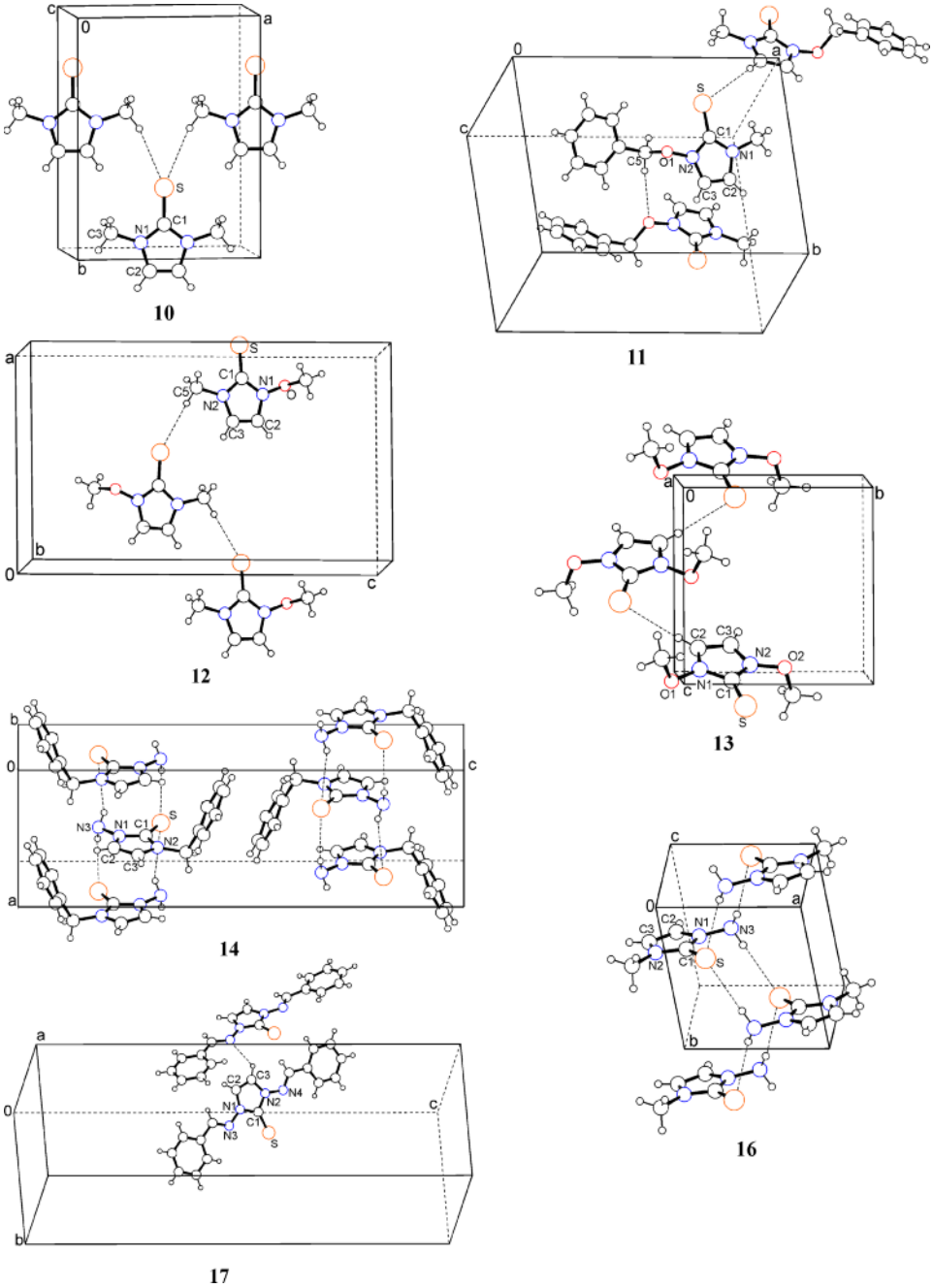


Fig. 2 (color online). Interactions in the crystal structures of imidazoline-2-thiones.

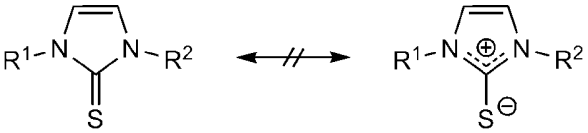
lographic data and refinement details are summarized in Table 1. Interatomic distances and angles in the heterocyclic rings are displayed in Fig. 1. The hydrogen bonding interactions in the crystal structures are shown in Fig. 2, and the pertinent parameters are collected in Table 2. Keeping in mind the potential pitfalls [50] of using the sum of van-der-Waals radii [51, 52] as the threshold for hydrogen bonds and remembering that

Table 1. Crystallographic data and data collection and structure refinement details.

Compound	**10**	**11**	**12**	**13**	**14**	**16**	**17**
CCDC no.	919557	919558	919559	919560	919561	919562	919563
Empirical formula	$C_5H_8N_2S$	$C_{11}H_{12}N_2OS$	$C_5H_8N_2OS$	$C_5H_8N_2O_2S$	$C_{10}H_{11}N_3S$	$C_4H_7N_3S$	$C_{17}H_{14}N_4S$
Formula weight	128.19	220.29	144.19	160.19	205.28	129.19	306.38
Crystal system	orthorhombic	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic	orthorhombic
Space group	*Cmcm*	$P2_1/c$	*Pbca*	*Pn*	*Pbca*	$P2_1/m$	*Pbca*
a, Å	8.4445(4)	13.3360(6)	10.9850(3)	6.5863(5)	6.9535(4)	6.9235(4)	10.2869(1)
b, Å	11.1216(6)	10.9427(5)	6.8233(2)	7.4806(6)	13.1888(8)	6.5520(3)	10.1127(1)
c, Å	6.7252(4)	7.6120(3)	18.1691(5)	7.8027(7)	22.2938(14)	7.1347(3)	29.5072(2)
α, deg	90	90	90	90	90	90	90
β, deg	90	93.541(4)	90	99.636(8)	90	110.287(3)	90
γ, deg	90	90	90	90	90	90	90
Volume, Å^3	631.61(6)	1108.71(8)	1361.85(7)	379.01(5)	2044.5(2)	303.57(3)	3069.58(5)
Z	4	4	8	2	8	2	8
$D_{calcd.}$, g cm^{-3}	1.35	1.32	1.41	1.40	1.33	1.41	1.33
Absorption coefficient, mm^{-1}	3.7	0.3	0.4	3.4	2.5	0.4	1.9
F(000), e	272	464	608	168	864	136	1280
Crystal size, mm^3	$0.44 \times 0.12 \times 0.02$	$0.50 \times 0.16 \times 0.16$	$0.36 \times 0.18 \times 0.12$	$0.36 \times 0.24 \times 0.20$	$0.18 \times 0.14 \times 0.08$	$0.15 \times 0.06 \times 0.03$	$0.24 \times 0.16 \times 0.12$
Radiation	CuK_α	MoK_α	MoK_α	CuK_α	CuK_α	MoK_α	CuK_α
θ range for data collection	6.6–67.4	3.3–25.4	3.7–25.4	5.6–67.1	4.0–67.6	3.0–25.0	3.0–67.5
Index ranges	$-10 \le h \le 9$ $-13 \le k \le 12$ $-8 \le l \le 7$	$-14 \le h \le 16$ $-11 \le k \le 13$ $-6 \le l \le 9$	$-10 \le h \le 13$ $-7 \le k \le 8$ $-21 \le l \le 21$	$-5 \le h \le 7$ $-8 \le k \le 8$ $-9 \le l \le 9$	$-7 \le h \le 8$ $-13 \le k \le 15$ $-20 \le l \le 26$	$-8 \le h \le 8$ $-7 \le k \le 7$ $-8 \le l \le 7$	$-12 \le h \le 12$ $-12 \le k \le 11$ $-34 \le l \le 35$
Reflections collected	1280	6529	7563	2165	13 043	1719	39 389
Independent reflections/R_{int}	336/0.029	2016/0.027	1244/0.028	940/0.036	1839/0.047	588/0.026	2765/0.033
Reflections [$I > 2\,\sigma(I)$]	318	1738	1105	918	1719	535	2603
Restraints/parameters	0/29	0/137	0/84	2/93	2/133	1/55	0/199
Goodness-of-fit on F^2	1.11	1.06	1.07	1.14	1.05	1.07	1.04
R_1/wR_2 [$I > 2\,\sigma(I)$]	0.032/0.086	0.033/0.084	0.028/0.070	0.032/0.085	0.037/0.095	0.027/0.062	0.032/0.085
R_1/wR_2 (all data)	0.033/0.089	0.040/0.088	0.033/0.073	0.032/0.086	0.040/0.100	0.032/0.065	0.034/0.087
$\Delta\rho_{max/min}$, e Å^{-3}	0.25/−0.32	0.23/−0.20	0.23/−0.22	0.22/−0.23	0.23/−0.30	0.17/−0.18	0.13/−0.26

Compound	Interaction	H···A	D···A	D–H···A	Symmetry code (A)
10	C3–H···S	2.9783(5)	3.923(2)	162.2(1)	$1/2+x, 1/2+y, z$
11	C5–H···O	2.630(1)	3.607(2)	168.9(1)	$x, 1/2-y, 1/2+z$
	C2–H···S	2.9208(4)	3.723(2)	142.9(1)	$2-x, 1/2+y, 3/2-z$
12	C5–H···S	2.8115(4)	3.771(2)	166.1(1)	$-1/2+x, 1/2-y, 1-z$
13	C2–H···S	2.7455(8)	3.673(4)	165.4(2)	$1/2+x, -y, -1/2+z$
14	N3–H···S	2.74(2)	3.500(1)	148(2)	$1/2+x, y, 3/2-z$
	N3–H···S	2.92(2)	3.645(1)	144(2)	$-1/2+x, y, 3/2-z$
	C3–H···S	2.8014(4)	3.697(2)	157.6(1)	$1/2-x, 1/2+y, z$
16	N3–H···S	2.80(1)	3.645(1)	158(2)	$1-x, 1/2+y, 2-z$
17	C3–H···N	2.572(1)	3.259(2)	129.46(8)	$1/2-x, -1/2+y, z$

Table 2. Hydrogen interaction geometries (Å, deg).



Scheme 2. Alleged resonance structures of 1,3-disubstituted imidazoline-2-thiones.

short contacts do not necessarily mean stabilizing interactions, we report here either hydrogen bonds which are at least 6 % shorter than the sum of van-der-Waals radii or otherwise label them as 'contacts'. It has been noted, however, that this may be too restrictive a criterion for weak interactions [53].

The structure of 1,3-dimethylimidazoline-2-thione (**10**) [46, 47] was re-determined at the same temperature as the new compounds to allow comparison of the data. This turned out to be a wise decision, because the effect of temperature on the angles in the ring system of this compound obviously is almost as large as the effect of the hetero-atom substituents in the other compounds. Thus, in the reported structures of **10** at room temperature the C–N–C angles within the ring were 108.4° [7] and 109.2° [46], whereas at 173 K we found 110.2(2)°. The other thiones reported here which bear *N*-alkyl substituents exhibit C–N–C ring angles from 110.4(1)° to 110.7(1)°. The planar molecules of **10** are arranged by weak intermolecular CH_3···S contacts in layers parallel to the (001) plane which are separated by 3.363 Å.

An *N*-alkyloxy substituent causes widening of the C–N–C ring angle at the N atom bearing the alkyloxy substituent by approximately 3°. Thus, in the structures of the benzyloxy **11**, methoxy **12** and dimethoxy derivative **13**, the C–N–C ring angles range from 112.7(1)° to 113.2(3)°. In the two independent molecules of the related 1,3-di(benzyloxy)imidazoline-2-thione [28], these angles are between 112.7(3)° and 113.5(2)°, which is in perfect agreement. Short CH_2···O and CH···S contacts were observed in **11**, CH_3···S hydrogen bonds in the direction of the crystallographic *a* axis in **12**, and CH···S hydrogen bonds forming zigzag chains in **13**. It is also noteworthy that 1,3-dimethoxyimidazoline-2-thione **13** adopts the *anti* conformation (the methoxy groups are rotated out of the ring plane on opposite sides by 86.2° and 86.5°, respectively) in the solid state. Previously, both *syn* and *anti* conformations have been observed for 1,3-dimethoxyimidazolium salts [54].

In the structures of the *N*-amino-substituted thiones **14**, **16** and **17**, the C–N–C ring angles at the N atom bearing the amino substituent range from 110.7(2)° to 111.2(1)°. In 1-amino-3-benzylimidazoline-2-thione (**14**) two chains of intermolecular NH···S interactions (one short, one long) propagating in opposite directions lead to stacking of overlapping rings in the [100] direction, with a centroid–centroid distance of 3.518 Å. The columns are linked by CH···S hydrogen bonds. The molecules of 1-amino-3-methylimidazoline-2-thione (**16**) are parallel to the (010) plane, with an interplanar distance of 3.276 Å and connected by two chains of symmetry-related NH···S hydrogen bonds in the [010] direction, but not overlapping (shortest centroid–centroid distance 6.797 Å). The small methyl groups allow an alternating arrangement of the rings on opposite sides of the hydrogen bond ribbon (in contrast to the larger benzyl groups in **14** which are oriented to the left and right of the ribbon forcing the rings to one side). An intermolecular CH···N hydrogen bond was observed in the crystal structure of the 1,3-bis(benzylideneamino) derivative **17**.

The C=S bond lengths in these seven thiones range from 1.66 to 1.69 Å in agreement with the accepted value of 1.68 Å in thioureas [55]. Earlier, this C=S bond has been considered remarkably long (compared with 1.60 Å in a trithiocarbonate as an ill-chosen

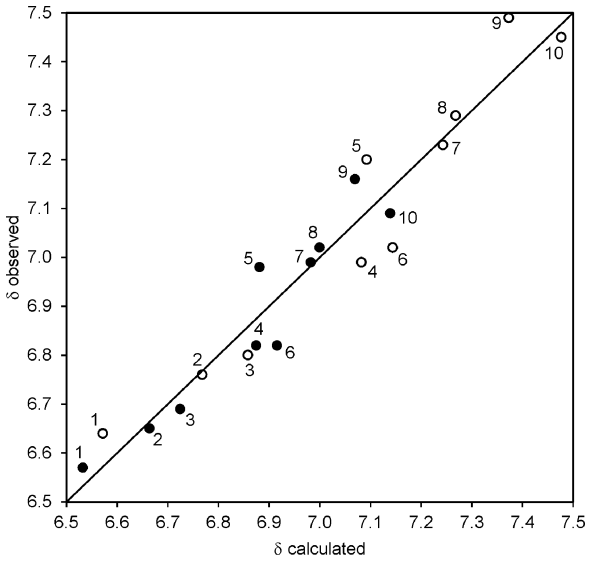


Fig. 3. Correlation of calculated and observed ^{1}H NMR shifts of 1,3-dimethylimidazoline-2-thione **10** (•) and 1,3-dimethoxyimidazoline-2-thione **13** (○) in different solvents: (1) CCl_4, (2) $CDCl_3$, (3) CD_2Cl_2, (4) CD_3CN, (5) [D_6]acetone, (6) [D_8]THF, (7) CD_3OD, (8) D_2O, (9) [D_7]DMF, (10) [D_6]DMSO.

reference compound), and thus believed to indicate a contribution of the mesoionic imidazolium-2-thiolate (Scheme 2) [7, 46]. This point keeps getting reiterated in the literature [38, 56]. However, a research in the Cambridge Structural Database resulted in a mean value of 1.68 ± 0.02 Å for imidazolinethiones (101 structures, no metal coordination, $R \leq 0.05$) and 1.67 ± 0.07 Å for compounds containing a propanethione fragment (105 structures, no metal coordination, $R \leq 0.05$). Thus, there is no evidence for an elongated C=S bond in imidazoline-2-thiones.

^{1}H NMR spectroscopy

The ^{1}H NMR signals of the thione ring protons are shifted upfield from those of the quaternary precursor salts by 0.5 – 0.8 ppm, which may be attributed to the loss of cationic character. It is noteworthy that ^{1}H NMR shifts of the thiones depend quite significantly on the solvent. It seemed to be of interest to analyze this behavior in terms of the Kamlet-Abboud-Taft parameters [57] of solvent properties, *i. e.* (hydrogen bond donor) acidity α [58], (hydrogen bond acceptor) basicity β [59], and dipolarity/polarizability π^* [60, 61]. Thus, spectra of **10** and **13** were recorded in ten common NMR solvents covering a wide range of these parameters. The parameters for non-deuterated solvents from a recent compilation [62] were applied to unravel the individual contributions of the terms in the linear solvation energy relationship (LSER) [57] by multiple regression analysis:

$$\delta(^1\mathrm{H}) = \delta_0 + s\pi^* + a\alpha + b\beta$$

From the data the following equations were derived (standard errors of δ_0, s, and b, correlation coefficient r, relative standard deviation σ of the correlation, and number N of data points given).

For **10**: $\delta(^1\mathrm{H}) = (6.462 \pm 0.077) + (0.252 \pm 0.120)\pi^* + (0.559 \pm 0.106)\beta$
$(r = 0.95,\ \text{rel. } \sigma = 0.97\,\%,\ N = 10)$

For **13**: $\delta(^1\mathrm{H}) = (6.467 \pm 0.099) + (0.375 \pm 0.154)\pi^* + (0.835 \pm 0.135)\beta$
$(r = 0.96,\ \text{rel. } \sigma = 1.21\,\%,\ N = 10)$

Both the standard deviations and correlation coefficients are satisfactory. It was to be expected that a thiolate would be affected by the hydrogen bond donating strength of the solvents. However, the influence of the α term was found to be negligible. Interestingly, the β term is predominant, and the resulting correlation of calculated *vs.* observed values is shown in Fig. 3. The dimethoxy compound **13** displayed higher sensitivity than the dimethyl compound **10**. Obviously, here the C–H···solvent interactions dominate, which sort of validates the C–H···S contacts observed in the crystal structures. In contrast, the α term constituted the major contribution to the observed solvatochromism of an unquestionable tetrazolium-5-thiolate [63]. Thus, there is no evidence of involvement of a mesoionic imidazolium-2-thiolate resonance structure here (Scheme 2).

Conclusion

The synthesis of fundamental 1,3-disubstituted imidazoline-2-thiones was investigated. The choice of method depended on the nature of the *N*-substituent (C, O, or N), and work-up was adapted according to solubility and impurities. Thus, no general method is available. These thiones are valuable building blocks for other 2-substituted imidazolium systems and ligands on their own. The bifunctional amino-thione

compounds offer access to new heterocyclic systems. Clearly, significant progress has been made in the thriving field of imidazole chemistry, adding new insights into an already flourishing area of heterocyclic chemistry. Reactions of the new thiones will be communicated in due course.

Experimental Section

NMR spectra were recorded with a Bruker Avance DPX 300 spectrometer. IR spectra were obtained with a Nicolet 5700 FT instrument. High-resolution mass spectra were measured with a Finnigan MAT 95 mass spectrometer. Elemental analyses were conducted at the University of Vienna, Austria.

1-Benzylimidazole and 1-methylimidazole were purchased from Aldrich, sulfur from Merck, and used as received. *O*-(2,4-Dinitrophenyl)hydroxylamine (DNPH) was freshly prepared according to the published procedure [64] and used within one week. 1-(Benzylideneamino)imidazole was obtained by the literature method [65]. 1-Methoxyimidazole and 1-methoxyimidazolium hexafluorophosphate were synthesized by catalytic hydrogenation of 1,3-dimethoxyimidazolium hexafluorophosphate [54]. The quaternary precursor salts 1,3-dimethylimidazolium iodide (**1a**) [9, 30, 66] or hexafluorophosphate (**1b**) [67–69] or methylsulfate (**1c**) [69], 1-benzyloxy-3-methylimidazolium hexafluorophosphate (**2**) [70], 1,3-dimethoxyimidazolium hexafluorophosphate (**4**) [54], and 1,3-bis(benzylideneamino)imidazolium chloride (**8**) [27] were synthesized as described. No spectroscopic data of **8** have been disclosed so far, and they are therefore given here. 1-Amino-3-methylimidazolium 2,4,6-trimethylbenzenesulfonate [71] is known, but we preferred the respective 2,4-dinitrophenolate (DNP) **7a** and the ensuing chloride **7b**, because DNPH is an extremely powerful, easy-to-prepare, and relatively inexpensive aminating agent, and the DNP is readily converted to the corresponding chloride.

*1-Methoxy-3-methylimidazolium iodide (**3**)*

A solution of 1-methoxyimidazole (0.44 g, 4.5 mmol) and methyl iodide (0.40 mL, 1.43 equiv.) in CH_2Cl_2 (5 mL) was stirred for 4 days at 20 °C. The solvent was evaporated, and the oily residue was repeatedly treated with Et_2O until it solidified to give a hygroscopic, tan powder. Yield: 0.79 g (73 %). M. p. 72 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.84 (s, 3H), 4.22 (s, 3H), 7.75 (t, J = 1.9 Hz, 1H), 8.22 (t, J = 1.9 Hz, 1H), 9.65 (unresolved t, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 36.6, 69.5, 118.4, 121.6, 132.9 ppm. – IR (neat): ν = 3123 w, 3093 w, 2940 w, 3057 m, 1568 w, 1327 m, 1152 m, 1023 m, 1011 m, 946 s, 823 m, 747 m, 617 s, 585 s cm^{-1}. – HRMS (FAB): m/z = 113.0662 (calcd. 113.0709 for $C_5H_9N_2O$, $[M]^+$).

*1-Amino-3-benzylimidazolium 2,4-dinitrophenolate (**5a**)*

A solution of 1-benzylimidazole (1.00 g, 6.3 mmol) and DNPH (1.26 g, 1.0 equiv.) in CH_2Cl_2 (10 mL) was stirred for 20 h at 20 °C. The product was filtered off, washed with Et_2O (10 mL), and dried. Yield: 1.71 g (76 %). M. p. 116–117 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 5.36 (s, 2H), 6.34 (d, J = 9.7 Hz, 1H), 6.9 (br, 2H), 7.40 (s, 5H), 7.65 (t, J = 1.8 Hz, 1H), 7.73 (t, J = 1.8 Hz, 1H), 7.79 (dd, J = 3.2 Hz, J = 9.8 Hz, 1H), 8.59 (d, J = 3.2 Hz, 1H), 9.30 (t, J = 1.4 Hz, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 52.1, 121.0, 124.2, 124.9, 126.3, 127.5, 127.6, 128.2 (2C), 128.7, 129.0 (2C), 135.0, 135.4, 136.0, 169.9 ppm. – IR (neat): ν = 3103 w, 3057 w, 1598 m, 1551 m, 1529 m, 1466 m, 1430 m, 1373 w, 1317 s, 1260 s, 1127 s, 1053 m, 910 w, 830 m, 751 m, 715 m, 694 s, 661 s, 617 s cm^{-1}. – HRMS (FAB): m/z = 174.1029 (calcd. 174.1026 for $C_{10}H_{12}N_3$, $[M]^+$).

*1-Amino-3-benzylimidazolium chloride (**5b**)*

A suspension of **5a** (1.60 g, 4.5 mmol) in 1 M HCl (45 mL) was stirred at 80 °C for 1 h. The mixture was filtered, the solids were well washed with hot 1 M HCl (2 × 10 mL) and H_2O (10 mL). The cold filtrate was extracted with Et_2O (10 mL) and taken to dryness under reduced pressure. The resulting oil crystallized upon treatment with CH_2Cl_2 to give a colorless powder. Yield: 0.90 g (96 %). M. p. 150–152 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 5.2 (br, 2H), 5.43 (s, 2H), 7.37–7.44 (m, 5H), 7.67 (t, J = 1.7 Hz, 1H), 7.79 (t, J = 1.7 Hz, 1H), 9.50 (t, J = 1.4 Hz, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 51.8, 120.9, 124.0, 128.3 (2C), 128.7, 129.0 (2C), 135.1, 135.2 ppm. – IR (neat): ν = 3185 w, 3085 m, 3004 m, 1656 w, 1553 m, 1455 w, 1311 w, 1209 w, 1163 m, 1069 m, 892 w, 778 w, 733 m, 712 s, 696 s, 667 m, 624 m, 615 m cm^{-1}. – HRMS (FAB): m/z = 174.1051 (calcd. 174.1026 for $C_{10}H_{12}N_3$, $[M]^+$).

*1-Benzylideneamino-3-methylimidazolium tetrafluoroborate (**6**)*

To a solution of 1-(benzylideneamino)imidazole (1.71 g, 10 mmol) in anhydrous CH_2Cl_2 (17 mL) Me_3O BF_4 (1.55 g, 1.05 equiv.) was added. The mixture was stirred under argon for 24 h at 20 °C. The colorless product was collected by filtration, washed with Et_2O, and dried under reduced pressure. Yield: 2.04 g (75 %). M. p. 108 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.91 (s, 3H), 7.58–7.69 (m, 3H), 7.89 (s, 2H), 7.92 (s, 1H), 8.45 (s, 1H), 9.16 (s, 1H), 9.68 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 36.3, 115.7, 123.4, 129.0 (2C), 129.4 (2C), 131.0, 133.3, 135.2, 161.4 ppm. – IR (neat): ν = 3161 w, 3111 w, 1584 w, 1552 m, 1451 w, 1226 w, 1035 s, 970 m, 853 m, 739 m, 692 m, 618

m cm^{-1}. – HRMS (FAB): $m/z = 186.1026$ (calcd. 186.1026 for $C_{11}H_{12}N_3$, $[M]^+$).

*1-Amino-3-methylimidazolium 2,4-dinitrophenolate (**7a**)*

A solution of 1-methylimidazole (2.00 g, 24 mmol) and DNPH (5.09 g, 1.05 equiv.) in CH_2Cl_2 (40 mL) was stirred for 24 h at 20 °C. The product was filtered off, washed with Et_2O (2 × 10 mL), and dried. Yield: 4.75 g (69 %). M. p. 108 – 109 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 3.81$ (s, 3H), 6.33 (d, $J = 9.7$ Hz, 1H), 6.9 (br s, 2H), 7.61 (s, 2H), 7.78 (dd, $J = 3.2$ Hz, $J = 9.7$ Hz, 1H), 8.59 (d, $J = 3.1$ Hz, 1H), 9.07 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 35.9$, 122.2, 123.6, 125.0, 126.5, 127.5, 135.8, 136.1, 170.3 ppm. – IR (neat): $\nu = 3243$ w, 3135 w, 3079 w, 1596 m, 1557 m, 1536 m, 1483 w, 1466 w, 1435 w, 1376 w, 1316 s, 1246 s, 1178 s, 1127 s, 1047 m, 918 m, 851 m, 830 s, 747 s, 624 s cm^{-1}. – $C_{10}H_{11}N_5O_5$ (281.22): calcd. C 42.71, H 3.94, N 24.90; found C 42.78, H 3.77, N 24.52. – HRMS (FAB): $m/z = 98.0879$ (calcd. 98.0713 for $C_4H_8N_3$, $[M]^+$).

*1-Amino-3-methylimidazolium chloride (**7b**)*

A suspension of **7a** (3.00 g, 11 mmol) in 1 M HCl (90 mL) was stirred at 80 °C for 1 h. The mixture was filtered, the solids were well washed with hot 1 M HCl (2 × 20 mL) and H_2O (20 mL), and the filtrate was taken to dryness under reduced pressure. The resulting oil crystallized on cooling and was washed with Et_2O (2 × 10 mL). Yield: 1.33 g (93 %). M. p. 120 – 122 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta =$ 3.82 (s, 3H), 5.1 (br s, 2H), 7.63 (s, 1H), 7.64 (s, 1H), 9.19 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 35.8$, 122.0, 123.5, 135.5 ppm. – IR (neat): $\nu = 3132$ m, 3042 s, 3004 m, 2943 w, 1655 w, 1564 m, 1365 w, 1295 w, 1182 s, 1066 m, 1005 m, 841 m, 766 s, 617 s cm^{-1}. – HRMS (FAB): $m/z = 98.0878$ (calcd. 98.0713 for $C_4H_8N_3$, $[M]^+$).

*1,3-Bis(benzylideneamino)imidazolium chloride (**8**)*

A solution of 1,3-diaminoimidazolium chloride (1.0 g, 7.4 mmol) in MeOH (20 mL) was treated with benzaldehyde (1.66 g, 2.1 equiv.) and concentrated HCl (1 drop) and stirred at room temperature for 3 days. The solvent was removed, and the residue was stirred with H_2O (20 mL) and Et_2O (20 mL) for 10 min. The product was collected by filtration, washed with H_2O and Et_2O, and dried to give 0.83 g (36 %) of a tan powder. M. p. 177 °C (lit. 193 – 196 °C [27]). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 7.59 – 7.68$ (m, 6H), 7.95 – 7.97 (m, 4H), 8.82 (s, 2H), 9.50 (s, 2H), 10.63 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 116.7$ (2C), 129.2 (4C), 129.5 (4C), 131.0 (2C), 132.0, 133.5 (2C), 162.3 (2C) ppm. – IR (neat): $\nu = 1615$ m, 1599 m, 1574 m, 1538 m, 1487 m, 1227 m, 1128 m, 760 s, 689 s cm^{-1}. – HRMS (FAB): $m/z = 275.1280$ (calcd. 275.1291 for $C_{17}H_{15}N_4$, $[M]^+$).

*1-Amino-3-methoxyimidazolium 2,4-dinitrophenolate (**9a**)*

A solution of 1-methoxyimidazolium hexafluorophosphate (1.0 g, 4.1 mmol) in H_2O (4 mL) was treated with $NaHCO_3$ (0.35 g) and extracted with CH_2Cl_2 (2 × 10 mL). The solution was dried over $MgSO_4$ and reduced to half its volume. DNPH (0.86 g, 4.3 mmol) was added, and the mixture was stirred for 24 h at 20 °C. On cooling to –30 °C the product precipitated and was filtered off, washed with Et_2O (3 × 5 mL), and dried. Yield: 0.56 g (46 %). M. p. 77 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 4.08$ (s, 3H), 6.97 (d, $J = 9.4$ Hz, 1H), 7.02 (s, 1H), 7.65 (s, 1H), 8.17 (dd, $J = 2.9$ Hz, $J = 9.5$ Hz, 1H), 8.28 (s, 1H), 8.66 (d, $J = 2.9$ Hz, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 68.4$, 116.0, 121.9, 122.9, 123.5, 128.8, 131.1, 134.7, 136.4, 161.7 ppm. – IR (neat): $\nu = 3138$ w, 1599 m, 1571 m, 1525 m, 1427 m, 1324 s, 1258 s, 952 s, 820 s, 608 s cm^{-1}. – HRMS (FAB): $m/z = 114.0671$ (calcd. 114.0662 for $C_4H_8N_3O$, $[M]^+$).

*1-Amino-3-methoxyimidazolium chloride (**9b**)*

A suspension of **9a** (0.48 g, 1.6 mmol) in 1 M HCl (20 mL) was stirred at 80 °C for 1 h. The mixture was filtered, the solids were well washed with hot 1 M HCl (2 × 5 mL) and H_2O (5 mL). The cold filtrate was extracted with Et_2O (2 × 2 mL) and taken to dryness under reduced pressure to give 0.24 g (99 %) **9b** as an oil. ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 4.24$ (s, 3H), 7.70 (s, 1H), 8.22 (s, 1H), 9.67 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta =$ 69.2, 118.0, 118.1, 131.2 ppm. – IR (neat): $\nu = 3072$ m, 3017 m, 2942 m, 2786 m, 2701 m, 2599 m, 1568 m, 1445 m, 1011 s, 950 s, 842 s cm^{-1}.

*1,3-Dimethylimidazoline-2-thione (**10**)*

A mixture of **1c** (1.0 g, 4.8 mmol), sulfur (160 mg, 1.04 equiv.), and K_2CO_3 (0.80 g, 1.2 equiv.) in MeOH (8 mL) was refluxed for 3 h. After removal of the solvent, the residue was recrystallized from boiling H_2O (*ca.* 10 mL necessary to obtain a clear solution). The colorless product was filtered, washed with H_2O (1 mL), and dried under reduced pressure to yield 0.55 g (89 %). Single crystals from hot water. M. p. 183 °C (lit. 178 – 180 °C [8], 182 – 183.5 °C [9], 182 – 183.8 °C [29]). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 3.44$ (s, 6H), 7.08 (s, 2H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 34.5$ (2C), 118.1 (2C), 161.8 ppm. – IR (neat): $\nu = 3113$ w, 1573 w, 1492 w, 1464 w, 1436 w, 1387 m, 1238 m, 1180 m, 1085 w, 749 m, 730 s, 661 s cm^{-1}. – HRMS (FAB): $m/z = 128.0437$ (calcd. 128.0403 for $C_5H_8N_2S$, $[M^+]$), 129.0497 (calcd. 129.0481 for $C_5H_9N_2S$, $[M+H]^+$).

*1-Benzyloxy-3-methylimidazoline-2-thione (**11**)*

A mixture of **2** (1.0 g, 3.0 mmol), sulfur (96 mg, 1.0 equiv.), and Et_3N (0.41 ml, 1.0 equiv.) in pyridine (5 mL) was stirred at 70 °C (bath temperature) for 2 h. After addition of H_2O (50 mL) the mixture was heated until a clear solution was obtained, filtered to remove a small amount of a brown oil, and allowed to cool to 20 °C. The colorless needles were collected by filtration, washed with H_2O, and dried. Yield: 0.57 g (86 %). Single crystals from acetone/H_2O at ambient temperature. M. p. 120 – 121 °C (dec.; lit. 121 – 122 °C [25]). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 3.45$ (s, 3H), 5.26 (s, 2H), 7.04 (d, $J = 2.5$ Hz, 1H), 7.23 (d, $J = 2.5$ Hz, 1H), 7.41 (m, 3H), 7.51 (m, 2H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 34.4$, 78.0, 114.9, 115.4, 128.5 (2C), 129.1, 129.8 (2C), 133.7, 157.3 ppm. – IR (neat): $\nu = 3150$ w, 3122 w, 3090 w, 1560 w, 1455 m, 1409 m, 1390 m, 1324 m, 1215 m, 1139 m, 1079 m, 1040 m, 999 w, 946 m, 907 m, 846 m, 821 m, 776 w, 742 s, 696 m, 673 s, 647 m, 592 m, 572 m cm^{-1}. – HRMS (FAB): $m/z = 221.0792$ (calcd. 221.0743 for $C_{11}H_{13}N_2OS$, $[M + H]^+$).

*1-Methoxy-3-methylimidazoline-2-thione (**12**)*

A mixture of **3** (300 mg, 1.25 mmol), sulfur (40 mg, 1.0 equiv.), and Et_3N (0.26 mL, 1.5 equiv.) in pyridine (1.5 mL) was stirred at 70 °C for 2 h. The solvent was evaporated under reduced pressure, and the residue was extracted with EtOAc (3 × 3 mL). The extract was washed with 1 M HCl (3 × 1 mL) and filtered through a short SiO_2 column to remove a brown impurity. The filtrate was taken to dryness to yield 100 mg (55 %) of an off-white powder. The product was crystallized by slow evaporation of a solution in Et_2O at 20 °C. M. p. 55 °C (lit. 57 °C [12]). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 3.44$ (s, 3H), 3.96 (s, 3H), 7.09 (d, $J = 2.6$ Hz, 1H), 7.44 (d, $J = 2.6$ Hz, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 34.3$, 64.4, 113.8, 115.7, 157.1 ppm. – IR (neat): $\nu = 2934$ w, 1549 m, 1413 s, 1390 s, 1331 m, 1261 m, 1148 m, 1084 m, 1040 m, 1019 m, 803 m cm^{-1}. – HRMS (EI): $m/z = 144.0387$ (calcd. 144.0352 for $C_5H_8N_2OS$, $[M]^+$).

*1,3-Dimethoxyimidazoline-2-thione (**13**)*

a) A mixture of **4** (1.0 g, 3.6 mmol), sulfur (117 mg, 1.0 equiv.), and K_2CO_3 (0.61 g, 1.2 equiv.) in MeOH (6 mL) was stirred at 70 °C for 2 h. The solids were filtered off and rinsed with MeOH (2 × 2 mL). The filtrate was taken to dryness under reduced pressure. The residue was mixed with H_2O (5 mL) and extracted with CH_2Cl_2 (4 × 5 mL). The extract was dried over $MgSO_4$ and the solvent evaporated to give 0.29 g (50 %) of a tan oil which solidified.

b) A mixture of **4** (1.0 g, 3.6 mmol), sulfur (117 mg, 1.0 equiv.), and Et_3N (0.53 mL, 1.05 equiv.) in pyridine (5 mL) was stirred at 70 °C for 2 h. The solvent was evaporated under reduced pressure, and the residue was extracted with EtOAc (4 × 5 mL). The extract was washed with 1 M HCl (2 × 5 mL) and passed through a SiO_2 column to remove a brown impurity. Removal of the solvent yielded 0.32 g (55 %) of a tan solid. Single crystals were obtained by cooling a hot CCl_4 solution to –20 °C. M. p. 96 – 98 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 3.98$ (s, 6H), 7.45 (s, 2H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 64.9$ (2C), 112.0 (2C), 153.1 ppm. – IR (neat): $\nu = 3126$ w, 3098 w, 3065 w, 2992 w, 2937 w, 1545 w, 1448 m, 1396 s, 1117 m, 1011 s, 936 s, 741 m, 715 s, 646 s, 592 m, 537 s cm^{-1}. – HRMS (EI): $m/z = 160.0244$ (calcd. 160.0301 for $C_5H_8N_2O_2S$, $[M]^+$).

*1-Amino-3-benzylimidazoline-2-thione (**14**)*

A mixture of **5b** (0.21 g, 1.0 mmol), sulfur (34 mg, 1.05 equiv.), and Et_3N (0.14 ml, 1.0 equiv.) in pyridine (2 mL) was stirred at 90 °C for 4 h. After addition of cold H_2O (15 mL) the mixture was extracted with EtOAc (2 × 15 mL). The extract was washed with 1 M HCl (2 × 10 mL) and taken to dryness. The oily residue yielded seed crystals overnight which were secured. The oil was heated in H_2O (3 mL), and MeOH (*ca.* 0.5 mL) was added until a clear solution was obtained which was allowed to cool to 20 °C. Addition of a seed crystal produced a precipitate which was filtered off, washed with H_2O (3 mL), and recrystallized from hot MeOH (2 mL). Yield: 0.11 g (54 %). Single crystals from hot MeOH. M. p. 105 – 106 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): $\delta = 5.17$ (s, 2H), 5.4 (br, 2H), 7.09 (s, 1H, 7.13 (s, 1H), 7.31 (s, 5H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): $\delta = 50.2$, 115.0, 118.4, 127.6, 127.8 (2C), 128.5 (2C), 136.9, 160.1 ppm. – IR (neat): $\nu = 3281$ w, 3165 w, 3123 w, 3087 w, 3061 w, 2938 w, 1613 w, 1563 w, 1494 w, 1446 m, 1406 s, 1338 m, 1233 s, 1180 m, 1126 m, 965 m, 936 m, 817 w, 737 s, 702 s, 675 s, 651 s, 605 m, 575 m, 532 s cm^{-1}. – HRMS (EI): $m/z = 205.0649$ (calcd. 205.0668 for $C_{10}H_{11}N_3S$, $[M]^+$).

*1-Benzylideneamino-3-methylimidazoline-2-thione (**15**)*

a) A mixture of **6** (1.0 g, 3.7 mmol), sulfur (118 mg, 1.0 equiv.), and K_2CO_3 (0.61 g, 1.2 equiv.) in MeOH (10 mL) was stirred at 70 °C for 2 h. Addition of H_2O (20 mL) gave an off-white precipitate which was collected by filtration. A suspension of this crude product in H_2O (100 mL) was stirred for 2 h at room temperature to remove inorganic salts. The product was filtered off and dried to yield 0.51 g (64 %) of a yellow powder.

b) A mixture of **6** (1.0 g, 3.7 mmol), sulfur (118 mg, 1.0 equiv.), and Et_3N (0.51 ml, 1.0 equiv.) in pyridine (5 mL) was stirred at 80 °C for 2 h. Cold H_2O (15 mL) was added, and stirring was continued for 2 h. The yellow precipitate was filtered off, washed with H_2O (5 mL), and dried. The crude

product was heated in MeOH (6 mL), and acetone (12 mL) was added to give an almost clear solution which was filtered and set aside overnight at 20 °C. The crystals were collected by filtration and dried. Yield: 0.60 g (75 %). M. p. 184 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.51 (s, 3H), 7.33 (s, 1H), 7.52 (m, 3H), 7.77 (s, 1H), 7.85 (m, 2H), 9.04 (s, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 34.5, 111.4, 118.9, 128.1 (2C), 129.0 (2C), 131.5, 133.0, 154.4, 160.8 ppm. – IR (neat): ν = 3158 w, 3116 w, 3103 w, 1448 w, 1411 m, 1390 w, 1367 m, 1277 w, 1225 m, 1143 m, 958 w, 878 w, 764 s, 690 s, 657 s, 586 m, 551 m cm^{-1}. – $C_{11}H_{11}N_3S$ (217.29): calcd. C 60.80, H 5.10, N 19.34; found C 60.62, H 5.02, N 19.11. – HRMS (FAB): m/z = 218.0781 (calcd. 218.0746 for $C_{11}H_{12}N_3S$, $[M+H]^+$).

*1-Amino-3-methylimidazoline-2-thione (**16**)*

a) A mixture of **7b** (200 mg, 1.5 mmol), sulfur (50 mg, 1.05 equiv.), and Et$_3$N (0.42 ml, 2.0 equiv.) in pyridine (2 mL) was stirred at 80 °C for 6 h. The volatiles were removed under reduced pressure, and the residue was extracted with EtOAc (5 × 3 mL). The extracts were washed with 1 M HCl (2 × 2 mL), dried over MgSO$_4$, and taken to dryness. Crystals of **16** were obtained by sublimation at 130 °C/30 mbar. Yield: 106 mg (55 %).

b) A suspension of **15** (100 mg, 0.5 mmol) in 1 M HCl (10 mL) was stirred overnight at 60 °C in an open vessel for azeotropic removal of benzaldehyde. The resulting colorless solution was extracted with EtOAc (5 × 3 mL), and the solvent was evaporated to yield 42 mg (71 %) of a colorless powder. Crystals of **16** were obtained by slow cooling of a hot solution in EtOAc to 20 °C. M. p. 157 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.46 (s, 3H), 5.3 (br, 2H), 7.03 (d, J = 2.3 Hz, 1H), 7.10 (d, J = 2.3 Hz, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 34.7, 115.8, 117.7, 159.8 ppm. – IR (neat): ν = 3266 w, 3162 w, 3143 w, 3088 m, 1458 m, 1422 w, 1383 m, 1357 m, 1230 m, 1154 m, 921 m, 747 m, 660 m, 521 s, 500 m cm^{-1}. – HRMS (FAB): m/z = 130.0420 (calcd. 130.0433 for $C_4H_8N_3S$, $[M+H]^+$).

*1,3-Bis(benzylideneamino)imidazoline-2-thione (**17**)*

A suspension of **8** (0.40 g, 1.3 mmol) and sulfur (41 mg, 1.0 equiv.) in pyridine (4 mL) containing Et$_3$N (0.18 mL, 1.0 equiv.) was stirred at room temperature for 2 days. Then H$_2$O (10 mL) was added, and the precipitate was filtered off, washed with H$_2$O (2 × 2 mL), and dried. Yield: 0.31 g (79 %). Single crystals by slow evaporation of a solution in acetone/MeOH. M. p. 214 – 216 °C (lit. 215 – 218 °C [27]). – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.56 (m, 6H), 7.88 (m, 4H), 7.99 (s, 2H), 9.11 (s, 2H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 112.5 (2C), 128.3 (4C), 129.1 (4C), 131.8 (2C), 132.9 (2C), 155.6 (2C), 159.3 ppm. – IR (neat): ν = 3174 w, 3145 w, 3043 w, 1599 w, 1568 w, 1449 w, 1408 m, 1394 m, 1352 s, 1279 m, 1195 m, 1172 m, 1125 m, 946 m, 883 m, 756 s, 691 s, 670 m, 636 m, 564 m cm^{-1}. – HRMS (FAB): m/z = 306.0950 (calcd. 306.0934 for $C_{17}H_{14}N_4S$, $[M]^+$, 307.1005 (calcd. 307.1012 for $C_{17}H_{15}N_4S$, $[M+H]^+$).

*1-Amino-3-methoxyimidazoline-2-thione (**18**)*

A mixture of **9b** (0.20 g, 1.3 mmol), sulfur (45 mg, 1.05 equiv.), and Et$_3$N (0.28 ml, 1.5 equiv.) in pyridine (1.5 mL) was stirred at 80 °C for 2 h. The volatiles were removed under reduced pressure, and the residue was extracted with EtOAc (3 × 3 mL). The extracts were washed with 1 M HCl (2 × 2 mL) and H$_2$O (2 mL), filtered through a short SiO$_2$ column, and taken to dryness to yield 37 mg (19 %) of an amber powder. M. p. 120 °C. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 3.97 (s, 3H), 5.7 (br, 2H), 7.09 (d, J = 2.7 Hz, 1H), 7.37 (d, J = 2.7 Hz, 1H) ppm. – ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 64.5, 111.8, 115.7, 155.8 ppm. – IR (neat): ν = 3140 w, 2935 w, 1596 m, 1398 m, 1329 m, 1204 m, 1132 m, 840 s, 681 m cm^{-1}. – HRMS (FAB): m/z = 145.0286 (calcd. 145.0304 for $C_4H_7N_3OS$, $[M]^+$), 146.0348 (calcd. 146.0383 for $C_4H_8N_3OS$, $[M+H]^+$).

Crystal structure determination

The crystal structures were determined using an Oxford Diffraction Gemini-R Ultra diffractometer. X-Ray diffraction data were collected with MoK_α (λ = 0.7107 Å) or CuK_α radiation (λ = 1.5418 Å) at 173 K. Absorption corrections were applied in all cases (multi-scan). The structures were solved by Direct Methods and refined by full-matrix least-squares techniques with the programs SIR2002 [72] and SHELXL-97 [73], respectively. All non-hydrogen atoms were assigned anisotropic displacement parameters in the refinement.

CCDC 919557–919563 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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