Synthesis and X-Ray Structure of 1,8-Bis(phenyltelluro)naphthalene and Its Peri Tellurium-Tellurium Interaction

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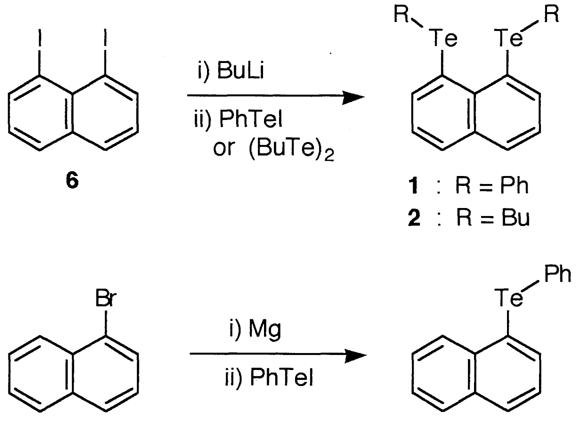
New 1,8-diaryl and dialkyl substituted ditelluronaphthalenes, 1,8-bis(phenyltelluro)naphthalene (**1**) and 1,8-bis(butyltelluro)-naphthalene, have been synthesized. The cyclic voltammogram of **1** showed the reversible electrochemical oxidation with remarkably low oxidation potential. The peri telluronio-tellurenyl interaction in the telluronium cation of **1** was identified by ^{125}Te NMR spectroscopy.

Although the transannular interaction or bond formation (e.g., dication) between heteroatoms in medium-sized heterocyclic compounds containing sulfur and/or selenium atoms has been studied,[1] such behavior by tellurium atom has received less attention. We previously reported the first isolation of tetraalkyl substituted ditelluride dication salt of 1,5-ditelluracyclooctane.[2] We have now made 1,8-bis(phenyltelluro)naphthalene (**1**) to study the peri tellurium-tellurium interaction in its oxidized species, since there is no report concerning the properties of 1,8-ditelluronaphthalenes. This paper describes the synthesis of **1** and the first observation of the peri tellurium-tellurium interaction in electrochemical oxidation and in concentrated sulfuric acid, together with the peri interaction between telluronio and tellurenyl groups in the telluronium salt of **1**.

The bis-telluride **1** was synthesized as follows (Scheme 1).[3] A solution of 1,8-dilithionaphthalene was prepared by treating 1,8-diiodonaphthalene (**6**)[4] (1.51 g, 4.0 mmol) with BuLi (7.5 mL, 12.0 mmol; 1.61 M in hexane) in anhydrous THF (100 mL) at -78 °C under an Ar atmosphere. To this lithium reagent was added a solution of PhTeI (8.0 mmol) prepared from PhTeTePh and I_2 in anhydrous THF (25 mL). The mixture was stirred for 12 h at -20 °C. After the usual work-up, the crude product was purified by silica-gel column chromatography (eluent, hexane-CCl_4) to give **1** in 21% yield.[5]



Scheme 1.

1,8-Bis(butyltelluro)naphthalene (**2**) was prepared by the similar procedures as the telluride **1** using dibutylditelluride, $(BuTe)_2$.[5] 1-Phenyltelluronaphthalene (**3**) was obtained from the reaction of 1-naphthylmagnesium bromide with PhTeI (Scheme 1).[5]

The X-ray crystallographic analysis of **1** indicates the following characteristic properties (Figure 1).[6] The peri Te···Te contact is 3.29 Å which is remarkably shorter than the sum of the van der Waals radii (4.40 Å) of tellurium. The Te-Te nonbonded distance here is unusually short. The naphthalene ring is twisted about the C(5)-C(10) axis. The X-ray data suggest that it may have interesting chemical properties.

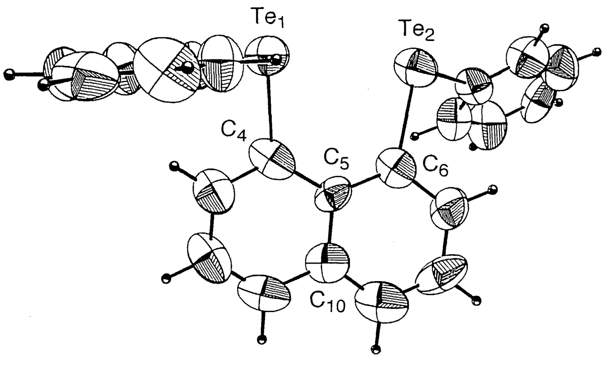
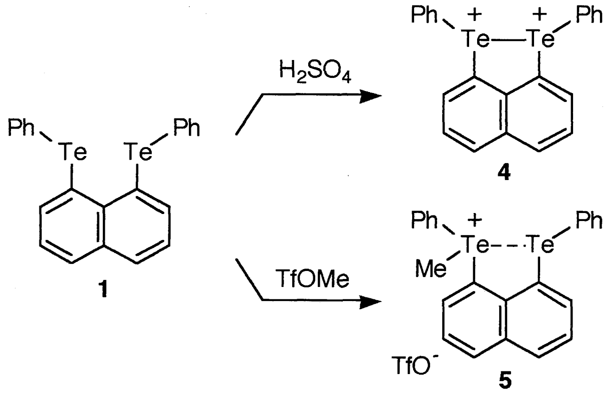


Figure 1. The crystal structure of bis-telluride **1**. Selected bond lengths (Å) and angles (deg): Te(1)-C(4) 2.14(1), Te(2)-C(6) 2.14(2), C(5)-C(6) 1.41(2), Te(1)-C(4)-C(5) 123.(1), Te(2)-C(6)-C(5) 124.(1), C(4)-C(5)-C(6) 128.(1). Selected torsional angles (deg): Te(1)-C(4)-C(5)-C(6) -12.0, C(4)-C(5)-C(6)-Te(2) -16.2.

The bis-telluride **1** was subjected to electrochemical oxidation by cyclic voltammetry (CV), since little is known about the electrochemical behavior of tellurides. When the cyclic voltammogram of **1** was measured in CH_3CN-0.1 M $NaClO_4$ with a glassy-carbon working electrode and Ag/0.01 M $AgNO_3$ in CH_3CN as a reference electrode (scan rate; 300 mV/s), one *reversible* oxidation peak appeared at the oxidation potential, +0.16 V.[7] The latter is lower than those of the mono-telluride **3** (Ep = +0.55 V) and diphenyltelluride, PhTePh (Ep = +0.56 V) which showed an irreversible oxidation wave.[8] Normally tellurides having alkyl and/or aryl groups show irreversible redox behavior. This facile oxidation and the electrochemically reversible oxidation of **1** are attributed to the destabilization of **1** by peri lone pair-lone pair repulsion and the stabilization of the oxidized species by neighboring-tellurium participation.

The bis-telluride **1** was readily oxidized electrochemically, it was thus treated with concd H_2SO_4 as an oxidant.[9] Specifically, the solution of **1** in concd D_2SO_4 was analyzed by ^{125}Te NMR spectroscopy.[10] The ^{125}Te NMR spectrum of **1** in $CDCl_3$ shows a single peak at 617 ppm (relative to Me_2Te), while the D_2SO_4 solution of **1** shows a single peak at 964 ppm. This is a remarkable downfield shift, consistent with a dicationic structure **4**.



Interestingly, the telluronium cation **5** showed the peri interaction between telluronio-tellurenyl groups as evidenced by its ^{125}Te NMR spectral data.[11] The proton-decoupled ^{125}Te NMR spectrum of **5** in $CDCl_3$ exhibits two peaks at 557 ppm (Te) and at 656 ppm (Te^+); particularly, each peak shows two clearly resolved satellite peaks due to the ^{125}Te-^{125}Te coupling (large coupling constant of $J_{\text{Te-Te}}$ = 1093 Hz) about each central peak. This is the first observation of ^{125}Te satellite due to the interaction between telluronio and tellurenyl groups.[12]

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References and Notes

1 H. Fujihara and N. Furukawa, *J. Mol. Struct. (Theochem)*, **186**, 261 (1989); H. Fujihara, R. Akaishi, T. Erata, and N. Furukawa, *J. Chem. Soc., Chem. Commun.*, **1989**, 1789.

2 H. Fujihara, T. Ninoi, R. Akaishi, T. Erata, and N. Furukawa, *Tetrahedron Lett.*, **32**, 4537 (1991).

3 It was very difficult to prepare the 1,8-bis(alkyl or aryltelluro)naphthalenes; e.g., 1,8-bis(methyltelluro)naphthalene was not obtained from the reaction of naphtho[1,8-*c*,*d*]-1,2-ditellurole with methyllithium: J. Meinwald, D. Dauplaise, F. Wudl, and J. J. Hauser, *J. Am. Chem. Soc.*, **99**, 255 (1977).

4 H. O. House, D. G. Koepsell, and W. J. Campbell, *J. Org. Chem.*, **37**, 1003 (1972).

5 **1**: mp 114-115 °C; ^{1}H NMR ($CDCl_3$) δ 7.09-7.21 (m, 8H), 7.55-7.58 (m, 4H), 7.66-7.70 (m, 2H), 8.02-8.05 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 119.8, 123.8, 126.4, 127.8, 129.4, 130.2, 135.4, 137.3, 140.1, 141.5. Anal. Found: C, 49.07; H, 2.94%. Calcd for $C_{22}H_{16}Te_2$: C, 49.34; H, 3.01%. **2**: liquid; ^{1}H NMR ($CDCl_3$) δ 0.74 (t, J=7.5 Hz, 6H), 1.23 (sext, J=7.5 Hz, 4H), 1.54 (quint, J=7.5Hz, 4H), 2.61 (t, J=7.5 Hz, 4H), 7.15 (t, J=7.4 Hz, 2H), 7.61 (d, J=7.4 Hz, 2H), 8.02 (d, J=7.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.4, 17.6, 25.1, 32.5, 118.2, 126.1, 129.5, 134.6, 139.9, 141.3; ^{125}Te NMR ($CDCl_3$) δ 409; FAB-MS, *m/z* 496 (M^+). **3**: liquid; ^{1}H NMR ($CDCl_3$) δ 6.98-7.17 (m, 4H), 7.34-7.38 (m, 2H), 7.51-7.55 (m, 2H), 7.64-7.70 (m, 2H), 7.91-7.94 (m, 1H), 8.13-8.17 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 114.8, 117.8, 125.7, 126.1, 126.4, 126.8, 127.5, 128.6, 129.3, 131.6, 133.5, 135.7, 137.2, 138.6; ^{125}Te NMR ($CDCl_3$) δ 568; MS, *m/z* 334 (M^+). Anal. Found: C, 57.95; H, 3.56%. Calcd for $C_{16}H_{12}Te$: C, 57.91; H, 3.64%.

6 Crystal data for **1**: $C_{22}H_{16}Te_2$, monoclinic, space group P21/c, a = 12.579(7), b = 11.252(5), c = 14.601(4) Å, β = 112.17(3)°, V = 1913.8 Å^3, Z = 4, D = 1.86 g/cm^3, Mo Kα radiation (λ = 0.71073 Å), CAD4 diffractometer, 1831 with $I > 3\sigma(I)$. The structure was solved by direct methods and refined anisotropically by full-matrix least squares using the MolEN program package. The final R value was 0.056.

7 The electrochemical property of **2** could not be studied, since **2** was insoluble in CH_3CN.

8 1,8-Bis(methylthio)naphthalene as a sulfur analogue of **1** showed the irreversible oxidation potential, Ep = +0.70 V: R. S. Glass, S. W. Andruski, J. L. Broeker, H. Firouzabadi, L. K. Steffen, and G. S. Wilson, *J. Am. Chem. Soc.*, **111**, 4036 (1989).

9 A. J. Bard, A. Ledwith, and H. J. Shine, *Adv. Phys. Org. Chem.*, **12**, 155 (1976).

10 **4**: ^{1}H NMR (D_2SO_4) δ 6.25 (d, J=7.6 Hz, 4H), 6.63 (t, J=7.6 Hz, 4H), 6.91 (t, J=7.6 Hz, 2H), 7.55 (t, J=7.8 Hz, 2H), 7.71 (d, J=7.8 Hz, 2H), 7.98 (d, J=7.8 Hz, 2H); ^{13}C NMR (D_2SO_4) δ 121.5, 123.9, 132.8, 134.3, 137.1, 137.8, 138.3, 142.4, 144.7, 146.9.

11 Treatment of **1** with 1 equiv of $CF_3SO_3CH_3$ (TfOMe) gave **5** (77%). **5**: mp 158-160 °C; ^{1}H NMR ($CDCl_3$) δ 2.81 (s, 3H), 7.11-7.17 (m, 5H), 7.36-7.59 (m, 7H), 7.84-7.87 (m, 1H), 8.07-8.14 (m, 2H), 8.54-8.57 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 18.4, 113.5, 117.9, 122.6, 123.3, 126.9, 127.6, 127.8, 128.2, 130.0, 130.6, 131.6, 133.0, 133.6, 133.9, 134.9, 136.6, 136.8, 138.1, 147.5. ^{19}F NMR ($CDCl_3$) δ 84.5 (relative to C_6F_6).

12 "The Chemistry of Organic Selenium and Tellurium Compounds," ed by S. Patai and Z. Rappoport, Wiley, New York (1986), Vol. 1 and (1987), Vol. 2.