Methylated Imidazolinium-Dithiocarboxylates: Two Representatives of a New Class of Ionic Liquids

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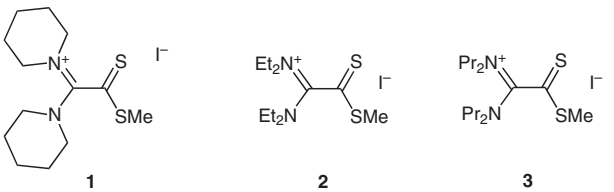
Abstract: The work describes the methylation of chiral and achiral imidazolinium-dithiocarboxylates. The resulting salts qualify as a novel class of ionic liquids after an anion metathesis was performed. Their NMR and UV/Vis spectra were studied.

Key words: ionic liquids, chirality, chiral cations, imidazolinium salts, zwitterions

Ionic liquids have emerged as a new promising class of organic material due to their potential as novel solvents for reactions and electrochemical processes.[1] Some of these liquids are expected to be 'green solvents', for example, due to their negligible vapor pressure.[2] The organic salts have a melting point below 100 °C. An additional advantage is the efficient recovery of some of these salts. Nevertheless, in a few examples it is known that the ionic liquids are not inert and react with some reagents,[3] which could be a disadvantage in some applications. The collection of ionic liquids based on the combinations of cations and anions has dramatically increased, and constantly new salts[4] and solvent mixtures[5] are prepared. In case the ionic liquids are chiral, they have an additional potential as chiral solvents, shift reagents, and catalysts.[6]

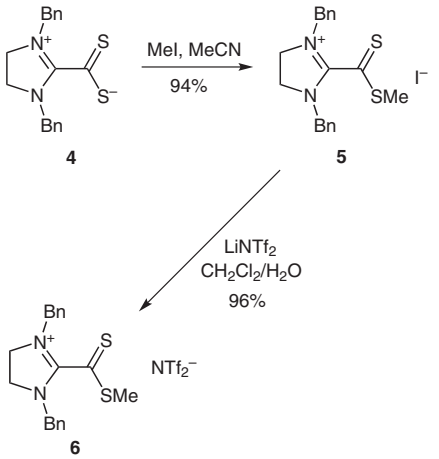
Due to our efforts in ionic liquids[7] and imidazolinium-dithiocarboxylates[8] we were interested to explore the possibility to prepare a new interesting class of ionic liquids from imidazolinium-dithiocarboxylates. The latter belong to the extraordinary class of carbene complexes of nonmetals[9] and can be formally prepared by the addition of an imidazolinium carbene to CS_2. The CS_2 group is nearly perpendicular to the imidazolinium ring. It is known that the CS_2 group can be methylated to give salts as shown in Figure 1. However, the examples in the literature are very limited and only simple salts with very high melting points were reported.[10]



1 2 3

Figure 1 Salts **1**–**3**

First, the simple zwitterion **4**[11] was prepared according to the literature. The zwitterion was then transferred into salt **5** with methyl iodide in 94% yield. The salt, as the starting zwitterion, was red and had a melting point of 145 °C. Through an anion metathesis, NTf_2 was introduced as an anion and the resulting red salt **6** was obtained in 96% yield with a water content of 0.069% (Scheme 1). The salt is liquid at room temperature and remains a liquid even at storage in a freezer at –28 °C for several months.



4 5 6

Scheme 1

Next, an enantiopure analogue was prepared. Starting from diamine **7** the zwitterion **8** was prepared in analogy to zwitterion **4**. Treating diamine **7** with of DMF dimethylacetal at 100 °C resulted in the carbene dimer, which was directly dissolved in xylene and reacted with CS_2 at 140 °C for 45 minutes to give the desired zwitterion **8** in 43% yield.[12] Treatment of **8** with methyl iodide gave the desired salt **9** in 92% yield. The salt has a melting point of 87 °C. In addition it was possible to change the counter anion by stirring salt **9** with KPF_6 or $LiNTf_2$ in a mixture of CH_2Cl_2 and water, which gave the desired salts **10** and **11** in 88 and 98% yield, respectively (Scheme 2). Interestingly, salt **10** with a PF_6 counter anion had a melting point of 74 °C, while salt **11** with the more lipophilic NTf_2 anion had a higher melting point of 109 °C. The salts were as stable as their so far reported analogues in the literature and no decomposition was observed at their melting points.

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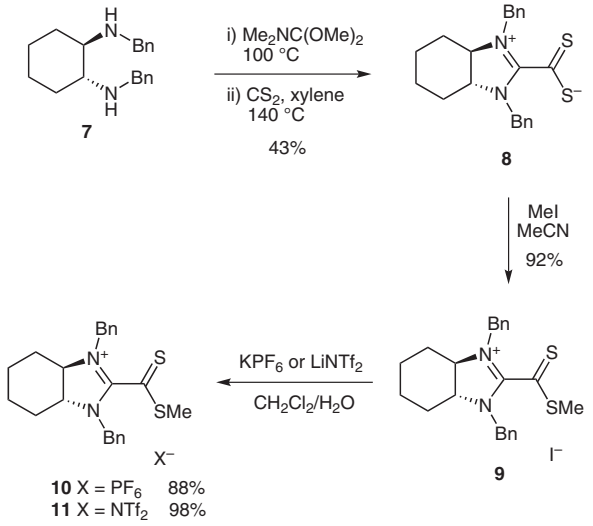

Scheme 2

The salts displayed some interesting behavior in the ^{1}H NMR spectra. While the diastereotopic benzylic protons came in salt **5** as a singlet at δ = 4.69, they showed in salt **6** a typical AB system, one doublet at δ = 4.65 and one at δ = 4.51. Although achiral, it is obvious that through desymmetrization a new chiral center would be formed at the benzylic position and the salt would possess an axial chirality along the axis of the imidazolinium ring and the CS_2Me group. In addition it was possible to observe in salts **9**, **10**, and **11** only very broad singlets for the benzylic protons, which is due to the slow rotation of the CS_2Me group at room temperature. However, this rotation is suppressed at 0 °C. A ^{1}H NMR spectrum at this temperature showed for salt **10** the first AB system with two doublets at δ = 5.00 and 4.88 and the second AB system with two doublets at δ = 4.84 and 4.70.

Because of the red color of the cation, due to charge transfer, it is also possible to observe different shifts in the UV/Vis spectra depending on the lipophilicity of the counter anions. In chloroform, salt **9** had a maximum at λ = 422 nm, salt **10** at 498 nm, and salt **11** at 504 nm. Changing the solvent to methanol, salt **9** had a maximum at λ = 500 nm.

In conclusion, we have demonstrated that methylated imidazolinium salts qualify as new chiral and room temperature ionic liquids. Because of their straightforward synthesis, it will be possible to prepare various analogues and to incorporate an axial chirality. Use of other alkylation agent instead of methyl iodide is also possible.[13] Due to their color it is possible to use these salts to determine the polarity of solvents and the lipophilic character of anions.[14]

All reactions were conducted under a protective atmosphere of dry N_2. MeCN and CH_2Cl_2 were distilled from CaH_2. Anhyd xylene was purchased from Sigma-Aldrich and used without further purification. Reactions were monitored by TLC with Merck silica gel 60 F_{254} plates. Flash column chromatography was performed on silica gel 60 (70–230 mesh ASTM). IR spectra were recorded on a Vector 22 FT-IR spectrophotometer from Bruker. ^{1}H NMR spectra were taken on an AMX 400 (400 MHz) or on an AC 250 P (200 MHz) spectrometer from Bruker in $CDCl_3$ and calibrated using the peak at 7.26 ppm as an internal reference. ^{13}C NMR spectra were taken on an AMX 400 (100 MHz) or on an AC 250 P (50 MHz) spectrometer from Bruker in $CDCl_3$ and calibrated using the peak 77.2 ppm as an internal reference. Mass spectra were recorded on MS 5889 B mass spectrometer from Hewlett Packard. Electron spray mass spectrometry was performed directly on a MS LC/MSD 1100 MSD mass spectrometer from Hewlett Packard. Elemental analysis were carried out on a 'Elementar Analyzer', model 1106 from Carlo Erba Instrumentazione at the Institute of Pharmaceutical Chemistry of the Technical University of Braunschweig and are reported as the average of two runs. Optical rotations were measured using a 1 dm path length (*c* is given as g/100 mL) on a PerkinElmer 243 B polarimeter in the reported solvent. UV/Vis spectra were recorded on a Hewlett Packard 8452A Diode Array Spectrophotometer. Melting points were taken on a Dr. Tottoli apparatus from Büchi and are uncorrected. H_2O content was determined via the Karl Fischer method. 1,3-Dibenzylimidazolinium-2-dithiocarboxylate (**4**)[11] and (1*R*,2*R*)-*N*,*N*-dibenzylcyclohexane-1,2-diamine (**7**)[15]were prepared according to the literature. All other chemicals were purchased from Aldrich, Fluka, Merck, or Lancaster.

1,3-Dibenzyl-2-(methylthiocarbonothioyl)imidazolinium Iodide (5)

MeI (0.5 mL, 8 mmol) was added to 1,3-dibenzylimidazolinium-2-dithiocarboxylate (**4**; 200 mg, 0.673 mmol) in MeCN (4 mL) to give, after 16 h, a deep red solution. The solvent was removed and the crude product obtained was washed with Et_2O (10 mL) to give the expected product as a red solid (269 mg, 0.63 mmol, 94%); mp 145 °C.

IR (KBr): 3424, 2897, 1612, 1264, 1122, 1059, 740 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.45–7.31 (m, 10 H, C_6H_5), 4.68 (s, 4 H, NC*H*$_2$Ph), 4.52–4.43 (m, 2 H, NC*H*$_2$C*H*$_2$N), 3.74–3.59 (m, 2 H, NC*H*$_2$C*H*$_2$N), 2.93 (s, 3 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 208.0 (CS_2), 164.4 (CN_2), 131.7 (C_6H_5), 129.4 (C_6H_5), 129.3 (C_6H_5), 128.6 (C_6H_5), 52.0 (N*C*H$_2$Ph), 48.4 (N*C*H$_2$*C*H$_2$N), 20.6 (CH_3).

MS (ESI, 0 V): *m*/*z* = 341 (M$^+$, 100%).

Anal. Calcd for $C_{19}H_{21}IN_2S_2$: C, 48.72; H, 4.52; N, 5.98. Found: C, 48.52; H, 4.57; N, 6.31.

1,3-Dibenzyl-2-(methylthiocarbonothioyl)imidazolinium Bis(trifluoromethylsulfonyl)amide (6)

An anion metathesis was performed with **5** (100 mg, 0.213 mmol) in CH_2Cl_2 (5 mL) with a solution of $LiNTf_2$ (92 mg, 0.319 mmol) in H_2O (5 mL). After stirring vigorously for 30 min, the organic phase was washed with H_2O (3 × 5 mL) and dried (MS 3 Å) to give the desired product as a red liquid (127 mg, 0.21 mmol, 96%).

IR (NaCl): 1599, 1350, 1190, 1133, 1054 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.44–7.36 (m, 6 H, C_6H_5), 7.31–7.26 (m, 4 H, C_6H_5), 4.65 (d, *J* = 14.0 Hz, 2 H, NC*H*$_2$Ph), 4.51 (d, *J* = 14.0 Hz, 2 H, NC*H*$_2$Ph), 4.21–4.01 (m, 2 H, NC*H*$_2$C*H*$_2$N), 3.71–3.62 (m, 2 H, NC*H*$_2$C*H*$_2$N), 2.96 (s, 3 H, CH_3).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 207.6 (CS_2), 163.5 (CN_2), 131.4 (C_6H_5), 129.6 (C_6H_5), 129.5 (C_6H_5), 128.6 (C_6H_5), 120.1 (q, *J* = 319.0 Hz, CF_3), 51.6 (N*C*H$_2$Ph), 47.7 (N*C*H$_2$*C*H$_2$N), 20.3 (CH_3).

MS (ESI, 0 V): *m*/*z* = 341 (M$^+$, 100%).

Anal. Calcd for $C_{21}H_{21}F_6N_3O_4S_4$: C, 40.57; H, 3.40; N, 6.76. Found: C, 40.93; H, 3.44; N, 6.81.

(3*R*,7*R*)-1,3-Dibenzyl-3,4,5,6,7,7-hexahydrobenzoimidazol-1-ium-2-dithiocarboxylate (8)

(1*R*,2*R*)-*N*,*N*-Dibenzylcyclohexane-1,2-diamine (**7**; 3 g, 10.2 mmol) was heated in the presence of DMF dimethylacetal (8.5 mL, 61.1 mmol) at 100 °C in a distillation set in order to remove MeOH and Me_2NH formed during the reaction. After 2 d, the temperature was raised to 115 °C and after slow evaporation, the mixture was dried overnight under vacuum at r.t. Thereafter, xylene (7.5 mL) and CS_2 (6 mL, 99.3 mmol) were added. After 45 min heating at 140 °C, the mixture was evaporated and the red solid was washed with hexane (20 mL) (1.45 g, 3.82 mmol, 38%); mp 209 °C; $[\alpha]_D^{22}$ +288 (*c* = 1.09, $CHCl_3$).

IR (KBr): 3423, 2945, 1521, 1454, 1365, 1261, 1065, 1047, 755, 713, 696 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.55–7.52 (m, 4 H, C_6H_5), 7.42–7.33 (m, 6 H, C_6H_5), 4.82 (d, *J* = 15.5 Hz, 2 H, NCH_2Ph), 4.65 (d, *J* = 15.5 Hz, 2 H, NCH_2Ph), 3.29–3.18 (m, 2 H, 2 NCH), 1.94–1.73 (m, 4 H, 2 $NCHCH_2$), 1.32–1.11 (m, 4 H, 2 $NCHCH_2CH_2$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 225.9 (CS_2), 169.9 (CN_2), 134.0 (C_6H_5), 128.9 (C_6H_5), 128.5 (C_6H_5), 66.9 (NCH_2Ph), 50.2 (NCH), 28.3 ($NCHCH_2$), 23.9 ($NCHCH_2CH_2$).

MS (EI): *m*/*z* (%) = 379 (M^+, 18), 289 (34), 106 (33), 91 (100).

Anal. Calcd for $C_{22}H_{24}N_2S_2$: C, 69.43; H, 6.36; N, 7.36. Found: C, 69.06; H, 6.39; N, 7.56.

(3*R*,7*R*)-1,3-Dibenzyl-2-(methylthiocarbonothioyl)-3,4,5,6,7,7-hexahydrobenzoimidazol-1-ium Iodide (9)

MeI (0.5 mL, 8 mmol) was added to **8** (200 mg, 0.525 mmol) in MeCN (4 mL) to give after 16 h, a very deep red solution. The solvent was removed and the obtained crude product was washed with Et_2O (10 mL) to give the expected product as a red solid (252 mg, 0.483 mmol, 92%); mp 87 °C; $[\alpha]_D^{22}$ –103 (*c* = 1.06, $CHCl_3$).

IR (KBr): 3423, 2938, 2859, 1547, 1453, 1264, 1098, 1030, 695 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.47–7.39 (m, 10 H, C_6H_5), 4.83 (br s, 5 H, NCH_2Ph, NCH), 3.55 (br s, 1 H, NCH), 2.86 (s, 3 H, SCH_3), 1.96–1.64 (m, 4 H, 2 $NCHCH_2CH_2$), 1.40–1.05 (m, 4 H, $NCHCH_2CH_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 208.7 (CS_2), 167.2 (CN_2), 130.7 (C_6H_5), 129.2 (C_6H_5), 128.9 (C_6H_5), 127.8 (C_6H_5), 68.7 (NCH_2Ph), 51.0 (NCH), 28.7 ($NCHCH_2CH_2$), 27.3 ($NCHCH_2CH_2$), 23.8 ($NCHCH_2CH_2$), 20.8 (SCH_3).

MS (ESI, 0 V): *m*/*z* = 395 (M^+, 100%).

Anal. Calcd for $C_{23}H_{27}N_2S_2$: C, 52.87; H, 5.21; N, 5.36. Found: C, 52.33; H, 5.23; N, 4.95.

(3*R*,7*R*)-1,3-Dibenzyl-2-(methylthiocarbonothioyl)-3,4,5,6,7,7-hexahydrobenzoimidazol-1-ium Hexafluorophosphate (10)

An anion metathesis was carried out on **9** (274 mg, 0.525 mmol) in CH_2Cl_2 (5 mL) with a solution of KPF_6 (126 mg, 0.68 mmol) in H_2O (5 mL). After stirring vigorously for 30 min, the organic phase was washed with H_2O (3 × 5 mL) and dried (MS 3 Å) to give the desired product as a red solid (251 mg, 0.46 mmol, 88%); mp 74 °C; $[\alpha]_D^{22}$ +62 (*c* = 1.05, $CHCl_3$).

IR (KBr): 3431, 2945, 1550, 1455, 1267, 838 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.41–7.29 (m, 10 H, C_6H_5), 4.71 (br s, 4 H, NCH_2Ph), 4.24 (br s, 1 H, NCH), 3.45 (br s, 1 H, NCH), 2.87 (s, 3 H, SCH_3), 1.93–1.67 (m, 4 H, 2 $NCHCH_2CH_2$), 1.32–1.04 (m, 4 H, $NCHCH_2CH_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 208.3 (CS_2), 166.7 (CN_2), 132.1 (C_6H_5), 129.3 (C_6H_5), 129.0 (C_6H_5), 127.7 (C_6H_5), 68.4 (NCH_2Ph), 50.4 (NCH), 28.6 ($NCHCH_2CH_2$), 27.5 ($NCHCH_2CH_2$), 23.7 ($NCHCH_2CH_2$), 20.2 (SCH_3).

MS (ESI, 0 V): *m*/*z* = 395 (M^+, 100%).

Anal. Calcd for $C_{23}H_{27}F_6N_2PS_2$: C, 51.10; H, 5.03; N, 5.18. Found: C, 51.21; H, 5.35; N, 5.11.

(3*R*,7*R*)-1,3-Dibenzyl-2-(methylthiocarbonothioyl)-3,4,5,6,7,7-hexahydrobenzoimidazol-1-ium Bis(trifluoromethylsulfonyl)amide (11)

An anion metathesis was performed with **9** (100 mg, 0.191 mmol) in CH_2Cl_2 (5 mL) with a solution of $LiNTf_2$ (113 mg, 0.393 mmol) in H_2O (5 mL). After stirring vigorously for 30 min, the organic phase was washed with H_2O (3 × 5 mL) and dried (MS 3 Å) to give the desired product as a red solid (126 mg, 0.187 mmol, 98%); mp 109 °C; $[\alpha]_D^{22}$ +50 (*c* = 1.185, $CHCl_3$).

IR (KBr): 3441, 2950, 1556, 1348, 1191, 1134, 1057 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 7.41–7.29 (m, 10 H, C_6H_5), 4.67 (br s, 4 H, NCH_2Ph), 4.09 (br s, 1 H, NCH), 3.48 (br s, 1 H, NCH), 2.88 (s, 3 H, SCH_3), 1.97–1.61 (m, 4 H, 2 $NCHCH_2CH_2$), 1.35–1.05 (m, 4 H, $NCHCH_2CH_2$).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 208.1 (CS_2), 166.8 (CN_2), 132.2 (C_6H_5), 129.3 (C_6H_5), 129.1 (C_6H_5), 127.7 (C_6H_5), 120.2 (q, *J* = 319 Hz, CF_3), 68.6 (NCH_2Ph), 50.5 (NCH), 28.5 ($NCHCH_2CH_2$), 27.7 ($NCHCH_2CH_2$), 23.6 ($NCHCH_2CH_2$), 20.2 (SCH_3).

MS (ESI, 0 V): *m*/*z* = 395 (M^+, 100%).

Anal. Calcd for $C_{25}H_{27}F_6N_3O_4S_4$: C, 44.43; H, 4.03; N, 6.22. Found: C, 44.59; H, 4.19; N, 6.40.

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