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Synthesis and crystal structure of *N*-phenyl-*N*′-(pyridin-2-ylmethyl)-*S*-methyl-thiouronium iodide

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ABSTRACT

Methylation of *N*-phenyl-*N*′-(pyridin-2-ylmethyl)thiourea led to a new low melting thiouronium iodide salt, whereas a further methylation of the nitrogen of the pyridine ring was not successful. This could be explained by the inactivity of the nitrogen atom due to the sterical shielding revealed by crystallographic data. Exchange of the iodide anion with bis(trifluoromethylsulfonyl)imide led to a thiouronium room temperature ionic liquid. Methylation of the urea analog *N*-phenyl-*N*′-(pyridin-2-ylmethyl)urea occurred on pyridine nitrogen, resulting in the expected pyridinium salt.

1. Introduction

Thiourea and urea compounds are widely applied in different fields of chemistry e.g. as amine scavengers, in catalytic processes or as germicides [1–3]. Moreover, they are very promising as metal scavenger e.g. for Hg, Ag or Cu [4–6]. Recently Rogers et al. [7] appended different urea and thiourea functional groups onto the imidazole ring, gaining interesting cations based on 1-alkyl-imidazolium-3-alkyl(thio)urea structures. Combining these cations with hexafluorophosphate as anion, they designed hydrophobic ionic liquids (ILs), which were liquid at room temperature and were efficiently applied for the extraction of Cd(II) and Hg(II) from aqueous solutions [7]. Furthermore, Ignatyev et al. have reported ionic liquids containing thiourea and urea moieties, suggesting their possible application as solvents or catalysts [8,9].

Generally, ILs are defined as molten salts with a melting point below 100 °C, mainly consisting of bulky and nonsymmetrical organic cations such as imidazolium, pyrrolidinium, pyridinium, ammonium or phosphonium, whereas various inorganic or organic anions are known. This group of compounds exhibits several outstanding properties such as an extremely low vapor pressure or extraordinary high thermal and electrochemical stabilities. Their physico-chemical properties such as viscosity, hydrophobicity or miscibility can be tuned by modifying the chemical structure of their constituents [10].

Following the idea of Rogers et al. [7], we have tried to synthesize similar compounds incorporating the urea and thiourea functionality but with a pyridine ring, using *N*-phenyl-*N*′-pyridin thiourea- and urea-based structures as starting materials. Several structural studies of this group of substances have already been presented in the literature and the influence of various substituents on inter- and intramolecular hydrogen bonding, and hence on crystal packaging has been discussed in detail [11–14].

Herein, we present the simple methylation of *N*-phenyl-*N*′-(pyridin-2-ylmethyl)thiourea and *N*-phenyl-*N*′-(pyridin-2-ylmethyl)urea resulting in low melting salts with different chemical structures. X-ray diffraction studies of the new thiouronium iodide salt together with comprehensive NMR-experiments were conducted and discussed. Anionic exchange of both low melting iodide salts with bis(trifluoromethylsulfonyl)imide led to a room temperature thiouronium-based ionic liquid [8] and an urea-based pyridinium salt.

2. Results and discussion

2.1. Synthesis

The starting material *N*-phenyl-*N*′-(pyridin-2-ylmethyl)thiourea **1** was prepared according to the literature [15]. Although the sulfur atom is actually a weak acceptor in alkylation reactions, it is well known that sulfur can act as extremely strong acceptor in systems like R1R2C=S, where R1 and R2 can form an extended

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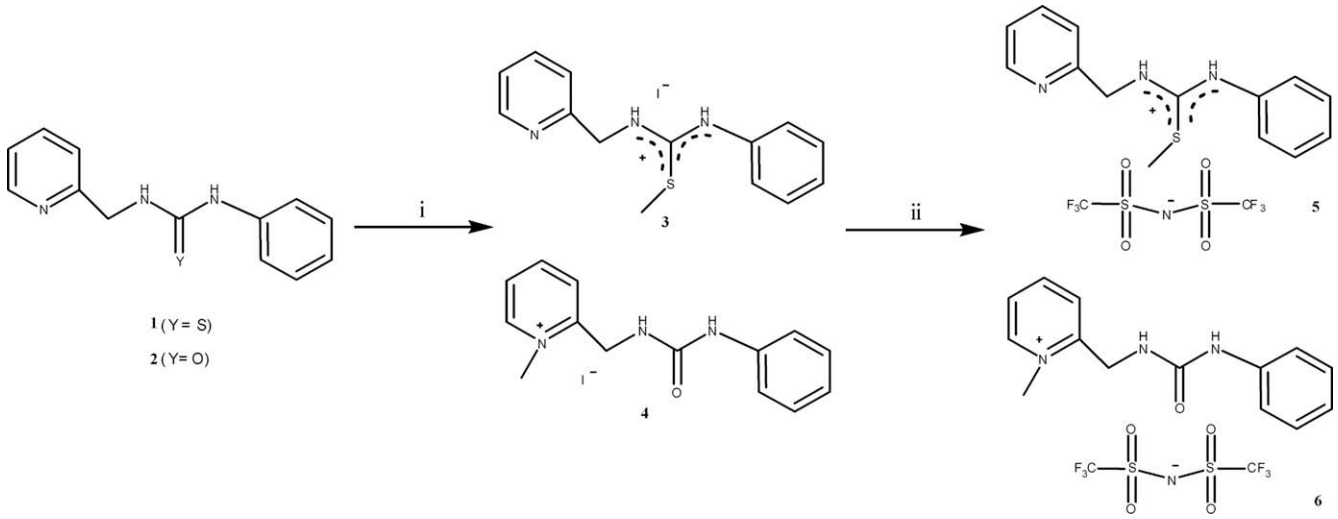
delocalized system with C=S, as it is the case for thioureas and thiosemicarbazones [16,17]. As expected, the methylation of compound **1** with the twofold mol equivalent of iodomethane in acetone resulted in the corresponding thiouronium compound **3** (Scheme 1). In contrast, methylation of the urea analog *N*-phenyl-*N*′-(pyridin-2-ylmethyl)urea **2** resulted in *N*-phenyl-*N*′-(1-methylpyridinium-2-ylmethyl)urea iodide **4**. Even in highly delocalized systems an oxygen atom is still a weak acceptor in alkylation reactions [18–21]. Generally, methylation of starting compounds *N*-phenyl-*N*′-(pyridin-2-ylmethyl)thiourea and the urea analog resulted in the corresponding iodide salts, however, with two different chemical structures (Scheme 1).

The difference in the methylation products of the thiourea and urea precursors is clearly observable in ^{1}H NMR spectra presented in Fig. 1. Whereas the methylated thiourea compound generally exhibited broad signals with the methyl group signal at 2.6 ppm, the methylated urea compound is characterized by sharp signals; the CH_3 protons resonate at 4.3 ppm. Methylation of the pyridine nitrogen in the urea compound was clearly confirmed by a long range ^{1}H, ^{13}C HMBC NMR measurement. Shift correlation signals of the N–CH_3 protons with carbon atoms of the pyridine ring were detected. In case of the methylated thiourea analog, most of the expected cross peaks in the HMBC NMR spectrum could not be observed due to the very broad ^{1}H NMR signals.

2.2. Crystal structure of *N*-phenyl-*N*′-(pyridin-2-ylmethyl)-*S*-methylthiouronium iodide, **3**

Beside the characteristic S–CH_3 resonance at 2.6 ppm, the structure of the synthesized thiouronium iodide compound was further confirmed by X-ray diffraction study, the result of which is shown in Fig. 2. Crystal data and details of data collection are listed in Table 1. Selected bond distances and angles along with hydrogen bond parameters are given in Table 2. The conformation of the compound is so, that the C6 of the phenyl ring and the S atom are in *anti* position with respect to N1–C6 bond, whereas C8 and the S atom are in *syn* position, with respect to N2–C8. This is in accord with the crystal structure of the starting compound, *N*-phenyl-*N*′-(pyridin-2-ylmethyl)thiourea, already described in the literature [11,12]. The formation of centrosymmetric dimers via N2H hydrogen bonding to an iodide atom (N2–H2···I1 3.483 Å) of a neighboring pair of ions is evident in Fig. 3. In contrast, in



Scheme 1. Synthesis of salts. Reagents and conditions: (i) two mol equivalents of iodomethane, acetone, reflux at 70 °C, 24 h, inert atmosphere (ii) one mol equivalent of lithium bis(trifluoromethylsulfonyl)imide, acetone/water, room temperature, over night.

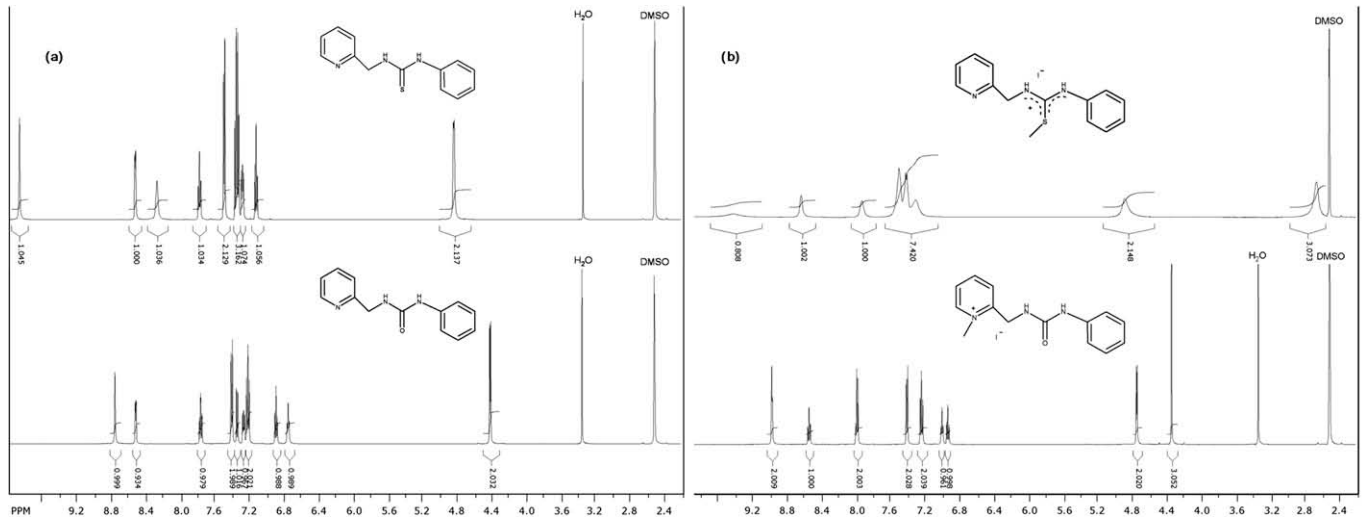


Fig. 1. ^{1}H NMR spectra of (a) starting compounds and (b) methylated products.

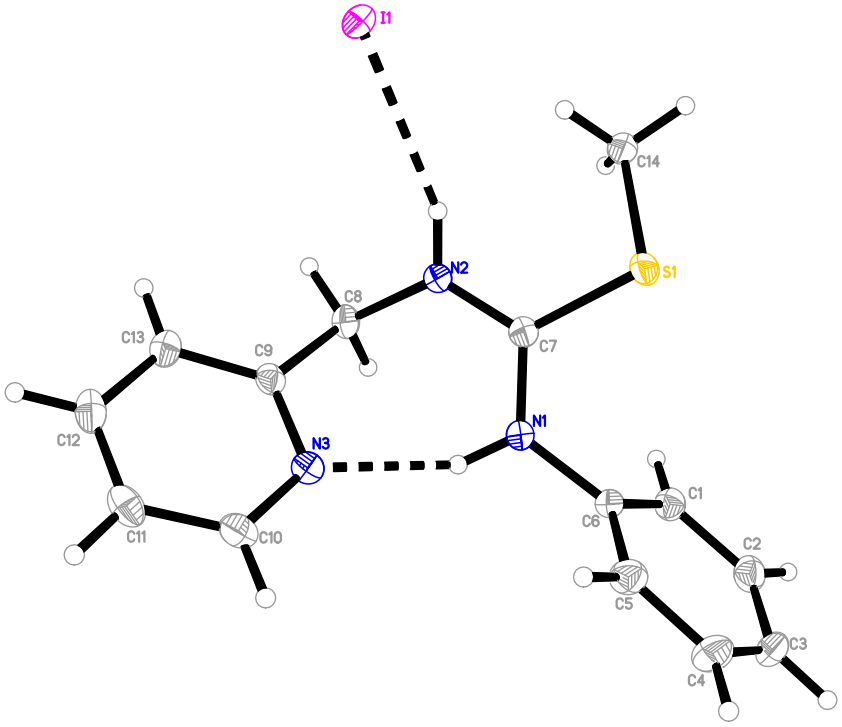


Fig. 2. Thermal ellipsoid diagram for compound **3** showing intramolecular hydrogen bonding as well as N2H···I1 bond with the iodide atom of the neighboring pair of ions, with atom numbering scheme and displacement ellipsoids at 30% probability level.

Table 1
Crystal data and details of data collection.

Empirical formula	$C_{14}H_{16}N_3SI$
f_w	385.26
Space group	$P2_1/c$
a (Å)	7.2671(8)
b (Å)	13.0720(15)
c (Å)	16.432(2)
β (°)	99.048(5)
V (Å3)	1541.6(3)
Z	4
ρ_{calcd} (g/cm^{-3})	1.66
Crystal size (mm)	0.30 × 0.12 × 0.10
T (K)	120(2)
μ (cm^{-1})	2.203
R_1[a]	0.0195
wR_2[b]	0.0464
GOF[c]	1.019

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[wF_o^2 - F_c^2)2]/\Sigma[w(F_o^2)2\ ]\}^{1/2}$.
[c] GOF (goodness of fit) = $\{\Sigma[wF_o^2 - F_c^2)2]/(n-p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.

Table 2
Selected bond distances (Å), bond angles (°) and hydrogen bond parameters.

Bond distances (Å)		Bond angles (°)	
S1–C7	1.7482 (14)	C7–S1–C14	102.24 (6)
S1–C14	1.8029 (14)	C6–N1–C7	125.57 (11)
N1–C7	1.3236 (16)	C7–N2–C8	124.76 (11)
N1–C6	1.4338 (16)	C2–C1–C6	119.29 (13)
N2–C7	1.3293 (17)	C1–C2–C3	120.25 (14)
N2–C8	1.4732 (17)	N1–C6–C1	120.56 (12)
C1–C6	1.3883 (19)	N1–C6–C5	118.46
C1–C2	1.3916 (19)	N1–C7–N2	120.49 (12)
C8–C9	1.5114 (18)	S1–C7–N1	118.20 (10)
C9–N3	1.3451 (17)	S1–C7–N2	121.22 (12)
C9–C13	1.3899 (18)	N2–C8–C9	115.66 (11)
N3–C10	1.3397 (18)	N3–C9–C13	122.26 (13)
C10–C11	1.3888 (21)	C8–C9–N3	115.94 (11)
		C8–C9–C13	121.70 (12)
		C9–N3–C10	118.18 (12)
		N3–C10–C11	123.19 (13)

Hydrogen bond parameters		Bond distances (Å)			Bond angles (°)	Symmetry code
D–H	A	d (D–H)	d (H…A)	d (D…A)	∠DHA	
N1–H100	N3	0.880	1.965	2.768 (12)	151.07	
N2–H200	I1	0.880	2.656	3.483 (17)	157.06	−1 + x, y, z

case of different uncharged *N*-2-alkylpyridyl-*N*′-arylthioureas, this kind of bond is built with the sulfur atom of a neighboring molecule [13,14]. This structural difference is in accordance with the second Etter hydrogen bonding rule, indicating the best hydrogen bond donor and best hydrogen bond acceptor would preferably form hydrogen bonds if there are no intramolecular hydrogen bonds possible, e.g. due to sterical shielding [22]. An iodide anion is clearly the better proton acceptor compared with a sulfur atom. These two driving forces resulted in the 3D packing structure presented in Fig. 3. Due to the spatial dispersion of hydrogen bonding and hence structure formation, the iodide anion is localized in the neighborhood of the N2 atom. Additionally, the strong intramolecular N1H···N3 hydrogen bond (2.768 Å) resulted in the rigid structure of the pyridine ring, inhibiting a free rotation of the ring. Due to the strong hydrogen bondings (and broad signals in NMR-experiments) the N1H signal was not observable in ^{1}H NMR spectra. This rigid structure and strong hydrogen bondings make the N3 atom of the pyridine ring practically "inactive" as electron donor. The attempt of a further methylation of the thiouronium compound on the nitrogen of the pyridine ring was not possible even under severe experimental conditions. For example, a maximum of approx. 10% of a dually methylated compound was gained in a methylation reaction of the thiouronium salt directly suspended in iodomethane (30-fold excess) under reflux for several days.

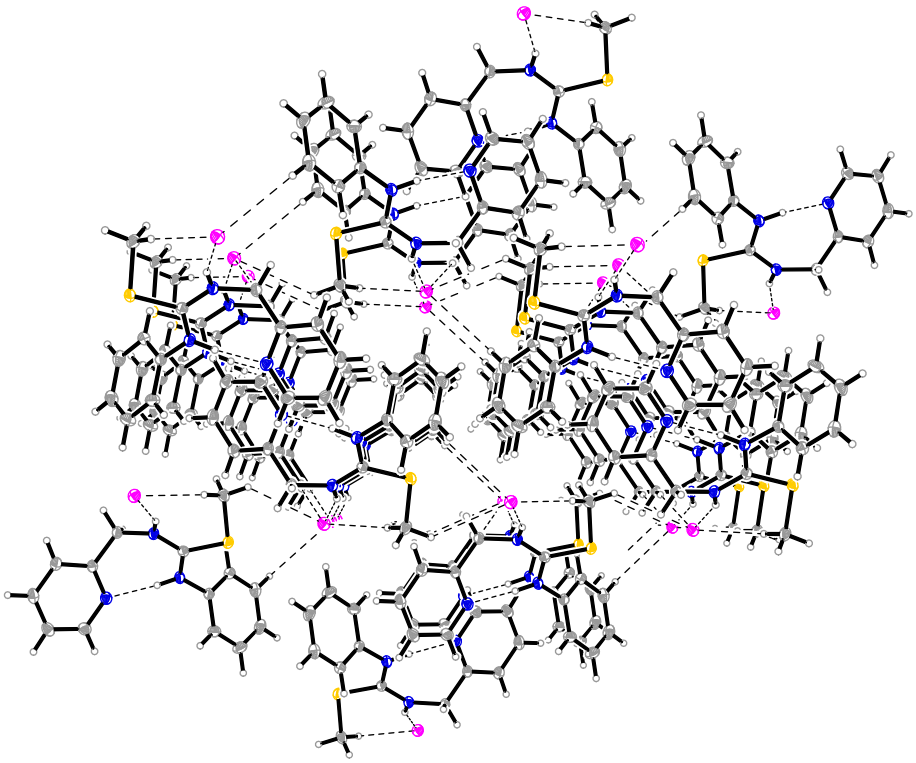


Fig. 3. Packing diagram for **3**.

The prepared low melting iodide salts can strictly not be regarded as ionic liquids as they have melting points over 100 °C (**3**: 133–135 °C; **4**: 155–156 °C). However, a simple anion exchange of iodide with bis(trifluoromethylsulfonyl)imide led to a significant decrease in the melting points. While the pyridinium–urea compound is solid at room temperature (melting point 104–105 °C), the prepared thiouronium compound is liquid at room temperature and can be regarded as ionic liquid. Thiouronium ionic liquids were already reported in the literature following different synthesis routes [8,9,23,24], describing their outstanding properties and possible application fields e.g. as solvents for synthetical and catalytical reactions (Friedel–Crafts acylation and alkylation, Diels–Alder cycloadditions, esterifications), as electrolytes or surfactants [8,24].

3. Summary

In summary, we have shown that the methylation of *N*-phenyl-*N*′-(pyridin-2-ylmethyl)thiourea occurred on the sulfur atom of the thiourea group. Crystallographic data revealed that the nitrogen of the pyridine ring is shielded due to the strong hydrogen bond and is therefore not easily available for a further methylation. Anion exchange led to a hydrophobic thiouronium room temperature ionic liquid. The methylation of the urea analog led to low melting pyridinium salts.

4. Experimental

4.1. General considerations

Dichloromethane for synthesis was distilled over P_2O_5 before use. All other chemicals were used as received without further purification. ^{1}H, ^{13}C and two-dimensional HMBC NMR spectra were recorded with a Bruker Avance III 500 MHz NMR spectrometer at 500.32 (^{1}H) and 125.81 (^{13}C), or 500.10 (^{1}H) and 125.75 (^{13}C) MHz (standard Bruker pulse programs) in DMSO-d_6 at 298 K, using the solvent residual peak for ^{1}H and ^{13}C as internal reference. Elemental analysis (C, H, N and S) was carried out by the Microanalytical Laboratory, University of Vienna [25]. ESI-MS-measurements were performed with an Esquire3000 ion trap mass spectrometer (Bruker Daltonics, Bremen, Germany) equipped with an orthogonal ESI source. Samples were diluted with methanol to ensure good spraying conditions and introduced via flow injection at a rate of 4 μL/min using a Cole-Parmer 74900 single-syringe infusion pump. Infrared spectra were measured with a Bruker Vertex 70 FTIR spectrometer (4000–400 cm^{-1}). Melting points were determined with a Melting Point B-540 instrument from Büchi, Switzerland.

4.2. The following procedure is representative of the synthesis of (*1*) and (*2*) [15,18]

2-(Aminomethyl)pyridine was dissolved in dry dichloromethane and cooled to 0 °C (ice bath). An equimolar amount of phenylisothiocyanate or phenylisocyanate, respectively, was slowly added and stirred at room temperature over night. After evaporation of the solvent, the solid product was dried under vacuum (10^{-3} mbar) for 24 h.

4.2.1. N-phenyl-N′-(pyridin-2-ylmethyl)thiourea (*1*)

White solid, yield 98%; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.85 (*d*, *J* = 4.7 Hz, 2H), 7.14 (*t*, *J* = 7.3 Hz, 1H), 7.30 (*t*, *J* = 7.2 Hz, 1H), 7.37 (m, 3H), 7.51 (*d*, *J* = 7.6 Hz, 2H), 7.79 (*t*, *J* = 7.5 Hz, 1H), 8.29 (s, 1H), 8.54 (*d*, *J* = 4.6 Hz,1H), 9.88 (s, 1H) ppm. ESI-MS: *m/z* calcd for $C_{13}H_{13}N_3S$: 244.33 (+); 242.33 (−); found: 244.2 (+); 242.1 (−). IR: 3172, 2994–2800, 1591, 1518, 1422; 1239 and 840–500 cm^{-1}. Anal. Calcd for $C_{13}H_{13}N_3S$: C, 64.16; H, 5.39; N, 17.27; S, 13.18; found: C, 64.21; H, 5.59; N, 17.36; S, 12.97.

4.2.2. N-phenyl-N′-(pyridin-2-ylmethyl)urea (*2*)

White solid, yield 98%; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.42 (*d*, *J* = 5.7 Hz, 2H), 6.76 (*t*, *J* = 5.7 Hz, 1H), 6.90 (*t*, *J* = 7.3 Hz, 1H), 7.21–7.29 (m, 3H), 7.36 (*d*, *J* = 7.8 Hz, 1H), 7.43 (*d*, *J* = 7.8 Hz, 2H),

7.78 (*t*, *J* = 7.8 Hz, 1H), 8.54 (*d*, *J* = 4.8 Hz, 1H), 8.77 (s, 1H) ppm. ESI-MS: *m/z* calcd for $C_{13}H_{13}N_3O$: 228.3 (+); 226.3 (−); found: 228.1 (+); 226.2 (−). IR: 3331, 3020–2900, 1631, 1624; 1594, 1568, 1440, 1239, 790–500 cm^{-1}. Anal. Calcd for $C_{13}H_{13}N_3O$: C, 68.70; H, 5.77; N, 18.49; found: C, 68.66; H, 5.57; N, 18.55.

4.3. The following procedure is representative of the synthesis of (**3**) and (**4**)

General methylation route: starting material (**1** oder **2**, respectively) was dissolved in acetone at 40 °C and a twofold mol equivalent of iodomethane was slowly added. The reaction was refluxed (70 °C, solvation of reactants at 50 °C) under inert atmosphere for 24 h. After evaporation of the solvent, the resulting solid was dried under vacuum (10^{-3} mbar) for 24 h.

4.3.1. N-phenyl-N′-(pyridin-2-ylmethyl)-S-methyl-thiouronium iodide (**3**)

White solid, yield 80%; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.66 (s, 3H), 4.88 (s, 2H), 7.32–7.51 (m, 7H), 7.94 (s, 1H), 8.65 (s, 1H), 9.44 (s, 1H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ = 14.9, 48.8, 122.7, 123.7, 126.8, 128.6, 130.1, 138.5, 149.1, 155.1 ppm. ESI-MS: *m/z* calcd for $C_{14}H_{16}N_3SI$: 258.4 (+); 126.9 (−); found: 258.1 (+); 126.8 (−). IR: 3105, 2977–2800, 1630; 1590, 1490, 1424; 1287, 760–570 cm^{-1}. Anal. Calcd for $C_{14}H_{16}N_3SI$: C, 43.64; H, 4.19; N, 10.91; S, 8.32; found: C, 43.64; H, 4.32; N, 10.82; S, 8.09.

4.3.2. N-phenyl-N′-(1-methylpyridinium-2-ylmethyl)urea iodide (**4**)

White solid, yield 83%; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.35 (s, 3H), 4.76 (*d*, *J* = 5.6 Hz, 2H), 6.95 (*t*, *J* = 7.3 Hz, 1H), 7.02 (*t*, *J* = 5.8 Hz, 1H), 7.26 (*d*, *J* = 7.8 Hz, 2H), 7.43 (*d*, *J* = 7.8 Hz, 2H), 8.01 (m, 2H), 8.56 (*t*, *J* = 7.5 Hz, 1H), 8.99 (br, 2H) ppm.^{13}C NMR (126 MHz, DMSO-d_6): δ = 41.1, 45.6, 118.5, 122.2, 126.1, 126.6, 129.2, 140.3, 145.7, 147.0, 155.6, 157.4 ppm. ESI-MS: *m/z* calcd for $C_{14}H_{16}N_3OI$: 242.3 (+); 126.9 (−); found: 242.1 (+); 126.8 (−). IR: 3302; 3181, 3120, 3060–2900, 1689, 1624; 1597, 1542, 1441, 790–500 cm^{-1}. Anal. Calcd for $C_{14}H_{16}N_3OI$: C, 45.54; H, 4.37; N, 11.38; found: C, 45.59; H, 4.19; N, 11.32.

4.4. The following procedure is representative of the synthesis of (**5**) and (**6**) [8,24]

Iodide salts were dissolved in appropriate solvents (**3** water; **4** water/acetone 1:1) and an equimolar amount of lithium bis(trifluoromethylsulfonyl)imide dissolved in water was added. The reaction mixture was stirred under inert atmosphere at room temperature for 24 h. The hydrophobic phase formed was separated and washed several times with ice-cold water. Products were dried under vacuum at 40 °C for 24 h (10^{-3} mbar).

4.4.1. N-phenyl-N′-(pyridin-2-ylmethyl)-S-methyl-thiouronium bis(trifluoromethylsulfonyl)imide (**5**)

Green liquid, yield: 73%; ^{1}H NMR (500 MHz, DMSO-d_6): δ = 2.64 (s, 3H), 4.87 (br, 2H), 7.29–7.51 (m, 7H), 7.93 (s, 1H), 8.65 (s, 1H), 9.42 (br, 1H).^{13}C NMR (126 MHz, DMSO-d_6): δ = 14.7, 48.8, 118.7, 121.2, 122.6, 123.7, 126.8, 128.6, 130.1, 138.5, 149.2, 155.3 ppm. ESI-MS: *m/z* calcd for $C_{16}H_{16}N_4O_4S_3F_6$: 258.4 (+); 280.2 (−); found: 258.2 (+); 279.7 (−). IR: 3348, 3070–2900, 1595, 1495, 1348, 1196, 1137, 1059, 739, 780–500 cm^{-1}. Anal. Calcd for $C_{16}H_{16}N_4O_4S_3F_6$: C, 35.68; H, 3.00; N, 10.41; S, 17.86; found: C, 36.00; H, 3.07; N, 10.34; S, 17.82.

4.4.2. N-phenyl-N′-(1-methylpyridinium-2-ylmethyl)urea bis(trifluoromethylsulfonyl)imide (**6**)

White solid, yield: 80%, ^{1}H NMR (500 MHz, DMSO-d_6): δ = 4.34 (s, 3H), 4.75 (*d*, *J* = 5.8 Hz, 2H), 6.95 (*t*, *J* = 7.5 Hz, 1H), 7.01 (*t*, *J* = 5.8 Hz, 1H), 7.27 (m, 2H), 7.43 (m, 2H), 7.99 (m, 2H), 8.55 (*t*, *J* = 7.7 Hz, 1H), 8.98 (*d*, *J* = 5.0 Hz, 2H) ppm. ^{13}C NMR (126 MHz, DMSO-d_6): δ = 41.0, 45.7, 118.5, 118.7, 121.2, 122.3, 126.2, 126.6, 129.5, 140.3, 146.0, 147.0, 155.7, 157.4 ppm. ESI-MS: *m/z* calcd for $C_{16}H_{16}N_4O_5S_2F_6$: 242.3 (+); 280.2 (−); found: 242.1 (+); 279.7 (−). IR: 3320, 3102–2950, 1650, 1567, 1597; 1517, 1447, 1348, 1188, 1135, 1057, 739, 780–500 cm^{-1}. Anal. Calcd for $C_{16}H_{16}N_4O_5S_2F_6$: C, 36.78; H, 3.09; N, 10.73; S, 12.28; found: C, 36.83; H, 3.06; N, 10.71; S, 12.26.

4.5. Crystallographic structure determination

A crystal suitable for X-ray diffraction measurements was obtained after recrystallisation of compound **3** in acetone at 50 °C and subsequently slowly evaporation of the solvent under cooling.

X-ray diffraction measurements were performed on a Bruker X8 APEXII diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å), controlled by a Pentium-based PC running the SAINT software package. A single crystal was positioned at 35 mm from the detector and 1921 frames were measured, each for 30 s over 1° scan for *N*-phenyl-*N*′-(pyridin-2-ylmethyl)-*S*-methyl-thiouronium iodide. Crystal data, data collection parameters and structure refinement details are given in Table 1. The structure was solved by direct method and refined on F2 by full-matrix least-squares techniques using the SHELXTL software package. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed at calculated positions or localized on difference Fourier maps and isotropically refined. The graphics were prepared by using ORTEP24.

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Appendix A. Supplementary data

All measured NMR spectra as well as the synthesis route and characterization of the dual methylation of *N*-phenyl-*N*′-(pyridin-2-ylmethyl)-*S*-methyl-thiouronium iodide (**3**) can be found in the supplementary data. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-747959. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2009.11.037.

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