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Absolute configuration and racemization mechanism of arenechalcogenic acids: resolution of tellurinic acid

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Abstract—An optically active arenetellurinic acid (+)-**1d** was obtained by means of liquid chromatography on a chiral column. The absolute configuration of the optically active tellurinic acid was assigned by comparing its circular dichroism spectrum with that of an optically active sulfinic acid, the absolute configuration of which was determined by X-ray crystallographic analysis. The absolute configurations of areneseleninic acids, which were previously obtained by chromatographic resolution, were assigned also on the basis of their circular dichroism spectra. The optically active tellurinic acid (*S*)-(+)-**1d** was stable toward racemization in hexane, although the racemization occurred in hexane/2-propanol. Kinetic studies on the racemization, the oxygen exchange reaction using $H_2{}^{18}O$, and theoretical studies revealed that a pathway involving an achiral tellurane formed by the addition of water to tellurinic acid exists for the racemization. The racemization mechanism of the optically active seleninic acid involving a seleninate anion, which was proposed previously, was confirmed by experiments using $H_2{}^{18}O$. The racemization mechanism of the optically active sulfinic acid in solution was concluded to be the same as that of the optically active seleninic acid. The difference in the racemization mechanism among the optically active chalcogenic acids is due to their ability to form hypervalent hydrate structures.

1. Introduction

Recently, many chiral tricoordinated selenium and tellurium compounds, such as oxides, onium salts, ylides, and imides, have been isolated, and their characteristics clarified.[1] Chalcogenic acids are also tricoordinated chalcogen compounds and have pyramidal structures. Therefore, chalcogenic acids have stereogenic centers on the chalcogen atoms. Previously, we have reported the resolution of areneseleninic acids by means of liquid chromatography on an optically active column, and found that the optically active areneseleninic acids racemize in solution.[2,3] It was also found that the racemization of areneseleninic acids is suppressed to some extent by the bulky substituents at the *ortho* position of the benzene ring, although no single enantiomers could be isolated as stable solids due to complete racemization during concentration of the eluates under reduced pressure. Recently, we also reported the isolation of optically active methaneseleninic acid as a stable solid by chiral crystallization.[4] To the best of our knowledge, there is no study concerning optically active tellurinic acids, which are analogues of seleninic acids. Moreover, there are few reports on the preparation of racemic tellurinic acids so far.[5] The scarcity seems to be due to that the tellurinic acids have polymeric structures and are insoluble in common organic solvents.

We examined the resolution of arenetellurinic acids by means of liquid chromatography on optically active columns and succeeded in obtaining an optically active tellurinic acid for the first time, the absolute configuration of which was assigned. The racemization mechanism of the optically active tellurinic acid was clarified. Herein, we report the resolution of tellurinic acid, together with the absolute configurations and the racemization mechanisms of the optically active chalcogenic acids.[6]

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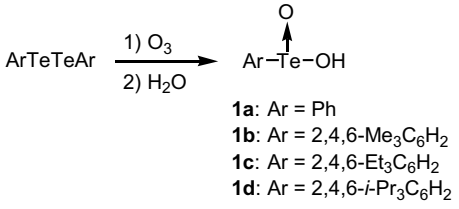
2. Results and discussion

2.1. Preparation of arenetellurinic acids

Arenetellurinic acids having bulky substituents of various sizes **1a**–**d** were prepared from corresponding diaryl ditellurides by oxidation with ozone and subsequent hydrolysis in yields of 24%, 63%, 61%, and 32%, respectively. Tellurinic acids **1a**–**d** showed broad signals in both the aromatic and aliphatic regions of their ^{1}H NMR spectra in $CDCl_3$, which may be because that the arenetellurinic acids are very polar molecules and associate in nonpolar solvent. The IR spectra of **1a**–**d** in the solid state (KBr) showed broad bands centering on 3360–3400 (OH) cm^{-1} as well as broad bands in the range of 500–800 cm^{-1}, which were assigned to ν (Te=O). The breadth of the bands of ν (Te=O) appeared to be due to intermolecular interactions in the solid state. Arenetellurinic acids **1a** and **1b** were insoluble in organic solvents without chloroform and dichloromethane. On the other hand, arenetellurinic acids **1c** and **1d** were soluble not only in halogenated solvents, but also in hexane and alcohol, which were used as the eluents for HPLC on optically active columns.



2.2. Resolution of arenetellurinic acids 1c and 1d by means of HPLC

Arenetellurinic acids **1c** and **1d** were subjected to chromatography on two types of chiral column (4.6×250 mm), one packed with amylose carbamate derivative-silica gel (Daicel Chiralpak AS) and the other packed with cellulose carbamate derivative-silica gel (Daicel Chiralcel OD), using hexane/2-propanol as the eluent. Their chromatograms showed only one peak in both cases. However, the ratio of the enantiomers was considered to differ between the former portion and the latter portion of the peak. When **1d** was subjected to chromatography on a larger column (10×250 mm), which was packed with cellulose carbamate derivative-silica gel using hexane as the eluent, the fraction corresponding to the first half of the peak showed a positive specific rotation $\{[\alpha]_{435}^{28} = +2.5 \times 10^3$ (c 1.2×10^{-3}, hexane)$\}$ and a negative Cotton effect at 238 nm on the circular dichroism spectrum (Fig. 1), whereas the following fractions showed no Cotton effect. On the other hand, arenetellurinic acid **1c** could not be optically resolved under the same conditions. In the case of the optically active seleninic acids, concentration of the eluates caused complete racemization.[2,3] By contrast, the molar ellipticity of (+)-**1d** was not reduced by concentration of the hexane solution, indicating that no racemization of the optically active tellurinic acid took place during the concentration of the eluate. To the best of our knowledge, this is the first report of the isolation of an optically active tellurinic acid, although the enantiomeric excess could not be determined.

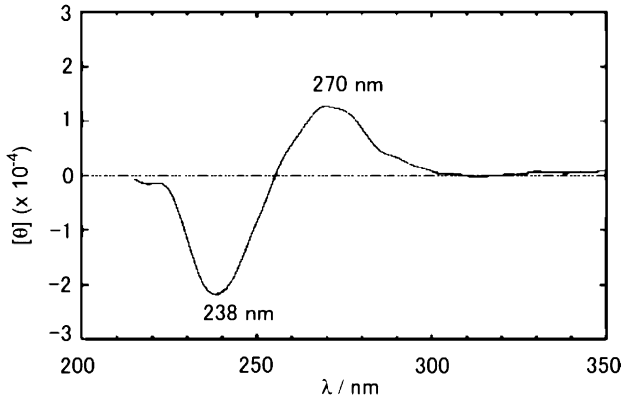


Figure 1. Circular dichroism spectrum of (+)-**1d** in hexane.

2.3. Absolute configurations of optically active arenetellurinic acid (+)-1d and optically active areneseleninic acids

As far as we know, there is no report of the relationship between the absolute configurations and the chiroptical properties of the optically active arenechalcogenic acids. On the other hand, there are many reports concerning the crystal structures of sulfinic acids, and some crystals of sulfinic acids belonging to chiral space groups.[7,8] For example, the crystal structure of arenesulfinic acid **2** with a crown-ether ring has been reported, and it was clarified that the crystal belongs to the chiral space group $P2_12_12_1$ although the chirality of **2** is not mentioned in the paper.[7] If the relationship between the chiroptical properties and the absolute configuration of an enantiomer of **2** could be determined, the absolute configurations of the arenechalcogenic acids would be clarified on the basis of the chiroptical properties. Therefore, arenesulfinic acid **2** was prepared and its chiral crystals obtained by recrystallization from ether according to the literature.[7] One of the single crystals showed a positive Cotton effect at around 240 nm in the solid state (KBr disk), while another one showed a negative Cotton effect in the same region (Fig. 2), whereas acetonitrile and ether solutions of the crystals showed no Cotton effect even within 5 s after dissolution. These results indicate that the optically active sulfinic acid **2** racemizes very rapidly in solution. The absolute configuration of **2**, which showed a negative Cotton effect at around 240 nm, was determined to be *S* by X-ray crystallographic analysis (Fig. 3). The two oxygen atoms of the OH and S=O groups could be discriminated on the basis of the bond distances between the sulfur atom and the oxygen atoms, while the hydrogen atom of the OH group was found on the D-map. Thus, on the basis of the similarity of their circular dichroism spectra, the absolute configuration of optically active tellurinic acid (+)-**1d**, which showed a negative Cotton effect

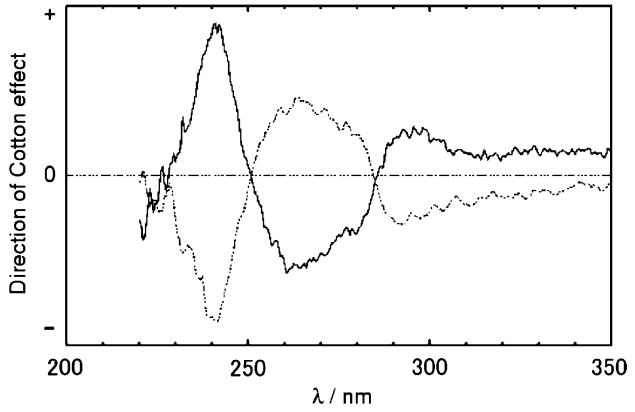


Figure 2. Circular dichroism spectra of the enantiomers of sulfinic acid **2** in the solid state (KBr disk).

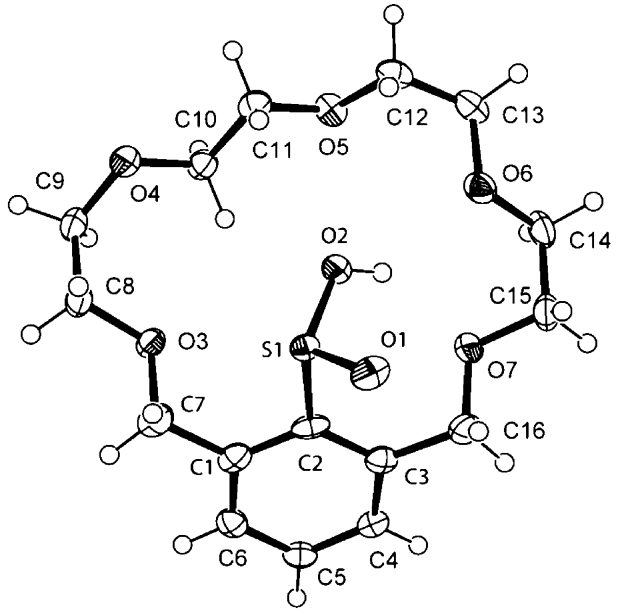
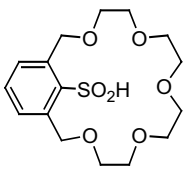


Figure 3. X-ray structure of (*S*)-**2**. Selected bond lengths (Å) and bond angles (°): S1–O1 1.4734(11), S1–O2 1.6231(10), S1–C2 1.8052(12), O1–S1–O2 110.56(7), O1–S1–C2 103.92(6), O2–S1–C2, 100.61(5).

at 238 nm, was determined to be *S*. The absolute configurations of optically active seleninic acids **3a–d** obtained by chromatographic resolution[2,3] have not been determined so far. In the same manner, the absolute configurations of the enantiomers of **3**, which showed negative Cotton effects at around 230–250 nm, were determined to be *S* while those of the enantiomers that showed positive Cotton effects in the same region were determined to be *R*.



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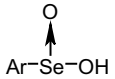


3a: Ar = 2,4,6-$Me_3C_6H_2$
3b: Ar = 2,4,6-$Et_3C_6H_2$
3c: Ar = 2,4,6-*i*-$Pr_3C_6H_2$
3d: Ar = 2,4,6-*t*-$Bu_3C_6H_2$

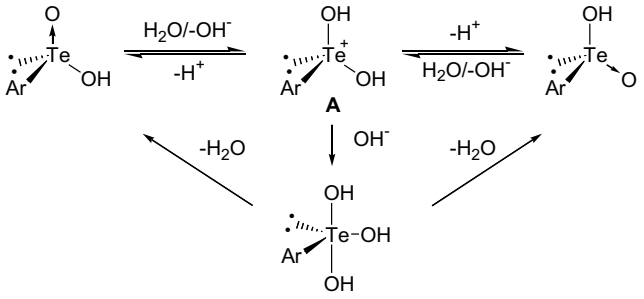
2.4. Racemization of optically active chalcogenic acids

The stability toward the racemization of optically active tellurinic acid (*S*)-(+)-**1d** was examined in solution. The change of the circular dichroism spectrum of (*S*)-(+)-**1d** in various solvents (ca. 2×10^{-5} M) was monitored at room temperature. No change in the ellipticity at 270 nm was observed on the circular dichroism spectrum of (*S*)-(+)-**1d** in hexane even after 3 days, indicating that no racemization occurred under the given conditions. However, the ellipticity in the same region was decreased with time in hexane/2-propanol (99/1), and showed a good linear relationship in the first-order rate plots. The kinetics for the racemization of (*S*)-(+)-**1d** was examined in order to clarify the mechanism. The first-order rate constants and half-lives for the racemization of (*S*)-(+)-**1d** are summarized in Table 1. The rate constant in 2-propanol/H_2O (4/1) ($2.16 \times 10^{-3}\,s^{-1}$) was much larger than that in hexane/2-propanol (99/1) ($1.18 \times 10^{-4}\,s^{-1}$), indicating that a small volume of residual water in the distilled 2-propanol may cause the racemization of the optically active tellurinic acid. Two mechanisms involving water for the racemization are proposed. One is the formation of an achiral tellurane by the addition of water to tellurinic acid, and the other is the formation of a tellurinate anion by the deprotonation of tellurinic acid with water. The oxygen exchange reaction of tellurinic acid was examined using $H_2{}^{18}O$ to check whether the tellurane is involved in the mechanism. When racemic tellurinic acid **1d** was dissolved in 2-propanol/$H_2{}^{18}O$ (4/1, 95 atom% ^{18}O) and allowed to stand for 2 h, the ratio of 2,4,6-*i*-$Pr_3C_6H_2Te^{16}O_2H$: 2,4,6-*i*-$Pr_3C_6H_2Te^{16}O^{18}OH$:2,4,6-*i*-$Pr_3C_6H_2Te^{18}O_2H$ was 5:3:5 based on the peak intensities on the MS spectrum, meaning that the oxygen atoms of tellurinic acid were indeed exchanged via an achiral tellurane formed by the addition of water. However, the rate of the reaction for tellurane formation is distinctly lower than the rate of the racemization. Comparing the rate constants of the racemization of (*S*)-(+)-**1d**, the rate constant in 2-propanol/H_2O (4/1) is approximately three times as large as that in 2-propanol/D_2O (4/1), showing that there is a primary kinetic isotope effect in

Table 1. First-order rate constants and half-lives for racemization of (*S*)-(+)-**1d**[a]

Solvent	$k_1 \times 10^4$ (s^{-1})	$t_{1/2}$ (min)
Hexane	No racemization (after 3 days)	
Hexane/2-propanol (99/1)	1.18	98.2
2-Propanol/H_2O (4/1)	21.6	5.34
2-Propanol/D_2O (4/1)	7.87	14.5

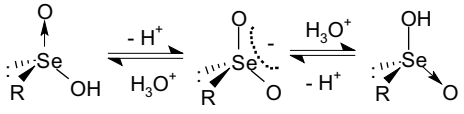
[a] In ca. 2×10^{-5} M solution at 25 ± 1 °C.



Scheme 1.

the racemization. Thus, the rate-controlling step of the racemization is the proton transfer from water to tellurinic acid, and the equilibrium between tellurinic acid and an achiral diol cation **A** probably participates in the racemization (Scheme 1).

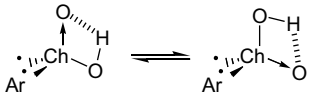
Previously, we proposed that the racemization of the optically active areneseleninic acid proceeds via the corresponding seleninate anion with the extrusion of a proton under dilute conditions (Scheme 2).[3] However, the pathway involving an achiral selenurane, which is formed by the addition of water to seleninic acid, might exist in the racemization of areneseleninic acid. Therefore, a further investigation was carried out in order to confirm the racemization mechanism of areneseleninic acid. A hexane/2-propanol (99/1) solution of enantiomerically pure (*R*)-**3c** was stirred in the presence of excess $H_2{}^{18}O$ (97 atom% ^{18}O) for 30 min at room temperature. However, no ion peak corresponding to seleninic acid containing ^{18}O was observed in the MS spectrum despite racemization taking place. This result indicates that the formation of selenurane by the addition of water does not occur under the given conditions. Therefore, the racemization of the optically active areneseleninic acids in solution was confirmed to proceed via a seleninate anion with the extrusion of a proton (Scheme 2).



Scheme 2.

As stated above, optically active sulfinic acid **2** racemized very rapidly in solution. Therefore, the racemization mechanism of optically active sulfinic acid **2** was also examined. When a 2-propanol solution of sulfinic acid **2** was stirred in the presence of excess $H_2{}^{18}O$ (95 atom% ^{18}O) for 2 h at room temperature, no ion peak corresponding to sulfinic acid containing ^{18}O was observed in the MS spectrum, indicating that addition of water to sulfinic acid does not occur under the given conditions. In general, arenesulfinic acids are more acidic than areneseleninic acids.[9] Therefore, the racemization of the optically active sulfinic acid in solution is concluded to proceed in the same manner as that of the optically active seleninic acid, that is, it proceeds via a sulfinate anion with the extrusion of a proton, although intermolecular proton transfer may participate in the racemization.

Vertex inversion and edge inversion, which are known to be the racemization mechanisms of some tricoordinated optically active chalcogen compounds,[10] and intramolecular proton transfer between the two oxygen atoms of the chalcogenic acids (Scheme 3) are also possible racemization mechanisms of the chalcogenic acids. The barriers for vertex inversion, edge inversion and intramolecular proton transfer of benzenechalcogenic acid were estimated by MO calculations (MP2/LANL2DZ) (Table 2). The activation energies of the inversions and intramolecular proton-transfer are higher than 23 kcal mol^{-1}, and are too high for rapid racemization to occur at room temperature.



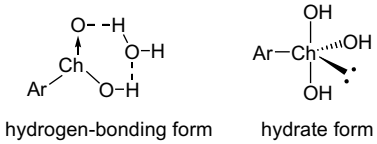
Scheme 3.

Table 2. Activation energies of vertex inversion, edge inversion, and intramolecular proton transfer of benzenechalcogenic acids (kcal mol^{-1})

	Vertex inversion	Edge inversion	Intramolecular proton transfer
$PhSO_2H$	59.6[a]	A[b]	23.8[c]
$PhSeO_2H$	71.8[a]	31.6[a]	25.0[c]
$PhTeO_2H$	81.8[a]	25.8[a]	27.0[c]

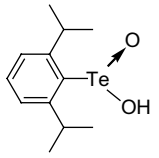
[a] Uncorrected values.
[b] The transition state was not found.
[c] The values were corrected for zero-point vibrational energies using a scaling factor of 0.9434 at the standard state (298.15 K, 1 atm).

The difference in the racemization mechanisms among the optically active chalcogenic acids can be explained by the ability to form hypervalent hydrate structures (sulfurane, selenurane, and tellurane) of the chalcogenic acids. The energy gaps of the hydrogen-bonding forms and the hydrate forms of the arenechalcogenic acids (Scheme 4) were estimated by MO calculations (MP2/LANL2DZ), and as a result, energy changes from the hydrogen-bonding forms to the hydrate forms of benzenesulfinic acid, benzeneseleninic acid, and benzenetellurinic acid **1a** were 17.8, 14.0, and −4.85 kcal mol^{-1}, respectively, meaning that tellurinic acid forms tellurane more readily than either sulfinic acid or seleninic acid



Scheme 4.

does. However, the results also show that tellurinic acid **1a** mainly exists in the hydrate form in the presence of water. In the case of a model molecule of tellurinic acid **4** with bulky substituents, the energy change from the hydrogen-bonding form to the hydrate form is almost nil ($-1.00\,kcal\,mol^{-1}$), indicating that bulky substituents are effective for suppressing the formation of achiral tellurane (hydrate form).



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3. Conclusion

The resolution of arenetellurinic acid was accomplished by means of liquid chromatography on a chiral column. The relationship between the absolute configurations and the circular dichroism spectra of the optically active arenechalcogenic acids was clarified on the basis of X-ray crystallographic analysis of an arenesulfinic acid. Kinetic studies on the racemization, the oxygen exchange reaction using $H_2{}^{18}O$, and theoretical studies revealed that a pathway involving an achiral tellurane exists for the racemization of the optically active arenetellurinic acid in solution, and the racemization of the optically active areneseleninic acid proceeds via a seleninate anion.

4. Experimental

4.1. General

Dichloromethane, hexane and 2-propanol were distilled from CaH_2 before use. Melting points were determined on a Yamato MP-21 melting point apparatus. UV–vis spectra were measured on a UV-3100PC UV-VIS-NIR scanning spectrometer. IR spectra were measured on a Perkin–Elmer spectrum GX FT-IR system. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX-500 FT NMR System. Mass spectra (MS) were determined on a JEOL JMS-LX1000 and a JEOL JMS-GCMATE system. Circular dichroism spectra were measured on a JASCO J-725 spectropolarimeter. Optical rotations were measured on a JASCO DIP-140 digital polarimeter and are given in $10^{-1}\,deg\,cm^2\,g^{-1}$.

4.2. General procedure for the preparation of arenetellurinic acids 1

Diaryl ditelluride (5 mmol) was dissolved in dichloromethane (100 mL) and ozone bubbled into the solution at −40 °C. After disappearance of color for the ditelluride, water (100 mL) was added to the solution, and the mixture stirred vigorously for 4 h at room temperature. The organic layer was separated and the organic component which remained in the aqueous layer extracted with dichloromethane (50 mL × 2). The combined organic layer was dried over anhydrous magnesium sulfate. The solution was concentrated to small volume (ca. 5 mL) under reduced pressure, at which point methanol (50 mL) was added. The fine precipitates formed were washed with methanol and dried in vacuo.

4.3. Benzenetellurinic acid 1a[5h]

Yield 24%; mp 270 °C (colorless powder; decomp.); ^1H NMR (500 MHz, $CDCl_3$): δ 2.55 (1H, br), 6.76 (5H, br); MS (EI, 30 eV) *m/z* 207, 205, 154, 77; MS (FAB) *m/z* 239 (M^+-H, ^{130}Te), 237 (M^+-H, ^{128}Te); IR (KBr) 3394 (br, OH), 3053, 1477, 1436, 1062, 735, 630 (br, Te=O) cm^{-1}.

4.4. 2,4,6-Trimethylbenzenetellurinic acid 1b

Yield 63%; mp 226 °C (colorless powder; decomp.); ^1H NMR (500 MHz, $CDCl_3$): δ 1.62 (3H, br), 2.17 (6H, br), 2.62 (1H, br), 6.68 (2H, br); MS (EI, 30 eV) *m/z* 248, 246, 119, 105, 91; MS (FAB) *m/z* 281 (M^+-H, ^{130}Te), 279 (M^+-H, ^{128}Te); IR (KBr) 3367 (br, OH), 2963, 2932, 2874, 2360, 1592, 1559, 1457, 1037, 1020, 871, 667 (br, Te=O) cm^{-1}.

4.5. 2,4,6-Triethylbenzenetellurinic acid 1c

Yield 61%; mp 201 °C (colorless powder; decomp.); ^1H NMR (500 MHz, $CDCl_3$): δ 0.75 (3H, br), 1.17 (6H, br), 1.70 (1H, br), 2.54 (4H, br), 3.00 (2H, br), 6.82 (2H, br); MS (EI, 30 eV) *m/z* 290, 288, 160, 133; MS (FAB) *m/z* 323 (M^+-H, ^{130}Te), 321 (M^+-H, ^{128}Te); IR (KBr) 3384 (br, OH), 2922, 2360, 2341, 1457, 1100, 1031, 846, 630 (br, Te=O), 542 cm^{-1}.

4.6. 2,4,6-Triisopropylbenzenetellurinic acid 1d

Yield 32%; mp 209 °C (colorless powder from methanol; decomp.); ^1H NMR (500 MHz, $CDCl_3$): δ −0.3 to 2.0 (18H, br), 2.81 (3H, br), 4.14 (1H, br), 7.03 (2H, br); MS (EI, 30 eV) *m/z* 332, 330, 203, 189, 91; MS (FAB) *m/z* 365 (^{130}Te, M^+-H), 363 (^{128}Te, M^+-H); IR (KBr) 3393 (br, OH), 2960, 2867, 2360, 1595, 1463, 1103, 878, 647 (br, Te=O) cm^{-1}; UV (hexane) λ_{max} 279 (sh, ε 3.30×10^3), 249 (sh, ε 1.08×10^4), 197 (ε 6.70×10^4) nm.

4.7. Resolution of 1d

A racemic sample of **1d** (30 mg) in hexane (0.5 mL) was charged to a chiral column packed with cellulose carbamate derivative-silica gel (Daicel Chiralcel OD; 10 × 250 mm) and eluted with hexane at a flow rate of 1.0 mL min^{-1}. Arenetellurinic acid (1 mg) was collected from the first half of the peak. The chemical structure was confirmed by ^1H NMR spectra after concentration.

4.8. (*S*)-(+)-1d

Mp 208 °C (colorless powder; decomp.); $[\alpha]_{435}^{28} = +2.5\times10^3$ (c 1.2×10^{-3}, hexane); CD (hexane) 270 ([θ]

1.27×10^4), 238 ([θ] -2.18×10^4) nm. Enantiomeric excess could not be determined by HPLC or ^{1}H NMR using Eu(hfc)$_3$.

4.9. 2-Sulfino-1,3-xylyl-18-crown-5 2[7]

To the THF (10 mL) solution of 2-bromo-1,3-xylyl-18-crown-5 (1.12 g, 3.00 mmol) was added dropwise BuLi (3.12 mmol) at -78 °C. The solution was stirred for 2 h, and sulfur dioxide bubbled into the solution for 10 min. The reaction mixture was slowly warmed to room temperature and concentrated under reduced pressure. The residue was dissolved into chloroform (15 mL) and extracted with 10% aqueous sodium hydroxide solution (15 mL × 2) and with water (20 mL × 2). The combined aqueous layer was concentrated to 20 mL under reduced pressure, acidified with 4 M hydrochloric acid (50 mL), extracted with chloroform (20 mL × 5). The solution was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. Recrystallization of the residue from ether afforded **2** (282 mg, 26%): mp 97–99 °C (from ether, lit. 101–104 °C); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.56–3.74 (16H, m), 4.75 (4H, br), 7.30 (2H, d, $J = 7.35$ Hz), 7.35 (1H, t, $J = 7.35$ Hz), 9.70 (1H, br); ^{13}C NMR (125 MHz, $CDCl_3$): δ 68.6, 69.5, 70.1, 70.2, 70.6, 130.4, 131.4, 137.1, 147.6; UV (MeCN) λ_{max} 270 (ε 2.98×10^3), 222 (ε 1.39×10^4), 197 (ε 6.53×10^4) nm.

4.10. Procedure for the measurement of circular dichroism spectrum of 2 in solid state

A mixture of a single crystal of **2** (ca. 1 mg) and 70 mg of KBr was ground and formed into disk with a radius of 6.5 mm and the KBr disk was used for measurement of circular dichroism spectrum.

4.11. X-ray crystallographic analysis of 2

Crystal data of **2** with negative Cotton effect: $C_{16}H_{24}O_7S$, $M_r = 360.41$; orthorhombic, space group $P2_12_12_1$, $a = 9.3667(11)$, $b = 12.5180(11)$, $c = 14.8160(13)$ Å, $V = 1737.2(3)$ Å^3, $Z = 4$, $T = 100$ K, $D_c = 1.378$ g cm^{-3}, $\mu = 0.221$ mm^{-1}, (Mo K$_\alpha$ 0.71073 Å). A prismatic crystal with dimensions of $0.50 \times 0.49 \times 0.38$ mm^3 was used for the data collection. A total of 4544 reflections were measured of which 3982 reflections ($R_{int} = 0.0098$) including Bijvoet pairs were independent and 3857 reflections with $I > 2\sigma(I)$. Lorentz and polarization corrections were made. Absorption correction was applied using a Ψ scan method with $T_{min} = 0.968$, $T_{max} = 0.997$. The H-atom of the sulfino group was located on the D-map and refined with an isotropic thermal parameter. Final refinement with 264 parameters against 3982 reflections gave $R = 0.0263$, $wR = 0.0613$, and $\Delta\rho_{min} = -0.17$, $\Delta\rho_{max} = 0.17$ eÅ^{-3}. Absolute structure parameter was 0.00(5). The sulfino group was found to be disordered into two atomic positions with the site occupancy factors of 0.783(2) [(*S*)-form] and 0.217(2) (incomplete structure). Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 250403.

4.12. Kinetic studies on racemization of (*S*)-(+)-1d

Kinetic studies of (*S*)-(+)-**1d** were examined in solutions (ca. 2×10^{-5} M) at 25 ± 1 °C. The rates of racemization were calculated on the basis of their circular dichroism spectra and plotted to the first-order rate equation.

4.13. Theoretical study

Geometries were optimized using the MP2[11] method with the LANL2DZ[12] basis set. All calculations were performed by using the GAUSSIAN 98[13] program on an IBM p690-681 (RegattaH) computer. Vibrational frequency analysis of each geometry of transition states of vertex inversion, edge inversion, and intramolecular proton-transfer of chalcogenic acids showed one imaginary frequency which corresponds to the vertex inversion or edge inversion mode, clearly indicating the real saddle-point in the reaction pathway. Differences in the zero-points energies between the saddle-points of inversions and the ground states are within 0.75 kcal mol^{-1} in each chalcogenic acid, and thus the energies are uncorrected.

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