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Synthesis of 1,2-Ditellurolane Derivatives

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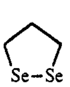
Abstract: Stable derivatives **4** and **5** of the elusive 1,2-ditellurolane (**3**) have been synthesized. Ditellurolane **4** was subjected to X-ray crystallographic analysis. The unusual blue color of these molecules has been attributed to the small dihedral angle associated with the rigid ring. The most remarkable reaction of these systems is the reversible monoprotonation of the Te–Te moiety.

Introduction

More than a century ago, Hagelberg[1] found that hydrolysis of 1,3-propanediyl bis(selenocyanate) afforded a yellow powder, to which Morgan and Burstall[2] assigned the structure of 1,2-diselenolane (**1**). Bergson and co-workers later disputed this conclusion and presented convincing evidence that this material is a polymer or oligomer which reversibly depolymerizes in solution to give heterocycle **1**, distinguishable by its unusually long-wavelength maximum at 440 nm.[3-6] In contrast, a number of 1,2-diselenolanes bearing buttressing substituents on the ring have been described, the most recent being the highly crystalline spiro derivative **2**.[7]



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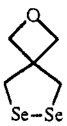

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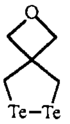

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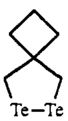

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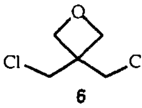
Far less is known concerning the tellurium analog of **1**, namely, 1,2-ditellurolane (**3**). The only reference to **3** is found in a paper by Merkel et al.,[8] in which the reaction of a 1,3-dihalopropane with a polytelluride anion gave a semisolid, deep red material which was blue in benzene solution and which gave analytical and mass spectral data consistent with structure **3**. The possibility that the red semisolid was a polymer, and that 1,2-ditellurolane was the blue species in solution, was not considered.

We now report our studies on the 1,2-ditellurolane system. These include attempts to isolate the elusive parent heterocycle **3**, as well as the synthesis and extensive characterization of the first stable, crystalline 1,2-ditellurolanes, **4**[9] and **5**.

Results and Discussion

Some time ago, we reported a convenient in situ synthesis of the tellurocyanate anion and its application to the preparation of benzyl tellurocyanate, the first alkyl tellurocyanate.[10] To our knowledge, no further alkyl tellurocyanates have been reported. In an attempt to prepare 1,3-propanediyl bis(tellurocyanate), 1,3-dibromopropane was reacted with potassium tellurocyanate in dry DMSO. Addition of water afforded an amorphous dark gray solid, which on Soxhlet extraction with carbon disulfide gave a deep blue solution showing absorption bands at 690, 601, and 400 nm. Evaporation of the solvent yielded an amorphous orange-red glass, which slowly redissolved on warming in carbon disulfide or benzene to give a blue solution. These observations are in general accord with those of Merkel et al.[8] and quite analogous to the behavior observed by Bergson in the corresponding case of the labile parent 1,2-diselenolane.

In the hope of stabilizing the 1,2-ditellurolane system by a buttressing effect, we examined the reaction of 3,3-bis(chloromethyl)oxetane (**6**) with potassium tellurocyanate in DMSO. On aqueous workup, the expected bis(tellurocyanate) **7** could not be isolated, but the purple-blue crystalline spiro ditellurolane **4** was obtained in yields of up to 65%. Compound **4**, mp 170 °C, formed deep blue solutions in a variety of solvents and crystallized well from ethanol or carbon disulfide. Its solution in benzene showed no ESR signal. Its UV–visible spectrum in CS_2 showed bands at 690, 601, and 400 nm, similar to those of the presumed unsubstituted 1,2-ditellurolane. Its ^1H NMR spectrum showed only two singlets at δ 3.65 and 4.38, while its decoupled ^{13}C NMR spectrum exhibited three signals at δ 83.36, 57.60, and 18.00. Its uncoupled ^{125}Te spectrum showed a single tellurium resonance as a triplet at δ 57.07 (J_{Te-H} = 27.5 Hz). The mass spectrum of the blue compound showed a strong ion cluster centered at 344, in support of structure **4**. It may be noted, however, that the combined spectroscopic data could not rule out the possibility that the compound might be the dimer **8**, containing an unusual four-tellurium core. However, unequivocal confirmation of the ditellurolane structure **4** was obtained by performing an X-ray crystallographic analysis (Figure 1).



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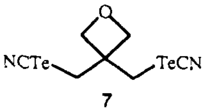

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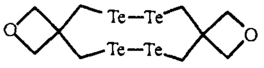

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Table I. Crystal Data and Summary of Data Collection Parameters for $C_5H_8OTe_2$

mol wt	339.3
space group	$P2_1/n$
cell constants	
a, Å	11.601 (4)
b, Å	5.859 (4)
c, Å	12.547 (4)
β, deg	116.20 (2)
V, Å^3	765
molecules/unit cell	4
D_c, g cm^{-3}	2.96
μ_c, cm^{-1}	75.9
radiation	Mo Kα
max cryst dimens, mm	0.50 × 0.50 × 0.30
scan width, deg	0.80 + 0.20 tan θ
std reflns	600, 440, 006
decay of stds	<2%
2θ range, deg	2–50
no. of reflns collcd	1548
no. of obsd reflns	1360
no. of params varied	73
R	0.082
R_w	0.080

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(1) Hagelberg, L. *Ber. Dtsch. Chem. Ges.* **1870**, *23*, 1083.
(2) Morgan, G. T.; Burstall, F. H. *J. Chem. Soc.* **1930**, 1497.
(3) Bergson, G.; Claeson, G. *Acta Chem. Scand.* **1957**, *11*, 911.
(4) Bergson, G. *Ark. Kemi* **1958**, *13*, 11.
(5) Bergson, G. *Ark. Kemi* **1962**, *19*, 195.
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(7) Günther, W. H. H.; Salzman, M. N. *Ann. N.Y. Acad. Sci.* **1972**, *192*, 25.
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(9) A preliminary description of **4** can be found in a patent: Lok, R.; Günther, W. H. H.; Freeman, J. P. U.S. 4,861,703; 1989. *Chem. Abstr.* **1990**, *112*, 148983$^{\gamma}$.
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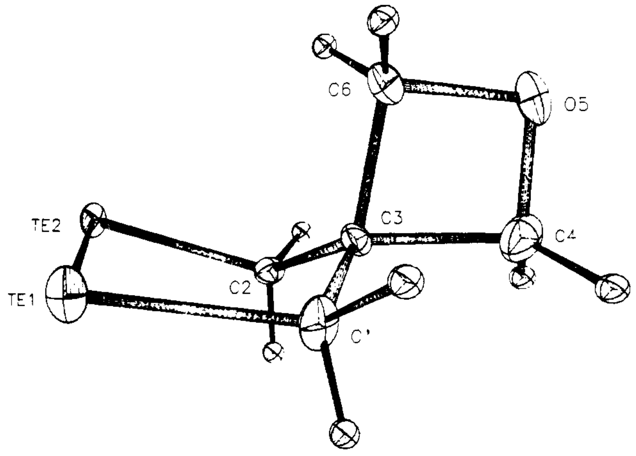
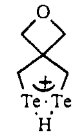


Figure 1.

Dark blue crystals were mounted in thin-walled glass capillaries prior to X-ray diffraction analysis. Details of usual procedures in our laboratory have been given previously.[11] A summary of data collection parameters and crystal data is presented in Table I. The structure was solved using SHELX-86. All atoms were treated with anisotropic thermal parameters. Hydrogen atoms in geometry-fixed positions were placed in calculated positions and were not refined. A final difference electron density map displayed no electron density that was unaccounted for.

Since the orange diethyl ditelluride shows an absorption maximum at 395 nm, the maximum exhibited by ditellurolane **4** at 690 nm represents a remarkable bathochromic shift of almost 300 nm. A similar but less dramatic shift (252 vs 440 nm) has been rationalized by LCAO-MO[12] and CNDO-MO[13] in the case of diselenides. To apply the general analysis used to the tellurium system, the small dihedral angle (8.5°) found in ditellurolane **4** results in considerable overlap of the two tellurium lone-pair p orbitals to give rise to doubly occupied π and π^* orbitals. The low-energy absorption band of **4** results from an electronic transition from the higher lying π^* orbital to a σ^* orbital, the energy of which is not dependent on the dihedral angle.

The existence of an unusual π-type conjugation between the two telluriums of **4** is in accord with the fact that a blue solution of the compound in acetonitrile becomes red-orange upon addition of a strong acid, with the UV–visible bands shifting to 521, 406, and 250 nm. The protonation is reversible, with the blue ditelluride bands reappearing on the addition of pyridine. The NMR of the protonated orange species showed that the δ 3.65 methylenes adjacent to the telluriums in the unprotonated form had moved downfield to coalesce with the oxetane protons at δ 4.38; addition of pyridine restored the δ 3.65 signal. These observations are consistent with protonation of the Te–Te bond to form a novel symmetrical π-complex of the type **9**; on the other hand, the possibility that the proton oscillates rapidly between the two Te atoms cannot be excluded. Unfortunately, the ^{125}Te signal of the orange species could not be observed, due to limited solubility. Several amorphous orange salts (i.e., tosylate and camphorsulfonate) were precipitated upon addition of ether. Only the perchlorate separated as nicely crystalline orange rhombs; however, *this salt detonated violently when touched with a spatula* (**CAUTION!**) and was not further examined.



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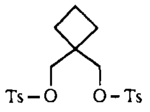

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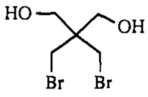

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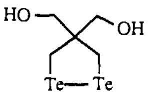

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Table II. Solvatochromic Behavior of Ditellurides **3–5**

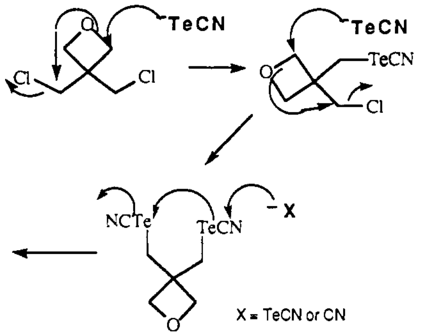
compound	solvent	λ_{max} (nm)
3	CS_2	690.5, 601.0
	benzene	667.0, 580 sh
	benzene + TFA	526, 407
4	CS_2	697, 602
	MeCN	641, 590
	CH_2Cl_2	665, 568
	MeOH	660, 580
5	CS_2	696, 603
	CH_2Cl_2	658, 567 sh
	CH_2Cl_2 + TFA	518, 398

A blue solution of **4** in tetrahydrofuran was reductively cleaved by sodium borohydride under nitrogen to the colorless ditellurolate. Introduction of air effected a rapid oxidation with the regeneration of the blue **4**.

The effect of the oxetane oxygen **4** on its electronic properties was probed by synthesizing its carbocyclic analog **5**. Thus, reaction of potassium tellurocyanate with 1,1-bis[(tosyloxy)methyl]cyclobutane (**10**) proceeded slowly and afforded directly, in modest yield, the purple ditellurolane **5**: mp 98 °C. The UV–visible spectra of both the unprotonated and protonated forms of **5** were identical to that of oxetane **4**, thus showing no effect on the ether oxygen on the ditellurolane system. All the compounds **3–5** showed solvatochromic behavior (see Table II).

Ditellurolane **5** was treated in methylene chloride solution with a solution of triflic acid in methylene chloride to give a red salt, analogous to **9**. Analytical determination of the acid:telluride ratio (see Experimental Section) led to a value of 1.04:1, supporting structures such as **9**.

The much faster and cleaner formation of **4** as compared to **5** may be the result of a sequence of steps involving nucleophilic attack of tellurocyanate at oxetane methylenes, as illustrated below. The fact that the formation of **4** involves the loss of the poorer leaving group (chloride vs tosylate) would seem to support this interpretation.



An attempt to form a ditellurolane from the acyclic dibromide **11** led to an insignificant amount of **12** under forcing conditions, identification being based solely on the UV spectrum, which was identical to those of **3**, **4**, and **5**. Steric factors are clearly of critical importance for the successful construction of the 1,2-ditellurolane structure.

Experimental Section

All melting points are uncorrected. NMR spectra were run in $CDCl_3$ solution. Ultraviolet spectra were run in the solvents specified. All organic extracts were dried over anhydrous sodium sulfate.

1,2-Ditellurolane (3). A solution of KTeCN[10] was prepared from tellurium (5.2 g, 0.04 mmol) and KCN (2.6 g, 0.04 mol) in dry DMSO (60 mL) under nitrogen. A solution of 1,3-dibromopropane (4.0 g, 0.02 mol) in DMSO (10 mL) was added to the cooled KTeCN solution. The mixture was stirred overnight. Water (60 mL) was added, and the brown precipitate was filtered and washed with more water. The solid was suspended in benzene (100 mL), treated with aqueous NaOH solution (10%, 100 mL), and gently warmed. The blue benzene layer was separated. The lower layer was extracted with more benzene until no more blue color was extracted. The combined benzene layer was washed, dried, filtered, and evaporated to give a brown gum (1.2 g). Extracts of this gum in common organic solvents (benzene, CS_2, CH_2Cl_2, $CHCl_3$) con-

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[11] Holton, J.; Lappert, M. F.; Ballard, D. G. H.; Pearce, R.; Atwood, J. L.; Hunter, W. E. *J. Chem. Soc., Dalton Trans.* **1979**, 45.

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tained **3** and were blue. UV: λ_{max} (CS_2) 690.5, 601 nm; λ_{max} (benzene) 667, 580, sh 318 nm; λ_{max} (benzene + TFA) 526, 407 nm. NMR: 3.843 (q, 2 H, $J = 6.2$ Hz), 3.42 (t, 4 H, $J = 6.2$ Hz).

2-Oxa-6,7-ditelluraspiro[3.4]octane (4). To a cooled solution (room temperature) of KTeCN in DMSO (50 mL),[10] which was generated from tellurium (5.1 g, 0.04 mol) and KCN (2.6 g, 0.04 mol) under nitrogen, was added 3,3-bis(chloromethyl)oxetane (3.1 g, 0.05 mol) in DMSO (25 mL). The dark mixture was stirred overnight and then heated to form a brown slurry. The mixture was diluted with water, and the dark solid was filtered. Crystallization from boiling ethanol furnished dark shiny crystals of **4** with a purplish sheen (5.1 g; yield 65%). Alternately, ditelluride **4** can also be extracted via Soxhlet extraction using CS_2 or $CHCl_3$. The yield of **4** varied from 25 to 65% depending on the quality of the bis(chloromethyl)oxetane, the duration of heating, etc. Compound **4**: mp >165 °C dec. UV: λ_{max} (CS_2) 697 (ϵ 308), 602 (279), 580 sh (223), 381 nm (2347). Raman: Te–Te bands at 181, 191 cm^{-1} (overtones at 363, 376 cm^{-1}). MS (^{130}Te): 344 (M^+, 40). NMR: ^1H 4.39 (s, 4 H), 3.65 (2, 4 H); ^{13}C 83.36, 57.6, 18.00; ^{125}Te (uncoupled) 57.07 ($J_{Te-H} = 27.5$ Hz). Anal. Calcd for $C_5H_8OTe_2$: C, 17.69; H, 2.36; Te, 75.23. Found: C, 17.3; H, 2.4; Te, 74.9.

6,7-Ditelluraspiro[3.4]octane (5). To a cooled solution of KTeCN in DMSO (30 mL) under nitrogen, which was generated from tellurium (1.30 g, 0.01 mol) and KCN (0.69 g, 0.011 mol), was added a solution of 1,1-bis[(tosyloxy)methyl]cyclobutane (**10**; 1.50 g, 0.0035 mol). The mixture was heated overnight at 90–100 °C under nitrogen and then stirred at room temperature for 1 day. The dark suspension was poured into dilute aqueous NaOH solution (100 mL, 1.5%). The precipitate was filtered, washed, dried, and extracted into CH_2Cl_2 using a Soxhlet extractor, until no more blue color was extracted. Concentration of the blue extract followed by addition of cyclohexane yielded ditellurolane derivative **5** (0.21 g; 21% yield) in two crops: mp 98 °C dec. UV: λ_{max} (CS_2) 696 (ϵ 308), 603 nm (270). MS (^{130}Te): *m/e* 342 (M^+, 28), 260 ($M^+ - 82$, 67). NMR: ^1H 3.46 (s, 4 H), 2.0–1.8 (m, 6 H); ^{13}C 56.42, 34.38, 23.45, 12.84; ^{125}Te (uncoupled) 50.01 (t, $J_{Te-H} = 29$ Hz). Anal. Calcd for $C_6H_{10}Te_2$: 339.888 943. Found: 339.887 131.

Action of Triflic Acid on 5. A suspension of **5** (40 mg) in CH_2Cl_2 (10 mL) was cautiously treated with a dilute solution of triflic acid in CH_2Cl_2 under sonification until a red precipitate resulted and the supernatant ceased to be blue. The salt was filtered, washed with more CH_2Cl_2 and hexane, and dried. A weighed quantity (0.054 g) of the salt was vibrated with distilled water when it reverted to **5**. This was filtered and washed with more distilled water. The aqueous filtrate containing triflic acid was titrated against standard NaOH solution (0.025 N) using phenolphthalein as the indicator, and it consumed 4.6 mL, leading to a H^+:**5** ratio of 1.045:1.0.

Acknowledgment. We thank the National Science Foundation (Grant CHE-9001714) for support of this work.

Supplementary Material Available: One figure, showing the unit-cell packing in **4**, and three tables, listing final fractional coordinates, bond distances and angles, and anisotropic thermal parameters for **4** (2 pages); a table of observed and calculated structure factors for **4** (8 pages). Ordering information is given on any current masthead page.

A Mechanistic Study of the Electrochemical Oxidation of 2,5-Bis(2-thienyl)pyrroles

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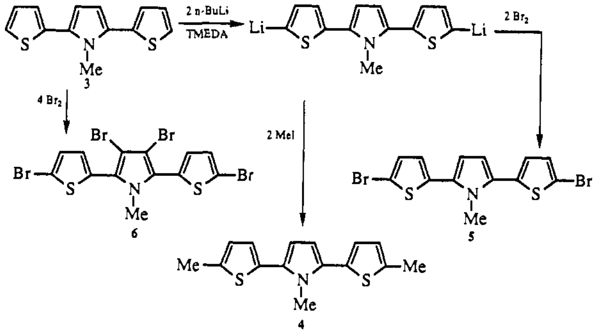
Received August 17, 1992

Abstract: A series of 2,5-bis(2-thienyl)pyrroles has been synthesized in which the α-thiophene protons and/or the β-pyrrole protons have been replaced by Me or Br substituents. A systematic electrochemical investigation of these compounds has yielded rate constants of 36 000 M^{-1} s^{-1} for linear coupling of the electrochemically generated cation radicals and 14 000–17 000 M^{-1} s^{-1} for branched coupling reactions of the cation radicals. These results constitute the first kinetic evidence for appreciable branched coupling of the electrochemical radical cations of an oligomer precursor of a conducting polymer.

Introduction

The chemistry of organic conducting polymers has been the subject of intensive worldwide investigation in recent years. With the exception of polyaniline, the polythiophenes and polypyrroles have received the most attention.[1] Hybrid polymers containing varying proportions of thiophene and pyrrole units are logical second generation materials of related structure. These have been produced not only by oxidative polymerization of simple mixtures of thiophene and pyrrole[2] but also from 2-(2-thienyl)pyrrole (**1**)[3] as well as the triheterocyclic precursor 2,5-bis(2-thienyl)pyrrole (**2**) and its *N*-alkyl derivatives.[4–6] Our interest has focused on the latter system for several reasons. First, polymers in this series have been reported to have conductivities which vary from 10^{-3} to 280 S/cm, depending on the dopant and the method of preparation. Second, the symmetrical nature of the tricyclic monomer **2** would be expected to lead to polymers of greater linearity and symmetry than that derived from the biheterocycle **1**, in which, as Pelter has noted, "...the order of the units is unknown, as well as the positions of linkage, the degree of branching, and the extent of crosslinking".[7] Such a view seems well justified since, while α,α' coupling is strongly favored for pyrroles on the monomer level,[8] theoretical calculations predict that as higher oligomers

Scheme I



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† Frank J. Seiler Research Laboratory/NE, USAF Academy, Fort Collins, CO 80840.

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