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Synthesis of a New Tellurium Heterocycle, *5H,7H*-Dibenzo[*b,g*][1,5]tellurathiocin, and Isolation and Reactivity of Its Tellurathia Dication Salt

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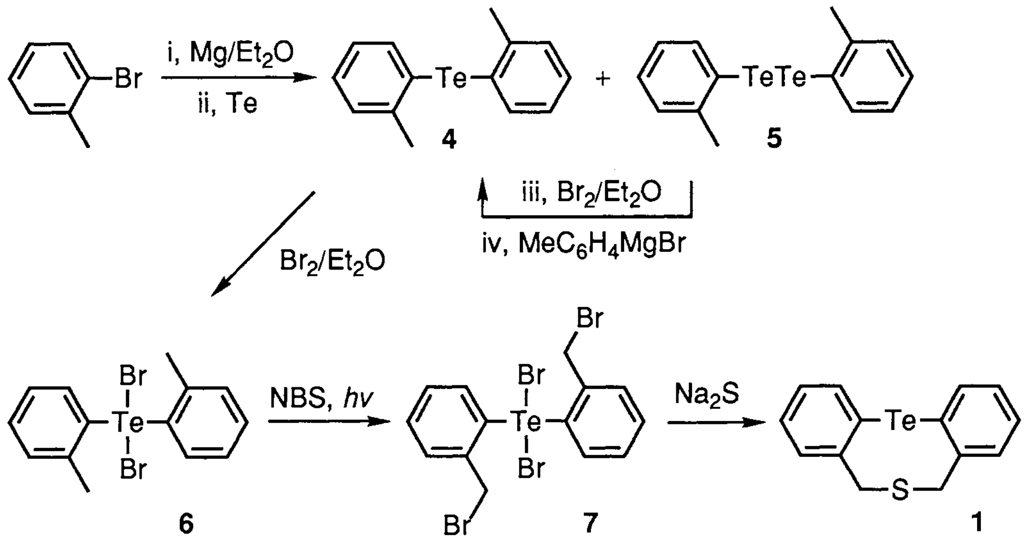
A new heterocycle containing tellurium and sulfur atoms, *5H,7H*-dibenzo-[*b,g*][1,5]tellurathiocin (**1**), has been synthesized. The transannular bond formation between tellurium and sulfur atoms was found in the reaction of **1** with concd H_2SO_4 by ^1H, ^{13}C, and ^{125}Te NMR spectroscopy. Two-electron oxidation of **1** with 2 equiv. of $NOPF_6$ gave the tellurathia dication salt **3** ($>Te^+-S^+<\ 2PF_6^-$) which acts as an oxidizing agent.

There is considerable interest on the transannular interaction or bond formation (*e.g.*, dication formation) between heteroatoms in medium-sized heterocyclic compounds containing nitrogen and/or sulfur atoms.[1-3] In contrast, the properties of medium-sized tellurium heterocycles are not well explored. Herein we describe the synthesis and the conformational properties of a new eight-membered ring tellurium heterocycle, *5H,7H*-dibenzo[*b,g*][1,5]tellurathiocin (**1**), and the first example of the dication containing a transannular Te-S bond in **1**. Dications consisting of two different positively charged heteroatoms have received less attention.[2b]

Compound **1** was synthesized as described in Scheme 1. Bis(2-methylphenyl)telluride (**4**) was obtained by the reaction of 2-methylphenylmagnesium bromide with tellurium.[4,5] Treatment of the telluride **4** with bromine in Et_2O gave bis(2-methylphenyl)tellurium dibromide (**6**) which was irradiated using a high-pressure mercury lamp after addition of *N*-bromosuccinimide (NBS) in CCl_4 to afford a tetra-bromide **7**.[5] Compound **7** (2.59 g, 4.13 mmol) in CH_2Cl_2 (100 mL) was treated with $Na_2S\cdot 9H_2O$ (2.18 g, 9.08 mmol) in EtOH (300 mL) using a high dilution technique at room temperature under an Ar atmosphere. The mixture was stirred at room temperature overnight. After usual work-up, the crude product was purified by silica-gel column chromatography (eluent, hexane/$CHCl_3$) to give **1**,[5] which was recrystallized from $CHCl_3$. Thus, the dibromide of tetracoordinated tellurium compound **7** was reduced to the telluride by Na_2S.

With regard to the conformational properties of **1**, the chair and the boat forms can exist.[6,7] The conformers can be assigned by the ^1H NMR spectral data for benzylic protons of the eight-membered ring.[6] The ^1H NMR (400 MHz) spectrum of **1** in $CDCl_3$ at 25 °C shows the benzylic methylene protons as a broad singlet at δ 3.66. At -50 °C, this resonance is split into two, at δ 3.49 and 3.81 (ABq, J=14 Hz), and at δ 4.13 and 4.95 (ABq, J=14 Hz); the former resonance is assigned to the boat form (75%), and the latter pair to the chair form (25%). These conformers can also be characterized by ^{125}Te NMR spectroscopy;[8] the ^{125}Te NMR spectrum of **1** in $CHCl_3$ at 25 °C shows a somewhat broad peak at δ 507.5 which becomes two singlet

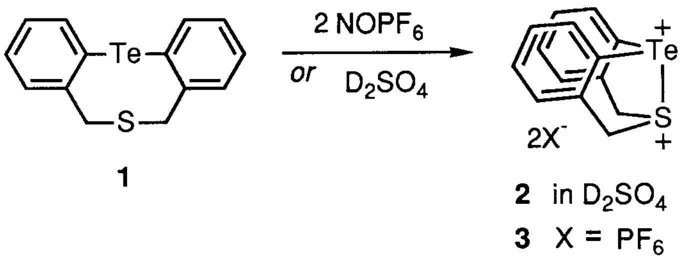


Scheme 1.

peaks at δ 493.5 (boat) and 528.3 (chair) at -50 °C, the ratio of the conformers being consistent with that obtained from the ^{1}H NMR spectrum. Analogous result was found in the ^{13}C NMR ($CDCl_3$) spectrum of **1** which shows two peaks at δ 34.1 and 44.5 for the methylene carbon atoms at -50 °C.

Dissolution of the tellurathiocin **1** in concd D_2SO_4 (98%)[9] at room temperature led to the formation of the transannular bond between tellurium and sulfur atoms, the dication **2**, as determined by the ^{1}H, ^{13}C, and ^{125}Te NMR spectroscopy; *i.e.*, the methylene proton signals of **1** in $CDCl_3$ disappeared and new AB quartet peaks appeared at δ 4.32 and 4.70 (J=16 Hz) in concd D_2SO_4, and the signal of the methylene carbon atoms shifted to 41.9 ppm from 38.4 ppm (**1** in $CDCl_3$ at 25 °C), while the ^{125}Te NMR spectrum showed a marked downfield shift at 1381.3 ppm as a singlet peak. These spectroscopic data indicate that **2** is a single conformer, boat form, in D_2SO_4 solution (Scheme 2) [**2**: ^{1}H; δ 4.32, 4.70 (ABq, J=16 Hz, 4H, CH_2), 7.18-7.24 (m, 6H, ArH), and 7.57-7.59 (m, 2H, ArH); ^{13}C; δ 41.9, 123.2, 127.3, 129.1, 129.9, 130.9, and 137.8]. This finding is quite different from that of the bis-sulfide analogue of **1**, 5*H*,7*H*-dibenzo[*b*,*g*][1,5]-dithiocin (**12**), *i.e.*, the ^{1}H and ^{13}C NMR spectra of its D_2SO_4 solution showed complex signals due to the instability of **12** in D_2SO_4. This result suggests that the cationic species of **1** is more stabilized by transannular bond between tellurium and sulfur atoms as compared with that of **12**.[10]

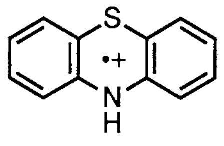
The dication of **1** was isolated as its PF_6^- salt by the two-electron oxidation of **1** with a one-electron-oxidizing agent, nitrosyl hexafluorophosphate, $NOPF_6$ (Scheme 2). A solution of $NOPF_6$ (125 mg, 0.71 mmol) in anhydrous CH_3CN (10 mL) was added to **1** (111 mg, 0.33 mmol) in anhydrous CH_2Cl_2 (50 mL) at -78 °C. The solution was stirred at 0 °C for 4.5 h. A white precipitate was formed. Evolution of NO gas was observed during the reaction. Upon filtration under anhydrous conditions and recrystallization from anhydrous CH_3CN-Et_2O, the dication **3** was obtained as a remarkably stable white solid, mp 165-167 °C (decomp).[11]



Scheme 2.

The dication salt **3** was characterized by spectroscopic and chemical means. The ^{1}H NMR (400 MHz) spectrum of **3** in CD_3CN exhibits absorptions at δ 4.54, 4.87 (ABq, *J*=16.7 Hz, 2H, CH_2), 4.55, 4.88 (ABq, *J*=16.7 Hz, 2H, CH_2), 7.53-7.62 (m, 6H,.ArH), and 7.95-7.98 (m, 2H, ArH). Its ^{1}H-^{1}H COSY spectrum established the relation of methylene protons in two sets of AB quartet suggesting that the conformer was fixed as an unsymmetric distorted boat form by the transannular Te-S bond. The ^{13}C NMR spectrum of **3** in CD_3CN shows peaks at δ 41.9, 130.0, 130.1, 131.0, 131.1, 132.0, and 140.6. The ^{31}P NMR spectrum of the PF_6^- anion of **3** in CD_3CN shows a phosphorus absorption at δ -149.0 (sept, J_{PF}=707 Hz; relative to H_3PO_4), in the region of ionic PF_6^-.

Interestingly, a solution of **3** in D_2O-CD_3CN was followed by NMR spectroscopy and no significant changes were observed over several hours, in which its spectrum is analogous to that of the dication **2** in D_2SO_4; especially two sets of AB quartet peaks became to one set of AB system. In contrast to **3**, disulfide dications were easily hydrolyzed to the corresponding *S*-oxides.[2,3)]



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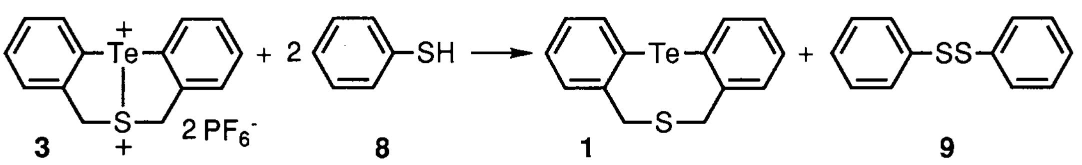
The reactivity of the tellurathia dication salt **3** was examined as follows. Treatment of benzenethiol (**8**) (2 equiv.) with **3** (1 equiv.) in CH_3CN under an Ar atmosphere at room temperature for 9 h afforded diphenyl disulfide (**9**) (93%) as the oxidation product and the tellurathiocin **1** (84%) as the reduction product (Scheme 3). Phenothiazine (**10**) was oxidized to its cation radical **11** with **3** as evidenced from the UV-visible spectrum which exhibits absorptions at λ_{max} = 439 and 516 nm in CH_3CN (lit.[12)] λ_{max} = 437 and 515 nm), since the oxidation potential of **10** is lower than that of the dication precursor.[10)] Thus, the dication **3** acts as an oxidant. However the reactivity of the dication of **12** was unknown, because it could not be isolated as a stable salt.



Scheme 3.

The results described herein show a new type of heteroatom dication stabilized by transannular bond between tellurium and sulfur atoms, although dications consisting of *two different positively charged heteroatoms* are quite rare.

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3) H. Fujihara, J.-J. Chiu, and N. Furukawa, *J. Am. Chem. Soc.*, **110**, 1280 (1988); H. Fujihara and N. Furukawa, *J. Mol. Struct. (Theochem)*, **186**, 261 (1989), and references cited therein.
4) This reaction gave also bis(2-methylphenyl)ditelluride (**5**) which was converted into the telluride **4** upon treatment with Br_2 followed by adding 2-methylphenylmagnesium bromide in Et_2O (Scheme1).
5) Compounds **1**: Mp 154-155 °C; ^1H NMR ($CDCl_3$) δ 3.66 (br s, 4H, CH_2) and 7.00-7.85 (m, 8H, ArH);[7] MS, *m/z* 342 (M^+). Anal. Found: C, 49.51; H, 3.21%. Calcd for $C_{14}H_{12}STe$: C, 49.47; H, 3.56%. **4**: ^1H NMR ($CDCl_3$) δ 2.42 (s, 6H, CH_3), 6.95 (t, *J*=7.4 Hz, 2H, ArH), 7.20 (t, *J*=7.4 Hz, 2H, ArH), 7.25 (d, *J*=7.4 Hz, 2H, ArH), and 7.48 (d, *J*=7.4 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 26.2, 118.4, 126.8, 128.4, 129.4, 138.2, and 142.6; MS, *m/z* 311 (M^+). Anal. Found: C, 54.43; H, 4.47%. Calcd for $C_{14}H_{14}Te$: C, 54.27; H, 4.55%. **6**: Mp 185.0-185.5 °C; ^1H NMR ($CDCl_3$) δ 2.83 (s, 6H, CH_3), 7.36-7.49 (m, 6H, ArH), and 7.90-7.92 (m, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 24.6, 127.9, 131.6, 131.8, 134.3, 135.2, and 140.4. Anal. Found: C, 35.76; H, 3.22%. Calcd for $C_{14}H_{14}Br_2Te$: C, 35.80; H, 3.00%. **7**: Mp 207.5 °C (decomp); ^1H NMR ($CDCl_3$) δ 5.21 (s, 4H, CH_2), 7.43-7.55 (m, 6H, ArH), and 8.02-8.05 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ 33.4, 130.2, 131.4, 132.0, 135.6, 138.0, and 140.7. Anal. Found: C, 26.77; H, 1.85%. Calcd for $C_{14}H_{12}Br_4Te$: C, 26.80; H, 1.93%.
6) R. P. Gellatly, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc., Perkin Trans. 1*, **1976**, 913; L. E. Brieaddy, B. S. Hurlbert, and N. B. Mehta, *J. Org. Chem.*, **46**, 1630 (1981).
7) The protons and carbons of the aromatic rings in the NMR spectra (400 MHz-^1H and 100 MHz-^{13}C) of **1** show two sets of signals due to the existence of two conformers; the detailed analysis will be reported elsewhere.
8) The ^{125}Te chemical shifts are relative to Me_2Te. The conformers were assigned by the integration of the tellurium peaks.
9) Concd H_2SO_4 acts either as an oxidant or as a strong acid: A. J. Bard, A. Ledwith, and H. J. Shine, *Adv. Phys. Org. Chem.*, **12**, 155 (1976).
10) The oxidation potentials (Ep *vs.* Ag/0.01 M $AgNO_3$) are +0.41 V for **1** and +0.90 V for **12**, indicating that **1** can be oxidized more readily than **12**.
11) Dication salt **3**: Anal. Found: C, 26.88; H, 1.83%. Calcd for $C_{14}H_{12}F_{12}P_2STe$: C, 26.70; H, 1.92%.
12) C. Bodea and I. Silberg, *Adv. Heterocycl. Chem.*, **9**, 321 (1968).

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