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Identification of the [1,3]dithiolo[4,5-*d*]dithiazolyl radical

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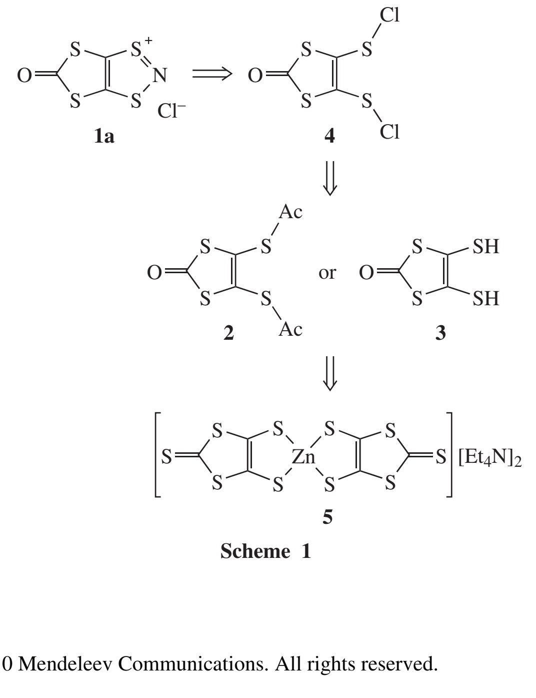
The synthesis of 5-oxo[1,3]dithiolo[4,5-*d*][1,3,2]dithiazol-1-ium chloride 1a from easily available zink chelate, TEA[Zn(DMIT)$_2$], has been developed; salt 1a has been converted to the first representative of [1,3]dithiolo[4,5-*d*]dithiazolyl radical, which was identified by EPR and CV data.

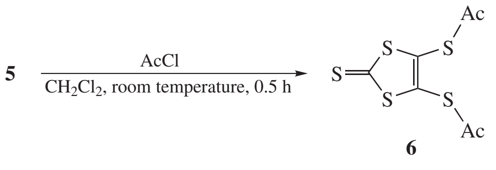
The 1,3,2-dithiazolyl radicals have received considerable attention in recent years as building blocks for the construction of both conducting and magnetic materials.[1] Together with some benzo[1,3,2]dithiazolyls several heterocyclic fused 1,3,2-dithiazolyl radicals, including quinolino,[2] 1,2,5-thiadiazolo,[3] thieno,[4] pyrazino[5] and pyridino[6] derivatives have been prepared. The most interesting physical properties have been achieved for 1,3,2-dithiazole condensed with 1,2,5-thiadiazole – the stable 1,3,5-trithia-2,4,6-triazapentalenyl radical.[7] As a rule, the crucial precursors for the synthesis of 1,3,2-dithiazolyl radicals are corresponding 1,3,2-dithiazolium salts. Here we report the synthesis of 5-oxo[1,3]dithiolo[4,5-*d*][1,3,2]dithiazol-1-ium salts and first identification of 5-oxo[1,3]dithiolo[4,5-*d*][1,3,2]dithiazol-1-yl radical.

The retrosynthetic analysis for ketone **1a** led us to a conclusion that the most reliable starting material would be *S*,*S*′-(2-oxo-1,3-dithiole-4,5-diyl) diethanethioate **2** (Scheme 1). Another possible precursor, 4,5-dimercapto-1,3-dithiol-3-one **3**, probably will be unstable as the corresponding thione derivative, 4,5-dimercapto-1,3-dithiole-3-thione.[8] In its turn 1,3-dithiole **2** could be prepared from easily available and stable zink chelate, TEA[Zn(DMIT)$_2$] **5**.[8]



Scheme 1

The reaction of zinc chelate **5** with acetyl chloride afforded previously unknown diacetyl derivative **6** in high yield (Scheme 2).†



Scheme 2

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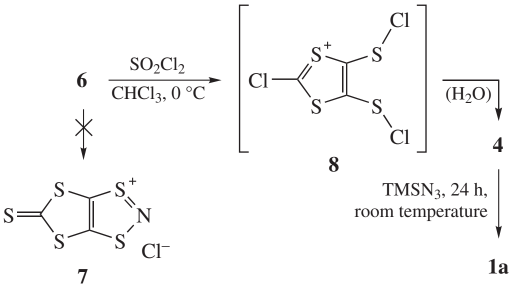
† *S,S′-(2-Thioxo-1,3-dithiole-4,5-diyl) diethanethioate* **6**. Acetyl chloride (2.4 ml, 30 mmol) was added dropwise to the solution of salt **5** (2.1 g, 3 mmol) in dichloromethane (30 ml) at 0 °C under argon. The reaction mixture was stirred at this temperature for 1.5 h and at room temperature for 2.5 h and poured into water (100 ml). The organic phase was separated, washed with H$_2$O, dried with Na$_2$SO$_4$ and evaporated. The residue was crystallized from hot hexane. Yield, 89%. Yellow solid, mp 78–80 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 2.45 (s, 6H, 2Me). ^{13}C NMR (75.5 MHz, CDCl$_3$) δ: 30.1 (2Me), 133.1 (two tertiary C_{sp^2}), 189.2 (C=O), 211.9 (C=S). MS (EI, 70 eV), *m*/*z* (%): 282 (M$^+$, 65), 240 (90), 198 (90), 122 (20), 88 (80), 76 (100), 64 (20), 44 (90). IR (KBr, ν/cm^{-1}): 3412 (C–H), 1716 (C=O). Found (%): C, 29.68; H, 2.21; S, 56.58. Calc. for C$_7$H$_6$O$_2$S$_5$ (%): C, 29.77; H, 2.14; S, 56.76.

S,S′-(2-Oxo-1,3-dithiole-4,5-diyl) diethanethioate **2**. Mercury(II) acetate (16 g, 50 mmol) was added to the solution of thione **6** (8.0 g, 37 mmol) in dichloromethane (100 ml) under argon. The reaction mixture was stirred at room temperature for 2 h, filtered and evaporated. The residue was crystallized from hot hexane. Yield, 67%. Colourless solid, mp 60–62 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 2.43 (s, 6H, 2Me). ^{13}C NMR (75.5 MHz, CDCl$_3$) δ: 30.0 (2Me), 125.5 (two tertiary C_{sp^2}), 189.6 (C=O), 189.9 (C=O). MS (EI, 70 eV), *m*/*z* (%): 266 (M$^+$, 5), 224 (60), 182 (5), 88 (10), 76 (20), 64 (5), 43 (100). IR (KBr, ν/cm^{-1}): 3420 (C–H), 1728 and 1668 (C=O). Found (%): C, 31.43; H, 2.37; S, 47.91. Calc. for C$_7$H$_6$O$_3$S$_4$ (%): C, 31.56; H, 2.27; S, 48.15.

*5-Oxo[1,3]dithiolo[4,5-*d*][1,3,2]dithiazol-1-ium chloride* **1a**. Sulfuryl chloride (0.31 ml, 3.8 mmol) was added dropwise to the solution of ketone **2** (0.5 g, 1.9 mmol) in dry acetonitrile (15 ml) at 0 °C under argon. The reaction mixture was stirred at this temperature for 1.5 h, and at 10 °C trimethylsilyl azide (0.37 ml, 2.8 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 1 h. The precipitate was filtered off, washed with MeCN (3×20 ml) and dried under reduced pressure. Yield, 85%. Yellow solid, mp 217–219 °C (decomp.). MS (EI, 70 eV), *m*/*z* (%): 229 (M$^+$, 5), 194 (15), 166 (20), 88 (60), 78 (55), 64 (25), 46 (100). IR (KBr, ν/cm^{-1}): 1688 (C=O). Found (%): C, 15.75; H, 6.13. Calc. for C$_3$ClNOS$_4$ (%): C, 15.68; N, 6.10.

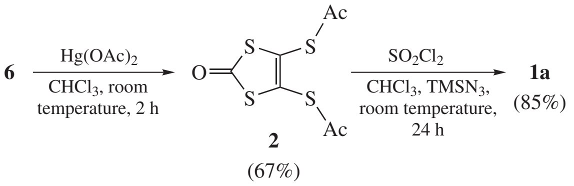
Thione **6** can be considered as an excellent intermediate for the synthesis of salt **7**, but when we treated it with sulfuryl chloride at 0 °C followed by addition of trimethylsilyl azide salt **1a** was unexpectedly formed in low yield (Scheme 3).



Scheme 3

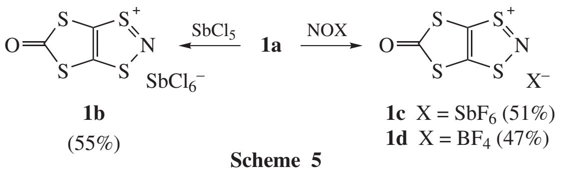
Apparently, the thione group in compound **6** is sensitive to chlorinating agents[8] to produce salt **8**, which may hydrolyze by water traces to ketone **4** with further reaction with trimethylsilyl azide to give salt **1a**.

To find the more rational way for the synthesis of salt **1a** and to improve the yield, we treated thione **6** with mercury(II) acetate in chloroform and isolated ketone **2** in good yield. Its reaction with trimethylsilyl azide afforded salt **1a** (Scheme 4).



Scheme 4

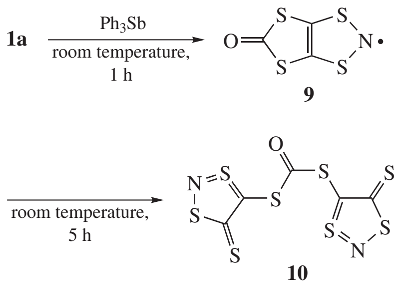
The structure of salt **1a** has been proved by elemental analysis, mass spectrometry and IR spectroscopy. This salt is insoluble in most of organic solvents. To obtain more soluble salts **1**, the exchange reactions of **1a** were investigated. The treatment of salt **1a** with antimony(V) chloride in chloroform afforded hexachloroantimonate **1b**, with nitrosonium hexafluoroantimonate and tetrafluoroborate, salts **1c** and **1d**, respectively (Scheme 5).[‡]



Scheme 5

Salts **1b–d** are soluble in organic solvents such as chloroform and acetonitrile, and their structures have also been confirmed by ^{13}C NMR spectroscopy.

Cyclic voltammetry (CV) studies of salt **1d** in acetonitrile showed a single quasi-reversible reduction peak at +0.095 V at room temperature, which is referred to one electron transfer and formation of radical **9** (Figure 1, Scheme 6). Its lifetime is sufficient to fix its formation on CV curve at the sweep speed of 0.1 V s^{-1}. However, after electrolysis at the controlled potential of +0.001 V, radical **9** was not detected in the catholyte, and the new peak at –0.35 V emerged (Figure 1, curves *2* and *3*). The same peak was received for compound **10** with the formula $C_5N_2OS_8$, which is the decomposition product of radical **9** (Scheme 6). According to the CV investigations, decomposition of radical **9** includes few fast steps through unstable intermediates (peaks at potentials of > +0.40 V), which is impossible to identify due to high speed of their transformations.



Scheme 6

Reduction of salt **1a** with triphenylantimony in degassed acetonitrile leads to a blue precipitate, which gave rise to the EPR spectrum of radical **9**, practically identical to the simulated spectrum with the same hyperfine coupling to the dithiazolyl ring nitrogen (Figure 2). After refluxing the reaction mixture for 4 h, the radical signal disappeared and a new violet compound with the formula $C_5N_2OS_8$ was isolated. On the grounds of elemental analysis and IR spectra, we have assigned to this compound the structure of bis(1,3,2-dithiazole-4-thione) **10**. Reduction of salt **1a** with sodium dithionite or copper powder in acetonitrile was also unsuccessful, but radical **9** has been detected by EPR spectroscopy.[§]

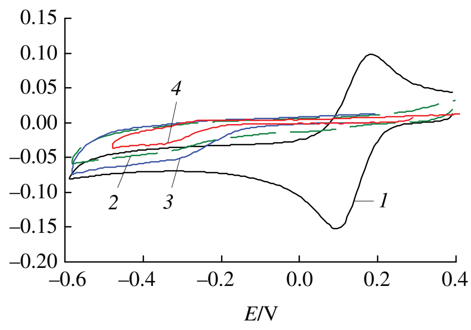


Figure 1 Cyclic voltammograms: (*1*) salt **1d** (1.6×10^{-3} M) in MeCN using 0.1 M Bu_4NBF_4 from 0.40 to –0.60 V; (*2*) after reduction on Pt electrode at +0.001 V; (*3*) after 1 h; (*4*) $C_5N_2OS_8$. Potentials were measured relative to a saturated calomel electrode.

[‡] *5-Oxo[1,3]dithiolo[4,5-*d*][1,3,2]dithiazol-1-ium salts* **1b–d**. The corresponding reagent (0.24 mmol) was added to a slurry of salt **1a** (50 mg, 0.22 mmol) in degassed chloroform (7 ml) at 0 °C under argon. The reaction mixture was stirred at this temperature for 1.5 h, and at 10 °C trimethylsilyl azide (0.37 ml, 2.8 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 10 h, the precipitate was filtered off and washed with cold degassed $CHCl_3$ (2×5 ml), dried and treated with degassed MeCN (2×10 ml), filtrate combined was evaporated under reduced pressure at the temperature < 30 °C.

*5-Oxo[1,3]dithiolo[4,5-*d*][1,3,2]dithiazol-1-ium hexachloroantimonate* **1b**. Yield, 55%. Yellow solid, mp 172–174 °C (decomp.). ^{13}C NMR (75.5 MHz, [$^2H_6$]acetone) δ: 173.5 (C=O); 188.9 (one tertiary C_{sp^2}). MS (EI, 70 eV), *m/z* (%): 230 ([$SbCl_3$]$^+$, 25), 191 (40), 156 (25), 121 (85), 88 (10), 64 (25), 48 (35), 35 (100). IR (KBr, ν/cm^{-1}): 1732 (C=O). Found (%): C, 7.20; N, 2.65. Calc. for $C_3Cl_6NOS_4Sb$ (%): C, 6.81; N, 2.65.

*5-Oxo[1,3]dithiolo[4,5-*d*][1,3,2]dithiazol-1-ium hexafluoroantimonate* **1c**. Yield, 51%. Yellow solid, mp 140–142 °C (decomp.). ^{13}C NMR (75.5 MHz, [$^2H_6$]acetone) δ: 173.5 (C=O), 188.8 (one tertiary C_{sp^2}). MS (EI, 70 eV), *m/z* (%): 194 ([M_{cat}]$^+$, 5), 166 (15), 88 (25), 78 (25), 64 (50), 46 (100). IR (KBr, ν/cm^{-1}): 1720 (C=O). Found (%): C, 8.38; N, 3.26; S, 29.82. Calc. for $C_3F_6NOS_4Sb$ (%): C, 8.25; N, 3.23; S, 29.71.

*5-Oxo[1,3]dithiolo[4,5-*d*][1,3,2]dithiazol-1-ium tetrafluoroborate* **1d**. Yield, 47%. Yellow solid, mp 147–149 °C (decomp.). ^{13}C NMR (75.5 MHz, [$^2H_6$]acetone) δ: 173.3 (C=O), 188.8 (one tertiary C_{sp^2}). MS (EI, 70 eV), *m/z* (%): 213 ([M_{cat} + F]$^+$, 5), 194 ([M_{cat}]$^+$, 5), 166 (55), 88 (25), 78 (20), 64 (50), 49 ([BF_2]$^+$, 100). IR (KBr, ν/cm^{-1}): 1680 (C=O). Found (%): C, 12.30; N, 5.17. Calc. for $C_3BF_4NOS_4$ (%): C, 12.82; N, 4.98.

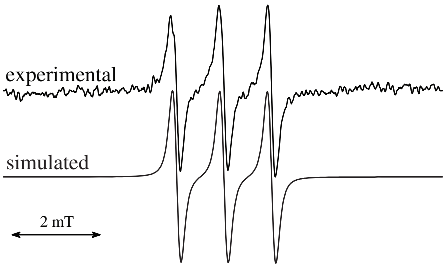


Figure 2 EPR spectrum of radical **9** in MeCN and its comparison with the simulated spectrum. The following simulation parameters have been used: isotropic *g*-tensor value $g_{\mathrm{iso}} = 2.0060$ and isotropic hyperfine constant $A_{\mathrm{iso}} = 1.08$ mT, Lorentzian linewidth is 0.27 mT.

[§] *5-({[(4-Sulfanylidene-4*H*-1λ^4,3,2-dithiazol-5-yl)sulfanyl]carbonyl}sulfanyl)-4*H*-1λ^4,3,2-dithiazole-4-thione* **10**. Triphenylantimony (108 mg, 0.3 mmol) was added to a slurry of salt **1a** (138 mg, 0.6 mmol) in degassed MeCN (7 ml) at 0 °C under argon. The reaction mixture was stirred at room temperature for 1 h, blue precipitate was filtered off, washed with abs. MeCN and dried. This precipitate gave rise to the EPR spectrum of the radical **9** shown in the Figure 2. If the reaction mixture was refluxed for 4 h, the new precipitate **10** was formed. Yield, 66%. Violet solid, mp 154–156 °C (decomp.). IR (KBr, ν/cm^{-1}): 1680 (C=O), 1640, 1420, 1320, 1250, 1120, 1070, 950, 750. Found (%): C, 16.83; N, 7.80; S, 69.89. Calc. for $C_5N_2OS_8$ (%): C, 16.65; N, 7.77; S, 71.14.

The X-band EPR spectrum was acquired on a Bruker ElexSys E500 spectrometer equipped with an ER049X microwave bridge and an SHQ cavity. Radical **9** was dissolved in dry acetonitrile (5 mmol dm^{-3}), and the EPR spectrum was recorded immediately without removing oxygen from the sample. The following parameters were used: microwave frequency, 9.878 GHz; microwave power, 6.325 mW; modulation frequency, 100 kHz; modulation amplitude, 0.1 mT (determined by microwave saturation test); conversion time, 81.92 ms; time constant, 20.48 ms; resolution, 1024 points. The solution of TEMPO in dry toluene was used as a reference sample ($g = 2.0060$). The spectra simulation was performed with the EasySpin package[9] using the simulation routine for isotropic fast-motional spectra and taking into account the hyperfine coupling with a nitrogen atom.

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