

Crystal structures of optically active diastereomeric telluronium and selenonium salts

Anion–cation interactions in the crystalline state

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Abstract

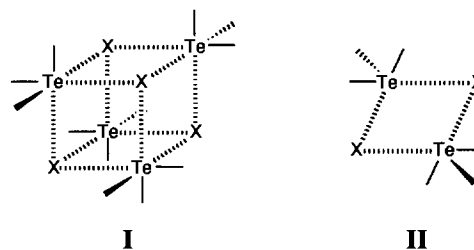
The tellurium atom in optically pure diastereomeric (*R*)-ethylmethylphenyltelluronium (*IS*)-camphor-10-sulfonate ((*R*)_{Te}-1) was found to interact with two oxygen atoms of the counter anions in the crystalline state, while that in the other diastereomeric isomer (*S*)_{Te}-1 interacts with three oxygen atoms. This difference in interactions is considered to be caused by steric factors (crystal packing) and not to be caused by electronic effects, since the telluronium cations have the same substituents and counter anions. The crystal packing structure of (*R*)_{Te}-1 showed *M*-helix geometry through anion–cation interactions, while that of (*S*)_{Te}-1 showed a 2D-sheet structure. The corresponding optically active selenonium salt (*R*)_{Se}-2 showed crystal packing similar to that of (*R*)_{Te}-1. © 1997 Elsevier Science S.A.

Keywords: Crystal structure; Optically active compound; Telluronium salt; Selenonium salt; Anion–cation interaction

1. Introduction

The crystal structures of many triorganotelluronium salts have been determined by X-ray crystallographic analyses [1–6], and anion–cation interactions (secondary bonding) in their crystalline states have received considerable attention [1–8].¹ In the crystalline state, telluronium salts with different anions show different anion–cation interactions; e.g. triethyltelluronium chloride [3] and bromide [4] each show a tetrameric structure, with distorted octahedral geometries around the tellurium atoms, through anion–cation interactions as in **I**, while the corresponding telluronium iodide [3] shows a dimeric structure with a distorted square pyramidal geometry around the tellurium atom as in **II**. Recently, we succeeded in isolating optically pure (*R*)- and (*S*)-ethylmethylphenyltelluronium (*IS*)-camphor-10-sulfonates ((*R*)_{Te}-1 and (*S*)_{Te}-1), and found that the isomers show peculiar behaviour with regard to anion–

cation interactions in solution [9]. The absolute configuration of (*R*)_{Te}-1, with an *R*-configuration around the tellurium atom, was determined by X-ray crystallographic analysis. In this paper, we report the crystal structures of (*S*)_{Te}-1 and corresponding selenonium salt (*R*)_{Se}-2. We found that the crystal structure of (*R*)_{Te}-1 showed square pyramidal geometry around the tellurium atom, while that of (*S*)_{Te}-1 showed octahedral geometry through anion–cation interactions, despite possessing the same counter anion and same substituents on the tellurium atoms. We also found that the crystal packing of the *R*-isomer showed a helix structure while the *S*-isomer showed a 2D-sheet structure through anion–cation interactions.



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¹ For a review of anion–cation interaction see Ref. [7].

2. Results and discussion

The absolute configuration around the tellurium atom in optically active telluronium salt (S)_{Te}-1, which was estimated previously [9], was determined by X-ray crystallographic analysis on the basis of the known stereochemistry of (*1S*)-camphor-10-sulfonate as an internal standard.

The tellurium atom of (R)_{Te}-1 interacts with two oxygen atoms of the two counter anions in the crystalline state, and the three carbon atoms and two oxygen atoms around the tellurium atom form a nearly square pyramidal geometry around the tellurium atom, as shown

in Fig. 1. The Te···O atomic distances in (R)_{Te}-1 are 2.88 and 3.05 Å. These values are 0.72 and 0.55 Å less than the sum of the van der Waals radii, and correspond to those of trimethyltelluronium nitrate which has an inorganic counter anion [6]. On the other hand, the crystal structure of the other optical isomer (S)_{Te}-1 shows three interactions between the tellurium atom and the oxygen atoms of the three counter anions, indicating octahedral geometry around the tellurium atom. The lengths of the Te···O secondary bonds in (S)_{Te}-1 are 3.00, 3.01 and 3.03 Å for one telluronium cation (molecule A), and 2.84, 3.02 and 3.09 Å for the other cation (molecule B). These values are also similar to those of

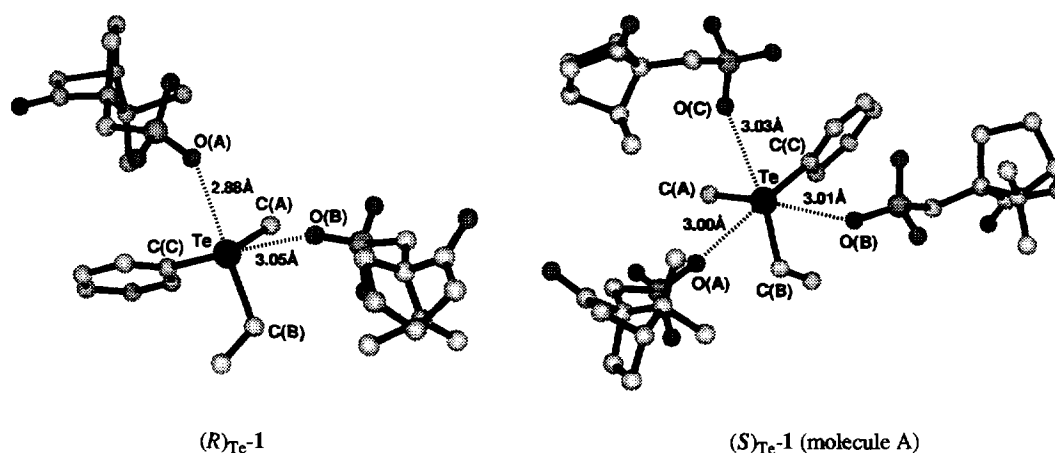


Fig. 1. Molecular structures of (R)_{Te}-1 and (S)_{Te}-1 showing anion-cation interactions with hydrogen atoms removed for clarity. (R)_{Te}-1 non-bonded angles (deg) around tellurium atom: O(A)-Te-O(B) 102.0, O(A)-Te-C(A) 75.0, O(A)-Te-C(B) 166.7, O(A)-Te-C(C) 78.8, O(B)-Te-C(A) 84.1, O(B)-Te-C(B) 85.6, O(B)-Te-C(C) 179.1. (S)_{Te}-1 (molecule A) non-bonded angles (deg) around tellurium atom: O(A)-Te-O(B) 106.0, O(A)-Te-O(C) 103.2, O(A)-Te-C(A) 80.4, O(A)-Te-C(B) 73.7, O(A)-Te-C(C) 172.7, O(B)-Te-O(C) 115.4, O(B)-Te-C(A) 165.5, O(B)-Te-C(B) 75.9, O(B)-Te-C(C) 76.8, O(C)-Te-C(A) 74.7, O(C)-Te-C(B) 168.6, O(C)-Te-C(C) 81.3.

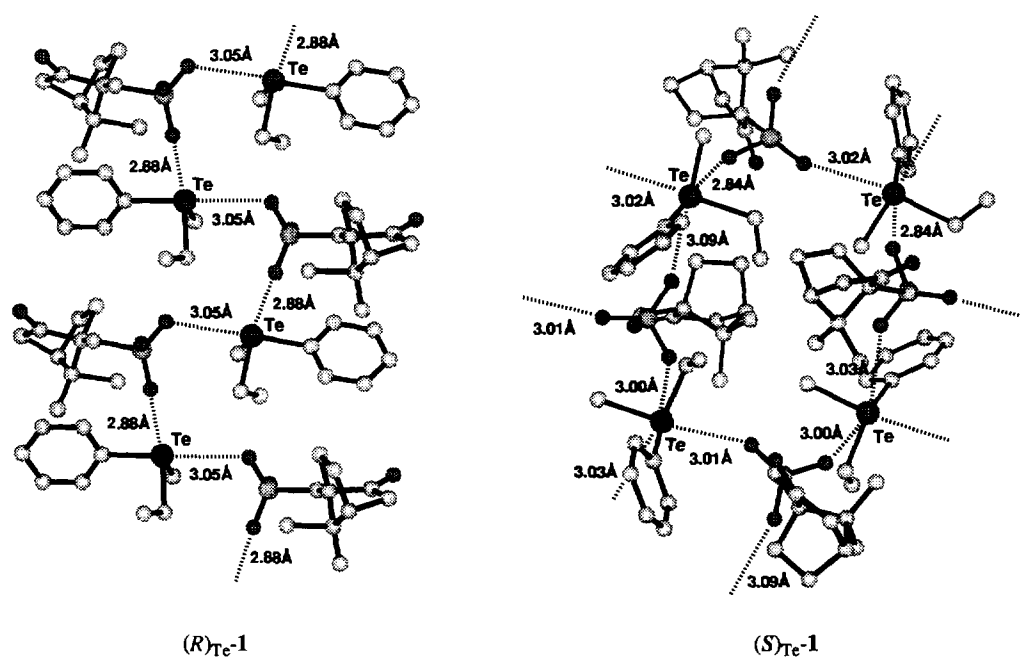


Fig. 2. Packing diagrams of (R)_{Te}-1 and (S)_{Te}-1 showing anion-cation interactions with hydrogen atoms removed for clarity.

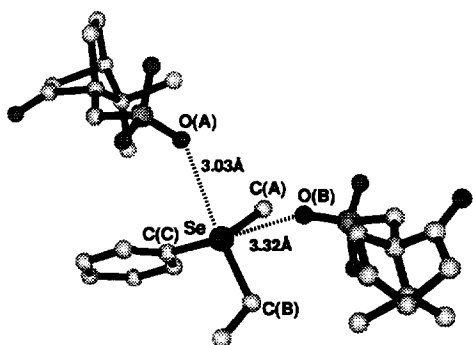


Fig. 3. Molecular structure of $(R)_{\text{Se}}\text{-2}$ showing anion–cation interactions with hydrogen atoms removed for clarity. Non-bonded angles (deg) around selenium atom: O(A)–Se–O(B) 99.4, O(A)–Se–C(A) 74.9, O(A)–Se–C(B) 170.9, O(A)–Se–C(C) 79.4, O(B)–Se–C(A) 85.8, O(B)–Se–C(B) 84.4, O(B)–Se–C(C) 172.9.

trimethyltelluronium nitrate [6]. This difference in the type of interaction between $(R)_{\text{Te}}\text{-1}$ and $(S)_{\text{Te}}\text{-1}$ is considered to be caused by steric factors (crystal packing) and not to be caused by electronic effects, since the counter anions of $(R)_{\text{Te}}\text{-1}$ and $(S)_{\text{Te}}\text{-1}$ are the same and the electronic effects due to the counter anions are considered to be almost identical. The crystal packing structures of $(R)_{\text{Te}}\text{-1}$ and $(S)_{\text{Te}}\text{-1}$ also show different geometries (Fig. 2). The *R*-isomer shows a helix structure through anion–cation interactions, and the crystal has *M*-helicity resulting from the chirality of $(R)_{\text{Te}}\text{-1}$. On the other hand, the *S*-isomer shows a 2D-sheet structure through anion–cation interactions.

The stereochemistry of (R) -ethylmethylphenyl-

selenium (*IS*)-camphor-10-sulfonate ($(R)_{\text{Se}}\text{-2}$) [10] was also clarified by X-ray analysis (Fig. 3). The geometry of the crystal structure of $(R)_{\text{Se}}\text{-2}$ is quite similar to that of the corresponding telluronium salt $(R)_{\text{Te}}\text{-1}$, and the crystal systems and space groups are also the same. However, the Se \cdots O atomic distances in $(R)_{\text{Se}}\text{-2}$ are 3.03 and 3.32 Å, which are longer than those in $(R)_{\text{Te}}\text{-1}$ even though the van der Waals radii and the covalent radii of selenium are smaller than those of tellurium. This tendency has also been observed in crystal structures of trimethylchalcogen–onium iodides (chalcogen = S [11], Se [12], Te [5,6]). These results indicate that the anion–cation interactions between the telluronium cation and counter anions are stronger than those between the corresponding selenium cation and counter anions, and can be explained on the basis of the electronegativities of selenium and tellurium, and magnitude of polarization of the salts. That is, the telluronium cation and the counter anion are more strongly polarized than in the case of the selenium salt because the tellurium atom is less electronegative than the selenium atom. Thus, the more positive telluronium cation more strongly draws the counter anion than the selenium cation.

3. Experimental section

Optically pure crystals of (S) -ethylmethylphenyltelluronium (*IS*)-camphor-10-sulfonate ($(S)_{\text{Te}}\text{-1}$) ($[\alpha]_{\text{D}} + 16.7$ (*c* 1.03, MeOH)) [9] and (R) -ethylmethylphenyl-

Table 1
Crystal data for $(R)_{\text{Te}}\text{-1}$, $(S)_{\text{Te}}\text{-1}$ and $(R)_{\text{Se}}\text{-2}$

	$(R)_{\text{Te}}\text{-1}$ ^a	$(S)_{\text{Te}}\text{-1}$	$(R)_{\text{Se}}\text{-2}$
Molecular formula	C ₁₉ H ₂₈ O ₄ STe	C ₁₉ H ₂₈ O ₄ STe	C ₁₉ H ₂₈ O ₄ SSe
Formula weight	479.97	479.97	431.45
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (#19)	<i>P</i> 2 ₁ (#4)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (#19)
<i>a</i> (Å)	11.767(3)	13.551(5)	11.520(2)
<i>b</i> (Å)	19.981(6)	11.722(2)	20.153(2)
<i>c</i> (Å)	8.826(4)	13.132(2)	8.706(1)
β (deg)		101.80(2)	
<i>V</i> (Å ³)	2075(1)	2042.0(9)	2021.2(4)
<i>Z</i>	4	4	4
<i>T</i> (°C)	23	23	20
<i>F</i> (000)	967	968	896
ρ (calcd) (g cm ⁻³)	1.54	1.56	1.42
Crystal dimensions (mm ³)	0.20 × 0.20 × 0.30	0.25 × 0.30 × 0.55	0.20 × 0.20 × 0.30
Radiation	Mo K α ($\lambda = 0.71069$ Å)	Mo K α ($\lambda = 0.71069$ Å)	Cu K α ($\lambda = 1.54178$ Å)
μ (cm ⁻¹)	15.50	14.49	36.42
Scan type	ω -2 θ	ω -2 θ	ω -2 θ
Total no. of reflections	2826	6675	1764
No. of unique observed reflections	2716 (<i>I</i> > 3 σ (<i>I</i>))	6236 (<i>I</i> > 3 σ (<i>I</i>))	1637 (<i>I</i> > 3 σ (<i>I</i>))
No. of least squares parameters	246	246	226
<i>R</i>	0.040	0.038	0.044
<i>R</i> _w	0.044	0.040	0.045

^a Crystal data for $(R)_{\text{Te}}\text{-1}$ was reported previously [9].

Table 2
Bond distances (Å) and angles (deg) of (*R*)_{Te}-1, (*S*)_{Te}-1 and (*R*)_{Se}-2 with esds in parentheses

	(<i>R</i>) _{Te} -1		(<i>S</i>) _{Te} -1		(<i>R</i>) _{Se} -2	
	Molecule A	Molecule B	Molecule A	Molecule B	Molecule A	Molecule B
Bond distances						
Ch(1)–C(1)	2.13(1)	2.09(1)	2.128(7)	1.926(8)		
Ch(1)–C(2)	2.17(1)	2.118(9)	2.20(2)	1.967(9)		
Ch(1)–C(4)	2.117(8)	2.126(8)	2.121(8)	1.930(7)		
S(1)–O(2) ^a	1.465(7)	1.424(8)	1.453(9)	1.452(6)		
S(1)–O(3) ^a	1.464(7)	1.466(8)	1.410(9)	1.445(6)		
S(1)–O(4) ^a	1.467(8)	1.428(6)	1.424(7)	1.458(6)		
S(1)–C(19)	1.79(1)	1.809(8)	1.781(8)	1.784(8)		
O(1)–C(11)	1.29(6)	1.33(3)	1.12(2)	1.24(2)		
C(2)–C(3)	1.50(2)	1.18(2)	1.31(2)	1.49(1)		
C(4)–C(5) ^b	1.39(1)	1.42(1)	1.37(1)	1.38(1)		
C(4)–C(9) ^b	1.35(1)	1.39(1)	1.36(1)	1.39(1)		
C(5)–C(6)	1.37(1)	1.46(2)	1.38(1)	1.40(1)		
C(6)–C(7)	1.40(2)	1.38(2)	1.39(2)	1.38(1)		
C(7)–C(8)	1.37(2)	1.36(2)	1.35(1)	1.38(1)		
C(8)–C(9)	1.42(1)	1.37(2)	1.41(1)	1.40(1)		
C(10)–C(11)	1.48(5)	1.51(2)	1.49(1)	1.52(2)		
C(10)–C(15)	1.53(3)	1.52(1)	1.56(2)	1.54(2)		
C(10)–C(16)	1.44(2)	1.49(1)	1.52(1)	1.42(1)		
C(10)–C(19)	1.54(1)	1.56(1)	1.53(1)	1.51(1)		
C(11)–C(12)	1.44(4)	1.58(4)	1.48(2)	1.41(3)		
C(12)–C(13)	1.61(4)	1.47(2)	1.50(2)	1.60(2)		
C(13)–C(14)	1.52(4)	1.54(2)	1.54(2)	1.47(2)		
C(13)–C(16)	1.49(2)	1.55(2)	1.53(2)	1.49(2)		
C(14)–C(15)	1.65(3)	1.59(2)	1.54(2)	1.57(2)		
C(16)–C(17)	1.42(3)	1.46(2)	1.54(2)	1.42(2)		
C(16)–C(18)	1.71(4)	1.60(1)	1.48(2)	1.63(2)		
Bond angles						
C(1)–Ch(1)–C(2)	95.2(4)	94.1(7)	92.0(4)	97.2(4)		
C(1)–Ch(1)–C(4)	96.6(4)	95.4(4)	97.0(3)	100.4(3)		
C(2)–Ch(1)–C(4)	93.7(4)	100.8(4)	94.3(5)	97.9(4)		
O(2)–S(1)–O(3)	112.7(5)	112.4(5)	110.9(5)	113.4(4)		
O(2)–S(1)–O(4)	112.9(5)	112.2(4)	114.3(5)	112.6(4)		
O(2)–S(1)–C(19)	105.9(5)	109.6(5)	104.8(4)	108.3(4)		
O(3)–S(1)–O(4)	112.5(5)	113.0(4)	111.9(5)	112.1(4)		
O(3)–S(1)–C(19)	104.2(4)	101.8(5)	106.1(5)	106.2(4)		
O(4)–S(1)–C(19)	107.9(5)	107.2(4)	108.1(4)	103.6(4)		
Ch(1)–C(2)–C(3)	112.9(8)	129(1)	112(1)	112.0(7)		
Ch(1)–C(4)–C(5)	121.1(6)	119.2(7)	123.9(6)	121.2(6)		
Ch(1)–C(4)–C(9)	117.3(7)	116.2(6)	116.6(6)	115.4(6)		
C(5)–C(4)–C(9)	121.6(8)	124.5(9)	119.4(8)	123.4(7)		
C(4)–C(5)–C(6)	120(1)	114(1)	120.8(8)	118.8(8)		
C(5)–C(6)–C(7)	120(1)	121(1)	118.6(9)	119.1(9)		
C(6)–C(7)–C(8)	119(1)	119(1)	122(1)	121.1(9)		
C(7)–C(8)–C(9)	121(1)	124(1)	117.8(9)	120.9(9)		
C(4)–C(9)–C(8)	118.8(9)	117.2(9)	121.3(8)	116.7(8)		
C(11)–C(10)–C(15)	97(4)	99(2)	109.7(8)	90(2)		
C(11)–C(10)–C(16)	87(4)	97(1)	96.6(8)	93(2)		
C(11)–C(10)–C(19)	108(1)	109(1)	109.0(8)	110(1)		
C(15)–C(10)–C(16)	115(1)	106.4(9)	102.0(9)	111(1)		
C(15)–C(10)–C(19)	116(1)	112.6(9)	116.0(8)	116.4(9)		
C(16)–C(10)–C(19)	124(1)	127.6(9)	121.6(7)	125.8(9)		
O(1)–C(11)–C(10)	126(3)	123(2)	126(1)	120(1)		
O(1)–C(11)–C(12)	117(3)	126(1)	122(1)	121(3)		
C(10)–C(11)–C(12)	116(3)	109(2)	110(1)	112(2)		
C(11)–C(12)–C(13)	95(3)	98(1)	98.3(9)	99(1)		
C(12)–C(13)–C(14)	96(2)	107(1)	111(1)	97(1)		
C(12)–C(13)–C(16)	93(2)	102(1)	103(1)	91(1)		
C(14)–C(13)–C(16)	111(1)	101.0(9)	103(1)	105(1)		

Table 2 (continued)

	(<i>R</i>) _{Te} -1		(<i>S</i>) _{Te} -1		(<i>R</i>) _{Se} -2	
	Molecule A	Molecule B	Molecule A	Molecule B	Molecule A	Molecule B
Bond angles						
C(13)–C(14)–C(15)	104(2)	104.6(9)	102(1)	108(1)		
C(10)–C(15)–C(14)	99(2)	102(1)	103(1)	99(1)		
C(10)–C(16)–C(13)	101(1)	97.8(8)	92.8(8)	102.6(9)		
C(10)–C(16)–C(17)	125(2)	116.4(9)	113(1)	121(1)		
C(10)–C(16)–C(18)	94(2)	108.9(7)	118.3(9)	102.1(1)		
C(13)–C(16)–C(17)	126(2)	116.9(9)	113(1)	120(1)		
C(13)–C(16)–C(18)	94(2)	105.7(9)	117(1)	99(1)		
C(17)–C(16)–C(18)	109(3)	110(1)	103(1)	106(1)		
S(1)–C(19)–C(10)	121.9(8)	117.4(7)	120.5(7)	122.9(7)		

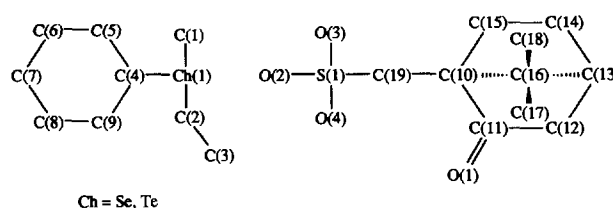
^a Atomic distances: Ch(1)–O(2) < Ch(1)–O(3) < Ch(1)–O(4).

^b Atomic distances: C(1)–C(5) < C(1)–C(9).

selenium (*1S*)-camphor-10-sulfonate ((*R*)_{Se}-2) ([α]_D +42.4 (c 1.03, MeOH)) [10] were obtained by fractional recrystallization of the corresponding diastereomeric mixtures.

3.1. X-ray crystallographic analyses

The molecular structure of (*R*)_{Te}-1 has been reported previously [9]. Each colourless crystal of (*S*)_{Te}-1 and (*R*)_{Se}-2 was mounted on a glass fibre. The crystal of (*S*)_{Te}-1 was subjected to intense data collection on a Mac Science MXC18 diffractometer and (*R*)_{Se}-2 was examined on a Rigaku AFC7R diffractometer. The unit cells were determined and refined from 25 randomly selected reflections obtained by automatic search, centre, index and least squares routines. Crystal data, data collection parameters and the results of the analyses are summarized in Table 1 together with those of (*R*)_{Te}-1. Bond distances and angles are summarized in Table 2.



Acknowledgements

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