Transannular Te−S Interaction in a New Tellurium Heterocycle, 5*H*,7*H*-Dibenzo[*b*,*g*][1,5]tellurathiocin

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A new heterocycle containing tellurium and sulfur atoms, 5*H*,7*H*-dibenzo[*b*,*g*][1,5]-tellurathiocin (**1**), has been synthesized. The chair and the boat forms of **1** can be characterized by ^{1}H, ^{13}C, and ^{125}Te NMR spectroscopy. A transannular bond between the tellurium and sulfur atoms was found in the reaction product of **1** with concentrated H_2SO_4 by ^{1}H, ^{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. The reaction of 12-oxo-5*H*,7*H*-dibenzo[*b*, *g*][1,5]tellurathiocin (**8**) with acetic anhydride afforded a 12,12-diacetoxy-substituted tellurane (**16**). Heating of a benzene solution of **16** gave a remote α-acetoxylated sulfide **18** and the parent 5*H*,7*H*-dibenzo[*b*, *g*][1,5]tellurathiocin (**1**). Reaction of tellurathiocin **1** with *t*-BuOCl gave exclusively its telluroxide **8**. Tellurathiocin **1** was reacted with Br_2 to give a 12,12-dibromo-substituted tellurane (**25**). Reaction of the tellurane **25** with aqueous NaOH gave the telluroxide **8** selectively, and variable-temperature ^{1}H NMR studies revealed that the telluroxide **8** was fixed in boat form. The ^{125}Te and ^{77}Se NMR spectra of 12-oxo-5*H*,7*H*-dibenzo[*b*,*g*][1,5]telluraselenocin (**28**) show a strong transannular interaction between the tellurium and selenium atoms.

Introduction

There has been considerable interest in 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 have not been well explored. We have reported the conformational properties of a new eight-membered-ring tellurium heterocycle, 5*H*,7*H*-dibenzo-[*b*, *g*][1,5]tellurathiocin (**1**), and the dication derived from it that contains a transannular Te−S bond.[4] Dications containing two different positively charged heteroatoms have received less attention.[2b] Furthermore, the preparation and structure of hypervalent organochalcogen compounds are of considerable current interest.[5,6] In particular, the synthesis and properties of various sulfuranes and selenanes have been extensively studied. However, the reactivity of tetracoordinated tellurium compounds has received less attention.[6] We have found that the reaction of 12-oxo-5*H*,7*H*-dibenzo[*b*, *g*][1,5]tellurathiocin (**8**) with acetic anhydride gave the 12,12-diacetoxy-substituted tellurane **16**, which led to the corresponding remote α-acetoxylated sulfide **18** and the tellurathiocin **1** on heating.[7] This paper reports the transannular Te−S interaction in tellurathiocin **1** and a new reaction mode for the group transfer from tellurane induced by transannular interaction. The selective oxidation of an eight-membered tellurium heterocycle, 5*H*,7*H*-dibenzo[*b*, *g*][1,5]tellurathiocin (**1**), to its telluroxide **8** via its tellurane and the conformational analysis of telluroxide **8** also are discussed.

Results and Discussion

Synthesis of 5*H*,7*H*-Dibenzo[*b*,*g*][1,5]tellurathiocin (1). Compound **1** was synthesized as described in Scheme 1. Bis(2-methylphenyl) telluride (**4**) was obtained by the reaction of (2-methylphenyl)magnesium bromide with tellurium. Treatment of telluride **4** with bromine in Et_2O gave bis(2-methylphenyl)tellurium dibromide (**6**). The latter was irradiated using a high-pressure mercury lamp after addition of *N*-bromosuccinimide (NBS) in CCl_4 to afford the tetrabromide **7**. Compound **7** in CH_2Cl_2 was reduced with $Na_2S{\cdot}9H_2O$ in EtOH using a high-dilution technique at room temperature to give **1**.

Conformational Properties of Tellurathiocin 1. With regard to the conformational properties of **1**, the chair and the boat forms can coexist.[8] The conformers can be assigned by the ^{1}H NMR spectral data for benzylic protons of the eight-membered ring.[8] The ^{1}H NMR (400 MHz) spectrum of **1** in $CDCl_3$ at 25 °C shows the benzylic methylene protons as a broad singlet at δ

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(1) Alder, R. W. *Tetrahedron* **1990**, *46*, 683.
(2) (a) Musker, W. K.; Wolford, T. L.; Roush, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 6416. (b) Musker, W. K.; Hirschon, A. S.; Doi, J. T. *J. Am. Chem. Soc.* **1978**, *100*, 7754.
(3) (a) Fujihara, H.; Chiu, J.-J.; Furukawa, N. *J. Am. Chem. Soc.* **1988**, *110*, 1280. (b) Fujihara, H.; Furukawa, N. *J. Mol. Struct (Theochem)* **1989**, *186*, 261 and references cited therein.
(4) Fujihara, H.; Takaguchi, Y.; Chiu, J.-J.; Furukawa, N. *Chem. Lett.* **1992**, 151.
(5) Hayes, R. A.; Martin, J. C. Sulfurane Chemistry. In *Organic Sulfur Chemistry, Theoretical and Experimental Advances*; Bernardi, F., Csizmadia, I. G., Mangini, A., Eds.; Elsevier: Amsterdam, 1985; Chapter 8.
(6) Patai, S., Rappoport, Z., Eds. *The Chemistry of Organic Selenium and Tellurium Compounds*; Wiley: New York, 1986; Vol. 1, Chapters 3 and 14.
(7) Fujihara, H.; Takaguchi, Y.; Furukawa, N. *Chem. Lett.* **1992**, 501.
(8) (a) Gellatly, R. P.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc., Perkin Trans. 1* **1976**, 913. (b) Brieaddy, L. E.; Hurlbert, B. S.; Mehta, N. B. *J. Org. Chem.* **1981**, *46*, 1630.

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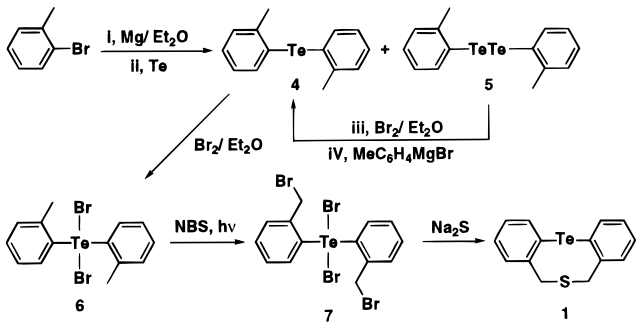
Scheme 1



3.66. At −50 °C, this resonance is split into two, at δ 3.49 and 3.81 (AB q, J = 13.6 Hz), and at δ 4.13 and 4.95 (AB q, J = 14.4 Hz); the former resonance is assigned to the boat form (75%)[9] and the latter pair to the chair form (25%), as shown in Figure 1. These conformers can also be characterized by ^{125}Te NMR spectroscopy. The ^{125}Te NMR spectrum of **1** in $CDCl_3$ at 25 °C shows a somewhat broad peak at δ 507.5 which becomes two singlet 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. An 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.

Oxidation Potential of Tellurathiocin 1. Electrochemical oxidation of the tellurathiocin **1** was studied by cyclic voltammetry. The peak potential of the first oxidation peak was determined at a glassy-carbon electrode, in CH_3CN-0.1 M $NaClO_4$ vs Ag/0.01 M $AgNO_3$. The oxidation potential of the tellurathiocin **1** is 0.41 V, which is 0.15 V lower than that of diphenyl telluride **29** (0.56 V). This is considered to be due to the transannular interaction between the tellurium and sulfur atoms. Although this phenomenon was also observed in the oxidation potential of the dithiocin **13** (1.05 V)[10] compared with that of diphenyl sulfide **30** (1.19 V), the lowering effect in the tellurathiocin **1** is almost equal to that in the dithiocin **13** in spite of the combination of the different heteroatoms. This may be due to the structural effect of the dibenzocyclooctane system.

Dication Formation of Tellurathiocin 1 with D_2SO_4. The tellurathiocin **1** was readily oxidized electrochemically, and thus it was treated with concentrated H_2SO_4 as an oxidant.

Dissolution of the tellurathiocin **1** in concentrated D_2SO_4 (98%) at room temperature led to the formation of a transannular bond between the tellurium and sulfur atoms, giving the dication in **2**, as determined by ^{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 = 17.0 Hz) in concentrated 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 δ 1381.3 as a singlet peak. These spectroscopic data indicate that **2** is a single conformer, boat form, in D_2SO_4 solution (Scheme 2). This finding is quite different from that of a bis(sulfide) analog of **1**, 5*H*,7*H*-dibenzo[*b*, *g*][1,5]-dithiocin (**13**); i.e., the ^{1}H and ^{13}C NMR spectra of its D_2SO_4 solution showed complex signals due to the instability of **13** in D_2SO_4. This result suggests that, compared with **13**, the cationic species derived from **1** is stabilized to a greater degree by the transannular bond between tellurium and sulfur atoms.

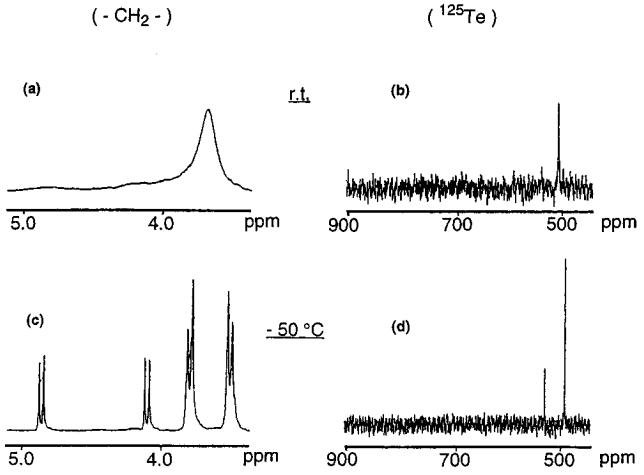
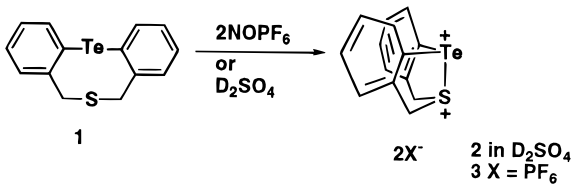


Figure 1. VT-NMR spectra of tellurathiocin **1**: (a) ^{1}H NMR spectrum of methylene at room temperature; (b) ^{125}Te NMR spectrum at room temperature; (c) ^{1}H NMR spectrum at −50 °C; (d) ^{125}Te NMR spectrum at −50 °C.

Scheme 2



Isolation of Tellurathia Dication Salts 3 and 10. The dication derived from **1** was isolated as its remarkably stable PF_6^- salt (**3**) by two-electron oxidation of **1** with a one-electron oxidizing agent, nitrosyl hexafluorophosphate ($NOPF_6$), at −78 °C (Scheme 2).

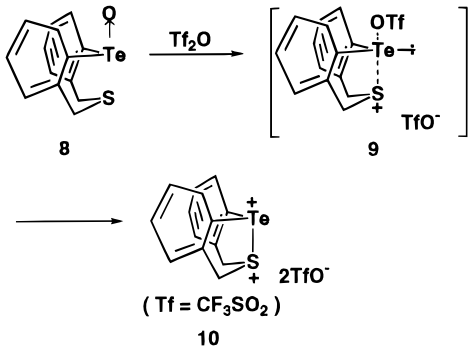
The dication salt **3** was characterized by spectroscopic and chemical means. The ^{1}H NMR (400 MHz) spectrum of **3** in CD_3CN exhibits reasonances at δ 4.57, 4.90 (AB q, J = 16.7 Hz, 2H, CH_2) and 4.58, 4.91 (AB q, J = 16.7 Hz, 2H, CH_2) as methylene protons. Its ^{1}H−^{1}H COSY spectrum established the relation of methylene protons in two sets of AB quartets suggesting that the conformer was fixed as an unsymmetric distorted boat form by a transannular Te−S bond.

Interestingly, a solution of **3** in D_2O−CD_3CN was monitored by NMR spectroscopy, and no significant chemical changes were observed over several hours, during which its spectrum is analogous to that of the dication in **2**; especially, two sets of AB quartet peaks became one AB system (δ 4.62, 4.95). In contrast to **3**, disulfide dications were easily hydrolyzed to the corresponding *S*-oxides.[11]

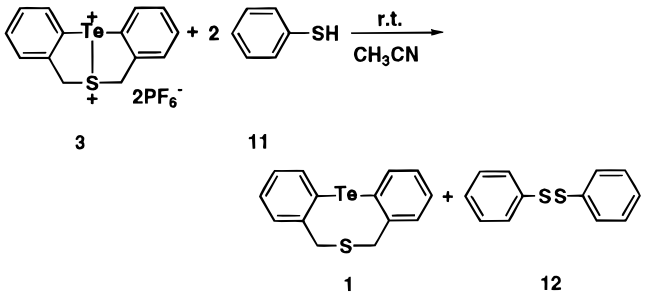
(9) The elucidation of conformational properties of such dibenzodithiocin (**13**) analogues was possible as a result of distinctive differences in the ^{1}H NMR spectral properties of the boat and chair forms. One of the conformers shows the nonequivalent methylenes as a distinct AB quartet due to rigidity of the conformer, while the other has a singlet or AB quartet with the small difference of chemical shifts for the methylene peak due to flexibility of the conformer. The former signals are assignable to the rigid chair conformer and the latter to the boat conformer. Such structural assignments were used and confirmed to be eligible for dibenzodithiocin **13** and its related compounds by Ollis et al. in the ref 8.

(10) Fujihara, H.; Kawada, A.; Furukawa, N. *Heterocycles* **1986**, *24*, 17.

Scheme 3

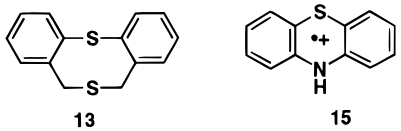


Scheme 4



Furthermore, the telluroxide **8** led to a tellurathia dication salt (**10**; 81%) upon treatment with trifluoromethanesulfonic anhydride at −20 °C (Scheme 3). This reaction may proceed via the initial formation of a (((trifluoromethyl)sulfonyl)oxy)telluronium salt (**9**), which is subsequently converted into the dication salt **10** by nucleophilic displacement of the $CF_3SO_3^-$ ion by the remote sulfur atom, i.e., by a transannular reaction.

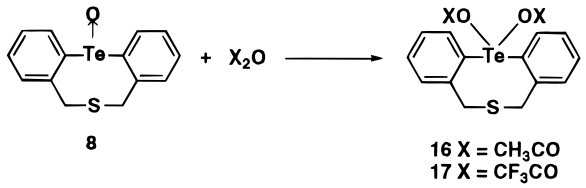
Reactivity of the Tellurathia Dication Salt 3. The reactivity of the tellurathia dication salt **3** was examined as follows. Treatment of benzenethiol (**11**; 2 equiv) with **3** (1 equiv) in CH_3CN under Ar at room temperature for 9 h afforded diphenyl disulfide (**12**; 93%) as the oxidation product and the tellurathiocin **1** (84%) as the reduction product (Scheme 4). Phenothiazine (**14**) was oxidized to its cation radical **15** by **3**, as evidenced by the UV−visible spectrum, which exhibits absorption at λ_{max} 439 and 516 nm in CH_3CN (lit. λ_{max} 437 and 515 nm), since the oxidation potential of **14** is lower than that of the dication precursor. Thus, the dication salt **3** acts as an oxidant. However, the reactivity of the dication of **13** was unknown, because it could not be isolated as a stable salt.



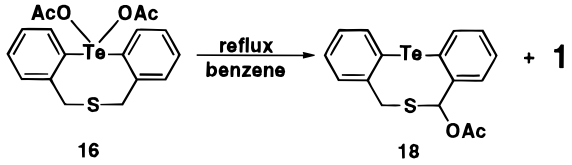
Synthesis of the 12,12-Diacetoxy-Substituted Tellurane 16 and 12,12-bis(trifluoroacetoxy)-Substituted Tellurane 17. Typically, treatment of telluroxide **8** with Ac_2O in anhydrous CH_2Cl_2 at room temperature for 3 h gave the tellurane **16** in 87% yield, as shown in Scheme 5. The bis(trifluoroacetoxy)-substituted tellurane (**17**) was formed in an analogous reaction of **8** with $(CF_3CO)_2O$.

(11) Ohkata, K.; Okada, K.; Akiba, K.-Y. *Heteroat. Chem.* **1995**, *6*, 145.

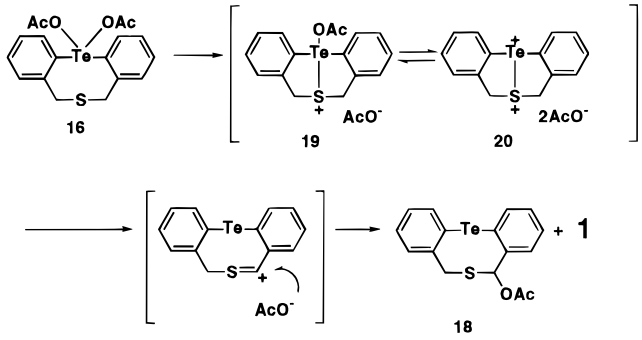
Scheme 5



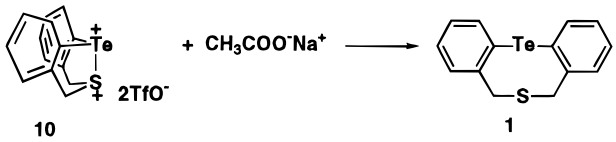
Scheme 6



Scheme 7



Scheme 8



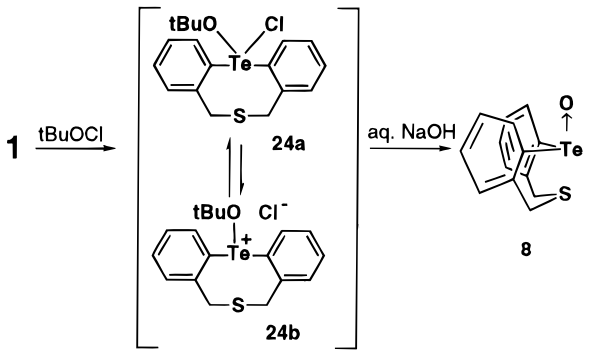
Migration of an Acetoxy Group from Tellurane 16 Induced by Transannular Interaction. Surprisingly, refluxing a solution of **16** in benzene afforded **18** (23%) and **1** (60%) (Scheme 6). Similarly, when **8** was allowed to react with a large excess of acetic anhydride at 100 °C for 36 h, **18** and **1** were obtained in 25% and 60% isolated yields, respectively. However, a distinct difference in reactivity between **16** and **17** was found; i.e., a benzene solution of **17** was stable even under reflux.

In order to explain the formation of **18** and **1** from **16**, we propose the following pathway: **16** is initially converted into a sulfoniotellurane (**19**) or a dication salt (**20**) by a transannular Te−S interaction (Scheme 7). Subsequently, proton abstraction from **19** or **20** and acetoxylation take place to give **18**. The neutral **1** is generated by the reduction of **20** with AcO^-. This is the case for the reaction of dication salt **10** with sodium acetate at 80 °C in CH_3CN: the reduction product **1** was formed in 66% yield (Scheme 8).

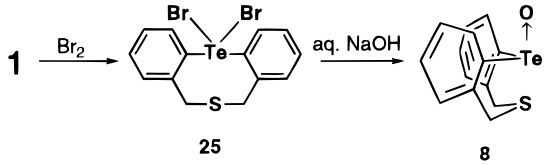
Synthesis of 12-Oxo-5*H*,7*H*-dibenzo[*b*,*g*][1,5]-tellurathiocin (8). t-BuOCl is widely used as an oxidant for conversion of telluride into telluroxide.[12] Thus, the treatment of tellurathiocin **1** with t-BuOCl in anhydrous CH_2Cl_2−MeOH (1:1 v/v) at 0 °C for 4 h gave the telluroxide **8** in 93% yield (Scheme 9). The

(12) (a) Detty, M. R. *J. Org. Chem.* **1980**, *45*, 274. (b) Kobayashi, M.; Ohkubo, H.; Shimizu, T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 503.

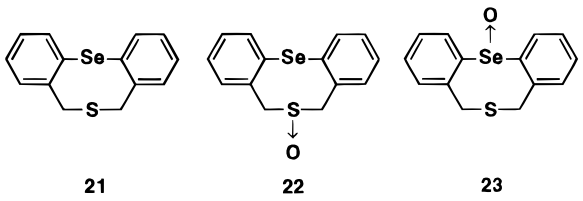
Scheme 9



Scheme 10



structure of **8** was confirmed by ^{1}H, ^{13}C, and ^{125}Te NMR spectroscopy, IR spectroscopy, and elemental analysis. Particularly, the ^{125}Te NMR spectroscopy is diagnostic for the structure determination of tellurium compounds. The ^{125}Te NMR shift of telluroxide **8** appears at 1154 ppm, similar to the shifts of diphenyl telluroxide (1035 ppm). None of the other oxidized product, e.g., sulfoxide, was obtained in these reactions. In contrast, the selenathiocin **21** led to a sulfoxide (**22**; 67%) and selenoxide (**23**; 33%) upon treatment with *m*-chloroperbenzoic acid in $CHCl_3$ at 0 °C.[13]



In order to explain the formation of **8** from tellurathiocin **1**, we propose the following pathway: **1** is initially converted into the tellurane **24a** or telluronium salt **24b**. Subsequently, hydrolysis of **24** takes place to give **8** (Scheme 9).

The possibility for the formation of tellurane **24a** is supported by the following experiment. The intermediate of the oxidation to telluroxide **8** was isolated as a remarkably stable tellurane (**25**) by the reaction of **1** with Br_2 (Scheme 10). The structure of **25** was characterized by ^{1}H, ^{13}C, and ^{125}Te NMR spectroscopy and elemental analysis. The ^{125}Te NMR shifts of **25** appear at 1289 ppm (relative to Me_2Te) in $(CH_3)_2SO$. This is a remarkable downfield shift, consistent with the tellurane structure **25**. This new tellurane formation was also found to occur in when tellurathiocin **1** is treated with iodine.

Furthermore, hydrolysis of tellurane **25** gave the telluroxide **8** in quantitative yield.

(13) Fujihara, H.; Mima, H.; Chiu, J.-J.; Furukawa, N. *Tetrahedron Lett.* **1990**, *31*, 2307.

(14) Fujihara, H.; Uehara, T.; Erata, T.; Furukawa, N. *Chem. Lett.* **1993**, 263.

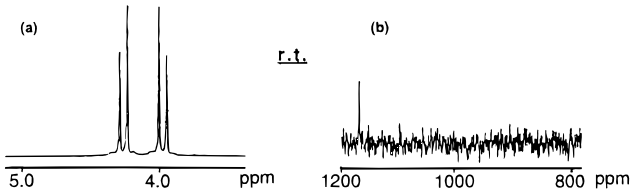
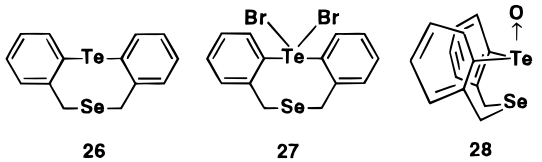


Figure 2. NMR spectra of telluroxide **8**: (a) ^{1}H NMR spectrum of methylene at room temperature; (b) ^{125}Te NMR spectrum at room temperature.

Conformational Properties of Telluroxide 8. With regard to the conformational properties of **8**, the chair and the boat forms can coexist.[8] The conformers can be assigned by the ^{1}H NMR spectral data for benzylic protons of the eight-membered ring.[8] The ^{1}H NMR (270 MHz) spectrum of **8** in $CDCl_3$ at 25 °C shows the benzylic methylene proton as an AB quartet at 3.98 and 4.14 ppm (AB q, J = 16.2 Hz) which is assigned to the boat form (100%)[9] (Figure 2). On the other hand, the ^{1}H NMR(400 MHz) spectrum of **1** in $CDCl_3$ at 25 °C shows the benzylic methylene proton as a broad singlet at δ 3.66 ppm due to the fast conformational exchange. This conformer, boat form, can also be characterized by ^{125}Te NMR spectroscopy; the ^{125}Te NMR spectrum of **8** in $CDCl_3$ at 25 °C shows a signal at 1154 ppm. An analogous result was found in the ^{13}C NMR ($CDCl_3$) spectrum of **8**, which shows one peak at 37.6 ppm for the methylene carbon atom at 25 °C. Furthermore, the peak separation in the ^{1}H NMR spectra of telluroxide **8** was not observed under variable temperature measurements (from −50 to 70 °C), indicating that the conformational change of boat form in telluroxides **8** is restricted by the transannular interaction. This result suggests that the boat form of the telluroxide **8** is more stabilized by a transannular bond between the tellurium and sulfur atoms as compared with the chair form.

In order to prove this transannular interaction of telluroxide **8**, we synthesized telluraselenocin **26**, which had selenium instead of sulfur at the benzylic position.[13] Telluraselenocin **26** was oxidized by the same procedure for the oxidation of tellurathiocin, e.g., reaction with t-BuOCl or halogen to obtain the telluroxide **28**. The structure of **28** was characterized by ^{1}H, ^{13}C, ^{77}Se, and ^{125}Te NMR spectroscopy, IR spectroscopy, and elemental analysis. The ^{125}Te NMR spectrum of **28** in $CDCl_3$ shows a single resonance at 1159 ppm, which is assigned to the telluroxide structure.



Interestingly, the telluroxide **28** showed a transannular interaction between telluroxy and selenide groups, as evidenced by its ^{77}Se and ^{125}Te NMR spectral data. The proton-decoupled ^{77}Se NMR spectrum of **28** in $CDCl_3$ exhibits one peak, particularly, which shows two clearly resolved satellite peaks due to the ^{77}Se−^{125}Te coupling (large coupling constant J_{Se-Te}, 467 Hz) about the central peak. The proton-decoupled ^{125}Te NMR spectrum of **28** in $CDCl_3$ exhibits one peak, particularly, which shows two clearly resolved satellite peaks due to

the $^{125}Te-^{77}Se$ coupling (large coupling constant, J_{Te-Se} = 467 Hz) about the central peak. This is the first observation of a ^{125}Te satellite due to an interaction between tellurinyl and selenide groups.

Structure of Tellurane 25. It should also be added that we could determine the structure of **25** as a tellurane structure using the reaction of telluraselenocin **26** instead of tellurathiocin **1**. There are a number of reasons for this determination. One is that the hydrolysis of **25** gave the telluroxide **8** selectively. Another reason is that no satellite peaks, $^{77}Se-^{125}Te$ coupling, of the selenium derivative **28** which had selenium instead of sulfur at the benzylic position were observed.

Conclusion

The results described herein show a transannular Te−S interaction of tellurathiocin **1**, e.g., conformational properties, migration of an acetoxy group, and a new type of heteroatom dication stabilized by a transannular bond, although transannular interactions between two different heteroatoms are quite rare.

Experimental Section

General Data. All melting points were uncorrected and were taken on a Laboratory Devices Mel-Temp II and a Yanaco micro melting point apparatus. IR spectra were measured on a JASCO FT/IR-5000 spectrometer. All NMR spectra were measured on a JEOL LMN-EX-270 or a Bruker MSL-400 spectrometer. Mass spectra were taken with a Hitachi RU-6MG, a Shimazu QP-2000, and a JEOL JMX SX102 mass spectrometer. Elemental analysis was carried out by the Chemical Analysis Center at the University of Tsukuba.

All reagents were obtained from Wako Pure Chemical Industries Ltd., Tokyo Kasei Co. Ltd., or Aldrich Chemical Co. The reagents used as reaction solvents were further purified by general methods.

Synthesis of Bis(2-methylphenyl) Telluride (4). To a solution of 0.80 M tolylmagnesium bromide (0.16 mol, 200 mL) was added dry tellurium powder (20.0 g, 0.16 mol) under an Ar atmosphere. After it was stirred for 6 h at room temperature, the mixture was treated with oxygen gas for 30 min. The mixture was poured onto cracked ice (200 g), and the solution was neutralized with aqueous HCl. The cooled mixture was separated by filtration, and the filtrate was extracted with ether. The organic layer was dried over anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; eluent hexane) to give bis(2-methylphenyl) telluride (**4**; 19.8 g, 64.0 mmol) in 40% yield: ^1H NMR (500 MHz, $CDCl_3$) δ 2.42 (s, 6H, CH_3), 6.95 (t, J = 7.4 Hz, 2H, Ar H), 7.20 (t, J = 7.4 Hz, 2H, Ar H), 7.25 (d, J = 7.4 Hz, 2H, Ar H), 7.48 (d, J = 7.48 Hz, 2H, Ar H); ^{13}C NMR ($CDCl_3$) δ 26.2, 118.4, 126.8, 128.4, 129.4, 138.2, 142.6; MS m/z 311 (M^+). Anal. Calcd for $C_{14}H_{14}Te$: C, 54.27; H, 4.55. Found: C, 54.43; H, 4.47.

Synthesis of Bis(2-methylphenyl)tellurium Dibromide (6). To a solution of bis(2-methylphenyl) telluride (**4**; 7.53 g, 24.3 mmol) in dry ether (200 mL) was added bromine (3.92 g, 24.5 mmol) under an Ar atmosphere. The yellow products were precipitated and separated from the solution by filtration. The crude products were recrystallized from chloroform to give yellow crystals of **6** (6.52 g, 13.9 mmol) in 57% yield: mp 185.0−185.5 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 2.83 (s, 6H, CH_3), 7.37 (t, J = 7.5 Hz, 4H, Ar H), 7.47 (t, J = 7.5 Hz, 2H, Ar H), 7.91 (d, J = 7.5 Hz, 2H, Ar H); ^{13}C NMR ($CDCl_3$) δ 24.6, 127.9, 131.6, 131.8, 134.3, 135.2, 140.4. Anal. Calcd for $C_{14}H_{14}Br_2Te$: C, 35.80; H, 3.00. Found: C, 35.76; H, 3.22.

Synthesis of Tetrabromide 7. Bis(2-methylphenyl)tellurium dibromide (**6**; 600 mg, 1.28 mmol) and *N*-bromosuccinimide (500 mg, 2.81 mmol) in dry CCl_4 (400 mL) were irradiated with a high-pressure mercury lamp ($\lambda \geq 300$ nm) at room temperature under an Ar atmosphere with stirring for 2 h. The resulting white precipitate was filtered, and the mixture was purified by column chromatography (silica gel, eluent; 20:1 chloroform/methanol) to afford white crystals of **7** (120 mg, 0.19 mmol) in 15% yield: mp 207.5 °C dec; ^1H NMR (60 MHz, $CDCl_3$) δ 5.20 (s, 4H, CH_2), 7.25−7.52 (m, 6H, Ar H), 7.90−8.14 (m, 2H, Ar H). Anal. Calcd for $C_{14}H_{14}Br_4Te$: C, 26.80; H, 1.93. Found: C, 26.77; H, 1.85.

Synthesis of Tellurathiocin 1. To a stirred solution of tetrabromide **7** (2.59 g, 4.13 mmol) in 100 mL of CH_2Cl_2 was added dropwise a solution of sodium sulfide (2.18 g, 9.08 mmol) in 300 mL of ethanol at room temperature using a high-dilution technique. The mixture became white and turbid; it was stirred at room temperature overnight. An insoluble polymer was filtered off, and the crude product was purified by silica-gel column chromatography (eluent 6:1 hexane/$CHCl_3$) to give **1**, which was recrystallized from $CHCl_3$ to give white crystals (120 mg, 0.35 mmol) in 8.5% yield: mp 154−155 °C; ^1H NMR (400 MHz, $CDCl_3$, at −50 °C) δ 3.49, 3.81 (AB q, J = 13.6 Hz, boat CH_2), 4.13, 4.95 (AB q, J = 14.4 Hz, 2H, chair CH_2), 6.93−7.28 (m, 6H, Ar H), 7.58−8.16 (m, 2H, Ar H); ^{13}C NMR ($CDCl_3$, at −50 °C) δ 34.1, 44.1, 117.6, 126.4, 126.6, 127.1, 128.3, 129.5, 129.8, 131.8, 132.4, 142.4, 142.7, 148.3; ^{125}Te NMR ($CHCl_3$, at −50 °C) δ 493.48, 528.29 (relative to Me_2Te); MS m/z 342 (M^+). Anal. Calcd for $C_{14}H_{12}STe$: C, 49.47; H, 3.56. Found: C, 49.51; H, 3.21. A telluradithiocin (**29**; 23 mg, 0.05 mmol) was also obtained as a minor product in 1.1% yield: mp 159 °C; ^1H NMR (400 MHz, $CDCl_3$, at −50 °C) δ 4.01, 5.14 (AB q, 2H, J = 12.0 Hz, chair CH_2), 4.57, 4.68 (AB q, 2H, J = 12.0 Hz, boat CH_2), 7.09−7.48 (m, 6H, Ar H), 8.19−8.34 (m, 2H, Ar H); ^{13}C NMR ($CDCl_3$, at −50 °C) δ 45.1, 54.7, 119.9, 121.2, 127.6, 128.3, 29.2, 130.4, 130.6, 141.8, 142.2, 143.0, 143.9; MS, m/z 374 (M^+). Anal. Calcd for $C_{14}H_{12}S_2Te$: C, 45.21; H, 3.25. Found: C, 45.41; H, 3.01.

Reaction of Tellurathiocin 1 with Concentrated H_2SO_4. When tellurathiocin **1** (22.0 mg, 0.0645 mmol) was dissolved in concentrated H_2SO_4 at room temperature, the solution turned yellow. The reaction mixture was examined by ^1H and ^{13}C NMR spectroscopy: ^1H NMR (500 MHz, D_2SO_4) δ 4.32, 4.70 (AB q, J = 17.0 Hz, 2H, CH_2), 7.18−7.24 (m, 6H, Ar H), 7.57−7.59 (m, 2H, Ar H); ^{13}C NMR (D_2SO_4) δ 41.6, 123.2, 127.3, 129.1, 129.9, 130.9, 137.8; ^{125}Te NMR (H_2SO_4) δ 1381.34 (relative to Me_2Te).

Reaction of Tellurathiocin 1 with Nitrosyl Hexafluorophosphate ($NOPF_6$). 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 −78 °C for 4.5 h. A white precipitate was formed. Evolution of NO gas was observed during the reaction. The crude product was almost pure, which was confirmed by a ^1H NMR spectrum. Upon filtration under anhydrous conditions and recrystallization from anhydrous CH_3CN-Et_2O, the dication hexafluorophosphate **3** was obtained as a remarkably stable white solid (20 mg, 0.03 mmol) in 9% yield: mp 165−167 °C; ^1H NMR (270 MHz, CD_3CN) δ 4.57, 4.90 (AB q, J = 16.7 Hz, 2H, CH_2), 4.58, 4.91 (AB q, J = 16.7 Hz, 2H, CH_2), 7.60−7.65 (m, 6H, Ar H), 7.99−8.02 (m, 2H, Ar H); ^{13}C NMR (CD_3CN) δ 41.9, 130.0, 130.1, 131.0, 131.1, 132.0, 140.6; ^{31}P NMR (CD_3CN) δ −149.8 (sept, J_{P-F} = 707 Hz; relative to H_3PO_4), in the region of ionic PF_6^-; ^{125}Te NMR (CH_3CN) δ 1257, 1259 (1:1) (relative to Me_2Te). Anal. Calcd for $C_{14}H_{12}F_{12}P_2STe$: C, 26.70; H, 1.92. Found: C, 26.88; H, 1.83.

Reaction of Telluroxide 8 with Trifluoromethanesulfonic Anhydride. To a solution of the telluroxide **8** (67 mg, 0.19 mmol) in 20 mL of anhydrous CH_2Cl_2 was added dropwise a solution of trifluoromethanesulfonic anhydride (54 mg, 0.19 mmol) in anhydrous CH_2Cl_2 at −78 °C under an Ar

atmosphere. The mixture turned pale yellow, and a white precipitate formed. The precipitate was filtered and dried in vacuo to afford the pale yellow solid **10** (50 mg, 0.08 mmol) in 41% yield: mp 142 °C dec; ^{1}H NMR (CD_3CN) δ 4.52, 4.89 (AB q, J = 16.5 Hz, 4H, CH_2), 7.57−7.66 (m, 6H, Ar H); ^{13}C NMR (CD_3CN) δ 42.8, 130.5, 131.3, 131.7, 132.3, 133.3, 142.3; ^{19}F NMR (CD_3CN) δ 87.8 (relative to C_6F_6); ^{125}Te NMR (CH_3CN) δ 1111 (relative to Me_2Te). Anal. Calcd for $C_{16}H_{12}F_6O_6S_3Te$: C, 30.12; H, 1.90. Found: C, 30.00; H, 1.96.

Reaction of the Tellurathiadication Salt 3 with Thiophenol (11). To a solution of the dication salt **3** (52.8 mg, 0.084 mmol) in 2 mL of anhydrous CH_3CN was added 2 equiv of thiophenol **11** (19.4 mg, 0.18 mmol) under an Ar atmosphere at 0 °C. After this mixture was stirred at 0 °C for 4 h, water was added to it. Then CH_2Cl_2 was added and the organic layer was extracted from NaCl-saturated solution and washed with $NaHCO_3$-saturated solution and water, successively. After the usual workup, the mixture was separated by column chromatography (silica gel, eluent; 6:1 hexane/chloroform) to afford the tellurathiocin **1** (24 mg, 0.071 mmol) in 84% yield and diphenyl disulfide **12** (17 mg, 0.082 mmol) in 93% yield. Each compound was characterized by ^{1}H NMR spectroscopy and GPC.

Reaction of the Tellurathia Dication Salt 3 with Phenothiazine (14). To a solution of the dication salt **3** (2.0 mL, 1.33 mM) in CH_3CN in a UV cell was added a solution of phenothiazine **14** (0.6 mL, 2 equiv., 6.8 mM) in CH_3CN. The solution became yellow. The reaction was followed by UV spectroscopy.

Synthesis of the 12,12-Diacetoxy-Substituted Tellurane 16. To a solution of the telluroxide **8** (100 mg, 0.28 mmol) in 10 mL of anhydrous CH_2Cl_2 was added dropwise acetic anhydride (30 mg, 0.29 mmol) at room temperature under an Ar atmosphere. The mixture was stirred at room temperature for 3 h. After the usual workup, the residue was recrystallized from dichloromethane and diethyl ether to afford white crystals of **16** (105 mg, 0.23 mmol) in 82% yield: mp 161 °C dec; ^{1}H NMR ($CDCl_3$) δ 1.85 (s, 6H, CH_3), 3.49, 4.03 (br AB q, 4H, CH_2), 7.36−7.54 (m, 6H, Ar H), 7.90−7.93 (m, 2H, Ar H); ^{13}C NMR ($CDCl_3$) δ 22.3, 31.1, 127.7, 132.7, 132.8, 133.2, 137.0, 141.3, 177.5. Anal. Calcd for $C_{18}H_{18}O_4STe$: C, 47.20; H, 3.96. Found: C, 46.86; H, 3.91.

Synthesis of the 12,12-Bis(trifluoroacetoxy)-Substituted Tellurane 17. To a solution of the telluroxide **8** (65 mg, 0.18 mmol) in 10 mL of anhydrous CH_2Cl_2 was added dropwise hexafluoroacetic anhydride (38 mg, 0.18 mmol) at room temperature under an Ar atmosphere. The mixture was stirred at room temperature for 1 h. After the usual workup, the residue was recrystallized from dichloromethane and diethyl ether to afford white crystals of **17** (72 mg, 0.13 mmol) in 70% yield: mp 193−193.5 °C dec; ^{1}H NMR (CD_2Cl_2) δ 4.09, 4.48 (AB q, J = 15.7 Hz, 4H, CH_2), 7.34−7.57 (m, 6H, Ar H), 8.23−8.26 (m, 2H, Ar H); ^{13}C NMR (CH_2Cl_2) δ 38.9, 130.3, 130.4, 131.1, 131.8, 132.4, 139.9, 160.9; ^{19}F NMR (CD_2Cl_2) δ 87.8 (relative to C_6F_6). Anal. Calcd for $C_{18}H_{12}F_6O_4STe$: C, 38.20; H, 2.14. Found: C, 38.33; H, 2.14.

Migration of an Acetoxy Group from Tellurane 16 on Heating. The solution of 12,12-diacetoxy-substituted tellurane **16** (102 mg, 0.26 mmol) in 30 mL of anhydrous benzene was heated at 80 °C under an Ar atmosphere with stirring for 15 h. After the usual workup, the residue was purified by column chromatography (silica gel, eluent benzene) to afford the tellurathiocin **1** (45 mg, 0.13 mmol) in 58% yield and the remote α-acetoxylated sulfide **18** (18 mg, 0.03 mmol) in 20% yield: mp 124 °C; IR (KBr) 1749 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.15 (s, 3H, CH_3), 4.05, 4.62 (AB q, J = 14.9 Hz, 2H, CH_2), 7.00−7.53 (m, 6H, Ar H), 7.68 (br s, 1H, CH), 8.00−8.10 (m, 2H, Ar H); MS m/z 400 (M^+). Anal. Calcd for $C_{16}H_{14}O_2STe$: C, 48.12; H, 3.51. Found: C, 47.97; H, 3.46.

Remote Pummerer Reaction of Tellurathiocin 1. The solution of telluroxide **8** (86 mg, 0.24 mmol) in 2.5 mL of acetic anhydride was heated at 100 °C under an Ar atmosphere with stirring for 16 h. After the usual workup, the residue was purified by column chromatography (silica gel, eluent benzene) to afford the remote α-acetoxylated sulfide **18** (16 mg, 0.04 mmol) in 17% yield and tellurathiocin **1** (49 mg, 0.14 mmol) in 60% yield.

Reduction of Dication 10 with CH_3COONa. To a solution of the dication salt **10** (23 mg, 0.036 mmol) in 10 mL of anhydrous benzene was added an excess of CH_3COONa (12 mg, 0.15 mmol) under an Ar atmosphere at room temperature with stirring at 80 °C for 20 h. After the usual workup, the mixture was separated by column chromatography (silica gel, eluent 6:1 hexane/chloroform) to afford the tellurathiocin **1** (8 mg, 0.024 mmol) in 66% yield, which was characterized by ^{1}H NMR spectroscopy and GPC.

Reaction of Tellurathiocin 1 with *t*-BuOCl. To a solution of tellurathiocin **1** (144 mg, 0.424 mmol) in anhydrous CH_2Cl_2 (20 mL) was added *t*-BuOCl (45.8 mg, 0.424 mmol) at 0 °C under an Ar atmosphere, and the mixture was stirred overnight. Subsequently, aqueous 2 N NaOH solution was added, and the resulting mixture was stirred at 0 °C for 10 min. The organic layer was extracted with CH_2Cl_2. After the usual workup, the crude products were recrystallized from $CH_2Cl_2-Et_2O$ to give telluroxide **8** (141 mg, 0.394 mmol) in 93% yield: mp 163 °C; IR (KBr) 754 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.98, 4.14 (AB q, J = 16.2 Hz, 4H, CH_2), 7.23−7.51 (m, 6H, Ar H), 8.36−8.39 (m, 2H, Ar H); ^{13}C NMR ($CDCl_3$) δ 37.6, 129.3, 129.4, 130.4, 130.5, 134.0, 139.9; ^{125}Te NMR ($CDCl_3$) δ 1154 (relative to Me_2Te). Anal. Calcd for $C_{14}H_{12}OSTe$: C, 47.25; H, 3.40. Found: C, 47.04; H, 3.36.

Reaction of Tellurathiocin 1 with Bromine. To a solution of tellurathiocin **1** (57 mg, 0.17 mmol) in dry dichloromethane (2 mL) was added bromine (29.5 mg, 0.18 mmol) under an Ar atmosphere. The yellow products precipitated and were separated by filtration. The crude products were recrystallized from chloroform to give yellow crystals of **25** (60 mg, 0.12 mmol) in 71% yield: mp 212 °C dec; ^{1}H NMR (DMSO-d_6) δ 4.69, 5.17 (AB q, J = 16.5 Hz, 4H, CH_2), 7.53−7.65 (m, 6H, Ar H), 8.38−8.41 (m, 2H, Ar H); ^{13}C NMR (DMSO-d_6) δ 42.1, 128.2, 129.7, 130.2, 131.2, 133.8, 141.6; ^{125}Te NMR (DMSO) δ 1289 (relative to Me_2Te). Anal. Calcd for $C_{14}H_{12}Br_2STe$: C, 33.65; H, 2.42. Found: C, 33.82; H, 2.36.

Hydrolysis of Tellurane 25. To the tellurane **25** (100 mg, 0.20 mmol) was added aqueous 10% NaOH solution (2 mL) at room temperature. After the mixture was stirred overnight, the resulting white precipitate was filtered and recrystallized from CH_2Cl_2 to afford the telluroxide **8** (60 mg, 0.169 mmol) in 84% yield.

Synthesis of the Telluraselenocin 26. To a stirred solution of tetrabromide **7** (1.00 g, 1.59 mmol) in 300 mL of CH_2Cl_2 was added dropwise a solution of sodium selenide (0.23 g, 1.80 mmol) in 100 mL of methanol at room temperature using a high-dilution technique. The mixture became white and turbid and was stirred at room temperature for 30 min. After the usual workup, the crude product was purified by silica gel column chromatography (eluent $CHCl_3$) to give **26**, which was recrystallized from $CHCl_3$ to give white crystals (322 mg, 0.832 mmol) in 52% yield: mp 162−163 °C dec; ^{1}H NMR (270 MHz, $CDCl_3$, at −50 °C) δ 3.74, 3.92 (AB q, J = 12.5 Hz, boat CH_2), 4.24, 5.18 (AB q, J = 13.2 Hz, chair CH_2), 6.96−7.35 (m, 6H, Ar H), 7.69−8.28 (m, 2H, Ar H); ^{13}C NMR ($CDCl_3$, at −50 °C) δ 27.8, 36.0, 117.7, 118.4, 127.0, 127.2, 127.4, 129.3, 130.0, 130.5, 133.5, 143.8, 150.0; ^{77}Se NMR ($CHCl_3$) δ 397.7, 424.6 (relative to Me_2Se); ^{125}Te NMR ($CHCl_3$) δ 559.3, 580.5 (relative to Me_2Te); MS m/z 388 (M^+). Anal. Calcd for $C_{14}H_{12}SeTe$: C, 43.47; H, 3.13. Found: C, 43.23; H, 2.79.

Reaction of the Telluraselenocin 26 with Bromine. To a solution of telluraselenocin **26** (216 mg, 0.558 mmol) in dichloromethane (15 mL) was added bromine (29 μL, 0.563 mol) under an Ar atmosphere. The yellow products precipitated and were separated by filtration. The crude products were recrystallized from dimethyl sulfoxide to give yellow

crystals of **27** (299 mg, 0.547 mmol) in 98% yield: mp 223 °C dec; ^{1}H NMR (270 MHz, DMSO-d_6) δ 4.64, 5.13 (AB q, J = 15.0 Hz, 4H, CH_2), 7.46−7.65 (m, 6H, Ar H), 8.50−8.53 (m, 2H, Ar H); ^{13}C NMR (DMSO-d_6) δ 39.7, 129.4, 130.9, 131.0, 131.9, 134.6, 143.2; ^{77}Se NMR (DMSO) δ 360.6 (t, J_{Se-H} = 25.5 Hz) (relative to Me_2Se); ^{125}Te NMR (DMSO) δ 1239 (relative to Me_2Te). Anal. Calcd for $C_{14}H_{12}Br_2SeTe$: C, 30.76; H, 2.21. Found: C, 30.93; H, 2.56.

Hydrolysis of the Tellurane 27. To the tellurane **27** (201 mg, 0.368 mmol) was added aqueous 10% NaOH solution (3 mL) at room temperature. After the mixture was stirred overnight, the resulting white precipitate was filtered and recrystallized from $CHCl_3$−Et_2O to afford the telluroxide **28** (73 mg, 0.181 mmol) in 49% yield: mp 157 °C dec; IR (KBr) 741 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.90, 4.25 (AB q, J = 14.2 Hz, 4H, CH_2), 7.20−7.47 (m, 6H, Ar H), 8.31−8.34 (m, 2H, Ar H); ^{13}C NMR ($CDCl_3$) δ 29.7, 129.0, 129.9, 130.3, 131.0, 135.5, 140.1; ^{77}Se NMR ($CHCl_3$) δ 233.0 (relative to Me_2Se); ^{125}Te NMR ($CHCl_3$) δ 1159 (relative to Me_2Te). Anal. Calcd for $C_{14}H_{12}OSeTe$: C; 41.70; H, 3.00. Found: C, 42.00; H; 3.06.

Reaction of the Telluraselenocin 26 with *t*-BuOCl. To a solution of telluraselenocin **26** (151 mg, 0.39 mmol) in dry CH_2Cl_2 (15 mL) was added *t*-BuOCl (42.1 mg, 0.39 mmol) at 0 °C under an Ar atmosphere. The mixture was stirred overnight, and then aqueous 2 N NaOH solution was added at 0 °C. The resulting mixture was stirred for 10 min. The organic layer was extracted with CH_2Cl_2 and worked up as usual. After drying it was dried under vacuum, the product was characterized to be the telluroxide **28** by NMR spectroscopy. Further purification by recrystallization with benzene produced colorless cubic crystals of telluroxide **28** (145 mg, 0.36 mmol) in 93% yield.

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