Heteroatom Chemistry
Volume 6, Number 5, 1995

First Synthesis and Structural Determination of 1,1′-Spirobis(3H-2,1-benzoxatellurole)-3,3′-dione ([10-Te-4(C2O2)])

Yutaka Takaguchi and Naomichi Furukawa*

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

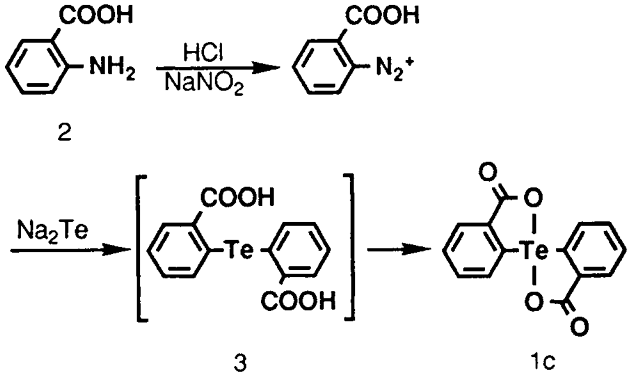
Received 27 December 1994; revised 18 February 1995

ABSTRACT

1,1′-Spirobis(3H-2,1-benzoxatellurole) -3, 3′-dione [10-Te-4(C2O2)] (**1c**) *with five-membered spirorings was prepared, and its molecular structure was determined by X-ray crystallographic analysis. The two types of arrangement of the ligands about the central tellurium atom show considerably distorted trigonal bipyramidal (TBP) geometries. The tellurane* **1c** *undergoes a ring-opening reaction on treatment with aqueous sodium hydroxide to afford the telluroxide* **10**, *which reacts with aqueous hydrochloric acid at room temperature to give again the tellurane* **1c** *in quantitative yield. © 1995 John Wiley & Sons, Inc.*

INTRODUCTION

Organic hypervalent compounds of chalcogens have received considerable attention in the past two decades [1–3]. In particular, the synthesis and properties of various spirosulfuranes and spiroselenanes have been extensively reported [4]. However, much less is known about the chemistry of spirotelluranes. Furthermore, while several dialkoxyspirotelluranes [10-Te-4(C2O2)] have been prepared [5], preparation of a diacyloxyspirotellurane has never been reported. This article describes the first isolation of the diphenyldiacyloxyspirotellurane **1c** and its structural determination by X-ray crystallographic analysis.



SCHEME 1

RESULTS AND DISCUSSION

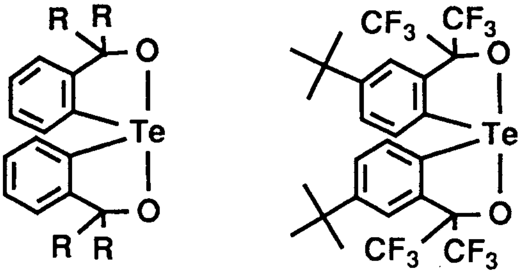
The title compound **1c** was synthesized, as shown in Scheme 1. The structure of **1c** was confirmed by ^{1}H, ^{13}C, and ^{125}Te NMR spectroscopy, mass spectroscopy, and elemental analysis. Particularly, the ^{125}Te spectroscopy is a diagnostic method to estimate the structure of tellurium compounds. The ^{125}Te NMR shift of spirotellurane **1c** appears at 951 ppm ($CDCl_3$) and 1021 ppm (CD_3OD), similar to the shifts of dialkoxyspirotelluranes (**4**), (**5**), and (**6**) (1196 ppm in C_6H_6, 1051 and 1190 ppm in $CDCl_3$) [5]. On the other hand, the mass spectrum of **1c** shows clearly the parent peak at *m/z* 370 (M^+, 1.30%) together with *m/z* 326 ($M^+ - 44$, 14.0%).

The structure of the compound **1c** was finally determined by X-ray crystallographic analysis [6]. The molecular structure of spirotellurane **1c**, similarly to other telluranes [5,7], exhibits a considerably distorted trigonal bipyramidal (TBP) geometry about the central tellurium atom, where the

---

*To whom correspondence should be addressed.

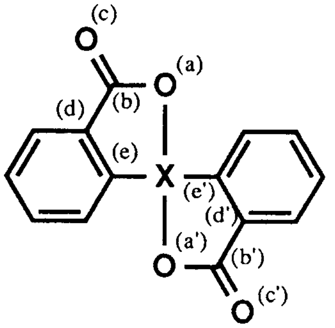
1042-7163/95/050481-04



4: R = CF3
5: R = CH3

6

STRUCTURAL FORMULA 1



1a: X=S
1b: X=Se
1c: X=Te

STRUCTURAL FORMULA 2

more electronegative acyloxy ligands are in the apical positions with the two aryl carbons and the lone electron pair in the equatorial ones. The tellurane **1c** was found to be composed of two nearly identical crystals. The ORTEP drawing of **1c** is shown in Figure 1. The apical Te(1)–O(1), Te(1)–O(3), Te(2)–O(1'), and Te(2)–O(3') bond distances are 2.106(7), 2.137(6), 2.112(7), and 2.129(7) Å, whereas the equatorial Te(1)–C(11), Te(1)–C(21), Te(2)–C(11'), and Te(2)–C(21') bond lengths are 2.10(1), 2.10(1), 2.09(1), and 2.096(9) Å, respectively. The apical Te–O distances related to hypervalent bonds were found to be slightly longer than the sum of the tellurium and oxygen covalent radii (2.10 Å). Bond angles O(1)–Te(1)–O(3), O(1')–Te(2)–O(3'), O(1)–Te(1)–C(11), C(1)–Te(1)–C(21), O(3)–Te(1)–C(11), O(3)–Te(1)–C(21), O(1')–Te(2)–C(11'), O(1')–Te(2)–C(21'), O(3')–Te(2)–C(11'), O(3')–Te(2)–C(21'), C(11)–Te(1)–C(21), and C(11')–Te(2)–C(21') are 161.3(3), 158.4(3), 79.3(4), 87.3(3), 88.6(3), 79.4(3), 79.6(3), 85.5(3), 87.3(3), 78.8(3), 94.2(4), and 95.6(4)°, indicating that **1c** is a considerably distorted TBP structure that is nearly identical with that of tetraphenyltellurane (**7**) as reported by Smith et al. [8].

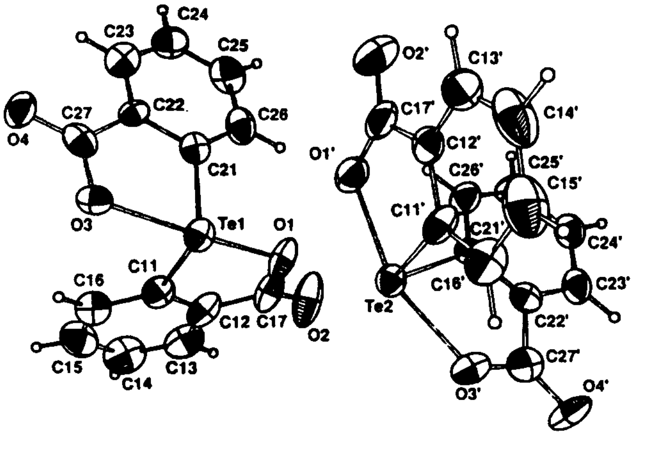


FIGURE 1 ORTEP drawing of **1c**.

The butterfly-like molecule of the symmetrical spirotellurane **1c** retains its C2 molecular symmetry in the crystal structures formed equally with the space group P2SC/n (No. 14). Due to the distorted TBP geometry, all of the O–Te–C bond angles in **1c** are nearly 90°, and the O–Te–O moieties are approximately linear. In most cases, the Te–O bonds are slightly bent toward the aromatic rings (the endocyclic O–Te–C bond angles are usually somewhat smaller than 90°). The five-membered rings in spirotellurane **1c** are almost coplanar, within experimental error, having endocyclic torsional angles (φ) smaller than 8°. The aromatic rings are nearly perpendicular to the equatorial plane, as shown by the C–Te–C–C torsional angles of 77–103°. The fusion of the planar spirorings with the benzene rings does not cause any steric strain.

Since the spirochalcogenuranes **1a**–**c** can be classified as [10-X-4(C2O2)] (X=S, Se, Te) species, they seem to be appropriate models for studying the efficiency of the central atom effect by comparing their molecular structures and resistance to hydrolysis. By X-ray structure determination, we can compare the geometric parameters about the chalcogen characteristic of the molecular structures of diaryldiacyloxychalcogenuranes and explain how the central atom of the spirorings influence these parameters. Selected bond lengths and bond angles that are characteristic of the spirochalcogenuranes **1a**–**c** are listed in Table 1.

The structural data of spirosulfurane (**1a**) and -selenane (**1b**) can be well interpreted on the basis of Musher's theory assuming hypervalent three-center four-electron bonds in the axial array. It must be noted that an apical O–X–O angle of **1c** is about 20° smaller than that of spirosulfurane **1a**. The gradual increase of O–X–O distances in the spirochalcogenuranes **1a**–**c** is accompanied by a similar decrease of O–X–O bond angles and X–C bond lengths.

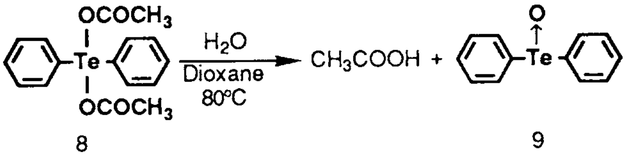
Thus, it may be concluded that the structural parameters about the chalcogen in spirochalcogenuranes [10-X-4(C2O2)] (X=S, Se, Te) with aromatic carbon and acyloxy-oxygen are not close to

TABLE 1 Selected Bond Distances and Angles for Spirosulfurane **1a**, Spiroselenane **1b**, and Spirotellurane **1c**

	Spirochalcogenuranes		
	1a	**1b**	**1c**
Bond distances (Å)			
X–O$_a$	1.842(3)	1.968(7)	2.106(7)
X–O$_{a'}$	1.842(3)		2.137(6)
X–C$_e$	1.794(5)	1.930(7)	2.10(1)
X–C$_{e'}$	1.794(5)		2.10(1)
O$_a$–C$_b$	1.320(9)	1.329(12)	1.35(1)
O$_c$–C$_b$	1.192(8)	1.198(10)	1.23(1)
C$_b$–C$_d$	1.46(3)	1.488(11)	1.46(2)
Bond angles (°)			
O$_a$–X–O$_{a'}$	177.7(4)	172.4(3)	161.3(3)
O$_a$–X–C$_e$	91.3(4)	91.4(3)	79.3(4)
O$_a$–X–C$_e$			87.3(3)
O$_a$–X–C$_e$			88.6(3)
O$_a$–X–C$_{e'}$	91.3(4)	83.8(3)	79.4(3)
C$_e$–X–C$_e$	106.9(4)	101.0(3)	94.2(4)
X–O$_a$–C$_b$	115.2(7)	115.4(5)	114.8(7)
O$_a$–C$_b$–C$_d$	111(1)	112.1(7)	114.8(9)
O$_c$–C$_b$–C$_d$		125.4(8)	125(1)

one another and are considerably influenced by the central atom.

Compound **1c** was quite stable to water and did not form the corresponding telluroxide, even on heating, which is in marked contrast to the behavior of the sulfur analog (**1a**). This result indicates that the equilibrium lies very far to the left, in analogy with dialkoxyspirosulfuranes (Scheme 2) [9]. On the other hand, the acyclic diaryldiacyloxytellurane (**8**) was hydrolyzed in dioxane-water to give diphenyl telluroxide (**9**) and acetic acid (Scheme 3). The ring effect of spirotellurane **1c** well accounts for such a decrease in reactivity. However, in the case of spirotellurane **1c**, on treatment with aqueous sodium hydroxide, the formation of telluroxide (**10**) was detected by ^{125}Te, ^{1}H, and ^{13}C NMR spectroscopy. Interestingly, telluroxide **10** returns to **1c** by neutralization with aqueous hydrochloric acid (Scheme 4). Therefore, the stability of diaryldiacyloxyspirochalcogenurane [10-Te-4(C2O2)] (X=S, Se, Te) is identical with that of tetraphenylchalcogenuranes.

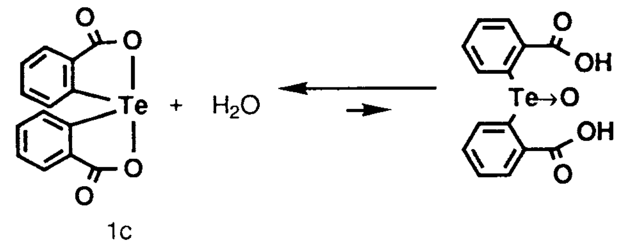


SCHEME 3

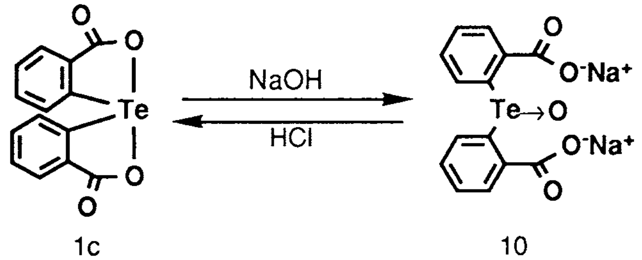
EXPERIMENTAL

1,1′-Spirobis(3H-2,1-benzoxatellurole)-3,3′-dione (**1c**). A solution of sodium nitrite (4.70 g, 61.8 mmol) in water (20 mL) was added dropwise to a white suspension of anthranilic acid (**2**) (8.23 g, 60.0 mmol) in water (40 mL) and concentrated hydrochloric acid (40 mL) at 0–5°C. After 1 hour, the yellow reaction mixture was allowed to react with sodium telluride, which was prepared by treatment of tellurium (3.83 g, 30.0 mmol) with sodium hydroxide (21.4 g, 534 mmol) and rongalite (27.4 g, 178 mmol) in water (100 mL) at 80°C. The whole mixture was stirred at 80°C for 30 min. The yellow products were precipitated with acid and separated from the solution by filtration. The crude products were purified by silica-gel column chromatography (methanol/chloroform 1:8) and recrystallized from methanol to give white crystalline (**1c**) (3.22 g, 8.76 mmol, 14.6%), mp 286–287°C; ^{1}H NMR (CD$_3$OD) δ 7.71 (t, J = 7.3 Hz, 2H), 7.86 (t, J = 7.3 Hz, 2H), 7.94 (d, J = 7.3 Hz, 2H), 8.08 (d, J = 7.3 Hz, 2H); ^{13}C NMR (CD$_3$OD) δ 131.8, 132.6, 134.3, 134.4, 137.0, 139.1, 174.6; ^{125}Te NMR (CD$_3$OD) δ 1021 (relative to Me$_2$Te); MS, *m/z* 370 (M$^+$). Anal. calcd for C$_{14}$H$_8$O$_4$Te: C; 45.72, H; 2.19%. Found: C, 45.55; H, 2.25%.

Although it has been reported that bis(2-carboxyphenyl)telluride (**3**) can be obtained by reacting potassium telluride with diazotized anthranilic acid [10], we could not obtain **3**. Probably, **3** was oxidized during the workup procedure by aerial oxygen to give the telluroxide that undergoes



SCHEME 2



SCHEME 4

dehydration resulting in the formation of **1**, as shown in Scheme 2.

Hydrolysis of Acyclic Diaryldiacyloxytellurane (**8**). A solution of tellurane **8** (31.0 mg, 0.114 mmol) in 15 mL of dioxane-water (9:1 v/v) was heated at 80°C for 5 hours. Telluroxide (**9**), which was identified as to its structure by comparing ^1H, ^{13}C, ^{125}Te nmr spectra with those of an authentic sample, could be obtained together with acetic acid in quantitative yield.

Formation of Bis(2-carboxyphenyl)telluroxide, Sodium Salt (**10**). A solution of sodium hydroxide (100 mg) in D_2O (0.50 mL) was added to spirotellurane **1c** (20 mg, 0.054 mmol). Telluroxide **10** was detected by its ^1H NMR (D_2O) spectrum, δ, 7.51–7.54 (m, 2H), 7.59–7.66 (m, 4H), 8.10–8.13 (m, 2H); ^{13}C NMR (D_2O) δ 132.5, 132.6, 133.3, 135.2, 138.8, 143.1, 176.1; ^{125}Te NMR (D_2O) δ 1258 (relative to Me_2Te). This solution was neutralized with aqueous hydrochloric acid, and white precipitates were separated from the solution by filtration to give again the tellurane **1c** in quantitative yield.

ACKNOWLEDGMENT

This work was supported by the Ministry of Education, Science and Culture, Japan (priority area: Grant No. 05236205).

REFERENCES

[1] R. A. Hayes and J. C. Martin: Sulfurane Chemistry, in F. Bernardi, I. G. Csizmadia, and A. Mangini (eds): *Organic Sulfur Chemistry, Theoretical and Experimental Advances*, Elsevier, Amsterdam, pp. 408–483 (1985).

[2] J. I. Musher, *Angew. Chem., Int. Ed. Engl., 8*, 1969, 54; M. M. L. Chen and R. Hoffmann, *J. Am. Chem. Soc., 98*, 1976, 1647; A. E. Reed and P. von R. Schleyer, *ibid., 112*, 1990, 1434; W. Kutzelnigg, *Angew. Chem., Int. Ed. Engl., 23*, 1984, 272; A. Demolliens, O. Eisenstein, P. C. Hiberty, J. M. Lefour, G. Ohanessian, S. S. Shaik, and F. Volatron, *J. Am. Chem. Soc., 111*, 1989, 5623.

[3] D. H. R. Barton, S. A. Glover, and S. V. Ley, *J. Chem. Soc. Chem. Commun.*, 1977, 266; D. Hellwinkel and G. Fahrbach, *Liebigs Ann. Chem., 712*, 1968, 1; I. Harigittai and B. Rozsondai: Structural Chemistry of Organic Compounds Containing Selenium or Tellurium, in S. Patai and Z. Rappoport (eds): *The Chemistry of Organic Selenium and Tellurium Compounds Volume 1*, Wiley, New York, pp. 63–155 (1986); J. Bergman, L. Engman, and J. Sidin: Tetra- and Higher-valent (Hypervalent) Derivatives of Selenium and Tellurium, in *ibid.*, pp. 517–558 (1986); D. B. Denney, D. Z. Denney, P. J. Hammond, and Y. F. Hsu, *J. Am. Chem. Soc., 103*, 1981, 2340; S. Ogawa, S. Sato, T. Erata, and N. Furukawa, *Tetrahedoron Lett., 33*, 1992, 1915.

[4a]A. Kálmán, K. Sasvari, and I. Kapovits, *Acta Crystallogr., B29*, 1973, 355; I. Kapovits, J. Rábai, D. Szabó, K. Czakó, Á. Kucsman, G. Argay, V. Fülöp, A. Kálmán, T. Koritsánszky, and L. Párkányi, *J. Chem. Soc., Perkin Trans. 2*, 1993, 847.

[4b]B. Dahlen and B. Lindgrew, *Acta Chem. Scand., 27 (6)*, 1973, 2218.

[4c]J. C. Martin and R. J. Arhart, *J. Am. Chem. Soc., 86*, 1971, 2339.

[4d]H. J. Reich, *J. Am. Chem. Soc., 95*, 1973, 964.

[5] R. S. Michalak, S. R. Wilson, and J. C. Martin, *J. Am. Chem. Soc., 106*, 1984, 7529

[6] Crystallographic Data for **1c**; Fw = 367.82, monoclinic, space group PSC/n, a = 9.037(1), b = 12.407(2), c = 22.316(3) Å, $V/Å^3$ = 2498.3, Z = 8, R = 0.056, Rw = 0.063 for 4606 reflections. Atom coordinates, bond lengths, bond and torsional angles, temperature factors of all atoms, and F_{obs}/F_{calc} values are deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

[7] S. Sato, N. Kondo, and N. Furukawa, *Organometallics, 13*, 1994, 3393.

[8] C. S. Smith, J.-S. Lee, D. D. Titus, and R. F. Ziolo, *Organometallics, 1*, 1982, 350.

[9] W. Y. Lam and J. C. Martin, *J. Org. Chem., 46*, 1981, 4462.

[10]W. V. Farrar, *Research (London), 4*, 1951, 177.