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Isolation and Structure of Bis(2,2'-biphenylylene)dichloro- and -difluoropertelluranes, [12–Te–6(C4X2), X = Cl, F] (λ^6-Tellane)

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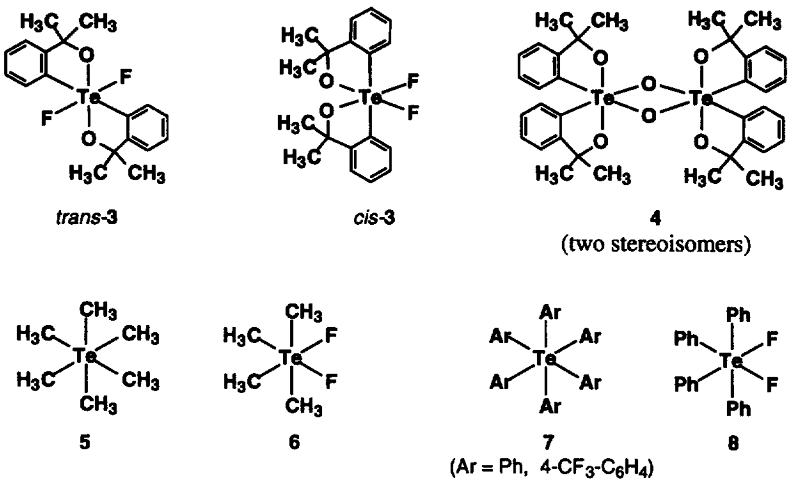
Abstract: Bis(2,2'-biphenylylene)tellurane (**1**; λ^4-tellane) reacts with sulfuryl chloride and xenon difluoride to give bis(2,2'-biphenylylene)dichloro- and -difluoropertelluranes, [12–Te–6(C4X2), X = Cl (**2a**), F (**2b**)] (λ^6-tellane) in high yields. The structures of the pertelluranes **2a** and **2b** were determined by single crystal X-ray crystallographic analysis, revealing that they have a distorted octahedral geometry and a *cis*-configuration with respect to the coordinated halogen atoms, and subsequently each was analyzed by an *ab initio* calculation. © 1997 Elsevier Science Ltd.

INTRODUCTION

There are only a few neutral hexavalent organic tellurium compounds among the hypervalent tellurium species, but tetravalent compounds which often exhibit a trigonal bipyramidal structure are more common.[1] The first hexavalent organotellurium(VI) species (λ^6-tellane) [12–Te–6(C2O2F2)] (**3**) and $[12\text{–Te–}6(\mathrm{C2O4})]_2$ (**4**) have been reported by Martin et al.[2] These compounds were synthesized by the reaction of the corresponding tetravalent tellurane [10–Te–4(C2O2)] with BrF_3 or ozone. The former structure was determined to be octahedral with *cis* configurations by X-ray crystallographic analysis. The synthesis of hexamethylpertellurane, [12–Te–6(C6)] (**5**), and tetramethyldifluoropertellurane, [12–Te–6(C4F2)] (**6**), has been reported by Morrison et al., and the molecular structure analysis of $(CH_3)_6Te$ was revealed by gas-phase electron diffraction[3] and its theoretical MO calculation has been performed by Schaefer et al.[4] However, no X-ray crystallographic analysis of this species have been reported until recently. Quite recently, Akiba and Seppelt et al. have reported that the reaction of LiC_6H_4-4-CF_3 with $TeCl_4$ and that of $F_2Te(C_6H_5)_4$ (**8**) with PhLi give hexakis[4-(trifluoromethyl)phenyl]pertellurane (**7**) and hexaphenylpertellurane, respectively. This is the first isolation of hexaarylpertellurane species.[5] The molecular structures of both pertelluranes were determined by X-ray crystallographic analysis.

We have been working on the syntheses, structures, and reactivities of the hypervalent chalcogen compounds (chalcogenurane).[6] Hellwinkel et al. reported that bis(2,2'-biphenylylene)tellurane (**1**) on treatment with 1 equiv of Br_2 or I_2 gave only the corresponding telluronium bromide or iodide and they did not obtain the corresponding pertellurane.[7] On the other hand, we have already reported that the reactions of tetraaryltellurane [10–Te–4(C4)] with various reagents are useful for the synthesis of new tetravalent telluranes containing oxygen atoms as ligands.[8] Furthermore, we reacted bis(2,2'-biphenylylene)tellurane (**1**) with sulfuryl chloride[9] and xenon difluoride, and obtained the new pertellurane **2**. Here we describe the first isolation of bis(2,2'-biphenylylene)dichloro- and difluoropertelluranes, [12–Te–6(C4X2), X = Cl (**2a**), F (**2b**)] (λ^6-tellane), and their crystal and molecular structures. Also included in this paper are the results of an *ab initio* calculation of the pertelluranes **2a** and **2b** showing the charge distribution of the molecules.

Chart 1



trans-3 *cis*-3 4 (two stereoisomers)

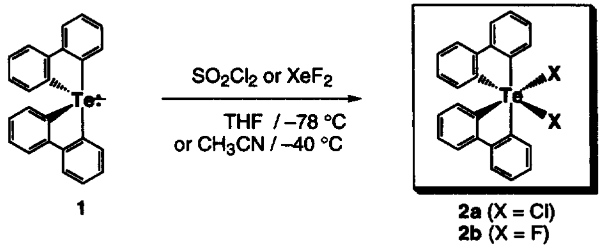
5 6 7 (Ar = Ph, 4-CF_3-C_6H_4) 8

RESULTS AND DISCUSSION

Synthesis and Spectra of Pertelluranes 2a and 2b

The tellurane **1** was reacted with 1 molar equiv of sulfuryl chloride in dry THF at –78 °C or xenon difluoride in dry CH_3CN at –40°C. After the removal of the solvent at room temperature, the corresponding tetraaryldichloropertellurane (**2a**) or tetraaryldifluoropertellurane (**2b**) was isolated as stable yellow crystals in 50% yield or colorless crystals in 54% yield, respectively, as shown in Scheme 1. These products were identified by ^1H, ^{13}C, ^{19}F and ^{125}Te NMR, mass spectroscopy, and elemental analysis.

Scheme 1



1

2a (X = Cl)
2b (X = F)

In the case of [12–Te–6(Y4Z2)] having Y and Z ligands (where Z is a more electronegative ligand than Y), it has been reported that the corresponding pertelluranes in the *cis* configuration tend to be more stable than the corresponding *trans* configuration and the results of various NMR spectra indicate that the two Y ligands on the Z–Te–Z plane are not equivalent to the other two Y ligands.[2,3,5] Examination of the ^1H and ^{13}C NMR spectra of the compounds **2a** and **2b** reveals that the two benzene rings in each biphenylylene groups are in nonequivalent states each other with 4 doublet and 4 triplet peaks seen in the ^{1}H spectra and a set of 12 peaks in the ^{13}C spectra. Furthermore, only the ^{1}H NMR chemical shift of the 3'-position in both *cis*-pertelluranes(VI) **2a** and **2b** appears at an unusually high field compared with those of bis(2,2'-biphenylylene)selenurane or -tellurane **1**, when at low temperature the pseudorotation is slower than the NMR time scale.[10] This result indicates that the 3'-proton is shielded by the aromatic ring of the neighboring biphenylylene group. Although the proton-decoupled ^{125}Te signal of **2a** in DMSO-d_6 appeared at 569.0 ppm as one peak, those of **2b** appeared at 699.8 ppm as the triplet peaks due to a spin-spin coupling between the tellurium and fluorine nuclei ($^{1}J_{\mathrm{Te-F}}$ = 2151 Hz) which are similar to the $^{1}J_{\mathrm{Te-F}}$ values of Me_4TeF_2 (1830 Hz)[3a] and Ph_4TeF_2 (2049 Hz)[5]. Furthermore, the ^{19}F signal of **2b** appeared at –47.2 ppm with the satellite peaks due to the same spin-spin coupling ($^{1}J_{\mathrm{F-Te}}$ = 2151 Hz) for the central peak. The ratio of these satellite peaks and central peak is in keeping with the natural abundance of the ^{19}F and ^{125}Te elements. The ^{13}C NMR signals for each of the 2- and 2'-positions on the biphenylylene groups in the compound **2b** appear at a low field as triplet peaks due to a spin-spin coupling between carbon and fluorine nuclei via the tellurium nucleus ($^{2}J_{\mathrm{C-F}}$ = 20.1 or 34.6 Hz) as shown in Figure 1. These results indicate that these 2- and 2'-carbon and fluorine atoms combine directly to the central tellurium atom. Compounds **2a** and **2b** were characterized by their parent peaks in their EI-MS spectra having isotope patterns identical with the calculated ones. In addition, **2a** and **2b** were also identified by elemental analysis.

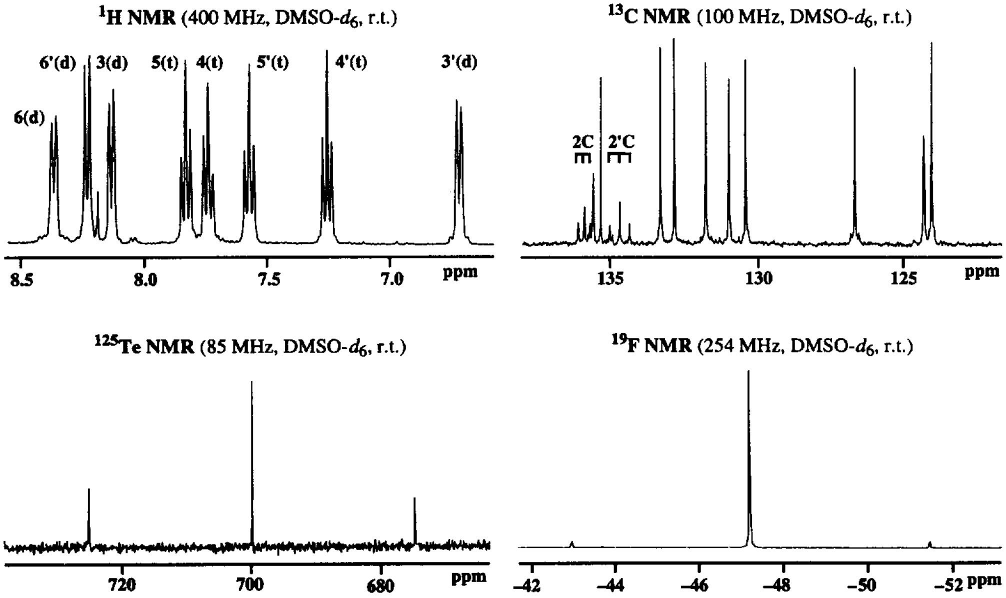


Figure 1. Various NMR spectra of **2b**.

On the basis of these results we can conclude that the compounds **2a** and **2b** are a hexacoordinated organopertelluranes having a *cis* configuration with respect to the two chlorine or fluorine atoms and that the inter- or intramolecular permutation of the ligands in Te(VI) is slow on the NMR time scale or is nonexistent.

Furthermore, we have succeeded in determining the structures of the products **2a** and **2b** by X-ray crystallographic analysis.

X-ray Crystallographic Analysis of Pertelluranes 2a and 2b

The molecular structure of **2a** as shown by an ORTEP plot has already been reported, together with a list of selected bond distances and angles.[9] In this report, the molecular structure of **2b** and the adopted numbering scheme for one enantiomer (Δ) are illustrated by an ORTEP plot in Figure 2.

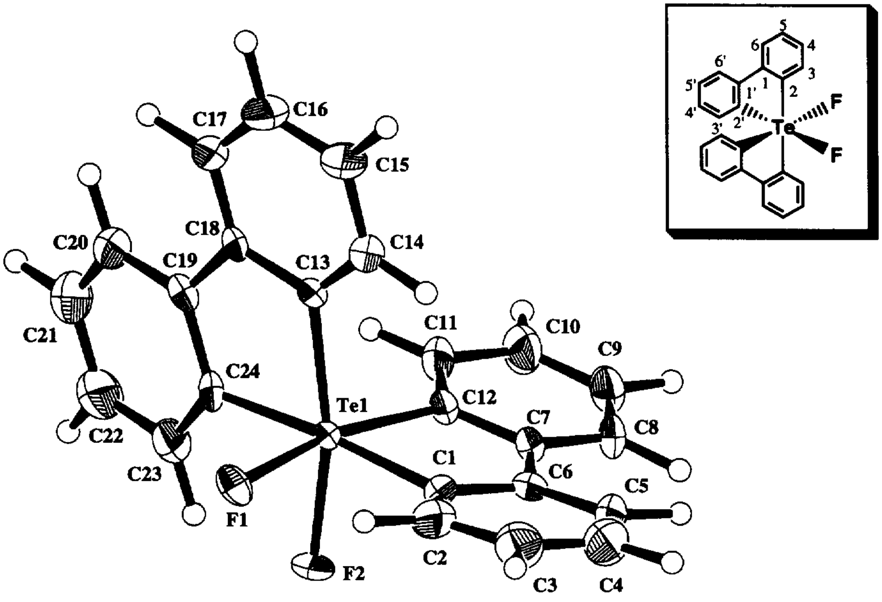


Figure 2. ORTEP view of pertellurane **2b** (Δ), showing each atom-numbering in the scheme. For clarity, the containing two water molecules are omitted.

The unit cell of **2a** consists of four molecules of $[Te(C_{12}H_8)_2Cl_2]$ and four CH_2Cl_2 molecules, each on a crystallographic 2-fold axis of symmetry. The racemic compound contains two types of tellurium centers, each having two biphenylylene ligands and two chlorine atoms in their coordination sphere in both the Δ and Λ configurations, respectively. The central tellurium atom has a distorted-octahedral coordination geometry with the two chlorine atoms *cis* to each other. The Te–Cl bond distance exhibited is 2.530(1) Å, which is longer than the Te–Cl single covalent bond (2.31 Å)[11] and the Te–Cl bond (2.33 ± 0.02 Å)[12] of $TeCl_4$, but is similar to the apical bond lengths (2.511 and 2.528 Å) found in $(CH_3)_2Cl_2Te$ and *trans*-$TeCl_4(SC(N(CH_3)_2)_2)_2$.[13] The average Te–C bond distance exhibited is 2.123(4) Å, which is similar to the Te–C single covalent bond (2.101 Å) and slightly shorter than the Te–C apical bond (2.24 Å) of bis(2,2'-biphenylylene)tellurane (**1**). A comparison of Te–C bond distances in the corresponding di-, tetra-, and hexavalent tellurium species shows that the variation of bond distances with increasing valency is irregular. The Te–C bond distances become longer in the order of dibenzotellurophene(II) (2.087 Å),[14] the pertellurane(VI) **2a**, and the tellurane(IV) **1**. These results agree with the order of Te–C bond distances of $(CH_3)_xTe$, (x = 2, 4, 6).[15]

On the other hand, the unit cell of **2b** contains four molecules of $[Te(C_{12}H_8)_2F_2]$ and two water molecules. The racemic compound contains two types of tellurium centers, each having two biphenylylene ligands and two chlorine atoms in their coordination sphere in both the Δ and Λ configurations, respectively. The central tellurium atom has a distorted-octahedral coordination geometry with the two fluorine atoms *cis* to each other and is similar to the configuration of **2a**. The average Te–F bond distance exhibited is 1.972 Å, which is similar to the Te–F single covalent bond (1.96 Å).[11] The average Te–C bond distance exhibited is 2.10(1) Å, which is nearly identical with that of the Te–C single covalent bond (2.101 Å) and is slightly shorter than the Te–C apical bond (2.24 Å) of bis(2,2'-biphenylylene)tellurane (**1**).

Table 1. Selected bond distances (Å) and angles (deg) with Esd's in parentheses for **2a** and **2b**[a]

2a				**2b**			
Te(1)–Cl(1)	2.530(1)	Te(1)–C(1)	2.130(3)	Te(1)–F(1)	1.969(6)	Te(1)–F(2)	1.975(6)
Te(1)–C(12)	2.116(4)	C(1)–C(2)	1.378(5)	Te(1)–C(1)	2.08(1)	Te(1)–C(12)	2.12(3)
C(1)–C(6)	1.400(5)	C(2)–C(3)	1.390(6)	Te(1)–C(13)	2.12(1)	Te(1)–C(24)	2.09(1)
C(3)–C(4)	1.369(7)	C(4)–C(5)	1.377(6)	C(1)–C(2)	1.39(2)	C(1)–C(6)	1.43(2)
C(5)–C(6)	1.398(5)	C(6)–C(7)	1.471(5)	C(2)–C(3)	1.42(2)	C(3)–C(4)	1.41(2)
C(7)–C(8)	1.396(6)	C(7)–C(12)	1.404(5)	C(4)–C(5)	1.37(2)	C(5)–C(6)	1.40(2)
C(8)–C(9)	1.385(7)	C(9)–C(10)	1.377(7)	C(6)–C(7)	1.49(2)	C(7)–C(8)	1.39(2)
C(10)-C(11)	1.398(6)	C(11)–C(12)	1.381(5)	C(7)–C(12)	1.38(1)	C(8)–C(9)	1.38(2)
				C(9)–C(10)	1.37(2)	C(10)–C(11)	1.41(2)
				C(11)–C(12)	1.35(2)		
Cl(1)–Te(1)–Cl(1)'	86.48(5)			F(1)–Te(1)–F(2)	83.7(3)		
Cl(1)–Te(1)–C(1)	90.3(1)			F(1)–Te(1)–C(1)	88.1(4)		
Cl(1)–Te(1)–C(1)'	87.8(1)			F(1)–Te(1)–C(24)	88.2(4)		
Cl(1)–Te(1)–C(12)	171.3(1)			F(1)–Te(1)–C(12)	168.5(3)		
Cl(1)–Te(1)–C(12)'	88.1(1)			F(1)–Te(1)–C(13)	89.9(4)		
C(1)–Te(1)–C(1)'	177.3(2)			C(1)–Te(1)–C(24)	175.9(4)		
C(1)'–Te(1)–C(12)	99.0(1)			C(1)–Te(1)–C(12)	82.9(4)		
C(1)–Te(1)–C(12)	82.7(1)			C(1)–Te(1)–C(13)	99.5(4)		
C(12)–Te(1)–C(12)'	98.1(2)			C(12)–Te(1)–C(24)	100.5(4)		
Te(1)–C(1)–C(2)	126.6(3)			Te(1)–C(1)–C(2)	127.3(9)		
Te(1)–C(1)–C(6)	109.8(3)			Te(1)–C(1)–C(6)	111.0(9)		

[a] Numbers in parentheses are the estimated standard deviations in the least significant digits.

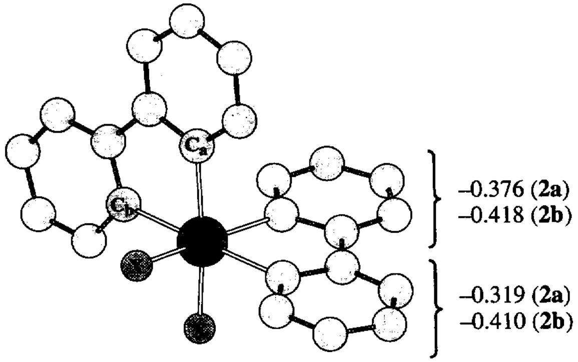
Furthermore, the respective bond angles of C(1)'–Te(1)–C(12) and C(1)–Te(1)–C(13) are equal to 99.0(1)° (**2a**) and 99.5(4)° (**2b**) which are smaller than those of the equatorial carbons and tellurium(IV) atom in the tellurane **1** (108.2(2)°).[8a] In addition, the hydrogen atoms at the 3'-position of *cis*-pertellurane(VI) **2a** are located nearer to the aromatic ring in the other biphenylylene group compared with the structure of bis(2,2'-biphenylylene)tellurane (**1**). This result explains the shielding of the protons at the 3'-position of **2a** and **2b** as described above.

In the preparation of the pertelluranes **2a** and **2b**, the formation of *trans* conformers was not observed at all. These results are quite different from those reported by Martin. This can be explained rationally, since the biphenylylene ligands in the compounds **2a** and **2b** should be more conformationally (sterically) congested than Martin's ligands, hence the respective *trans* conformers once produced as intermediates are expected to be immediately converted to the corresponding stable *cis* conformers.

Ab Initio Calculation of Pertelluranes 2a and 2b

In order to understand the electronic structure of each pertellurane compound, single-point *ab initio* calculations were carried out using the crystal structures of **2a** and **2b**. The calculations were carried out at the RHF/3-21G(*) level using Spartan 3.1.[16] Atomic charges were calculated by the natural population analysis.[17] This method is particularly preferred to the traditional Mulliken population analysis for analyzing the electronic wave function of hypervalent molecules which have strongly polar bonds.[18]

The charges of the Te atoms in **2a** and **2b** were calculated to be +2.456 and +2.918, respectively. Thus, the Te atoms are strongly positively charged. This is not so surprising, considering that the atomic charge of sulfur in SF_6 was calculated to be about +2.9.[18] All the atoms bonded to the central Te atom are negatively charged (ranging from –0.430 to –0.631) as shown in Figure 3. Thus, the six bonds around the Te atom are strongly polar. The positive charge of the Te atom of **2b** bonded to the more electronegative fluorine atoms is larger than that of **2a**, and the Te–C bonds in **2b** are more polar than those of **2a**. The charges of the carbon atoms other than C_a and C_b range from –0.02 to –0.25, and those of the hydrogen atoms from +0.23 to +0.29.



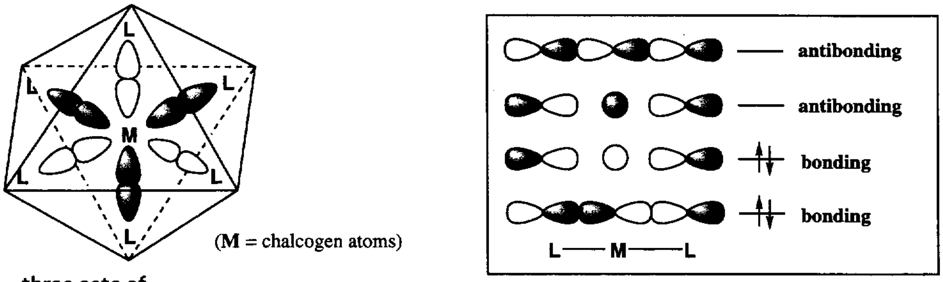
Atoms/Bonds	2a	2b
	charges	
Te	+2.456	+2.918
Cl	–0.533	–
F	–	–0.631
C_a	–0.462	–0.503
C_b	–0.430	–0.487
	bond orders	
Te-Cl	0.675	–
Te-F	–	0.875
Te-C_a	0.817	0.840
Te-C_b	0.762	0.790

Figure 3. The charge distribution (natural population analysis) and Mulliken bond orders of the pertelluranes **2a** (X = Cl) and **2b** (X = F) (average values for **2b**).

The total 5d-orbital populations of tellurium are very small, 0.052 for **2a** and 0.058 for **2b**, and the d orbitals are not primarily concerned with the Te–X (X = Cl, F) and Te–C bonds. The valence d orbital populations are much smaller than those in SF_6 (about 0.25).[18] This is partly due to the absence of p_π lone pairs on the ligand carbon atoms in the present cases; in SF_6 the sulfur $3d_\pi$ orbitals accept charges from fluorine p_π lone pair orbitals. However, participation of d_σ orbitals are also much smaller in the present molecules.

The Mulliken bond orders of Te–X are 0.675 (**2a**) and 0.875 (**2b**, average value). The Te–C_a bonds which lie on the X–Te–X plane have larger bond orders (0.817; **2a**, 0.840; **2b**) than the Te–C_b bonds (0.762; **2a**, 0.790; **2b**) which are perpendicular to the X–Te–X plane. This is consistent with the Mayer's considerations for symmetric and unsymmetric three-center four-electron (3c–4e) bonds.[19] However, according to the Mayer's analysis in which only a p orbital was considered for the central atom, the sum of bond orders of the two bonds in a 3c–4e bond has a maximum value of one. Moreover, the 5d orbitals are not primarily involved in the hypervalent bonds as mentioned above. The large values of bond orders for Te–X and Te–C may be ascribed to the participation of the 5s orbital of tellurium as may be seen from the following discussion. The role of the 3s orbital in SF_6 was discussed in Ref. 18.

The dodecet species such as the pertellurane(VI) species are considered to have three sets of 3c–4e bonds which are perpendicular to each other giving an octahedral structure. Strictly speaking, however, the 3c–4e bonds in dodecet species differ from that in decet species such as the tellurane(IV) species. In decet species, the valence s orbital of the central atom is not involved in the 3c–4e bond. On the other hand, in the octahedral dodecet species, the s orbital is empty if only the p orbitals are utilized in description of the three 3c–4e bonds. Actually, the s orbital can be mixed with the nonbonding orbital in the Rundle–Musher 3c–4e model.[20] Namely, the nonbonding orbital splits into bonding and antibonding orbitals as shown in Figure 4. Indeed, the occupancies of the 5s natural atomic orbitals of tellurium in **2a** and **2b** are 1.201 and 1.103, respectively. These values are consistent with the *extended Rundle–Musher Model* description shown in Figure 4. Because of the participation of the s orbital in the three 3c–4e bonds, the bonds in dodecet species are thought to be stronger than the apical hypervalent bonds in decet species. This agrees well with the experimental finding that the Te–C bonds in **2a** and **2b** are shorter than the apical Te–C bonds in **1**. Hexacoordinated chalcogen species seem to be generally more stable than the corresponding tetracoordinated species.



~three sets of
three center four electron bond~

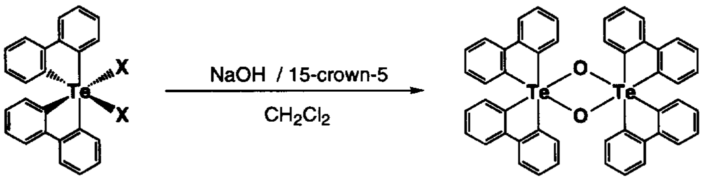
Extended Rundle-Musher Model

Figure 4. Octahedral structure and *Extended Rundle-Musher Model* of 3c-4e bond

Hydrolyses of Pertelluranes 2a and 2b

In order to understand the reactivities of each pertellurane compound, we tried to hydrolyze the pertelluranes **2a** and **2b** with alkali. Generally, the tetracoordinated chalcogen compounds with two halogen atoms as ligands have been known to be easily hydrolyzed in water or basic solution to give the corresponding chalcogen oxides. However, the pertelluranes **2a** and **2b** are very stable and do not react with water at all. Therefore, we tried to react these pertelluranes with alkali (NaOH) in an organic solvent. This reaction is very slow and the half-life of the substrates is about one week. But this reaction proceeded for one day in the presence of 0.2 equimolar amount of 15-crown-5 as a catalyst to obtain bis(2,2'-biphenylylene)tellurane *Te*-oxide dimer (**9**) which has been already reported by us, quantitatively,[21] as shown in Scheme 2. The *Te*-oxide dimer **9** was assigned by various NMR spectra, FABMS, and elemental analysis.

Scheme 2



2a (X = Cl)
2b (X = F)

9

The present results provide a new procedure for the syntheses, structures, reactivities, and theoretical studies of organopertellurane (λ^6-tellane). Further work in this area is currently underway in our laboratory.

EXPERIMENTAL SECTION

General Methods. All NMR spectra were obtained with a JEOL LMN-EX-270 or a Bruker ARX-400 spectrometer. Mass spectra were taken with a JEOL JMX SX102 mass spectrometer. X-ray crystallographic analysis was performed on an Enraf-Nonius CAD4 automatic or a Rigaku AFC-7R diffractometer. Elemental analyses were carried out by the Chemical Analytical Center at the University of Tsukuba. All melting points are uncorrected. Each chemical shift was determined by two dimensional shift correlation (^1H-^1H- and ^{13}C-^1H-COSY) spectra.

Materials. All solvents and reagents were dried and purified according to standard methods. Bis(2,2'-biphenylylene)tellurane **1** was prepared according to ref 7.

Bis(2,2'-biphenylylene)dichloropertellurane (2a): To a solution of bis(2,2'-biphenylylene)tellurane **1** (340 mg, 0.79 mmol) in anhydrous THF (25 ml) was added one equimolar amount of sulfuryl chloride (63 µl, 0.79 mmol) by a syringe under argon at −78 °C. After stirring for 1 h at room temperature, the mixture was filtrated and the solvent was removed under argon to give the corresponding pertellurane **2a** (0.40 g) as pale yellow solids in a 50% yield. Recrystallization from anhydrous THF/CH_2Cl_2 gave yellow cubic crystals. Mp

214–216 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6, room temperature) δ 6.63 (d, J = 7.6 Hz, 2H, 3'-Ar H), 7.32 (t, J = 7.6 Hz, 2H, 4'-Ar H), 7.62 (t, J = 7.6 Hz, 2H, 5'-Ar H), 7.92 (t, J = 6.7 Hz, 2H, 4-Ar H), 7.94 (t, J = 6.7 Hz, 2H, 5-Ar H), 8.36 (d, J = 7.6 Hz, 2H, 6'-Ar H), 8.53 (d, J = 6.7 Hz, 2H, 3-Ar H), 8.61 (d, J = 6.7 Hz, 2H, 6-ArH); ^{13}C NMR (67.8 MHz, DMSO-d_6, room temperature) δ 124.4, 125.0, 125.3, 126.7, 130.7, 131.4, 132.5, 132.6, 133.0, 133.6, 137.1, 147.7; ^{125}Te NMR (85 MHz, DMSO, room temperature) δ 569.0 (relative to Me_2Te); MS (m/z) 504 (M^+), 469($M^+ - 35$), 433($M^+ - 71$), 282($M^+ - 222$); Anal. Calcd for $C_{24}H_{16}Cl_2Te$: C, 51.08; H, 3.09; Found: C, 51.11; H, 3.01.

Bis(2,2'-biphenylylene)difluoropertellurane (2b): To a suspension of bis(2,2'-biphenylylene)tellurane **1** (410 mg, 0.95 mmol) in anhydrous CH_3CN (50 ml) one equimolar amount of xenon difluoride (0.16 mg, 0.95 mmol) was added via an additional flask under argon at –40 °C. The suspension of tellurane **1** turned colorless and was precipitated as a white powder. After stirring for 1 h at room temperature, the mixture was filtrated under argon to give the corresponding pertellurane **2b** (450 mg) as a colorless powder in a 54% yield. Recrystallization from anhydrous CH_2Cl_2 gave colorless cubic crystals. Mp 313–316 °C (decomp.); ^{1}H NMR (400 MHz, DMSO-d_6, room temperature) δ 6.73 (d, J = 7.5 Hz, 2H, 3'-ArH), 7.26 (t, J = 7.5 Hz, 2H, 4'-ArH), 7.58 (t, J = 7.5 Hz, 2H, 5'-ArH), 7.75 (t, J = 7.5 Hz, 2H, 4-ArH), 7.84 (t, J = 7.5 Hz, 2H, 5 -ArH), 8.14 (d, J = 7.5 Hz, 2H, 3-ArH), 8.24 (d, J = 7.5 Hz, 2H, 6'-ArH), 8.38 (d, J = 7.5 Hz, 2H, 6-ArH); ^{13}C NMR (100 MHz, DMSO-d_6, room temperature) δ 124.0, 124.3, 126.6, 130.4, 130.9, 131.7, 132.8, 133.3, 134.7 (t, J_{C-F} = 34.6 Hz, 2'C), 135.4, 135.6, 136.0 (t, J_{C-F} = 20.1 Hz, 2C); ^{19}F NMR (254 MHz, DMSO-d_6, room temperature) δ –47.2 (s, J_{F-Te} = 2151 Hz) (relative to $CFCl_3$); ^{125}Te-NMR (85 MHz, DMSO-d_6, room temperature) δ 699.8 (t, J_{Te-F} = 2151 Hz) (relative to Me_2Te); MS (m/z) 472 (M^+); Anal. Calcd for $C_{24}F_2H_{16}Te(H_2O)_2$: C, 56.97; H, 3.98. Found: C, 57.32; H, 3.40.

Reactions of the pertelluranes 2a and 2b with NaOH: To a solution of bis(2,2'-biphenylylene)dihalopertellurane **2a** (111 mg, 0.19 mmol) or **2b** (50 mg, 0.11 mmol) in CH_2Cl_2 (50 ml) an excess of sodium hydroxide (**2a**; 160 mg, 3.78 mmol) or (**2b**; 85 mg, 2.12 mmol) were added with a catalytic amount of 15-crown-5 ether (**2a**; 8 µl, 0.04 mmol) or (**2b**; 4 µl, 0.02 mmol) at room temperature. After stirring for 1 day at room temperature, water was added to the suspension and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. Each residue was recrystallized from Et_2O/Hexane to give the bis(2,2'-biphenylylene)tellurane *Te*-oxide dimer (**9**) of 85 mg (from **2a**) in 99% yield or 47 mg (from **2b**) in 99% yield as colorless crystals. Mp 272–275 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$, room temperature) δ 6.58 (d, J = 7.5 Hz, 2H, 3'-ArH), 6.73 (t, J = 7.5 Hz, 2H, 4-ArH), 6.83 (t, J = 7.5 Hz, 2H, 4'-ArH), 7.18 (t, J = 7.5 Hz, 2H, 5'-ArH), 7.28 (t, J = 7.5 Hz, 2H, 5-ArH), 7.45 (d, J = 7.5 Hz, 2H, 6'-ArH), 7.82 (d, J = 7.5 Hz, 2H, 6-ArH), 7.92 (d, J = 7.5 Hz, 2H, 3'-ArH); ^{13}C NMR (100 MHz, $CDCl_3$, room temperature) δ 121.9, 122.1, 127.2, 128.6, 128.8, 130.0, 130.9, 133.5, 134.5, 135.8, 140.0, 140.1; ^{125}Te NMR (126 MHz, $CDCl_3$, room temperature) δ 593.2 (relative to Me_2Te); FABMS (m/z) 901 ($[M+H]^+$), 451 ($[M/2+H]^+$), (matrix; 2-nitrophenyl octyl ether).

X-ray crystallographic data for compounds 2a and 2b: Single crystals of **2a** were formed by recrystallization from a dry THF/CH_2Cl_2 solution. A transparent light yellow crystal of dimensions 0.20 x 0.30 x 0.70 mm was analyzed on an Enraf-Nonius CAD4 four-circle diffractometer at 296 K. The crystallographic data and numerical details for the compound **2a** are given in ref 9. The structure was solved by direct methods. The initial E map revealed that the Te atoms are on the respective symmetry sites (0.5, y', 0.25) with one unique chlorine atom bonded to each. The remaining non-hydrogen atoms were located in subsequent different Fourier syntheses. Hydrogen atoms were added at calculated positions (C–H = 0.97, 1.08 Å for carbons with tetrahedral and planar geometries, respectively) but not refined. The neutral atom scattering factors used in the refinements were taken from Cromer and Waber[22] and corrected for anomalous dispersion.[23] Only the 1916 reflections with $I > 3.00\sigma(I)$ were used in the refinements. The final cycle of refinement included 137 variable parameters and converged with $R = 0.025$ and $Rw = 0.032$. The remaining maximum and minimum electron density features in the final difference Fourier map are equal to 0.44 and –0.36 e/Å^3, respectively, with the maxima located at a distance of 1.07 Å from the tellurium atom.

Table 2. X-ray Crystallographic Data for Diffraction Studies of **2a** and **2b**

compd	**2a**	**2b**
formula	$[C_{24}H_{16}Cl_2Te]\cdot CH_2Cl_2$	$C_{24}H_{16}F_2OTe$
fw	587.83	485.99
cryst syst	monoclinic	monooclinic
space group	*C2/c* (No. 15)	$P2_1/c$ (No. 14)
a, Å	15.626(2)	7.473(1)
b, Å	11.650(1)	16.759(7)
c, Å	13.865(2)	16.498(3)
β, deg	112.14(1)°	102.10(1)
V, Å^3	2337.9(5)	2020.4(9)
Z	4	4
*D*calcd, g cm^{-3}	1.67	1.598
F(000)	1152	952
temp, °C	23±1	23±1
radiation (λ, Å)	Mo Kα (0.710 73)	Cu Kα (1.54178)
cryst dimens, mm	0.20 x 0.30 x 0.70	0.20 x 0.15 x 0.30
μ, cm^{-1}	15.1	118.87
scan type	ω–2θ	ω–2θ
scan rate	2-20 deg/min	2-20 deg/min
scan width, deg	0.7 + 0.460 tanθ	1.42 + 0.30 tanθ
Maxi 2θ, deg	50.0	60.0
tot no. of rflns	2259	3992
no. of unique rflns	2167	3688
no. of params refined	252	263
rflns included	1956 with $Fo^2 > 2.5\sigma(Fo^2)$	2568 with $Fo^2 > 3.0\sigma(Fo^2)$
agreement factors[a]		
R	0.025	0.052
Rw	0.032	0.066

[a] $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $Rw = [\Sigma\omega(|Fo| - |Fc|^2)/\Sigma\omega Fo^2]^{1/2}$.

On the other hand, single crystals of **2b** were formed by recrystallization from a dry THF/CH_2Cl_2 solution. A transparent light yellow crystal of dimensions 0.20 x 0.15 x 0.30 mm was analyzed on a Rigaku AFC7S four-circle diffractometer using graphite monochromated Cu-K$_\alpha$ radiation at 296 K. The structure was solved by direct methods and all non-hydrogen atoms were located using Fourier techniques and refined anisotropically. Hydrogen atoms were added at calculated positions (C–H = 1.08 Å) but not refined. The solvent was identified by I.R.(υ(O–H) = 3490 cm^{-1}) and X-ray analysis as a water molecule disordered over the two sites, O(1) and O(2). The neutral atom scattering factors used in the refinements were taken from Cromer and Waber[22] and corrected for anomalous dispersion.[23] Only the 2568 reflections with $I > 3.00\sigma(I)$ were used in the refinements. The final cycle of refinement included 263 variable parameters and converged with R = 0.052 and Rw = 0.066. The remaining maximum and minimum electron density features in the final difference Fourier map are equal to 1.17 and –1.21 e/Å^3, respectively, with the maxima located at a distance of 0.89 Å from O(2). X-ray crystallographic data for diffraction studies of **2a** and **2b** are shown in Table 2.

All calculations were performed on an Indy workstation using the teXsan crystallographic software package from Molecular Structure Corp. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at Cambridge Crystallographic Data Centre.

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