Supporting Information
to
Access to Pure and Highly Volatile Hydrochalcogenide Ionic Liquids

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1. Devices and methods
Elemental analyses (C, N, H, S) were carried out by the service department for routine analysis and mass spectrometry with a vario MICRO cube (ELEMENTAR). The samples were weighed into tin capsules inside a nitrogen filled glove box (Labmaster 130, MBRAUN).

Melting points were determined with a BÜCHI Melting Point B540.

Combined TGA/ DSC measurements were performed with a NETZSCH STA 409 CD in aluminium oxide crucibles, with an argon flow rate of 40 mL/min and a heating rate of 10 K/min; TGA decomposition points are given as onset temperature, DSC data is given as peak value.

$^1$H and $^{13}$C-NMR spectra were recorded in automation with a Bruker Avance 300 spectrometer, $^{77}$Se NMR-spectra were recorded by the service department for NMR-analyses with a Bruker DRX 400 spectrometer. All spectra were recorded at ambient temperature. $^1$H and $^{13}$C-NMR spectra were calibrated using residual protons and solvent signals, respectively (DMSO-$d_6$: $\delta_H$ 2.50 ppm, $\delta_C$ 39.52 ppm).$^1$ NMR spectra of $^{77}$Se were referenced externally against dimethyl selenide.

IR spectra were recorded on a Bruker APLPHA FT-IR spectrometer with Platinum ATR-sampling.

2. Starting materials
All solvents were dried according to common procedures$^2$ and passed through columns of aluminium oxide, 3 Å molecular sieve and R3-11G-catalyst (BASF) or stored over molecular sieve (3 or 4 Å) until use. Reagents were used as received unless stated otherwise. 1-Ethyl-3-methylimidazolium methylcarbonate in methanol solution (30%) was donated by BASF. 1-Butyl-3-methylimidazolium methylcarbonate in methanol solution (50%) was purchased from IOLiTEC, $N$-butylpyrrolidine from ACROS. 1-Ethyl-2-methylimidazole was synthesised in analogy to a published procedure.$^3$ Methylcarbonate ionic liquids were synthesised following the general procedure of R. Kalb.$^4$ Bis(trimethylsilyl) selenide was synthesised in analogy to the corresponding sulphide.$^5$
Hydrogen sulphide was fed into a 30% solution of 1-ethyl-3-methylimidazolium methylcarbonate (26.9 g, 43.4 mmol) in methanol for 40 minutes. All volatiles were removed in vacuo and the residue recrystallised from a mixture of acetonitrile and diethyl ether at −30 °C. The solution was decanted and the crystals dried in fine vacuum. [EMIm][HS] (4.62 g, 32.0 mmol, 74%) was obtained as colourless solid. Mp 91-93 °C (from acetonitrile/diethyl ether, 2 K/min). DSC (10 K/min): 92.8 °C (endoth.). TGA (10 K/min): 162.1 °C (decomp.). 

1H-NMR (300.1 MHz, DMSO-d6) δH = −3.85 (s, 1H, HS), 1.39 (t, 3JHH = 7.3 Hz, 3H, CH2CH3), 3.88 (s, 3H, NMe), 4.24 (q, 3JHH = 7.3 Hz, 2H, CH2CH3), 7.87 (s, 1H, H4/5), 7.99 (s, 1H, H4/5), 9.97 (s, 1H, H2) ppm.

IR: νmax/cm⁻¹: 3022m, 2859m, 2565w (SH), 1570s, 1464m, 1420m, 1339m, 1178s, 1030w, 874m, 800s, 704w, 622vs.

For sublimation [EMIm][HS] (535 mg, 3.71 mmol) was placed in a long Schlenk tube and heated to 70 °C at 1·10⁻³ mbar. A colourless substance sublimed to the cooler parts of the flask. After 18 hours 465 mg (3.22 mmol, 87%) of purified, colourless [EMIm][HS] could be isolated. The light brown remainder (30 mg) consisted primarily of unchanged starting material. Mp: 92-93 °C. Elem. anal. found C, 50.0; H, 8.4; N, 19.4; S, 22.2. The IR and NMR spectra stayed unchanged.

3.2 Synthesis of 1-ethyl-2,3-dimethylimidazolium hydrosulphide ([EMMIIm][HS], 2).

1-Ethyl-2,3-dimethylimidazolium methylcarbonate (12.7 g, 63.4 mmol) was dissolved in methanol (20 mL) and hydrogen sulphide was fed into the solution for 75 minutes. All volatile components were removed in vacuum, and the residue recrystallised from a mixture of acetonitrile and diethyl ether. [EMMIIm][HS] was isolated as light orange crystals in a yield of 4.60 g (29.1 mmol, 46%). Mp 125-126 °C (from acetonitrile/diethyl ether, 2 K/min). DSC (10 K/min): 127.6 °C (endoth.). TGA (10 K/min): 179.5 °C (decomp.). 

Elem. anal. found C, 53.1; H, 9.1; N, 18.0; S, 19.0; C7H14N2S1 requires C, 53.1; H, 8.9; N, 17.7; S, 20.3. IR:
\( \nu_{\text{max}}/\text{cm}^{-1} \): 2971s, 2563m (HS), 1721w, 1580m, 1533m, 1327w, 1299m, 1253s, 1197m, 1128m, 954w, 818vs, 661m, 500w. \(^1\)H-NMR (300.1 MHz, DMSO-\(d_6\)) \( \delta_H = -4.07 \) (s, 1H, HS), 1.33 (t, \( J_{\text{HH}} = 7.3 \) Hz, 3H, CH\(_2\)CH\(_3\)), 2.60 (s, 3H, C-Me), 3.76 (s, 3H, NMe), 4.16 (q, \( J_{\text{HH}} = 7.3 \) Hz, 2H, CH\(_2\)CH\(_3\)), 7.69 (s, 1H, H4/5), 7.73 (s, 1H, H4/5). \(^1\)C-NMR (75.5 MHz, DMSO-\(d_6\)) \( \delta_C = 9.0 \) (1C, C-Me), 14.8 (1C, CH\(_2\)CH\(_3\)), 34.6 (1C, NMe), 121.1 (1C, C4/5), 123.4 (1C, C4/5), 136.7 (1C, C2) ppm.

For sublimation [EMMIIm][HS] (349 mg, 2.21 mmol) was placed in a long Schlenk tube and heated to 85 °C at 1·10\(^{-3}\) mbar. A colourless substance sublimed to the cooler parts of the flask. After 60 hours 284 mg (1.79 mmol, 81%) of purified, colourless [EMMIIm][HS] could be isolated. The red remainder consisted partly of [EMMIIm][HS] but mostly unidentifiable side and decomposition products. \( \text{Mp} \) 127-128 °C. \textbf{Elem. anal.} found C, 53.1; H, 9.1; N, 18.1; S, 20.4; \( C_7H_{14}N_2S \) requires C, 53.1; H, 8.9; N, 17.7; S, 20.3. The IR and NMR spectra stayed unchanged.

\textbf{3.3 Synthesis of 1-butyl-3-methylimidazolium hydrosulphide ([BMIm][HS], 3).}

A 50% solution of 1-butyl-3-methylimidazolium methylcarbonate (8.39 g, 39.1 mmol) in methanol was mixed with additional methanol (10 mL) and hydrogen sulphide was fed into the solution for 45 minutes. All volatiles were removed \textit{in vacuo} and the residue recrystallised from a mixture of acetonitrile and diethyl ether at \(-30 \) °C. The solution was decanted and the crystals dried in fine vacuum. [BMIm][HS] (3.54 g, 53%) was obtained as colourless solid. \( \text{Mp} \) 54-55 °C (from acetonitrile/ diethyl ether, 2 K/min). \textbf{DSC} (10 K/min): 56.0 °C (endoth.). \textbf{TGA} (10 K/min): 157.4 °C (decomp.). \textbf{Elem. anal.} found C, 55.8; H, 9.6; N, 16.7; S, 18.55; \( C_8H_{16}N_2S \) requires C, 55.8; H, 9.4; N, 16.3; S, 18.6. \textbf{IR:} \( \nu_{\text{max}}/\text{cm}^{-1} \): 2928m, 2806m, 2559w (HS), 1665w, 1556s, 1453m, 1418w, 1362w, 1165vs, 1011m, 908m, 801s, 753m, 655s, 630s. \(^1\)H-NMR (300.1 MHz, DMSO-\(d_6\)) \( \delta_H = -3.92 \) (s, 1H, HS), 0.88 (t, \( J_{\text{HH}} = 7.3 \) Hz, 3H, CH\(_2\)CH\(_3\)), 1.18-1.30 (m, 2H, CH\(_2\)CH\(_3\)), 1.71-1.81 (m, 2H, NCH\(_2\)CH\(_2\)), 3.88 (s, 3H, NMe), 4.20 (t, \( J_{\text{HH}} = 7.2 \) Hz, 2H, NCH\(_2\)CH\(_2\)), 7.81 (s, 1H, H4/5), 7.90 (s, 1H, H4/5), 9.76 (s, 1H, H2) ppm. \(^1\)C-NMR (75.5 MHz, DMSO-\(d_6\)) \( \delta_C = 13.2 \) (1C, CH\(_2\)CH\(_3\)), 18.7 (1C, CH\(_2\)CH\(_3\)), 31.3 (1C, NCH\(_2\)CH\(_2\)), 35.6 (1C, NMe), 48.3 (1C, NCH\(_2\)CH\(_2\)), 121.1 (1C, C4/5), 123.4 (1C, C4/5), 136.7 (1C, C2) ppm.

For sublimation [BMIm][HS] (549 mg, 3.19 mmol) was placed in a long Schlenk tube and heated to 50 °C at 1·10\(^{-3}\) mbar. A colourless substance sublimed to the cooler parts of the flask. After 48 hours 420 mg (1.79 mmol, 77%) of purified, colourless [BMIm][HS] could be
isolated. The light green remainder consisted of unchanged starting material. \textbf{Mp} 54-55 °C. \textbf{Elem. anal.} found C, 55.8; H, 9.5; N, 16.7; S, 18.3; \(\text{C}_8\text{H}_{16}\text{N}_2\text{S}_1\) requires C, 55.8; H, 9.4; N, 16.3; S, 18.6. The IR and NMR spectra stayed unchanged.

3.4 \textit{Synthesis of 1-ethyl-3-methylimidazolium hydroselenide ([EMIm][HSe], 4).}

A 30\% solution of 1-ethyl-3-methylimidazolium methylcarbonate (3.68 g, 5.93 mmol) was cooled in an ice bath and degassed thoroughly. Bis(trimethylsilyl)selenide (1.63 g, 7.23 mmol) was added in small portions within 15 minutes and the resulting mixture was stirred at 0 °C for 30 minutes and further 30 minutes at ambient temperature. After removal of volatile contents the residue was recrystallised from an acetonitrile/diethylether mixture at −30 °C. [EMIm][HSe] (796 mg, 70\%) was obtained as a colourless solid. \textbf{Mp} 101-102 °C (from acetonitrile/diethyl ether, 2 K/min). \textbf{Elem. anal.} found C, 37.7; H, 6.3; N, 15.0; \(\text{C}_6\text{H}_{12}\text{N}_2\text{Se}_1\) requires C, 37.7; H, 6.3; N, 14.7. \textbf{IR}: \(\nu_{\text{max}}/\text{cm}^{-1}\): 3049m, 2962m, 2274w (HSe), 1569m, 1418w, 1362w, 1339w, 1259m, 1173s, 1091m, 1027m, 863m, 789vs, 704m, 645m, 620vs. \(^{1}H\text{-NMR}\) (300.1 MHz, DMSO-\(d_6\)) \(\delta_H = -6.56\) (s, 1H, HSe), 1.40 (t, \(^3J_{HH} = 7.3\text{ Hz}, 3\text{H}, \text{CH}_2\text{CH}_3\)), 3.87 (s, 3H, NMe), 4.22 (q, \(^3J_{HH} = 7.3\text{ Hz}, 2\text{H}, \text{CH}_2\text{CH}_3\)), 7.77 (t, \(^3J_{HH} = 1.7\text{ Hz}, 1\text{H}, H4/5\)), 7.87 (t, \(^3J_{HH} = 1.7\text{ Hz}, 1\text{H}, H4/5\)), 9.46 (s, 1H, H2) ppm. \(^{13}C\text{-NMR}\) (75.5 MHz, DMSO-\(d_6\)):\(\delta_C = 15.1\) (1C, CH\(_2\)CH\(_3\)), 35.7 (1C, NMe), 44.0 (1C, CH\(_2\)CH\(_3\)), 121.9 (1C, C4/5), 123.4 (1C, C4/5), 136.2 (1C, C2) ppm. \(^{77}\text{Se-NMR}\) (76.3 MHz, DMSO-\(d_6\)): \(\delta_{\text{Se}} = -312.3\) ppm.

For sublimation [EMIm][HSe] (418 mg, 2.19 mmol) was placed in a long Schlenk tube and heated to 95 °C at 1·10\(^{-3}\) mbar. A colourless substance sublimed to the cooler parts of the flask. After 80 hours 330 mg (1.73 mmol, 79\%) of purified, colourless [EMIm][HSe] could be isolated. The light green remainder consisted of unchanged starting material. \textbf{Mp} 101-103 °C. \textbf{Elem. anal.} found C, 37.6; H, 6.3; N, 15.2.; \(\text{C}_6\text{H}_{12}\text{N}_2\text{Se}_1\) requires C, 37.7; H, 6.3; N, 14.7. The IR and NMR spectra stayed unchanged.

3.5 \textit{Synthesis of N-butyl-N-methylpyrrolidinium hydrosulphide ([BMPyr][HS], 5).}

\(N\)-Butyl-\(N\)-methylpyrrolidinium methylcarbonate (15.1 g 69.5 mmol) was dissolved in methanol (40 mL) and hydrogen sulphide fed into the solution for one hour. All volatiles were removed \textit{in vacuo} and the residue recrystallised from a mixture of acetonitrile and diethyl ether at −30 °C. The solution was decanted and the crystals dried in fine
vacuum. [BMPyr][HS] (5.65 g, 46%) was obtained as colourless solid. **Mp** 153-155 °C (decomp., from acetonitrile/ diethyl ether, 2 K/min). **DSC** (10 K/min): 166.5 °C (endoth.). **TGA** (10 K/min): 153.4 °C (decomp.). **Elem. anal.** found C, 61.8; H, 12.3; N, 8.1; S, 17.7; C_{9}H_{21}N_{1}S_{1} requires C, 61.6; H, 12.1; N, 8.0; S, 18.3. **UV-Vis:** $\lambda_{\text{max}}$ (DMSO)/nm 264. **IR:** $\nu_{\text{max}}$/cm$^{-1}$: 2959vs, 2934s, 2873m, 2560w (HS), 1459vs, 1379w, 1260w, 1060m, 1004s, 910s, 743m, 587w. $^1$H-NMR (300.1 MHz, DMSO-$d_6$) $\delta_{H}$ = -4.03 (s, 1H, HS), 0.92 (t, $^3J_{HH}$ = 7.4 Hz, 3H, CH$_2$CH$_3$), 1.24-1.38 (m, 2H, CH$_2$CH$_3$), 1.60-1.74 (m, 2H, NCH$_2$CH$_2$), 2.00-2.14 (m, 4H, CH$_2$(3,4)), 3.02 (s, 3H, NMe), 3.30-3.60 (m, 6H, NCH$_2$CH$_2$, CH$_2$(2,5)) ppm. $^{13}$C-NMR (75.5 MHz, DMSO-$d_6$) $\delta_{C}$ = 13.4 (1C, CH$_2$CH$_3$), 19.2 (1C), 21.0 (1C), 24.8 (1C), 47.4 (t, $^2J_{CN}$ = 3.9 Hz, 2C, C3/4), 62.6 (t, $^2J_{CN}$ = 2.8 Hz, 2C, C2/5), 63.2 (t, $^2J_{CN}$ = 3.1 Hz, 1C) ppm.

Upon attempting to sublime the substance analogously to the prior imidazolium salts the condensation of colourless droplets at cooler parts of the Schlenk flask was observed. These were identified as a mixture of decomposition products. No traces of the former salt could be detected.
4. Crystal Structures

Single crystals of [EMIm][HS] (1), where grown by sublimation, the resulting structure was analogous but of higher quality when compared to crystals grown from a saturated methanol solution. Crystals of 2 were obtained by layering a solution of the compound in acetonitrile with diethyl ether. [BMPyr][HS] (5) crystallised from an oversaturated acetonitrile solution at room temperature. The data collection for the single crystal structure determinations was performed in rotation method on a Bruker D8 QUEST diffractometer by the X-ray service department of the Fachbereich Chemie, University of Marburg. The spectrometer is equipped with a Mo-$\text{K}_\alpha$ X-ray micro source (0.71073 Å, Incotec), a fixed chi goniometer and a PHOTON 100 CMOS detector. Bruker software (Bruker Instrument Service, APEX2, SAINT) was used for data collection, cell refinement and data reduction. The structures were solved with SIR-977 or SIR20118 refined with SHELXL-20149 and finally validated using PLATON10 software, all within the WinGX11 software bundle. EnCIFer aided in the editing and validation of the CIF files.12 Absorption corrections where applied beforehand within the APEX2 software (multi-scan).13 Graphic representations were created using Diamond 4.14 C-bound H-atoms were constrained to parent site; The sulphur bound H-atom in [EMIm][HS] was located in the Fourier map and refined independently. Analogous treatment of the sulphur bound H-atom in [BMPyr][HS], did not lead to a stable position for the H-atom and convergence of the structure, possibly attributable to the strong disorder of the cation along a mirror plane (figure S1 and S2). In this case the H-atom was located in the Fourier map and coordinates and displacement were fixed before the next refinement cycles. In all graphics the ellipsoids are shown for the 50% probability level. Hydrogen atoms are shown with arbitrary radius, only those bound to hetero atoms or involved in hydrogen bonds are shown in the graphic representations. Selected crystal data and experimental parameters are listed in table S1. Crystallographic data for the structures presented in this paper have been deposited with the Cambridge Crystallographic Data Centre. CCDC-141450 and 141454 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%5Frequest/cif.
Table S1. Crystal data for the structures of compounds 1 and 5.

|                              | [EMIm][HS] (1)                  | [BMPyr][HS] (5)                  |
|-----------------------------|---------------------------------|---------------------------------|
| Formula                     | C6 H12 N2 S                      | C9 H21 N S                      |
| FW / g mol⁻¹                | 144.24                          | 175.33                          |
| Crystal system              | monoclinic                      | tetragonal                      |
| Space group                 | P 21/n                          | P 42/m b c                      |
| Colour, habit               | colourless block                | colourless needle               |
| Crystal size / mm³          | 0.21 x 0.20 x 0.10              | 0.38 x 0.14 x 0.12              |
| a / Å                       | 8.6023(3)                       | 15.6635(6)                      |
| b / Å                       | 7.6710(2)                       | 15.6635                         |
| c / Å                       | 12.7600(4)                      | 8.9408(5)                       |
| α /°                        | 90                              | 90                              |
| β /°                        | 107.8620(10)                    | 90                              |
| γ /°                        | 90                              | 90                              |
| V / Å³                      | 801.42(4)                       | 2193.6(2)                       |
| Z                           | 4                               | 8                               |
| Dcalc / g cm⁻³              | 1.195                           | 1.062                           |
| Min./max. Transm.           | 0.6361/ 0.7457                   | 0.6668/ 0.7456                   |
| μ / cm⁻¹                    | 0.323                           | 0.244                           |
| F(000)                      | 312                             | 784                             |
| T / K                       | 100(2)                          | 100(2)                          |
| θ range /°                  | 2.54 : 26.33                    | 2.60 : 25.99                    |
| range h,k,l                 | -11:11; -10:10; -17:17         | -16:19; -18:19; -11:11          |
| Refl. Coll.                 | 18404                           | 16725                           |
| Refl. Indep.                | 1993                            | 1154                            |
| Refl. 1 > 2σ(I)             | 1777                            | 871                             |
| Data / restr. / param.      | 1993/ 0/ 88                     | 1154/ 2/ 90                     |
| ReL                        | 0.0447                          | 0.0514                          |
| R1 (obs)                    | 0.0318                          | 0.0601                          |
| wR2 (all)                   | 0.0876                          | 0.1680                          |
| GooF (F²)                   | 1.066                           | 1.056                           |
| Res. e⁻ dens. (min./ max.)   | -0.238/ 0.338                   | -0.368/ 0.248                   |
| CCDC                        | 1414150                         | 1414154                         |

Table S2. Hydrogen bonds in the solid state structure of [EMIm][HS] (1).

| D-H···A       | d(D--A) /Å | d(H--A) /Å | (DHA)° |
|---------------|------------|------------|--------|
| [EMIm][HS]    |            |            |        |
| C2-H2···S1'   | 2.68       | 3.520(1)   | 148.2  |
| C4-H4···S1''  | 2.79       | 3.731(1)   | 172.7  |
| C6-H6B···S1   | 2.88       | 3.786(1)   | 152.7  |

I: x+1/2, -y+3/2, z-1/2; II: -x+1, -y+1, -z+1.
Figure S1. Crystal structure of [EMIm][HS] (1) viewing along the b-axis.

Figure S2. Crystal structure of [BMPyr][HS] (5) viewing along the c-axis and disorder of the pyrrolidinium cation along a mirror plane.
5. Details concerning the sublimation process

All sublimed imidazolium salts could unambiguously be identified as the original hydrochalcogenide salt. The NMR and IR spectra fully coincide; the elemental composition was proven by elemental analysis (CHNS). The melting points were increased by ca. 1 K after sublimation demonstrating the already high purity of the originally isolated hydrochalcogenide salts. The residue after a first sublimation consists mainly of unsublimed starting material, only in case of [EMMIm][HS] (2) a larger amount of unidentified side products was observed. Typically the isolated sublimate accounted for more than 80% of the employed amount. After a second sublimation no visible residue remained, 95% of the deployed substance could be re-isolated.

![Figure S3. Crystals of [EMIm][HS] (1) after sublimation.](image)

![Figure S4. [EMMIm][HS] (2) before and after sublimation.](image)
Figure S5. [BMIm][HS] (2) before and after sublimation.

Figure S6. Crystalline [BMIm][HS] (3) after sublimation.

Figure S7. [EMIm][HSe] (4) before and after sublimation.
In case of [BMPyr][HS] the condensed substance consists primarily of the acyclic aminothiolo S7, which results from a ring opening $S_N2$ attack at one of the pyrrolidinium C atoms next to the nitrogen atom. This reaction behaviour is well documented for pyrrolidinium cations. It can be traced back to an increased ring strain in comparison with related 6-ring piperidinium, where primarily a demethylation occurs.\textsuperscript{15}

![Scheme S1. Thermal decomposition of [BMPyr][HS] (5), only the main product is shown.](image)

We also investigated the vaporisation behaviour of the hydrosulphide salts 1 and 5 under ambient pressure, in order to mimic the conditions in the TGA measurements for $\Delta H_{\text{vap}}$ determination (\textit{vide infra}). Larger samples were placed in a Schlenk tube with a coldfinger at $-30 \, ^\circ\text{C}$ reaching as far as 1 cm above the substance. The tube was then heated to 100 °C and after reaching the final temperature the pressure was adjusted to atmospheric conditions. After several hours, when a sufficient amount of material was visible on the cold finger, the experiment was stopped and the complete condensate analysed by NMR spectroscopy. Figures S9 compares the $^1\text{H}$-NMR spectra of pure [EMIm][HS] and the collected substance, figure S10 correspondingly compares the spectra of [BMPyr][HS] and its decomposition products.
Figure S9. $^1$H-NMR spectra of pure [EMIm][HS] (blue) and the substance collected after the attempted sublimation at ambient pressure (red). The variation of the chemical shift of the aromatic imidazolium protons is due to the difference in concentration of the two samples.

Figure S10. $^1$H-NMR spectra of pure [BMPyr][HS] (blue) and the decomposition products collected after the attempted sublimation at ambient pressure (red).
6. Isothermal TGA measurements for $\Delta H_{vap}$ determination

Isothermal TGA experiments for determination of vaporisation enthalpies were conducted using a TGA/SDTA 851 equipped with a LF/1100 °C oven from METTLER TOLEDO. The measurements were carried out in encapsulated 40 µL Al crucibles, which have been perforated with a 0.64 mm opening for a defined effusion at isothermal steps. Dry nitrogen was used as carrier gas with a flow rate of 50 mL/min. The calibration of the experimental setup was undertaken with ferrocene as calibration substance with known vapour pressure, following the NIST recommendation.\textsuperscript{16} Ferrocene was purchased from ACROS ORGANICS (98%).

For all experiments the purest available samples were chosen; in case of the imidazolium salts, the salts were sublimed once before further use. In case of [BMPyr][HS] a double recrystallisation of the sample was carried out. As further test substance for the TGA experiments, [BMIm][TFSI] was purchased from IOLITEC (99.5%) and dried 24 h in fine vacuum at 90 °C prior to the TGA experiment. All measurements were conducted with a stepwise temperature programme of isothermal plateaus (10 min) and a heating rate of 10 K/min. The mass loss rate per unit area $\frac{1}{A} |\frac{dm}{dt}|$ is related to the apparent vapour pressure $P_T$ via equation (1):\textsuperscript{16a}

$$\log\left(\frac{1}{A} |\frac{dm}{dt}| \right)_T + C \propto \log P_T$$  \hspace{1cm} (1)

Here, $C$ is a device specific constant.

From Arrhenius plots of the mass loss rates per unit area, the vaporisation enthalpy $\Delta H_{vap}$ could be extracted according to the Clausius-Clapeyron equation (2), where $C'$ is a sample specific constant.

$$\log \left(\frac{1}{A} |\frac{dm}{dt}| \right) = \frac{\Delta H_{vap}}{R} \cdot \frac{1000}{T} + C'$$  \hspace{1cm} (2)

The determined $\Delta H_{vap}$ values were corrected to 298 K via equation (3).

$$\Delta H_{vap}(298 \, K) = \Delta H_{vap}(T_{av}) + \Delta C_m(298 \, K - T_{av})$$  \hspace{1cm} (3)

The value of the molar heat capacity difference $\Delta C_m$ was set to -0.1 kJ•mol$^{-1}$, which has evolved as a rough standard approximation in this field of research, although not undisputed.\textsuperscript{17}
To allow for a comparison of the apparent vapour pressures between different substances, the molar weight of the gas-phase molecules has to be considered. Here, we assumed contact ion pairs to constitute the gas phase. Therefore, the IL-specific molar masses were employed to the Arrhenius plots of the molar loss rates per unit area $\log\left(\frac{1}{A} \cdot \left| \frac{dn}{dt} \right| \right) = \log\left(\frac{1}{A} \cdot \left| \frac{dm}{dt} \cdot \frac{1}{M} \right| \right)$, presented in figure S11-right, compared with the mass loss rate (figure S11-left). Comparing substances 1, 2, 5, ferrocene and [BMIm][TFSI] shows the striking difference between the classical IL test substance [BMIm][TFSI] and the hydrochalcogenides investigated in this work (figure S12).

**Figure S11.** Arrhenius plots of the mass loss rate (left) and the molar loss rates (right) per unit area of compounds 1 to 5, the melting temperature of [BMIm][HS] lies outside of the current graph borders at 3.05.

**Figure S12.** Arrhenius plots of the molar loss rates per unit area, comparing the hydrosulphides 1, 2, 5, ferrocene and [BMIm][TFSI].
7. Computational methods

Structure optimisation for the most stable conformations of [EMIm][HS] single ion pairs (SIPs) in the gas phase (figure S13) as well as reaction path search for the decomposition processes occurring during the vaporisation were studied with the quantum chemistry programme Gaussian 09. These calculations for gas phase structures were performed within density functional theory on a BP86/def2-TZVP level. Molecular structures for stationary points on the Born-Oppenheimer hypersurface were obtained such that the root mean square (RMS) of all force components with respect to internal coordinates dropped below $10^{-5} \text{E}_h \cdot \text{a}_0^{-1}$ and $10^{-5} \text{E}_h \cdot \text{rad}^{-1}$. Convergence criteria in the self-consistent field (SCF) procedure were that RMS changes in the density matrix between two successive SCF cycles remained below $10^{-6}$. The integration scheme is “UltraFine”, i.e. a pruned (99, 590) grid for the numerical integration step involved in the construction of the exchange correlation potential. All stationary points were characterised by harmonic vibrational frequency calculations and minimum energy reaction paths were obtained via the steepest gradient descent approach. To identify the type of bonding interaction present in the SIP b) (figure S13), the program AIMALL was employed to perform the QTAIM (Quantum Theory of Atoms in Molecules) analysis according to R. F. W. Bader. Additionally to that, a natural bond orbital analysis in NBO 3.1 and an energy decomposition analysis (EDA) in ADF were performed.

Calculations concerning cohesive energies were performed with the Vienna Ab initio Simulation Package (VASP). The experimental crystal structures of compounds 1 and 3, which were determined in the course of this work, were used as input. The structure of 1 is submitted with this publication (vide supra). The CIF files of all structures have been deposited with the CCDC and can be obtained under CCDC 1414150 to 1414153. Structure optimisations were performed for monoclinic [EMIm][HS] (1) and [EMIm][HSe] (4) and orthorhombic [EMMIm][HS] (2) and [BMIm][HS] (3) crystal structures, as well as for single ion pairs in the gas phase. These calculations were performed within the non-spin polarised density functional theory and the Generalised Gradient Approximation PBE (GGA-PBE) together with the projector-augmented-wave (PAW) method as implemented in the Vienna Ab initio Simulation Package (VASP.5.3.5). A kinetic energy cut-off of 480 eV is used for convergence of the total energy within 1 meV. Gamma k-point meshes of 4 x 4 x 6 for [EMMIm][HS], 4 x 6 x 4 for [EMIm][HSe] and 4 x 4 x 4 for the two other crystal unit cells are used for Brillouin zone integration to calculate the electronic ground states. Long-range
van-der-Waals interactions were accounted for by employing the zero damping DFT-D3 scheme of Grimme.  

Cohesive energies ($E_{coh}$) are assumed to be approximately equal to the sublimation enthalpies ($\Delta H_{sub}$) and were calculated using the relation

$$\Delta H_{sub} \approx E_{coh} = E_{unit} - E_{bulk}/N_{unit},$$

where $E_{unit}$ is the energy of a single ion pair in the most stable conformation in vacuum and $E_{bulk}$ is the energy per unit cell of the respective salt. $N_{unit}$ is the number of formula units in the simulation cell of the given crystalline structure ($N_{Unit} = 8$ for [EMMIm][HS], and $N_{Unit} = 4$ for the others). $E_{unit}$ was calculated in a simulation cell, which is sufficiently large to avoid artificial interactions between a SIP and its periodic images. For the same purpose, the cut-off radius of the force field within the context of the PBE-D3 scheme was reduced. Equilibrium structures were obtained using the conjugate gradient optimisation. All atoms were fully relaxed until the change in forces on the ionic displacements was below 0.01 eV/Å. No other constraints were imposed for structure optimisation calculations in the bulk systems. The optimized lattice parameters (a, b, c, $\beta$) for the crystal structures (table S3) show a slight deviation from the experimental values.

### Table S3. Structural parameters of the unit cells of compounds 1 to 4 after structure optimisation (experimental values in parenthesis).

| Compound               | a/ Å   | b/ Å   | c/ Å   | $\beta$/° |
|------------------------|--------|--------|--------|------------|
| [EMIm][HS] (1)         | 8.58 (8.60) | 7.54 (7.67) | 12.67 (12.76) | 107.7 (107.9) |
| [EMMIm][HS] (2)        | 7.84 (8.02) | 13.32 (13.43) | 16.46 (16.64) | -          |
| [BMIm][HS] (3)         | 9.84 (9.91) | 12.04 (12.14) | 8.16 (8.23)   | -          |
| [EMIm][HSe] (4)        | 8.57 (8.60) | 7.60 (7.78) | 13.20 (13.30) | 108.4 (108.2) |
7.1 Gas phase structure optimisation of [EMIm][HS] single ion pairs

Figure S13. Most stable ion pairs of [EMIm][HS] (without ZPE correction).
Table S4. Total electronic energies of the [EMIm][HS] SIPs (without ZPE correction).

|    | \( E/ E_h \) | \( E_{rel} \) kJ·mol\(^{-1} \) |
|----|-------------|------------------|
| a  | -743.703593 | 0.0              |
| b  | -743.702876 | 1.9              |
| c  | -743.702057 | 4.0              |
| d  | -743.701422 | 5.7              |
| e  | -743.697161 | 16.9             |
| f  | -743.696625 | 18.3             |
| g  | -743.683208 | 53.5             |
| h  | -743.682816 | 54.6             |
| i  | -743.682783 | 54.6             |
| j  | -743.682511 | 55.4             |
| k  | -743.681308 | 58.5             |

7.2 \( S_N^2 \) reactions and carbene formation as decomposition pathways

Figure S14. Decomposition of [EMIm][HS] by nucleophilic attack at the methyl group.
Figure S15. Decomposition of [EMIm][HS] by nucleophilic attack at the ethyl group.

Table S5. Total electronic energies of the S_N2-type reactions (without ZPE correction).

| Attack at the methyl group | $E/ E_h$ | $E_{rel} / \text{kJ mol}^{-1}$ |
|---------------------------|-----------|-----------------------------|
| Ion pair (most stable one) | −743.703593 | 0.0 |
| Pre-reaction complex     | −743.661534 | 110.4 |
| Transition structure     | −743.656123 | 124.6 |
| Post-reaction complex    | −743.732113 | −74.9 |
| Products (separated)     | −743.728935 | −66.5 |

| Attack at the ethyl group |
|----------------------------|
| Ion pair (most stable one) | −743.703593 | 0.0 |
| Pre-reaction complex     | −743.683208 | 53.5 |
| Transition structure     | −743.652775 | 133.4 |
| Post-reaction complex    | −743.729330 | −67.6 |
| Products (separated)     | −743.727514 | −62.8 |
Figure S16. Energy profile of the carbene formation.

Table S6. Total electronic energies of the carbene formation (without ZPE correction).

| Attack at the methyl group | $E/\,E_h$ | $E_{\text{rel}}/\,\text{kJ}\cdot\text{mol}^{-1}$ |
|---------------------------|-----------|-----------------------------------|
| Ion pair (most stable one) | −743.703593 | 0.0                              |
| H–bonded SIP              | −743.697161 | 16.9                             |
| Singlet carbene           | −743.685269 | 48.1                             |
| Triplet carbene           | −743.552676 | 396.2                            |

7.3 Formation of 1-ethyl-3-methylimidazole-2-thione

As already noted by Hollóczki et al., a neutral thiol species A, resulting from nucleophilic attack of the hydrosulphide at the C2 position (scheme S2) cannot be stabilised.\textsuperscript{30} This forced reaction is accompanied by slight increase in energy by about 28.2 \text{kJ}\cdot\text{mol}^{-1}, with the corresponding structure not being a stationary point on the potential energy hypersurface.
Scheme S2. Formation of an imidazole-2-thiole by nucleophilic attack of $\text{HS}^-$ at the C2-carbon.

The reaction becomes thinkable if another hydrosulphide anion is included, which will act as Brønstedt base and concertedly deprotonates the thiole to anion $\text{B}$ (scheme S3). According to DFT calculations, in the gas phase this reaction would be accompanied by an overall energy loss of $-6.3$ kJ·mol$^{-1}$.

Scheme S3. Formation of an imidazole-2-thiolate by nucleophilic attack of $\text{HS}^-$ at the C2-carbon and concertedly deprotonation by another hydrosulphide anion.

Thiolate $\text{B}$ will act as a strong hydride donor and reacts with the strongest acid present in the system, which is again the hydrosulphide anion ($pK_a (\text{HS}^-) \approx 14$, $p\text{Ka} ([\text{EMIm}]^+) = 23$). Thiole $\text{A}$ will certainly show a lower $pK_a$ value, but its questionable existence and, if at all, very low abundance renders it an improbable reaction partner. The forming sulphide dianion will immediately attack the next [EMIm] cation initiating an autocatalytic cycle (scheme S4). The overall energy balance of the reaction is computed to be exothermic by $-51.01$ kJ/mol.

Scheme S4. Generation of the thione 6 and initiation of an autocatalytic decomposition cycle.

Table S7 summarises the computed energies of the single components and table S8 reports the total energies of the reactions depicted in schemes S2 to S4.

Table S7. Total electronic energies of the single components (without ZPE correction).

| Component                     | $E/E_h$ |
|-------------------------------|---------|
| Most stable SIP [EMIm][HS]    | $-743.703593$ |
| Thiole $\text{A}$             | $-743.692868$ |
| Hydrosulphide anion (HS$^-$)  | $-398.871600$ |
| Thiolate $\text{B}$           | $-743.128954$ |
| Hydrogen sulphide (H$_2$S)    | $-399.448640$ |
| Thione 6                      | $-742.545439$ |
| Hydrogen (H$_2$)              | $-1.177586$ |
Table S8. Total energies of the reactions depicted in schemes S2 to S4.

| Reaction of scheme S2 | $E/ E_h$ | $\Delta E_{\text{rel}}$ kJ·mol$^{-1}$ |
|----------------------|----------|-------------------------------------|
| [EMIm][HS] SIP       | $-743.703593$ | $0.0$                              |
| Thiole A             | $-743.692868$ | $28.2$                             |

| Reaction of scheme S3 | $E/ E_h$ | $\Delta E_{\text{rel}}$ kJ·mol$^{-1}$ |
|----------------------|----------|-------------------------------------|
| Separated reactants  | $-1142.575196$ | $0.0$                              |
| Separated products   | $-1142.577594$ | $-6.3$                             |

| Reaction of scheme S4 | $E/ E_h$ | $\Delta E_{\text{rel}}$ kJ·mol$^{-1}$ |
|----------------------|----------|-------------------------------------|
| Separated reactants  | $-1486.832550$ | $0.0$                              |
| Separated products   | $-1486.851979$ | $-51.0$                             |

### 7.4 Analysis of the bonding interaction in the single ion pair b) and thiol A

The formation of a 1-ethyl-3-methylimidazol-2-thiole was anticipated as a possible intermediate during the generation of the respective thione. However, the structure with separated ion and a C–S distance of 2.26 Å (equivalent to ion pair b) of figure S13) is more stable than the covalently bound molecule, where the bond length was fixed to 1.82 Å, which was assumed a typical C–S single bond length. Figure S17 visualises the relative energy change with varying C–S distance.

![Figure S17. Relative energy of the [EMIm][HS] SIP b) in dependency of the C–S distance ($E_{\text{rel}} = 0$ corresponds to the most stable SIP a) of figure S13).](image)

Comparing the bond length with other ionic pairs, where the anion is not located above the ring-system of the imidazolium, the abnormality gets fortified. There, the C–S bond length is always larger than 3 Å, which indicates that ion pair b) has a more covalent character than other ionic pairs like the H-bonded ion pair c). To identify the type of bonding interaction present in the structure b) a Bader analysis,\textsuperscript{21} a natural bond orbital analysis\textsuperscript{22} and an energy
decomposition analysis were performed, comparing structure b), methanethiol and sodium hydrosulphide. A bond critical point was found between sulphur and the carbon of interest, with an electron (charge) density $\rho = 7.64 \cdot 10^{-2} \, (-e) \cdot a_0^{-3}$ and a Laplacian of the electron density of $\nabla^2 \rho = 3.63 \cdot 10^{-2} \, (-e) \cdot a_0^{-5}$. The criterion for a covalent bonding interaction is that $\rho/(-e) \cdot a_0^{-3}$ should be higher than 0.2 and $\nabla^2 \rho/(-e) \cdot a_0^{-5}$ should be negative. This indicates the carbon-sulphur interaction to be mostly of ionic character (figure S18). For methanethiol the values $\rho = 1.73 \cdot 10^{-1} \, (-e) \cdot a_0^{-3}$ and $\nabla^2 \rho = -2.57 \cdot 10^{-1} \, (-e) \cdot a_0^{-5}$ and for sodium hydrosulphide the values $\rho = 3.07 \cdot 10^{-2} \, (-e) \cdot a_0^{-3}$ and $\nabla^2 \rho = 1.38 \cdot 10^{-1} \, (-e) \cdot a_0^{-5}$ were calculated. These fit to the expectations of mainly covalent and ionic interactions, respectively.

![Figure S18. Bader analysis of the ion pair b), methanethiol and sodium hydrosulphide (from left to right).](image)

The NBO analysis (figure S19), in contrast reveals a $\sigma$-like bond orbital, indicating a covalent bond. It is overt, that the orbital is highly deformed; the electron density is located more on the sulphur atom due to its higher electronegativity.
The energy decomposition analysis (EDA) of the three compounds finally confirms an intermediate state between a covalent bond and an ionic character of the interaction. The H–bonded ion pair e) in comparison shows a significantly higher electrostatic contribution (Tabel S9).

**Table S9. Energy decomposition analysis of Ion pairs b), e), methanethiol and sodium hydrosulphide.**

|                      | Ion pair b) | Ion pair e) | Methanethiol | Sodium hydrosulphide |
|----------------------|-------------|-------------|--------------|----------------------|
| $E_{total}$/kJ•mol$^{-1}$ | $-116.0$    | $-102.8$    | $-285.1$     | $-133.7$            |
| $E_{pauli}$/kJ•mol$^{-1}$ | $127.2$     | $48.9$      | $187.9$      | $30.4$               |
| $E_{el.static}$/kJ•mol$^{-1}$ | $-160.5$    | $-110.3$    | $-223.8$     | $-146.5$            |
| (66.0%)               | (72.7%)     | (47.3%)     | (89.3%)      |                      |
| $E_{orbital}$/kJ•mol$^{-1}$ | $-82.8$     | $-41.4$     | $-249.2$     | $-17.6$             |
| (34.0%)               | (27.3%)     | (52.7%)     | (10.7%)      |                      |
| $E_{diss}$/kJ•mol$^{-1}$ | $99.2$      | $95.8$      |              |                      |

Also the bond indices of the carbon-sulphur bond according to Wiberg$^{22a}$ produce an intermediate value for the ion pair b) (BI = 0.5681). The values for methyl-thiol (BI = 1.0486) and sodium hydrosulphide (BI = 0.3576) clearly indicate covalent and ionic interactions, respectively.
8. EI-MS-Spectra

[EMIm][HS], 1

Data 19/04/22_EE_649_Su
Comment:
Description:
Ionization Mode: EI
History Centroid|Peak Height|Centroid|Resolution|Average|Method|1.0|3.46|3.56
Charge number: 1
Element: C 2, H 5, N 1, O 1

Exact Mass: 33.9877
Chemical Formula: H2S

Exact Mass: 81.0447
Chemical Formula: C4H10N1+

Exact Mass: 142.0555
Chemical Formula: C6H16N3S

Composition: H, S
Mono Isotopic Mass: 33.08772
Average Mass: 34.09198
Nominal Mass: 34
Created by Administrator

| Mass  | Intensity | Relative Intensity | Calcd. Mass | Mass Difference (m/z) | Mass Difference (ppm) | Possible Formula |
|-------|-----------|--------------------|-------------|-----------------------|------------------------|-----------------|
| 33.08772| 31.8223 | 30.34 | 33.08772 | -0.96 | -16.82 | H2S |
[EMMIm][HSI], 2

H$_2$S

Chemical Formula: H$_2$S
Exact Mass: 33.9877

Chemical Formula: Cy$_2$H$_2$N$_2^+$
Exact Mass: 124,1000

Chemical Formula: Cy$_2$H$_2$N$_2^+$
Exact Mass: 123,0922
### [BMIm][HS], 3

**Data:** 150511_EL_701_Su
**Comment:**
**Description:**
**History:** Averages.MS(1): ±0.36, ±0.39; ±1.41
**Acquired:** 2015-06-12
**Operator:** AccuTOF
**Calibration:** File: Pea_i00-20150601
**Created:** 2015-06-16 1:30:44 PM

**Change number:** 1
**Tolerance:** 5.00 ppm, 3.00 ppm, 2.00 ppm

#### Unsaturation Number: -1.5, 20.0 (Fraction Both)

| Mass  | Intensity | Calc. Mass | Mass Difference (mDa) | Possible Formula |
|-------|-----------|------------|-----------------------|-----------------|
| 170.08745 | 111.05561 | 170.08777 | -0.32 | C32H32B2Cl2N2S |

**Data:** 150511_EL_701_Su
**Comment:**
**Description:**
**History:** Averages.MS(1): ±0.36, ±0.49
**Acquired:** 6/29/2015
**Operator:** AccuTOF
**Calibration:** File: Pea_i00-20150601
**Created:** 2015-06-12 10:04:40 AM

**Change number:** 1
**Tolerance:** 3.00 ppm

#### Unsaturation Number: -1.5, 20.0 (Fraction Both)

### Composition H5S
**Mono Isotopic Mass:** 23.08772
**Average Mass:** 23.08168

**Created:** 6/29/2015 10:27:13 AM

| Mass  | Intensity | Relative Intensity | Calc. Mass | Mass Difference (mDa) | Mass Difference (ppm) | Possible Formula |
|-------|-----------|--------------------|------------|-----------------------|------------------------|-----------------|
| 33.98760 | 513436.05 | 25.14 | 33.98772 | -0.62 | -1.87 | C3H7ClS |
| 55.94336 | 2017151.42 | 76.15 | 55.95265 | 0.46 | 0.86 | C3H4Cl2N |
| 60.95979 | 2049549.44 | 160.02 | 60.95279 | 0.49 | 0.81 | C3H4ClN2 |
| 137.12002 | 591153.11 | 21.62 | 137.12076 | 0.95 | 0.69 | C3H4Cl2N3SO |

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S31
\[\text{[EMim][HSe], 4}\]
9. NMR-Spectra

\([\text{EMIm}][\text{HS}]\), 1

**\(^1\text{H}-\text{NMR}, 300.1\text{ MHz}, \text{DMSO-}d_6\)**

\[\text{HS}^-\]

\[\text{N} \quad \text{N} \quad \text{H} \quad \text{S} \quad \text{N} \quad \text{N} \quad \text{H} \quad \text{S}\]

**\(^{13}\text{C}-\text{NMR}, 75.5\text{ MHz}, \text{DMSO-}d_6\)**

\[\text{HS}^-\]

\[\text{N} \quad \text{N} \quad \text{H} \quad \text{S}\]
$[^{[EMMIm]}[HS]]$, 2

$^1$H-NMR, 300.1 MHz, DMSO-$d_6$

$^{13}$C-NMR, 75.5 MHz, DMSO-$d_6$
$[\text{BMIm}][\text{HS}]_3$

$^1\text{H-NMR}, 300.1 \text{ MHz},$
$\text{DMSO-d}_6$

$^{13}\text{C-NMR}, 75.5 \text{ MHz},$
$\text{DMSO-d}_6$
[EMIm][HSe], 4

**1H-NMR, 300.1 MHz, DMSO-\textit{d}_6**

**13C-NMR, 75.5 MHz, DMSO-\textit{d}_6**
$[\text{BMPyr}]/[\text{HS}], 5$

$^{77}\text{Se}-\text{NMR}, 76.3$ MHz, DMSO-$d_6$

$^1\text{H}-\text{NMR}, 300.1$ MHz, DMSO-$d_6$
10. IR-Spectra

- [EMIm][HS] (1) after sublimation
- [EMIm][HS] (1) before sublimation
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