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Hypervalent Bond Formation and Interaction between Heavier Group 16 Elements in the Dihalides and Oxide of 5*H*,7*H*-Dibenzo[*b*,*g*][1,5]-ditellurocin and - telluraselenocin

Hisashi FUJIHARA,* Toshinori UEHARA, Tomoki ERATA,† and Naomichi FURUKAWA*
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305
†Institute of Applied Physics, University of Tsukuba, Tsukuba, Ibaraki 305

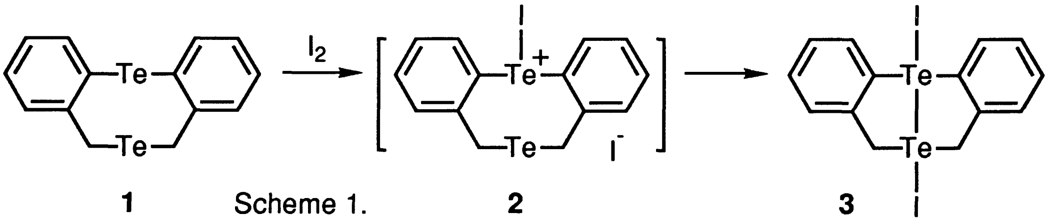
The reaction of 5*H*,7*H*-dibenzo[*b*,*g*][1,5]ditellurocin with I_2 resulted in the formation of the diiodo-ditellurane as a new class of bis-hypervalent chalcogenide. Treatment of the dibromo-derivative of 5*H*,7*H*-dibenzo[*b*,*g*][1,5]telluraselenocin with aqueous NaOH solution afforded exclusively the telluroxide which showed the strong transannular hypervalent interaction between the tellurinyl group and the selenyl group as evidenced by ^{77}Se and ^{125}Te NMR spectroscopy.

Transannular interaction or bond formation (*e.g.*, hypervalent bond) between heteroatoms in medium-sized heterocyclic compounds containing nitrogen, phosphorus, and sulfur atoms has been well studied.[1,2] However, the properties of medium-sized tellurium heterocycles have received less attention. We have now synthesized new eight-membered ring tellurium heterocycles, 5*H*,7*H*-dibenzo[*b*,*g*][1,5]ditellurocin (**1**) and 5*H*,7*H*-dibenzo[*b*,*g*][1,5]telluraselenocin (**4**), to investigate the conformational property, and the transannular interaction and bond formation between heavier group 16 elements. Herein we report the synthesis and the conformational properties of **1** and **4**, together with the characterization of a new ditellurane with Te(IV)-Te(IV) bond of **1**, and the transannular hypervalent interaction between the tellurinyl group and the selenyl group in the telluroxide **6**.

Compounds **1** and **4** were synthesized as follows. Bis(2-bromomethylphenyl)tellurium dibromide[3] (1.00 g, 1.59 mmol) in $CHCl_3$ (300 mL) was treated with Na_2Te (0.28 g, 1.59 mmol) or Na_2Se in EtOH (80 mL) using a high dilution technique at room temperature under an Ar atmosphere. The mixture was stirred at room temperature for 30 min. After usual work-up, the crude product was purified by silica-gel column chromatography (eluent, CH_2Cl_2) to give **1** or **4**.[4]

In the conformational properties for eight-membered rings of **1** and **4**, two typical different conformers such as chair and boat-forms can exist.[5] The conformers can be assigned by the ^1H NMR spectral data for benzylic protons of the eight-membered ring.[5] The ^1H NMR spectrum of **1** in $CDCl_3$ at 25 °C shows the benzylic methylene protons as a broad singlet at δ 4.08 and an AB type absorption at δ 4.22 and 5.48 (J=12 Hz); the former resonance is assigned to the boat form (53%), and the latter pair to the chair form (47%) (Table 1). These conformers can also be characterized by ^{125}Te NMR spectroscopy;[6] the ^{125}Te NMR spectrum of **1** in $CHCl_3$ at 25 °C shows *four* peaks at δ 553 (boat) and 565 (chair) for -TeAr, and δ 677 (boat) and 703 (chair) for -$TeCH_2Ar$, respectively, the ratio of the conformers being consistent with that obtained from the ^1H NMR spectrum.[6]

Treatment of the tellurocin **1** (100 mg, 0.23 mmol) with iodine (64 mg, 0.25 mmol) in CH_2Cl_2 (20 mL) under an Ar atmosphere at room temperature for overnight resulted in the formation of the diiodo-ditellurane **3** as an orange solid (96% yield), mp 132.5-133 °C (decomp) (Scheme 1).[7,8] The compound **3** was analyzed by ^1H, ^{13}C, and ^{125}Te NMR spectroscopy (Table 1) and elemental analysis. The benzylic methylene proton signals of **1** in $CDCl_3$ disappeared and new singlet peak appeared at δ 4.99 of **3** in $(CD_3)_2SO$, and the signal of the methylene carbon atoms shifted to 45.9 ppm from 12.1 and 14.1 ppm of **1**, in which those spectra indicate that **3** is a single conformer, *i.e.*, boat form. More significant spectroscopic evidence for the formation of **3** was obtained in the ^{125}Te NMR spectrum. The proton-decoupled ^{125}Te NMR spectrum of **3** in Me_2SO exhibits two resonances at δ 602 (-TePh) and at δ 946 (-TeCH$_2$Ph) (ratio 1:1) indicating the downfield shift; those resonances are assigned to the *tellurane* structure,[9b] particularly, the *satellite* peaks due to the *^{125}Te-^{125}Te coupling* (large coupling constant of $J_{Te\text{-}Te}$ = 1283 Hz) are observed.[9b,10,11] This result clearly indicates the bond formation between two tellurium atoms. The iodine of **3** does not exist as the ion form, since the ^{127}I NMR spectrum of **3** in Me_2SO shows no absorption of iodide ion. The ditellurane **3** may be formed as follows: **1** reacts with I_2 to generate the iodo-telluronium(III) ion (**2**) which is stabilized by the remote tellurium atom to give finally diiodo-ditellurane (IV) (**3**) (Scheme 1). This ditellurane **3** is a new class of hypervalent



Scheme 1.

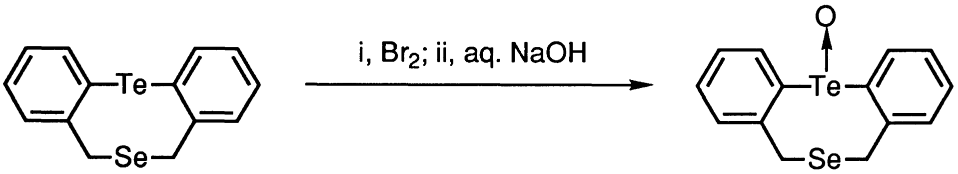
Table 1. NMR Spectral Data for Compounds **1**, **3**, **4**, **5**, and **6**[a]

Compd	Chemical shift, δ ^1H	^{13}C	^{125}Te / *^{77}Se*
1	4.08 (brs), 4.22, 5.48 (ABq, *J*=12 Hz), 6.86-7.27 (m), 7.78-8.25 (m)	12.1, 14.1, 117.0, 118.5, 126.5, 126.8, 127.0, 129.3, 129.4, 130.6, 137.2, 144.2, 147.7, 152.6	553, 565 677, 703
3	4.99 (brs, 4H), 7.30 (t, *J*=8 Hz, 2H), 7.44 (t, *J*=8 Hz, 2H), 7.63 (d, *J*=8 Hz, 2H), 7.93 (d, *J*=8 Hz, 2H)	45.9, 127.6, 128.9, 130.3, 131.5, 137.1, 142.7	602, 946
4	3.74, 3.92 (ABq, *J*=13 Hz), 4.24, 5.18 (ABq, *J*=13 Hz), 6.96-7.35 (m), 7.69-8.28 (m)	27.8, 36.0, 117.7, 118.4, 127.0, 127.2, 127.4, 129.3, 130.4, 130.5, 133.5, 143.8, 145.8, 150.0	559, 581 / *398, 425 (Se)*
5	4.64, 5.13 (ABq, *J*=15 Hz, 4H), 7.46-7.65 (m, 6H), 8.50-8.53 (m, 2H)	39.7, 129.4, 130.9, 131.0, 131.9, 134.6, 143.2	1239 / *361 (Se)*
6	3.90, 4.24 (ABq, *J*=14 Hz, 4H), 7.22 (d, *J*=8 Hz, 2H), 7.32 (t, *J*=8 Hz, 2H), 7.45 (t, *J*=8 Hz, 2H), 8.33 (d, *J*=8 Hz, 2H)	29.7, 129.0, 129.9, 130.3, 131.0, 135.5, 140.1	1159 / *233 (Se)*

[a] ^1H, ^{13}C, ^{77}Se, and ^{125}Te NMR data for **1**, **4**, and **6** in $CDCl_3$; for **3** and **5** in $(CD_3)_2SO$.

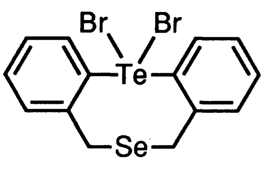
tellurium compound. Although hypervalent organosulfur compounds, sulfuranes, in group 16 elements have been widely studied in structural and theoretical aspects, a little attention has been devoted to multicoordinated tellurium compounds.[9,12,13] In contrast, much less is known about the chemistry of bis-hypervalent bonds with adjacent two hypervalent bonding species.[14]

Thus, the transannular bond formation between two tellurium atoms of **1** was found in the reaction of **1** with iodine. Therefore, in order to confirm the transannular interaction between two different chalcogen atoms, the telluraselenocin **4** has been prepared. The multinuclear NMR spectral data of **4** indicate the existence of two conformers, boat form (58%) and chair form (42%), in $CHCl_3$ at -50 °C (Table 1). The conformational study of selenium and tellurium heterocycles using ^{77}Se and ^{125}Te NMR spectroscopic method is little known.

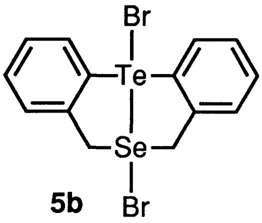


4 **6**

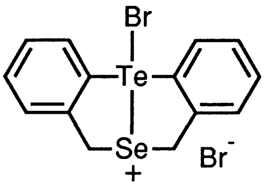
Scheme 2.



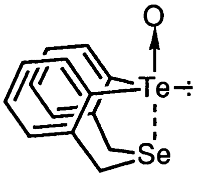
5a



5b



5c



6

The reaction of **4** (1 equiv.) with bromine (1 equiv.) in CH_2Cl_2 at room temperature afforded the dibromo-derivative **5** (90%).[15] Both ^1H, ^{13}C, ^{77}Se, and ^{125}Te NMR spectra of **5** shows a single conformer (Table 1). The tetracoordinated tellurium species should be formed as evidenced by the ^{125}Te NMR spectrum of **5**, though the discrete structure of **5** can not be assigned clearly as **5a** or **5b** or **5c**.[16] The dibromo-derivative **5** led to exclusively the telluroxide **6** (80%) upon treatment with aqueous NaOH solution at room temperature (Scheme 2), none of the selenoxide of **4** was obtained.[17,18] The telluroxide **6** was stable and **6** exists solely as a single conformer, *boat* form, from -50 to +100 °C as evidenced from the variable-temperature ^1H NMR spectra, while the telluraselenocin **4** shows the existence of two conformers.[19] This finding can be rationally explained in terms of the transannular interaction between the tellurinyl group and the selenyl group of **6**, since such interaction was confirmed by both ^{77}Se and ^{125}Te NMR spectroscopy; *e.g.*, the ^1H-decoupled ^{77}Se NMR spectrum of **6** in $CHCl_3$ showed the satellite peaks due to the ^{77}Se-^{125}Te coupling ($J_{Se\text{-}Te}$ = 467 Hz).[9b,10] This is the first evidence for the transannular interaction between tellurinyl and selenyl groups using multinuclear NMR technique.

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References

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3) H. Fujihara, Y. Takaguchi, J.-J. Chiu, T. Erata, and N. Furukawa, *Chem. Lett.*, **1992**, 151.

4) Compound **1**: Mp 153-153.5 °C (decomp); MS, *m/z* 440 (M^+). Anal. Found: C, 38.51; H, 2.76%. Calcd for $C_{14}H_{12}Te_2$: C, 38.62; H, 2.78%. **4**: Mp 162-163 °C (decomp); MS, *m/z* 390 (M^+). Anal. Found: C, 43.23; H, 2.79%. Calcd for $C_{14}H_{12}SeTe$: C, 43.47; H, 3.13%.

5) 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).

6) The ^{77}Se and ^{125}Te chemical shifts are relative to Me_2Se and Me_2Te, respectively. The conformers were assigned by the integration of the selenium and tellurium peaks. The peak of benzylic telluride of **1** was determined by off-resonance method.

7) It has been known that the reaction of aliphatic or aromatic monotellurides with halogens gave dialkyl or diaryl tellurium(IV) dihalides; the stability of which depends markedly on the alkyl group and on the halogen.[9,13] Those discrete tellurium(III) intermediates such as telluronium ions have been undetected.

8) **3**: Anal. Found: C, 24.30; H, 1.71%. Calcd for $C_{14}H_{12}I_2Te_2$: C, 24.40; H, 1.75%.

9) a) "The Chemistry of Organic Selenium and Tellurium Compounds," ed by S. Patai and Z. Rappoport, Wiley, New York (1986), Vol. 1, Chaps. 3 and 14. The term tellurane has been used for tetracoordinate tellurium (IV) compounds. b) Chapter 6 of Ref. 9a.

10) Both Se and Te atoms possess spin-1/2 nuclei with natural abundance (7.6% for ^{77}Se and 7.0% for ^{125}Te).

11) Akiba and co-workers reported that the existence of a N-S bond of ^{15}N-labeled 6,7-dihydro-6,12-dimethyl-5*H*-dibenzo[*b*,*g*][1,5]thiazocinium PF_6^- salt in solution was confirmed by $^{15}N\text{-}S\text{-}CH_3$ coupling $^2J_{CN}$.[1d)]

12) R. A. Hayes and J. C. Martin, "Sulfurane Chemistry" in "Organic Sulfur Chemistry, Theoretical and Experimental Advances," ed by F. Bernardi, I. G. Csizmadia, and A. Mangini, Elsevier, Amsterdam (1985), Chap. 8.

13) "The Organic Chemistry of Tellurium," K. J. Irgolic, Gordon and Breach Science Publishers, New York, (1974).

14) Perkins and Martin reported the existence of S(IV)-S(IV) bisulfurnayl dimer, in equilibrium with sulfuranyl radical as evidenced by ESR and NMR spectroscopy; C. W. Perkins and J. C. Martin, *J. Am. Chem. Soc.*, **108**, 3211 (1986).

15) **5**: Mp 223 °C. Anal. Found: C, 30.93; H, 2.56%. Calcd for $C_{14}H_{12}Br_2SeTe$: C, 30.76; H, 2.21%.

16) Akiba and co-workers studied the transannular bond formation between the antimony and the nitrogen in the halogeno derivatives of dibenz[*c*,*f*][1,5]azastibocine; K. Ohkata, M. Ohnishi, and K.-y. Akiba, *Tetrahedron Lett.*, **29**, 5401 (1988).

17) **6**: Mp 157 °C; FT-IR (KBr) 741 cm^{-1}. Anal. Found: C, 42.00; H, 3.06%. Calcd for $C_{14}H_{12}OSeTe$: C, 41.70; H, 3.00%.

18) The reaction of **3** with aqueous NaOH solution gave a complex mixture which could not be characterized.

19) Akiba and co-workers reported that the transannular interaction between the sulfinyl group and the amino group in *N*-methyl 5*H*,7*H*-dibenzo[*b*,*g*][1,5]thiazocine was confirmed by ^1H NMR spectroscopy and X-ray analysis.[1a)]

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