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Synthesis and Structural Characterization of 1-Arylimidazole-2-thiones and *N,N'*-Aryldiethoxyethylthioureas with Electronically Diverse Substituents: A Manifold of Hydrogen Bonding Networks

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Abstract

The 1-arylimidazole-2-thiones, (Hmim^{Ar}) [Ar = 3,4,5-C₆H₂(OMe)₃, 2,4-C₆H₃(NO₂)(OMe), 2,4,6-C₆H₂Cl₃ and 3,5-C₆H₃(CF₃)₂], which feature electronically diverse substituents, may be obtained *via* acid-catalyzed ring closure of the corresponding *N,N'*-aryldiethoxyethylthiourea derivatives, ArN(H)C(S)N(H)CH₂CH(OEt)₂, (H₂detu^{Ar}), which in turn are obtained *via* treatment of aminoacetaldehyde diethyl acetal, H₂NCH₂CH(OEt)₂, with the respective arylisothiocyanates (ArNCS). The molecular structures of all of the above *N,N'*-aryldiethoxyethylthioureas and 1-arylimidazole-2-thiones have been determined by X-ray diffraction, thereby demonstrating that the substituents have a profound effect on the crystal structures. For example, each of the *N,N'*-aryldiethoxyethylthiourea derivatives adopts a different hydrogen bonding pattern. Specifically, the hydrogen-bonding network in (i) H₂detu^{ArCl₃} consists of chains of 9-membered rings, with an [R₂²(9)] motif, that feature one N–H ⋯ O and one N–H ⋯ S interaction, (ii) H₂detu^{ArOMe,NO₂} consists of chains of 6-membered rings, with an [R₂¹(6)] motif, that feature two head-to-tail N–H ⋯ S interactions, (iii) H₂detu^{Ar(CF₃)₂} consists of a dimer that features two pairs of N–H ⋯ O interactions, of which each pair is a component of an 8-membered ring with an [R₂²(8)] motif, and (iv) H₂detu^{Ar(OMe)₃} consists of a chain of head-to-head dimeric rings with a basic [R₂²(16)] motif, a notable feature of which is that sulfur does not play a role as a hydrogen bond acceptor. Each of the 1-arylimidazole-2-thiones exists as a “head-to-head” hydrogen-bonded dimer in the solid state, with an [R₂²(8)] motif. However, while the hydrogen-bonded motifs for Hmim^{ArCl₃} and Hmim^{Ar(OMe)₃} are planar, those for Hmim^{Ar(CF₃)₂} and Hmim^{ArOMe,NO₂} are extremely puckered, with fold angles of 24.2° (mean value) and 45.7°, respectively.

Introduction

1-R-imidazole-2-thiones (Hmim^R),^{1,2,3,4,5} which are often referred to in terms of their tautomeric 2-mercapto-1-R-imidazole form (Figure 1),⁶ despite the fact that the thione form

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Electronic Supplementary Information (ESI). X-ray data in the form of CIF files for all compounds, CCDC #991539-991546; fully labeled figures of all compounds, crystal packing diagrams, and tables of intermolecular interactions.

is dominant,³ represent an important class of molecules that has found widespread applications in fields ranging from medicinal to coordination chemistry.

For example, with respect to medicinal applications, the parent methyl derivative, methimazole (also known as tapazole), is a widely used antithyroid drug,^{7,8} and a variety of other derivatives are potent multisubstrate inhibitors of β -hydroxylase,^{2c,3d,9} octopamine agonists^{3b} and CCR2 antagonists.^{2b,10} In addition, imidazole-2-thiones are used as reagents for the synthesis of compounds that are employed in imaging by positron emission tomography.¹¹ With respect to applications in coordination chemistry, Hmim^R derivatives have been used as ligands (in both protonated and deprotonated forms)¹² for a variety of metals. For example, in terms of mercury chemistry, coordination of Hmim^R has been shown to promote protolytic cleavage of Hg–C bonds.¹³ 1-R-imidazole-2-thiones have also been employed to construct a family of *bis*(mercaptoimidazolyl)hydroborato and *tris*(mercaptoimidazolyl)hydroborato ligands, [Bm^R] and [Tm^R], that respectively provide [S₂] and [S₃] donor arrays, of which the latter have been used to provide synthetic analogues of zinc enzymes (*e.g.* 5-aminolevulinate dehydratase and the ADA DNA repair protein)^{14,15} and organomercurial lyase (*Mer B*).^{13a} Furthermore, [Tm^R] ligands have also been used to afford access to metallaboratranes that feature novel retrodative M→B bonds.¹⁶ In view of the diverse applications of this class of molecules, it is surprising that only one structurally characterized 1-arylimidazole-2-thione derivative is listed in the Cambridge Structural Database,¹⁷ namely Hmim^{Tol}.^{18,19} Therefore, we report here the synthesis and structural characterization of a variety of Hmim^{Ar} compounds that contain electronically diverse substituents (Figure 2). In addition, we also describe the structures of the corresponding *N,N'*-aryldiethoxyethylthiourea intermediates. Compounds of this class have not been previously structurally characterized, despite the fact that *N,N'*-disubstituted thioureas have varied applications.^{20,21} Some examples of these applications include their use (*i*) as antibacterial,^{22,23,24} antifungal,^{24,25} antiviral,^{26,27,28} anti-HIV,²⁸ antimalarial,²³ antituberculous,^{28,29} antihistamine,³⁰ and anticancer²⁷ agents, (*ii*) in organocatalysis,^{31,32,33} and (*iii*) in crystal engineering.^{34,35}

Results and Discussion

Synthesis of 1-arylimidazole-2-thiones, Hmim^{Ar}

The 1-arylimidazole-2-thiones, Hmim^{Ar} [Ar = 3,4,5-C₆H₂(OMe)₃, 2,4-C₆H₃(NO₂)(OMe), 2,4,6-C₆H₂Cl₃ and 3,5-C₆H₃(CF₃)₂], may be obtained *via* the two-step process illustrated in Scheme 1.^{3,36} Specifically, treatment of aminoacetaldehyde diethyl acetal, H₂NCH₂CH(OEt)₂, with the respective arylisothiocyanate (ArNCS) gives the *N,N'*-aryldiethoxyethylthiourea derivative, ArN(H)C(S)N(H)CH₂CH(OEt)₂, (H₂detu^{Ar}), which is converted to the 1-arylimidazole-2-thione by acid-catalyzed ring closure. In each case, both the 1-arylimidazole-2-thione, Hmim^{Ar}, and the intermediate thiourea, H₂detu^{Ar}, can be isolated in good yields by crystallization.

Molecular structures of *N,N'*-aryldiethoxyethylthioureas, H₂detu^{Ar}

Despite the fact that thioureas have considerable synthetic utility^{3,31-33} and applications in crystal engineering,^{34,35} there are no structurally characterized examples of *N,N'*-

aryldiethoxyethylthioureas listed in the Cambridge Structural Database.¹⁷ The structures of N,N' -aryldiethoxyethylthioureas are also of interest because the presence of multiple potential hydrogen bond acceptor groups is expected to influence the hydrogen bonding patterns in their extended structures. In this regard, X-ray diffraction studies reveal that the molecular structures of H_2detu^{Ar} are highly dependent on the nature of the aryl substituent, as illustrated in Figure 3 and Figure 4.

With respect to the orientation of the thiourea substituents, previous studies have demonstrated that N,N' -disubstituted thioureas may exist in solution in different rotameric forms, which have been classified as *trans-trans*, *trans-cis* and *cis-cis*, based on their H–N–C–S dihedral angles, as illustrated in Figure 5.³⁷ Of these, the *trans-trans* and *trans-cis* rotamers typically have comparable energies, while the *cis-cis* has a significantly higher energy, such that the vast majority of N,N' -disubstituted thioureas exist in the solid state as either *trans-trans* or *trans-cis* rotamers;^{34,38} these rotamers are also respectively referred to as *syn* and *anti* with respect to the relative positions of the N–H groups.³⁹ On this basis, $H_2detu^{ArCl_3}$ and $H_2detu^{Ar(OMe)_3}$ are classified as adopting a *trans-cis* (*anti*) disposition of N–H groups (Figure 3), while $H_2detu^{Ar(CF_3)_2}$ and H_2detu^{ArOMe,NO_2} adopt a *trans-trans* (*syn*) disposition (Figure 4).

The C=S bond lengths in the thiourea compounds reported here are in the range 1.67 – 1.70 Å (Table 1) and are comparable to those of other thiourea derivatives (1.68 Å).⁴⁰ Furthermore, the distances pertaining to the various N ⋯ S and N ⋯ O hydrogen bonding interactions (Table 1) are also comparable to literature values (3.44 Å^{40,41} and 2.95 Å,⁴² respectively).

In addition to the *syn/anti* differences in the molecular structures, the compounds also exhibit significant differences with respect to their hydrogen bonding interactions, as illustrated in Figures 7 – 10.⁴³ For reference, *trans-trans* (*syn*) rotamers are typically observed to form linear⁴⁴ chains in which both N–H groups interact with a single thiocarbonyl sulfur in a bifurcated⁴⁵ manner, whereas *trans-cis* (*anti*) rotamers typically form dimers (Figure 6);³⁴ in terms of graph-set notation,⁴⁶ these networks are classified as $C(4)[R_2^1(6)]$ and $[R_2^2(8)]$, respectively. It is, therefore, evident from examination of Figures 7 – 10 that the aryldiethoxyethylthioureas reported here comprise much more varied hydrogen bonding networks than those presented in Figure 6. Specifically, the N–H groups of the thiourea moiety may interact with different combinations of hydrogen bond acceptors, such that each compound exhibits a distinctive network, as summarized in Table 1 and Table 2.

For example, rather than adopt the chain-like structure that is typical for *trans-trans* (*syn*) rotamers (Figure 6), $H_2detu^{Ar(CF_3)_2}$ exists as a discrete dimeric species with approximate C_2 symmetry (Figure 7). Thus, rather than hydrogen bond with the sulfur, the N–H groups of each thiourea moiety form intermolecular N–H ⋯ O hydrogen bonds with two oxygen atoms of a single diethoxyethyl group, $CH_2CH(OEt)_2$, thereby resulting in an 8-membered ring with an $[R_2^2(8)]$ motif.

In contrast, $\text{H}_2\text{detu}^{\text{ArOMe,NO}_2}$, which also possesses a *syn* disposition of N–H groups, does not exhibit any intermolecular N–H $\cdots$ O hydrogen bonding interactions with either the $\text{CH}_2\text{CH}(\text{OEt})_2$, OMe or NO_2 groups.⁴⁷ Instead, the pair of N–H groups exhibit intermolecular “head-to-tail” hydrogen bonding interactions with a single sulfur atom, thereby resulting in a chain of 6-membered rings, each one of which possesses an $[R_2^1(6)]$ motif (Figure 8). The overall hydrogen bonding network is described by the binary graph set $C_2^2(8)[R_2^1(6)]$ and is well-precedented for thioureas that possess a *syn* disposition of N–H groups (Figure 6).⁴⁸

$\text{H}_2\text{detu}^{\text{ArCl}_3}$ exists as a *trans-cis (anti)* rotamer, but rather than form a simple dimer by the centrosymmetric interaction of two thiourea [S/NH] pairs (Figure 6), $\text{H}_2\text{detu}^{\text{ArCl}_3}$ forms a structure that results from an interaction between a pair of [S/NH] and [O/NH] moieties, thereby resulting in a 9-membered ring with an $[R_2^2(9)]$ motif that features one N–H $\cdots$ O and one N–H $\cdots$ S interaction. In addition to the oxygen atom of the ethoxy groups allowing for an unusual type of ring structure, it also provides a means to create an extended chain structure by virtue of there being an additional hydrogen bond acceptor present. Thus, whereas the dimeric structures observed for other *trans-cis (anti)* rotamers utilize only one N–H bond per urea (Figure 6), both N–H bonds are utilized for $\text{H}_2\text{detu}^{\text{ArCl}_3}$, such that the hydrogen bonding network is described by the binary graph set $C_2^2(11)[R_2^2(9)]$.

The extended structure of $\text{H}_2\text{detu}^{\text{Ar(OMe)}_3}$ is unique because, in contrast to the other derivatives that form chains ($\text{H}_2\text{detu}^{\text{ArCl}_3}$ and $\text{H}_2\text{detu}^{\text{ArOMe,NO}_2}$), it does not utilize sulfur as a hydrogen bond acceptor.⁴⁹ Rather, each thiourea moiety of $\text{H}_2\text{detu}^{\text{Ar(OMe)}_3}$ exhibits two intermolecular N–H $\cdots$ O hydrogen bonding interactions, one with an oxygen atom of the diethoxyethyl group and one with an oxygen atom of a methoxy group (Figure 10). The overall result may be described as a polymeric chain of “head-to-head” $\text{H}_2\text{detu}^{\text{Ar(OMe)}_3}$ dimeric units, each of which is composed of a 16-membered ring with a basic $[R_2^2(16)]$ motif.

Molecular structures of 1-arylimidazole-2-thiones

The molecular structures of Hmim^{Ar} [$\text{Ar} = 3,4,5\text{-C}_6\text{H}_2(\text{OMe})_3$, $2,4\text{-C}_6\text{H}_3(\text{NO}_2)(\text{OMe})$, $2,4,6\text{-C}_6\text{H}_2\text{Cl}_3$ and $3,5\text{-C}_6\text{H}_3(\text{CF}_3)_2$] have been determined by X-ray diffraction, as illustrated in Figures 11 – 14.

Each of the compounds exists as a “head-to-head” hydrogen bonded dimer in the solid state, with an $[R_2^2(8)]$ motif, which is common for this class of compound.⁵⁰ However, while the hydrogen-bonded dimers of $\text{Hmim}^{\text{ArCl}_3}$ and $\text{Hmim}^{\text{Ar(OMe)}_3}$ are planar, those of $\text{Hmim}^{\text{Ar(CF}_3)_2}$ and $\text{Hmim}^{\text{ArOMe,NO}_2}$ are extremely puckered, as illustrated for the latter in Figure 15.

For example, the fold angle about the S $\cdots$ S vector for $\text{Hmim}^{\text{ArOMe,NO}_2}$ is 45.7° (Table 3). Nevertheless, despite the varying deviations from planarity among the Hmim^{Ar} compounds reported here, their N–H $\cdots$ S hydrogen bond distances do not vary dramatically (Table 3). Although a possible explanation for the large deviation for $\text{Hmim}^{\text{ArOMe,NO}_2}$ could be attributed to the presence of an *ortho* NO_2 substituent, it should be recognized that the

methyl derivative, Hmim^{Me}, also exhibits a highly bent [$R_2^2(8)$] ring, with a fold angle of 58.2°, ⁵¹ which indicates that steric factors are not likely responsible. Thus, it is evident that the nonplanarity of the 8-membered hydrogen bond rings in this system is dictated by packing forces rather than any electronic effect that influences the N–H $\cdots$ S hydrogen bonding interactions.

Conclusions

In summary, the structures of imidazole-2-thiones that feature electronically diverse 1-aryl substituents, namely Hmim^{Ar} [Ar = 3,4,5-C₆H₂(OMe)₃, 2,4-C₆H₃(NO₂)(OMe), 2,4,6-C₆H₂Cl₃ and 3,5-C₆H₃(CF₃)₂], have been determined by X-ray diffraction and shown to exist as “head-to-head” hydrogen-bonded dimers in the solid state, with [$R_2^2(8)$] motifs. The *N,N'*-aryldiethoxyethylthiourea precursors (H₂detu^{Ar}) have also been analyzed by X-ray diffraction, thereby demonstrating that the structures are strongly influenced by the nature of the aryl substituents, especially with respect to intermolecular hydrogen bonding interactions. For example, H₂detu^{Ar(CF₃)₂} is a dimer that features 8-membered rings, H₂detu^{ArOMe,NO₂} consists of chains of 6-membered rings, H₂detu^{ArCl₃} consists of chains of 9-membered rings, and H₂detu^{Ar(OMe)₃} consists of chains of 16-membered rings. In addition to these different hydrogen bonding networks, the substituents also influence the *trans-trans* (*syn*) and *trans-cis* (*anti*) preferences. Thus, H₂detu^{ArCl₃} and H₂detu^{Ar(OMe)₃} adopt a *trans-cis* (*anti*) disposition of N–H groups, whereas H₂detu^{Ar(CF₃)₂} and H₂detu^{ArOMe,NO₂} adopt a *trans-trans* (*syn*) disposition. *N,N'*-aryldiethoxyethylthioureas have not been previously structurally characterized and the variety of hydrogen bonding networks observed here have ramifications with respect to the use of such compounds in crystal engineering.

Experimental Section

General Considerations

NMR spectra were measured on Bruker 400 DRX and Bruker Avance 500 DMX spectrometers. ¹H NMR spectra are reported in ppm relative to SiMe₄ (δ = 0) and were referenced internally with respect to the protio solvent impurity (δ 7.16 for C₆D₅H and 2.50 for Me₂SO-*d*₅). ¹³C NMR spectra are reported in ppm relative to SiMe₄ (δ = 0) and were referenced internally with respect to the solvent (δ 39.52 for Me₂SO-*d*₅). ¹⁹F NMR spectra are reported in ppm relative to CFC₃ (δ = 0) and were obtained by using the Σ /100% value of 94.094011. ⁵³ Coupling constants are given in hertz. All chemicals were purchased from Sigma-Aldrich.

X-ray structure determinations

Single crystal X-ray diffraction data were collected on a Bruker Apex II diffractometer and crystal data, data collection and refinement parameters are summarized in Table 4. All data were corrected for absorption (SADABS) and the structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 6.12). ⁵⁴ Hydrogen atoms attached to carbon were refined in calculated positions (AFIX 43 for sp CH groups, AFIX 23 for sp² CH₂ groups, AFIX 13 for sp³ CH groups, and AFIX 137 for methyl groups) with a

displacement parameter of $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$ for CH and CH₂ groups and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{iso}}(\text{C})$ for CH₃ groups. The positional parameters of hydrogen atoms attached to nitrogen were refined freely, while the displacement parameters were either freely refined or assigned values of $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{N})$. The CF₃ groups of H₂detu^{Ar(CF₃)₂} and Hmim^{Ar(CF₃)₂} were disordered and were modeled by using SADI, SIMU, ISOR and RIGU commands for the disordered components. Molecular structures were viewed using SHELXTL⁵⁴ and Mercury.⁵⁵

Syntheses

H₂detu^{ArCl₃}—Aminoacetaldehyde diethyl acetal (6.5 g, 49 mmol) was added *via* syringe over a period of 1 minute to a rapidly stirred solution of 2,4,6-trichlorophenyl isothiocyanate (13.1 g, 55 mmol) in EtOH (250 mL). The mixture was refluxed for 3 hours under an inert atmosphere. After this period, the solvent was removed *in vacuo* and the residue obtained was dissolved in CH₂Cl₂ (100 mL). Pentane (100 mL) was added to the solution, thereby resulting in the formation of a suspension that was placed overnight at −15°C. The mixture was filtered and the precipitate was dried *in vacuo* to give H₂detu^{ArCl₃} as a white solid (17.7 g, 98%). Colorless crystals of H₂detu^{ArCl₃} suitable for X-ray diffraction were obtained *via* slow diffusion of hexanes into a solution in CH₂Cl₂. Anal. calcd. for H₂detu^{ArCl₃}: C, 42.0; H, 4.6; N, 7.5. Found: C, 42.0; H, 4.3; N, 7.5. ¹H NMR (Me₂SO-*d*⁶): δ 1.14 [br s, 6H of C(H)(OCH₂CH₃)₂], 3.53 [br s, 4H of C(H)(OCH₂CH₃)₂], 3.64 [br s, 2H of NCH₂C(H)(OCH₂CH₃)₂], 4.70 [br s, 1H of C(H)(OCH₂CH₃)₂], 7.71 [br s, 2H of C₆H₂Cl₃], 7.87 [br s, 1H of NH], 9.27 [br s, 1H of NH]. ¹³C{¹H} NMR (Me₂SO-*d*⁶): δ 15.3 [CH₃ of C(H)(OCH₂CH₃)₂], 46.9 [CH₂ of NCH₂C(H)(OCH₂CH₃)₂], 62.0 [CH₂ of C(H)O(CH₂CH₃)₂], 99.7 [CH of C(H)(OCH₂CH₃)₂], 128.2 [CH of C₆H₂Cl₃], 128.4 [CH of C₆H₂Cl₃], 132.4 [C of C₆H₂Cl₃], 136.0 [C of C₆H₂Cl₃], not observed [C=S].

Hmim^{ArCl₃}—A rapidly stirred solution of H₂detu^{ArCl₃} (16.7 g, 45 mmol) in a mixture of EtOH:H₂O (250 mL, 9:1) was treated with HCl_{aq} (3.4 mL of 12.1 M, 41 mmol) and the mixture was refluxed for 3 hours under an inert atmosphere, resulting in the slow formation of a white precipitate. After this period, the mixture was filtered and the precipitate was dried *in vacuo* to give Hmim^{ArCl₃} as a white solid (13.4 g, 94%). Colorless crystals of Hmim^{ArCl₃} suitable for X-ray diffraction were obtained *via* slow evaporation of a solution in Me₂SO on a watch glass. Anal. calcd. for Hmim^{ArCl₃}: C, 38.7; H, 1.8; N, 10.0. Found: C, 38.3; H, 1.7; N, 9.8. ¹H NMR (Me₂SO-*d*⁶): δ 7.11 [t, ³J_{H-H} = 2, 1H of C₃H₃N₂S], 7.15 [t, ³J_{H-H} = 2, 1H of C₃H₃N₂S], 7.91 [s, 2H of C₆H₂Cl₃], 12.5 [s, 1H of NH]. ¹³C{¹H} NMR (Me₂SO-*d*⁶): δ 116.3 [CH of C₃H₃N₂S], 118.7 [CH of C₃H₃N₂S], 128.7 [CH of C₆H₂Cl₃], 132.7 [C of C₆H₂Cl₃], 134.9 [C of C₆H₂Cl₃], 135.1 [C of C₆H₂Cl₃], 162.9 [C=S].

H₂detu^{Ar(OMe)₃}—Aminoacetaldehyde diethyl acetal (1.8 g, 14 mmol) was added *via* syringe over a period of 1 minute to a rapidly stirred solution of 3,4,5-trimethoxyphenyl isothiocyanate (3.3 g, 15 mmol) in EtOH (200 mL). The mixture was refluxed for 2 hours under an inert atmosphere. After this period, the solvent was removed *in vacuo* and the residue obtained was dissolved in dichloromethane (100 mL). Pentane (100 mL) was added to the solution, thereby resulting in the formation of a suspension. The mixture was filtered and the precipitate was dried *in vacuo* to give H₂detu^{Ar(OMe)₃} as a white solid (4.5 g, 93%).

Colorless crystals of $\text{H}_2\text{detu}^{\text{Ar(OMe)}_3}$ suitable for X-ray diffraction were obtained *via* slow diffusion of hexanes into a solution in CH_2Cl_2 . Anal. calcd. for $\text{H}_2\text{detu}^{\text{Ar(OMe)}_3}$: C, 53.6; H, 7.3; N, 7.8. Found: C, 53.4; H, 7.1; N, 7.7. ^1H NMR ($\text{Me}_2\text{SO}-d^6$): δ 1.13 [t, $^3J_{\text{H-H}} = 7$, 6H of $\text{C(H)(OCH}_2\text{CH}_3)_2$], 3.50 [m, 2H of $\text{NCH}_2\text{C(H)(OCH}_2\text{CH}_3)_2$], 3.59 [m, 4H of $\text{C(H)(OCH}_2\text{CH}_3)_2$], 3.64 [s, 3H of *para*- $\text{C}_6\text{H}_2(\text{OCH}_3)_3$], 3.75 [s, 6H of *meta*- $\text{C}_6\text{H}_2(\text{OCH}_3)_3$], 4.71 [t, $^3J_{\text{H-H}} = 5$, 1H of $\text{C(H)(OCH}_2\text{CH}_3)_2$], 6.75 [s, 2H of $\text{C}_6\text{H}_2(\text{OCH}_3)_3$], 7.49 [s, 1H of NH], 9.60 [s, 1H of NH]. $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{Me}_2\text{SO}-d^6$): δ 15.3 [CH_3 of $\text{C(H)(OCH}_2\text{CH}_3)_2$], 46.3 [CH_2 of $\text{NCH}_2\text{C(H)(OCH}_2\text{CH}_3)_2$], 55.8 [CH_3 of $\text{C}_6\text{H}_3(\text{OCH}_3)_3$], 60.0 [CH_3 of $\text{C}_6\text{H}_3(\text{OCH}_3)_3$], 61.6 [CH_2 of $\text{C(H)(OCH}_2\text{CH}_3)_2$], 99.7 [CH of $\text{C(H)(OCH}_2\text{CH}_3)_2$], 101.1 [CH of $\text{C}_6\text{H}_2(\text{OCH}_3)_3$], 134.5 [C of $\text{C}_6\text{H}_3(\text{OCH}_3)_3$], 134.6 [C of $\text{C}_6\text{H}_2(\text{OCH}_3)_3$], 152.7 [C of $\text{C}_6\text{H}_2(\text{OCH}_3)_3$], 180.3 [$\text{C}=\text{S}$].

Hmim^{Ar(OMe)₃}—A rapidly stirred solution of $\text{H}_2\text{detu}^{\text{Ar(OMe)}_3}$ (4.8 g, 13 mmol) in a mixture of EtOH:H₂O (200 mL, 9:1) was treated with HCl_{aq} (1.4 mL of 12.1 M, 17 mmol) and the mixture was refluxed for 3 hours under an inert atmosphere. After this period, the volatile components were removed *in vacuo* from the resulting yellow solution. The residue obtained was dissolved in EtOH (*ca.* 50 mL) and placed overnight at -15°C , thereby depositing a white precipitate. The mixture was filtered and the precipitate was dried *in vacuo* to give $\text{Hmim}^{\text{Ar(OMe)}_3}$ as a white solid (2.3 g, 65%). Colorless crystals of $\text{Hmim}^{\text{Ar(OMe)}_3}$ suitable for X-ray diffraction were obtained *via* slow diffusion of hexanes into a solution in CH_2Cl_2 . Anal. calcd. for $\text{Hmim}^{\text{Ar(OMe)}_3}$: C, 54.1; H, 5.3; N, 10.5. Found: C, 53.9; H, 5.3; N, 10.2. ^1H NMR ($\text{Me}_2\text{SO}-d^6$): δ 3.70 [s, 3H of *para*- $\text{C}_6\text{H}_2(\text{OCH}_3)_3$], 3.80 [s, 6H of *meta*- $\text{C}_6\text{H}_2(\text{OCH}_3)_3$], 7.00 [s, 2H of $\text{C}_6\text{H}_2(\text{OCH}_3)_3$], 7.05 [d, $^3J_{\text{H-H}} = 2$, 1H of $\text{C}_3\text{H}_3\text{N}_2\text{S}$], 7.29 [d, $^3J_{\text{H-H}} = 2$, 1H of $\text{C}_3\text{H}_3\text{N}_2\text{S}$], 12.36 [br s, 1H of NH]. $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{Me}_2\text{SO}-d^6$): δ 56.1 [CH_3 of $\text{C}_6\text{H}_2(\text{OCH}_3)_3$], 60.1 [CH_3 of $\text{C}_6\text{H}_2(\text{OCH}_3)_3$], 103.7 [CH of $\text{C}_6\text{H}_2(\text{OCH}_3)_3$], 115.2 [CH of $\text{C}_3\text{H}_3\text{N}_2\text{S}$], 119.7 [CH of $\text{C}_3\text{H}_3\text{N}_2\text{S}$], 133.5 [C of $\text{C}_6\text{H}_2(\text{OCH}_3)_3$], 136.6 [C of $\text{C}_6\text{H}_2(\text{OCH}_3)_3$], 152.6 [C of $\text{C}_6\text{H}_2(\text{OCH}_3)_3$], 161.5 [$\text{C}=\text{S}$].

$\text{H}_2\text{detu}^{\text{Ar(CF}_3)_2}$ —Aminoacetaldehyde diethyl acetal (4.6 g, 35 mmol) was added *via* syringe over a period of 1 minute to a rapidly stirred solution of 3,5-bis(trifluoromethyl)phenyl isothiocyanate (8.8 g, 32 mmol) in EtOH (250 mL). The mixture was refluxed for 2 hours under an inert atmosphere. After this period, the solvent was removed *in vacuo* and the residue obtained was dissolved in Me_2CO (100 mL) to give a pale yellow solution. Pentane (*ca.* 100 mL) was added to the solution until the onset of precipitation was observed. At this point, the mixture was placed at -15°C for 2 days, after which the resulting suspension was filtered to give $\text{H}_2\text{detu}^{\text{Ar(CF}_3)_2}$ as colorless crystals, suitable for X-ray diffraction, that were dried *in vacuo* (9.7 g, 74%). Anal. calcd. for $\text{H}_2\text{detu}^{\text{Ar(CF}_3)_2}$: C, 44.6; H, 4.5; N, 6.9. Found: C, 44.8; H, 4.4; N, 7.0. ^1H NMR ($\text{Me}_2\text{SO}-d^6$): δ 1.15 [t, $^3J_{\text{H-H}} = 7$, 6H of $\text{C(H)(OCH}_2\text{CH}_3)_2$], 3.53 [m, 2H of $\text{NCH}_2\text{C(H)(OCH}_2\text{CH}_3)_2$], 3.64 [m, 4H of $\text{C(H)(OCH}_2\text{CH}_3)_2$], 4.71 [t, $^3J_{\text{H-H}} = 5$, 1H of $\text{C(H)(OCH}_2\text{CH}_3)_2$], 7.71 [s, 1H of *para*- $\text{C}_6\text{H}_3(\text{CF}_3)_2$], 8.10 [br s, 1H of NH], 8.27 [s, 2H of *ortho*- $\text{C}_6\text{H}_3(\text{CF}_3)_2$], 10.21 [br s, 1H of NH]. $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{Me}_2\text{SO}-d^6$): δ 15.2 [CH_3 of $\text{C(H)(OCH}_2\text{CH}_3)_2$], 46.4 [CH_2 of $\text{NCH}_2\text{C(H)(OCH}_2\text{CH}_3)_2$], 61.7 [CH_2 of $\text{C(H)(OCH}_2\text{CH}_3)_2$], 99.4 [CH of $\text{C(H)(OCH}_2\text{CH}_3)_2$], 116.1 [CH of $\text{C}_6\text{H}_3(\text{CF}_3)_2$], 121.8 [CH of

$\text{C}_6\text{H}_3(\text{CF}_3)_2$, 123.2 [q, $^1\text{J}_{\text{C-F}} = 273$, $\text{C}_6\text{H}_3(\text{CF}_3)_2$], 130.2 [q, $^2\text{J}_{\text{C-F}} = 33$, C- CF_3 of $\text{C}_6\text{H}_3(\text{CF}_3)_2$], 141.8 [C of $\text{C}_6\text{H}_3(\text{CF}_3)_2$], 180.8 [C=S]. $^{19}\text{F}\{^1\text{H}\}$ NMR ($\text{Me}_2\text{SO}-d^6$): δ -61.8.

Hmim^{Ar}(CF₃)₂—A rapidly stirred solution of $\text{H}_2\text{detu}^{\text{Ar}(\text{CF}_3)_2}$ (5.6 g, 14 mmol) in a mixture of EtOH:H₂O (200 mL, 9:1) was treated with HCl_{aq} (1.4 mL of 12.1 M, 17 mmol) and the mixture was refluxed for 2 hours under an inert atmosphere. After this period, the solvent was removed *in vacuo* and the residue obtained was dissolved in EtOAc (100 mL). Pentane (100 mL) was added to the solution, which was placed overnight at -15°C , thereby depositing colorless crystals of Hmim^{Ar}(CF₃)₂, which were suitable for X-ray diffraction (3.0 g, 69%). Anal. calcd. for Hmim^{Ar}(CF₃)₂: C, 42.3; H, 1.9; N, 9.0. Found: C, 42.3; H, 1.8; N, 8.9. ^1H NMR ($\text{Me}_2\text{SO}-d^6$): δ 7.16 [t, $^3\text{J}_{\text{H-H}} = 2$, 1H of $\text{C}_3\text{H}_3\text{N}_2\text{S}$], 7.58 [t, $^3\text{J}_{\text{H-H}} = 2$, 1H of $\text{C}_3\text{H}_3\text{N}_2\text{S}$], 8.15 [s, 1H of *para*- $\text{C}_6\text{H}_3(\text{CF}_3)_2$], 8.52 [s, 2H of *ortho*- $\text{C}_6\text{H}_3(\text{CF}_3)_2$], 12.62 [br s, 1H of NH]. $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{Me}_2\text{SO}-d^6$): δ 116.0 [CH of $\text{C}_3\text{H}_3\text{N}_2\text{S}$], 119.2 [CH of $\text{C}_3\text{H}_3\text{N}_2\text{S}$], 121.1 [septet, $^3\text{J}_{\text{C-F}} = 4$, *para*-CH of $\text{C}_6\text{H}_3(\text{CF}_3)_2$], 122.9 [q, $^1\text{J}_{\text{C-F}} = 273$, $\text{C}_6\text{H}_3(\text{CF}_3)_2$], 126.5 [q, $^3\text{J}_{\text{C-F}} = 4$, *ortho*-CH of $\text{C}_6\text{H}_3(\text{CF}_3)_2$], 130.5 [q, $^2\text{J}_{\text{C-F}} = 33$, C- CF_3 of $\text{C}_6\text{H}_3(\text{CF}_3)_2$], 139.1 [C-N of $\text{C}_6\text{H}_3(\text{CF}_3)_2$], 162.2 [C=S]. $^{19}\text{F}\{^1\text{H}\}$ NMR ($\text{Me}_2\text{SO}-d^6$): δ -61.4.

H₂detu^{ArOMe,NO₂}—Aminoacetaldehyde diethyl acetal (15.8 g, 118 mmol) was added *via* syringe over 1 minute to a rapidly stirred solution of 4-methoxy-2-nitrophenyl isothiocyanate (24.7 g, 118 mmol) in EtOH (300 mL). The mixture was refluxed for 90 minutes under an inert atmosphere. After this period, the solvent was removed *in vacuo* and the residue obtained was dissolved in CH₂Cl₂ (100 mL). Pentane (*ca.* 100 mL) was added to the solution until the onset of precipitation was observed. At this point, the mixture was placed at -15°C overnight, after which the resulting bright yellow suspension was filtered and dried *in vacuo* to give H₂detu^{ArOMe,NO₂} as flocculent, yellow crystals (28.4 g, 70%). Yellow crystals suitable for X-ray diffraction were obtained *via* slow diffusion of hexanes into a solution in CH₂Cl₂. Anal. calcd. for H₂detu^{ArOMe,NO₂}: C, 49.0; H, 6.2; N, 12.2. Found: C, 49.1; H, 6.1; N, 12.3. ^1H NMR ($\text{Me}_2\text{SO}-d^6$): δ 1.15 [t, $^3\text{J}_{\text{H-H}} = 7$, 6H of C(H)(OCH₂CH₃)₂], 3.54 [m, 4H of C(H)(OCH₂CH₃)₂], 3.64 [m, 2H of NCH₂C(H)(OCH₂CH₃)₂], 3.85 [s, 3H of $\text{C}_6\text{H}_3(\text{NO}_2)(\text{OCH}_3)$], 4.66 [t, $^3\text{J}_{\text{H-H}} = 5$, 1H of C(H)(OCH₂CH₃)₂], 7.27 [dd, $^3\text{J}_{\text{H-H}} = 9$, $^4\text{J}_{\text{H-H}} = 3$, 1H of $\text{C}_6\text{H}_3(\text{NO}_2)(\text{OCH}_3)$], 7.49 [d, $^4\text{J}_{\text{H-H}} = 3$, 1H of $\text{C}_6\text{H}_3(\text{NO}_2)(\text{OCH}_3)$], 7.57 [d, $^3\text{J}_{\text{H-H}} = 9$, 1H of $\text{C}_6\text{H}_3(\text{NO}_2)(\text{OCH}_3)$], 8.13 [m, 1H of NH], 9.51 [s, 1H of NH]. $^{13}\text{C}\{^1\text{H}\}$ NMR ($\text{Me}_2\text{SO}-d^6$): δ 15.3 [CH₃ of C(H)(OCH₂CH₃)₂], 46.8 [CH₂ of NCH₂C(H)(OCH₂CH₃)₂], 56.0 [CH₃ of $\text{C}_6\text{H}_3(\text{NO}_2)(\text{OCH}_3)$], 61.9 [CH₂ of C(H)(OCH₂CH₃)₂], 99.7 [CH of C(H)(OCH₂CH₃)₂], 108.6 [CH of $\text{C}_6\text{H}_3(\text{NO}_2)(\text{OCH}_3)$], 119.7 [CH of $\text{C}_6\text{H}_3(\text{NO}_2)(\text{OCH}_3)$], 126.1 [C of $\text{C}_6\text{H}_3(\text{NO}_2)(\text{OCH}_3)$], 131.6 [CH of $\text{C}_6\text{H}_3(\text{NO}_2)(\text{OCH}_3)$], 145.1 [C of $\text{C}_6\text{H}_3(\text{NO}_2)(\text{OCH}_3)$], 156.8 [C of $\text{C}_6\text{H}_3(\text{NO}_2)(\text{OCH}_3)$], 182.5 [C=S].

Hmim^{ArOMe,NO₂}—A rapidly stirred solution of H₂detu^{ArOMe,NO₂} (27.1 g, 79 mmol) in a mixture of EtOH:H₂O (300 mL, 9:1) was treated with HCl_{aq} (6.0 mL of 12.1 M, 73 mmol). The mixture was refluxed for 3 hours under an inert atmosphere, resulting in the formation of a light orange precipitate. The mixture was allowed to cool to room temperature and filtered. The precipitate was washed with EtOH (*ca.* 50 mL) and dried *in vacuo* to give

Hmim^{ArOMe,NO₂} as a yellow-orange solid (18.4 g, 93%). Orange crystals suitable for X-ray diffraction were obtained *via* slow evaporation of a solution in Me₂SO on a watch glass. Anal. calcd. for Hmim^{ArOMe,NO₂}: C, 47.8; H, 3.6; N, 16.7. Found: C, 47.4; H, 3.3; N, 16.3. ¹H NMR (Me₂SO-*d*₆): δ 3.92 [s, 3H of C₆H₃(NO₂)(OCH₃)], 7.08 [t, ³J_{H-H} = 2, 1H of C₃H₃N₂S], 7.24 [t, ³J_{H-H} = 2, 1H of C₃H₃N₂S], 7.43 [dd, ³J_{H-H} = 9, ⁴J_{H-H} = 3, 1H of C₆H₃(NO₂)(OCH₃)], 7.51 [d, ³J_{H-H} = 9, 1H of C₆H₃(NO₂)(OCH₃)], 7.67 [d, ⁴J_{H-H} = 3, 1H of C₆H₃(NO₂)(OCH₃)], 12.37 [s, 1H of NH]. ¹³C{¹H} NMR (Me₂SO-*d*₆): δ 56.4 [C₆H₃(NO₂)(OCH₃)], 110.3 [CH of C₆H₃(NO₂)(OCH₃)], 115.6 [CH of C₃H₃N₂S], 119.8 [CH of C₃H₃N₂S], 119.9 [CH of C₆H₃(NO₂)(OCH₃)], 123.6 [C of C₆H₃(NO₂)(OCH₃)], 131.5 [CH of C₆H₃(NO₂)(OCH₃)], 146.4 [C of C₆H₃(NO₂)(OCH₃)], 159.4 [C of C₆H₃(NO₂)(OCH₃)], 162.9 [C=S].

Supplementary Material

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Figure 1.
Tautomers of Hmim^R.

Figure 2.
Hmim^{Ar} ligands.

Figure 3.
Molecular structures of $\text{H}_2\text{detu}^{\text{ArCl}_3}$ (left) and $\text{H}_2\text{detu}^{\text{Ar(OMe)}_3}$ (right).

Figure 4. Molecular structures of $\text{H}_2\text{detu}^{\text{Ar}(\text{CF}_3)_2}$ (top) and $\text{H}_2\text{detu}^{\text{ArOMe.NO}_2}$ (bottom).

Figure 5.
Rotamers of thioureas.

Figure 6.
Typical hydrogen bonding networks in thioureas.

Figure 7.
Hydrogen bonding network for $\text{H}_2\text{detu}^{\text{Ar}(\text{CF}_3)_2}$.

Figure 8.
Hydrogen bonding network for $\text{H}_2\text{detu}^{\text{ArOMe,NO}_2}$.

Figure 9.
Hydrogen bonding network for $\text{H}_2\text{detuArCl}_3$.

Figure 10.
Hydrogen bonding network for $\text{H}_2\text{detu}^{\text{Ar}(\text{OMe})_3}$.

Figure 11.
Molecular structure of hydrogen bonded Hmim^{ArCl₃}.

Figure 12.
Molecular structure of hydrogen bonded $\text{Hmim}^{\text{Ar}(\text{OMe})_3}$.

Figure 13.

Molecular structure of hydrogen bonded Hmim-Ar(CF₃)₂. Only two of the six crystallographically independent molecules are shown.

Figure 14.
Molecular structure of hydrogen bonded Hmim^{ArOMe,NO₂}.

Figure 15.

View of the non-planar hydrogen bonded [$R_2^2(8)$] motif in $\text{Hmim}^{\text{ArOMe.NO}_2}$.

Scheme 1.
 Synthesis of $\text{H}_2\text{detu}^{\text{Ar}}$ and Hmim^{Ar} .

Table 1

Selected metrical data for H₂detu^{Ar} derivatives [R = CH₂CH(OEt)].

	<i>d</i> (N ... O)/Å	<i>d</i> (N...O)/Å	<i>d</i> (N ... S)/Å	<i>d</i> (NH ... O)/Å	<i>d</i> (NH ... S)/Å	<i>d</i> (C=S)/Å	N ₁ -C-N ₂ /°
H ₂ detu ^{Ar} Cl ₃	3.012(2), (ArN ... OEt)		3.246(2) (NR)	2.24(2) (ArN ... OEt)		1.691(2)	116.66(19)
H ₂ detu ^{Ar} (OMe) ₃	3.015(2), 2.976(2) (RN ... OMe)	2.900(2), 2.882(2) (ArN ... OEt)		2.32(2), 2.21(2) (RN ... OMe)	2.01(2), 2.060(19) (ArN ... OEt)	1.6938(17), 1.6904(17)	116.75(15), 123.40(13)
H ₂ detu ^{Ar} (CF ₃) ₂	3.141(2), 3.002(2) (RN ... OEt)	2.955(2), 3.070(2) (ArN ... OEt)		2.21(2), 2.31(2) (RN ... OEt)	2.29(2), 2.10(2) (ArN ... OEt)	1.6693(19), 1.677(2)	112.43(16), 113.06(17)
H ₂ detu ^{Ar} (CF ₃) ₂	3.070(2), 3.142(2) (RN ... OEt)	3.002(2), 2.956(2) (ArN ... OEt)		2.29(2), 2.32(2) (RN ... OEt)	2.20(2), 2.10(2) (ArN ... OEt)	1.6697(18), 1.6766(19)	112.43(15), 113.09(16)
H ₂ detu ^{Ar} OMeNO ₂			3.348(3) (NR), 3.541(3) (NAr)		2.52(3) (NR), 2.80(2) (NAr)	1.684(3)	113.4(3)

Table 2

Hydrogen bonding networks for H₂detu^{Ar} derivatives.

	Unitary Network	Binary Network
H ₂ detu ^{ArCl₃}	C(4)C(7)	C ₂ ² (11)[R ₂ ² (9)]
H ₂ detu ^{Ar(OMe)₃}	DDDD	C ₂ ² (14)R ₂ ² (16)R ₄ ⁴ (22)R ₄ ⁴ (22)R ₄ ⁴ (30)R ₄ ⁴ (30)
H ₂ detu ^{Ar(CF₃)₂}	DDDD	R ₂ ² (8)R ₂ ² (8)R ₂ ² (10)R ₂ ² (12)R ₂ ² (12)R ₂ ² (14)
H ₂ detu ^{ArOMe,NO₂}	C(4)C(4)	C ₂ ² (8)[R ₂ ¹ (6)]

Table 3

Selected metrical data for Hmim^{Ar} derivatives.

	$d(\text{C}=\text{S})/\text{\AA}$	$\text{N}_1-\text{C}-\text{N}_2/^\circ$	$d(\text{N} \cdots \text{S})/\text{\AA}$	$d(\text{H} \cdots \text{S})/\text{\AA}$	$\text{N}-\text{H} \cdots \text{S}/^\circ$	Fold Angle/ $^\circ$	Artwist/ $^\circ$
Hmim ^{Ar} Cl ₃	1.6881(12)	104.96(10)	3.2511(11)	2.413(19)	174.1(17)	0.00	89.13
Hmim ^{Ar} OMe ₃	1.6896(17)	104.94(14)	3.2662(15)	2.36(2)	171.2(17)	0.00	56.77
Hmim ^{Ar} (CF ₃) ₂	1.692(2), 1.692(2)	105.23(18), 104.87(18)	3.278(2), 3.284(2)	2.50(1), 2.45(3)	178(3), 168(3)	22.87	43.65, 45.94
	1.692(2), 1.689(2)	104.85(19), 104.72(18)	3.291(2), 3.260(2)	2.46(3), 2.43(3)	178(3), 160(3)	23.47	42.28, 49.09
	1.692(2), 1.690(2)	105.19(19), 105.5(2)	3.370(2), 3.206(2)	2.54(4), 2.39(4)	167(4), 170(3)	26.19	44.52, 58.72
Hmim ^{Ar} OMe ₂ NO ₂	1.698(2)	105.1(2)	3.292(2)	2.39(3)	173(3)	45.72	68.07

(a) angle between planes defined by S1-C1-N1 $\cdots$ S2 and S2-C2-N2 $\cdots$ S1.

(b) angle between planes defined by the 5-membered heterocycle and 6-membered aryl rings.

Table 4

Crystal, intensity collection and refinement data.

	H₂detu^{Ar}Cl₃	H₂detu^{Ar}(OMe)₃	H₂detu^{Ar}(CF₃)₂	H₂detu^{Ar}OMeNO₂
crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
formula	C ₁₃ H ₁₇ Cl ₃ N ₂ O ₂ S	C ₁₆ H ₂₆ N ₂ O ₅ S	C ₁₅ H ₁₈ F ₆ N ₂ O ₂ S	C ₁₄ H ₂₁ N ₃ O ₅ S
formula weight	371.70	358.45	404.37	343.40
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	6.769(2)	10.344(3)	12.5507(13)	13.241(4)
<i>b</i> /Å	23.886(8)	12.952(4)	13.4265(14)	15.160(4)
<i>c</i> /Å	10.834(4)	13.814(4)	21.715(2)	8.398(2)
α /°	90	95.357(4)	90	90
β /°	90.947(5)	95.836(4)	98.920(2)	101.009(4)
γ /°	90	92.996 (4)	90	90
<i>V</i> /Å ³	1751.4(10)	1829.5(9)	3615.0(6)	1654.7(8)
<i>Z</i>	4	4	8	4
temperature (K)	150(2)	150(2)	150(2)	150(2)
radiation (λ , Å)	0.71073	0.71073	0.71073	0.71073
ρ (calcd.) g cm ⁻³	1.410	1.301	1.486	1.378
μ (Mo K α), mm ⁻¹	0.646	0.204	0.250	0.224
θ max, deg.	30.67	30.36	30.03	28.28
no. of data collected	27726	28972	55289	8040
no. of data	5411	10893	10539	4104
no. of parameters	200	458	713	219
<i>R</i> _I [<i>I</i> > 2 σ (<i>I</i>)]	0.0505	0.0498	0.0509	0.0558
<i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0986	0.1144	0.1153	0.0641
<i>R</i> _I [all data]	0.0991	0.1013	0.0844	0.1648
<i>wR</i> ₂ [all data]	0.1151	0.1356	0.1331	0.0834
<i>R</i> _{int}	0.0703	0.0547	0.0412	0.1117
GOF	1.015	1.027	1.019	1.003

	Hmim^{Ar}Cl₃	Hmim^{Ar}(OMe)₃	Hmim^{Ar}(CF₃)₂	Hmim^{Ar}OMeNO₂
crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
formula	C ₉ H ₅ Cl ₃ N ₂ S	C ₁₂ H ₁₄ N ₂ O ₃ S	C ₁₁ H ₆ F ₆ N ₂ S	C ₁₀ H ₉ N ₃ O ₃ S
formula weight	279.56	266.31	312.24	251.26
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	7.4408(8)	7.2383(6)	8.4302(5)	13.747(5)
<i>b</i> /Å	20.454(2)	7.9459(7)	23.8152(15)	12.625(4)
<i>c</i> /Å	7.1759(8)	22.324(2)	36.666(2)	13.632(5)
α /°	90	90	90	90
β /°	91.0376(14)	93.0750(10)	90	106.496(5)
γ /°	90	90	90	90
<i>V</i> /Å ³	1091.9(2)	1282.12(19)	7361.4(8)	2268.7(14)

	Hmim ^{ArCl₃}	Hmim ^{Ar(OMe)₃}	Hmim ^{Ar(CF₃)₂}	Hmim ^{ArOMe,NO₂}
Z	4	4	24	8
temperature (K)	130(2)	150(2)	130(2)	130(2)
radiation (λ , Å)	0.71073	0.71073	0.71073	0.71073
ρ (calcd.) g cm ⁻³	1.701	1.380	1.690	1.471
μ (Mo K α), mm ⁻¹	0.993	0.254	0.329	0.285
θ max, deg.	30.51	30.61	32.63	26.37
no. of data collected	17407	7575	117976	12681
no. of data	3337	3945	22429	2330
no. of parameters	139	170	1247	158
R_I [$I > 2\sigma(I)$]	0.0276	0.0426	0.0381	0.0449
wR_2 [$I > 2\sigma(I)$]	0.0722	0.0914	0.0882	0.1128
R_I [all data]	0.0283	0.0745	0.0358	0.0550
wR_2 [all data]	0.0728	0.1042	0.0872	0.1182
R_{int}	0.0327	0.0417	0.0256	0.0670
GOF	1.128	1.049	1.082	1.120
Flack parameter	–	–	0.34(4)	–