Synthesis and Reactivity of Chiral Tellurium Azomethines: Pseudopolymorphism of [*o*-((((1*S*,2*R*)-2-Hydroxy-2-phenyl-1-methylethyl)amino)methinyl)phenyl]tellurium(IV) Bromide

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A range of novel chiral tellurium compounds having an azomethine functional group in the position *ortho* to tellurium has been synthesized by the reaction of the tellurium-containing aldehydes bis(*o*-formylphenyl) telluride (**1**) and *o*-(butyltelluro)benzaldehyde (**4**) with chiral amines (*R*)-(+)-(1-pheylethylamine) and (1*R*,2*S*)-(−)-norephedrine, respectively. The precursor aldehydes were prepared by using a reported procedure with slight but advantageous modifications. During the preparation of *o*-(butyltelluro)benzaldehyde, interesting side products, namely bis(*o*-formylphenyl) ditelluride ethylene acetal **5**, bis(*o*-formylphenyl) tritelluride (**6**), and bis(*o*-formylphenyl) ditelluride (**7**) were isolated in moderate yields. The ditelluride **7** has been characterized by single-crystal X-ray diffraction studies. The liquid Schiff bases **10** and **11** were further characterized by derivatizing with liquid bromine. The title compound was obtained in excellent yield by reacting the Schiff base **11** with elemental bromine. Detailed NMR studies indicated the presence of a rigid environment for the hydroxyl group. Single-crystal X-ray determinations of the crystals obtained from the different batches indicated the presence of the two pseudopolymorphic forms **13a** and **13b**, respectively. In the case of **13a** there is one molecule of CH_3CN as solvent of crystallization, whereas in **13b** half a molecule of CH_3CN per molecule of the title compound lies along the 2-fold axis. In **13a** the hydroxyl hydrogen is hydrogen-bonded to the nitrogen of the solvent molecule, whereas in **13b** it is hydrogen-bonded to the bromine of the neighboring molecule.

Introduction

The syntheses and applications of chiral organoselenium ligands and reagents have attracted considerable current interest.[1,2] Whereas the ligand chemistry of analogous achiral tellurium ligands has been extensively studied in recent years,[3] developments in the area of chiral tellurium ligands have lagged behind. Earlier we reported the attempted synthesis of some “hybrid” chiral tellurium ligands and structural characterization of one of the derivatives.[4] Recently, synthesis of optically active tellurium-containing binaphthyls,[5] and bis[2-(1-(dimethylamino)ethyl)ferrocenyl] dichalcogenides[6] and their applications in chiral induction have been investigated. Very recently, the first examples of chirality transfer in allylic telluroxides[7] and diastereoselective imination of a chiral cinnamyl ferrocenyl telluride[8] have been reported. In view of the recent

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applications of chiral tellurium and selenium ligands in asymmetric catalysis, we contemplated the synthesis of conformationally more rigid polydentate chiral tellurium azomethines, incorporating mixed donor atoms, which may provide a high degree of stereocontrol in organic reactions.

Although achiral tellurium azomethines have been known for some years,[9,10] no chiral tellurium Schiff bases have been reported. In this paper we report the synthesis of the first examples of chiral multidentate Schiff bases and their derivatives incorporating several chiral centers and Te, N, and O donor atoms.

Experimental Section

General Methods. Air-sensitive reactions were carried out under an inert atmosphere. Solvents were purified and dried by standard techniques. All chemicals used, *o*-bromotoluene (Fluka), *n*-butyllithium (Merck), (*R*)-(+)-(1-pheylethyl)amine (Fluka), (1*R*,2*S*)-(−)-norephedrine (Aldrich), and the chiral shift reagent tris[3-((heptafluoropropyl)hydroxymethylene)-(+)-camphorato]europium(III) (Aldrich), were reagent grade and were used as received. Tellurium powder (Wilson Laboratories) was purified by washing with concentrated hydrochloric acid to remove TeO_2, followed by several washings with water to remove the acid and finally with methanol, and diethyl ether, and dried before use. *o*-Bromobenzyl bromide, *o*-bromobenzaldehyde and *o*-bromobenzaldehyde acetal[11] were prepared by reported methods. TeI_2 was prepared by reacting tellurium and iodine. The melting points are uncorrected and were determined on a Veego melting point apparatus using a capillary tube. Elemental analyses were performed on a Carlo Erba elemental analyzer, Model 1106. The IR spectra were recorded on a Perkin-Elmer 681 spectrometer. The solid samples were examined as KBr pellets. Nuclear magnetic resonance spectra, ^{1}H (299.94 MHz), ^{13}C (75.42 MHz), and ^{125}Te (94.75 MHz), were recorded on a Varian VXR 300S spectrometer. Chemical shifts are cited with respect to $SiMe_4$ as internal standard (^{1}H and ^{13}C) and $Te(S_2CNEt_2)_2$ as external standard (^{125}Te). The ^{1}H NMR spectra of the solutions containing chiral Schiff bases and the chiral shift reagent were recorded using (0.25:1)−(1:1) molar ratios of the shift reagent to the tellurium compound. Optical rotations were measured on a JASCO Model DIP 370 digital polarimeter. Mass spectra were obtained on a Jeol D-300(EI/CI) spectrometer and are reported as *m*/*e* (ion percent relative intensity). In the case of an isotopic pattern, the value given is for the most intense peak, except for the molecular ion, where all the peaks are given.

Preparation of Bis(*o*-formylphenyl)telluride Ethylene Acetal.[11] To a solution of ethylene acetal of *o*-bromobenzaldehyde (4.7 g, 20.5 mmol) in dry ether (100 mL) placed in a three-necked 250 mL flask fitted with a reflux condenser, rubber septum and nitrogen gas inlet, at room temperature, was added dropwise with stirring a 1.6 M solution of *n*-butyllithium (14 mL, 22.4 mmol) over a period of 5 min. The mixture was stirred for additional 5 min to obtain a cloudy white slurry. Then TeI_2 (3.93 g, 10.3 mmol) was added under a brisk flow of nitrogen in small portions. After it was refluxed for 30 min, the solution was cooled, poured into ice water (500 mL), and extracted with diethyl ether (3 × 50 mL). The ether extract was dried over anhydrous sodium sulfate and concentrated *in vacuo*. The residue was washed thoroughly with hexane (3 × 10 mL) to afford a pale yellow solid, which was recrystallized from an acetone−pentane (1:1) mixture to give colorless crystals of bis(*o*-formylphenyl)telluride ethylene acetal (2.4 g, 54.9, mp 79 °C (lit.[11] 79−80 °C)). Anal. Calcd for $C_{18}H_{18}O_4Te$: C, 50.76; H, 4.26. Found: C, 50.72; H, 4.31. ^{1}H NMR ($CDCl_3$): δ 7.56−7.04 (m, 8H, aromatic H), 5.93 (s, 2H, ArCH<), 4.10−3.91 (m, 8H, OCH_2CH_2O). ^{13}C NMR ($CDCl_3$): δ 140.1, 138.9, 129.8, 127.5, 126.7, 118.1 (aromatic C), 105.6 (CH<), 65.0 (OCH$_2$C).

Preparation of Bis(*o*-formylphenyl) Telluride (1). Hydrolysis of bis(*o*-formylphenyl)telluride ethylene acetal (2.4 g, 5.63 mmol) was performed by following the reported procedure[11] to give **1** as yellow crystals (1.5 g, 79, mp 115 °C (lit.[11] 117−118 °C)). Anal. Calcd for $C_{14}H_{10}O_2Te$: C, 49.77; H, 2.98. Found: C, 49.62; H, 2.93. ^{1}H NMR ($CDCl_3$): δ 10.27 (s, 2H, aldehydic H), 8.0−7.35 (m, 8H, aromatic H); ^{13}C NMR ($CDCl_3$): δ 195.3 (aldehydic C), 138.7, 137.3, 134.6, 132.7, 128.2, 124.4 (aromatic C). ^{125}Te NMR ($CDCl_3$): δ −686. IR (KBr): 1694, 1654 cm^{-1} (ν(C=O)).

Preparation of *o*-(Butyltelluro)benzaldehyde Ethylene Acetal (2). *o*-Bromobenzaldehyde ethylene acetal (5.17 g, 22.6 mmol) and *n*-BuLi (15.4 mL, 24.6 mmol) were reacted as described above for the preparation of bis(*o*-formylphenyl)telluride ethylene acetal. Tellurium powder (2.8 g, 22.6 mmol) was added slowly with vigorous stirring. After it was refluxed for 30 min, the solution was cooled and poured into ice water (500 mL). The resulting organic layer and the dichloromethane extracts (3 × 20 mL) from the aqueous layer were combined, washed with water, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The light orange solid which precipitated out from the reaction mixture on standing overnight afforded novel compounds **5**, **6**, and **7** (described later). The residual reddish yellow mother liquor gave compounds **2**, **3**, and **4** on the usual workup.

Synthesis of *o*-(Butyldibromotelluro)benzaldehyde Ethylene Acetal (3). Crude **2**, which was obtained as a viscous liquid from the above reaction, was converted to the dibromide derivative **3** by adding bromine (2.89 g, 18.1 mmol) in chloroform (30 mL) dropwise to a stirred solution of crude **2** (5.7 g) in chloroform (10 mL). After the mixture was stirred for 2 h, hexane (30 mL) was added. The yellow solid that precipitated out on cooling was filtered, washed with hexane, and recrystallized from a chloroform−hexane mixture (1:1): yield 6.5 g, 76% (based on crude **2**); mp 100 °C). Anal. Calcd for $C_{13}H_{18}O_2Br_2Te$: C, 31.63; H, 3.67. Found: C, 32.2; H, 4.0. ^{1}H NMR ($CDCl_3$): δ 7.91−7.49 (m, 4H, aromatic H), 6.46 (s, 1H, ArCH<), 4.16−4.03 (m, 4H, OCH_2-C), 3.73 (t, J = 7.6 Hz, 2H, CH_2-Te), 2.28−2.17 (m, 2H, CCH_2C), 1.70−1.58 (m, 2H, CCH_2CH$_3$), 1.07 (t, J = 7.3 Hz, 3H, CH_3-CH$_2$). ^{13}C NMR ($CDCl_3$): δ 138.8, 131.3, 130.8, 129.9, 128.1 (aromatic C), 102.0 (CH<), 64.8 (OCH$_2$), 44.9 (TeCH$_2$), 26.7 (CH$_2$CH$_2$CH$_2$), 24.4 (CH$_2$$CH_2CH_3$), 13.5 ($CH_3CH_2$).

Preparation of *o*-(Butyltelluro)benzaldehyde (4). Compound **3** (6 g, 12.2 mmol) was taken up in dichloromethane (20 mL) and the solution shaken repeatedly with an excess of aqueous $Na_2S{\cdot}9H_2O$ (5%) until the aqueous phase became colorless. The organic layer was washed with water, dried over anhydrous sodium sulfate, and concentrated under vacuum to give **2** as a reddish yellow liquid (3.3 g, 81.5%). The acetal **2** (3.3g, 9.9 mmol) was hydrolyzed with HCl (6 N, 7 mL) as reported[9c] and purified by flash column chromatography over silica (60−120 mesh, petroleum ether−ethyl acetate 95:5) to give **4** as a reddish yellow liquid (2.6 g, 91%).

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Synthesis of Bis(*o*-formylphenyl) Ditelluride Ethylene Acetal (5). Recrystallization of the light orange solid obtained during the preparation of **2** from chloroform−hexane (1:1) afforded pure **5** as the major product: yield 1.5 g, 24%; mp 120 °C). Anal. Calcd for $C_{18}H_{18}O_4Te_2$: C, 39.06; H, 3.28. Found: C, 39.1; H, 3.3. ^1H NMR ($CDCl_3$): δ 8.0−7.10 (m, 8H, aromatic H), 5.87 (s, 2H, ArC*H*<), 4.24−4.01 (m, 8H, OC*H*$_2$-C*H*$_2$O); ^{13}C NMR ($CDCl_3$): δ 139.9, 138.7, 130.5, 127.4, 127.1, 107.7 (aromatic C), 105.4 (*C*H<), 65.1 (O*C*H$_2$C); ^{125}Te NMR ($CDCl_3$): δ −506.

Synthesis of Bis(*o*-formylphenyl) Tritelluride (6) and Bis(*o*-formylphenyl) Ditelluride (7). A stirred solution of the crude light orange solid (2 g, 3.6 mmol) obtained during the preparation of **2**, in a carbon tetrachloride (15 mL) and methanol (45 mL) mixture, was refluxed with HCl (6 N, 5 mL) for 2 h. To this water was added (20 mL), and the reaction mixture was further refluxed for 5 min. After it was cooled, the mixture was washed with water (3 × 50 mL); the organic layer was separated and dried azeotropically with benzene (15 mL). The solvent was evaporated to afford a reddish yellow solid. This solid on recrystallization from acetic acid first gave red needles of the novel tritelluride **6**, and column chromatography of the mother liquor over neutral alumina (chloroform−petroleum ether, 1:1) followed by recrystallization from chloroform gave bis(*o*-formylphenyl) ditelluride (**7**) as yellow needles.

For **6**: yield 0.15 g, 7% (based on crude **5**); mp 115 °C). Anal. Calcd for $C_{14}H_{10}O_2Te_3$: C, 28.35; H, 1.70. Found: C, 28.79; H, 1.57. ^1H NMR ($CDCl_3$): δ 10.62 (s, 2H, aldehydic H), 8.44−7.50 (m, 8H, aromatic H). IR (KBr): 1584 cm^{-1} (ν(C=O); MS (EI): *m/e* 594, 592, 591 (M^++ 1, 1.6%), 362 ($[C_6H_4CHOTe_2]^+$, 21%), 235 $[C_6H_4(Te)CHO]^+$, 92%), 127 (Te^+, 27%), 105 ($[C_6H_4CHO]^+$, 99.5%), 77 ($[C_6H_5]^+$, 100%).

For **7**: yield (0.8 g, 48 (based on crude **5**); mp 152 °C (lit.[12] mp 147−152°C). Anal. Calcd for $C_{14}H_{10}O_2Te_2$: C, 36.13; H, 2.17. Found: C, 35.74; H, 2.12. ^1H NMR ($CDCl_3$): δ 10.13 (s, 2H, aldehydic H), 8.04−7.26 (m, 8H, aromatic H). ^{13}C NMR (DMSO-d_6): δ 195.2 (aldehydic C) 139.9, 138.2, 137.2, 135.4, 128.0,111.6 (aromatic C); ^{125}Te NMR (DMSO-d_6): δ −409. IR (KBr): 1653 (ν(C=O)). MS (EI): *m/e* 468, 466(m), 464, 462 (M^+ + 1), 234 $[C_6H_4(Te)CHO]^+$.

Synthesis of bis[2-(((*R*)-methylbenzylamino)methinyl)-phenyl] Telluride (8). Bis(*o*-formylphenyl) telluride (1 g, 2.96 mmol) was refluxed azeotropically in benzene (200 mL) with (*R*)-(+)-(1-pheylethyl)amine (0.79 g, 6.5 mmol) and two drops of acetic acid using a Dean−Stark trap until the completion of the reaction (by IR). The mixture was washed with water (3 × 100 mL) to remove the unreacted amine. The remaining water from the organic layer was removed azeotropically, and finally benzene was evaporated under vacuum to give a pale yellow viscous liquid of the Schiff base **8** (1.55 g, 96%). Anal. Calcd for $C_{30}H_{28}N_2Te$: C, 66.22; H, 5.19; N, 5.15. Found: C, 65.03; H, 4.99; N, 4.78. ^1H NMR ($CDCl_3$): δ 8.69 (s, 2H, azomethine H), 7.83−7.12 (m, 18H, aromatic H), 4.61 (q, *J* = 6 Hz, 2H, C*H*(CH$_3$)), 1.62 (d, *J* = 6 Hz, 6H, CH$_3$). ^{13}C NMR ($CDCl_3$): δ 162.3 (azomethine C), 144.5, 138.0,130.7, 130.2, 128.3, 127.3, 126.8, 125.6 (aromatic C), 69.0 (*C*HMe), 25.2 (*C*H$_3$). ^{125}Te NMR ($CDCl_3$): δ −233 (relative to $Te(S_2CNEt_2)_2$). IR (neat): 1634 cm^{-1} (ν(C=N)); MS (EI): *m/e* 547, 546 (m), 544, 543, 542, 541, 540 (M^+, ^{130}Te), 441 ($M^+ - C_8H_9$), 336 ($[TeC_6H_4CH{=}NCHMePh]^+$), 232 ($[C_6H_4CH{=}NTe]^+$), 207 ($[C_6H_4CH{=}NCHMePh]^+$), 105 ($[C_8H_9]^+$, 100%). $[\alpha]_D{}^{25} = -52.7$ (*c* = 2.5%, $CHCl_3$).

Synthesis of Bis[*o*-((((1*S*,2*R*)-2-hydroxy-2-phenyl-1-methylethyl)amino)methinyl)phenyl] Telluride (9). This was synthesized by reacting bis(*o*-formylphenyl)telluride (0.1 g, 0.296 mmol) and (1*R*,2*S*)-(−)-norephedrine (0.098 g, 0.65 mmol) in a fashion similar to that described for the above reaction and recrystallized from hexane to give a light yellow solid of **9**: yield 0.12 g, 67.1%, mp 72−80 °C. Anal. Calcd for $C_{32}H_{32}N_2O_2Te$: C, 63.61; H, 5.34; N, 4.64. Found: C, 63.50; H, 5.7; N, 4.8. ^1H NMR ($CDCl_3$): δ 8.62 (s, 2H, azomethine H), 7.80−7.17 (m, 18H, aromatic H), 4.85 (d, *J* = 4.4 Hz, 2H, *H*COH), 3.72−3.66 (m, 2H, C*H*(CH$_3$)), 2.9 (bs, 2H, O*H*), 1.15 (d, *J* = 6.6 Hz, 6H, CH$_3$). ^{13}C NMR ($CDCl_3$): δ 163.2 (azomethine C), 141.1, 138.0, 137.7, 131.0, 130.3, 128.0, 127.5, 127.3, 126.5, 125.3 (aromatic C), 77.0 (*C*HOH), 70.6 (*C*HMe), 16.3 (*C*H$_3$). ^{125}Te NMR ($CDCl_3$): δ −239.2 (relative to $Te(S_2CNEt_2)_2$. IR (KBr): 3404 (ν(OH), b), 1643 cm^{-1} (ν(C=N)); MS (EI): *m/e* 607, 606, 605, 604 (major), 603, 602, 601 (M^+, ^{128}Te), 498 ($M^+ - C_6H_5CHOH$), 469 ($M^+ - C_6H_5CHOHCHMe$), 456 ($M^+ - C_6H_5CHOHCHMeN$), 366 ($[C_6H_4(Te)CH{=}NCHMeCHOHPh]^+$), 320 ($[C_6H_4(CH)TeC_6H_4CH{=}N]^+$), 293 ($[C_6H_4TeC_6H_4CH]^+$), 260 ($[C_6H_4(Te)CH{=}NCHMe]^+$), 232 $[C_6H_4(Te)CH{=}N]^+$, 100%), 220 ($[C_6H_4(Te)CH]^+$), 204 ($[C_6H_4Te]^+$), 165 ($[C_6H_5CHOHCHMeN{=}CH]^+$), 135 ($[C_6H_5CHOHCHMe]^+$), 107 $[C_6H_5CHOH]^+$. $[\alpha]_D{}^{25} = +58.8$ (*c* = 2.5, $CHCl_3$).

Synthesis of *o*-[((*R*)-Methylbenzylamino)methinyl]-phenyl Butyl Telluride (10). This was synthesized by refluxing *o*-(butyltelluro)benzaldehyde (0.76 g, 2.62 mmol) and (*R*)-(+)-(1-pheylethyl)amine (0.33 g, 2.73 mmol) in benzene with 2 drops of acetic acid as described for the preparation of **8**. After the usual workup, the product was obtained as a viscous reddish yellow liquid (1 g, 97%). ^1H NMR ($CDCl_3$): δ 8.51 (s, 1H, azomethine H), 7.63−7.20 (m, 9H, aromatic H), 4.66 (q, *J* = 6.5 Hz, 1H, C*H*Me), 2.66−2.57 (m, 2H, TeC*H*$_2$), 1.84−1.76 (m, 2H, CHC*H*$_2$Me), 1.7−1.68 (d, *J* = 6.5 Hz, 3H, C*H*$_3$CH), 1.51−1.25 (m, 2H, C*H*$_2$Me), 0.95 (t, *J* = 6.6 Hz, 3H, C*H*$_3$CH$_2$). ^{13}C NMR ($CDCl_3$): δ 160.5 (azomethine C), 144.8, 136.3, 133.4, 132.5, 129.9, 128.4, 126.9, 126.8, 125.1, 121.0 (aromatic C), 69.7 (*C*HMe), 32.3 (CH$_2$*C*H$_2$CH$_2$), 26.2 (CH$_2$*C*H$_2$-CH$_3$), 25.8 (*C*H$_3$CH), 13.6 (*C*H$_3$-CH$_2$), 8.3 (*C*H$_2$Te). ^{125}Te NMR ($CDCl_3$): δ −356.3 (relative to $Te(S_2CNEt_2)_2$). IR (neat): 1654.5 (ν(C=N)). MS (EI): *m/e* 338, 337, 336 (m), 334, 333, 332 ($M^+ - C_4H_9$, ^{128}Te), 232 ($[C_6H_4(Te)CH{=}N]^+$), 149 ($[C_6H_5CH_2C_4H_9]^+$), 120 ($[C_6H_5CHMeN]^+$), 105 ($[C_6H_5CHMe]^+$, 100%). $[\alpha]_D{}^{25} = -175.2$ (*c* = 2.4%, $CHCl_3$).

Synthesis of *o*-[(((1*S*,2*R*)-2-Hydroxy-2-phenyl-1-methylethyl)amino)methinyl]phenyl Butyl Telluride (11). *o*-(Butyltelluro)benzaldehyde (1 g, 3.45 mmol) and (1*R*,2*S*)-(−)-norephedrine (0.6 g, 3.97 mmol) were treated in a manner similar to that described above for the synthesis of **8** to obtain **11** as a reddish brown viscous liquid (1.4 g, 95.9%). ^1H NMR ($CDCl_3$): δ 8.49 (s, 1H, azomethine H), 7.65−7.17 (m, 9H, aromatic H), 4.90 (d, *J* = 3.9 Hz, 1H, C*H*OH), 3.75 (m, 1H, C*H*(CH$_3$)), 2.65 (t, *J* = 7.8 Hz, 2H, TeC*H*$_2$), 1.86−1.81 (m, 2H, CHC*H*$_2$CH$_2$), 1.54−1.42 (m, 2H, C*H*$_2$Me), 1.20 (d, *J* = 6.6 Hz, 3H, C*H*$_3$CH), 0.96 (t, *J* = 7.3 Hz, 3H, C*H*$_3$CH$_2$). ^{13}C NMR ($CDCl_3$): δ 161.1 (azomethine C), 140.8, 136, 133.5, 132.4, 130.1, 128, 127.1, 126.3, 125.2, 120.5 (aromatic C), 76.7 (*C*HOH), 70.8 (*C*HMe), 32.1 (CH$_2$*C*H$_2$CH$_2$), 25.6 (CH$_2$*C*H$_2$CH$_3$), 15.9 (*C*H$_3$CH), 13.5 (*C*H$_3$CH$_2$), 8.6 (*C*H$_2$Te). ^{125}Te NMR ($CDCl_3$): δ −368.4 (relative to $Te(S_2CNEt_2)_2$). IR (KBr): 3319 (ν(OH)), 1638 cm^{-1} (ν(C=N)). MS: *m/e* 369, 368 (major), 367, 366, 365, 364, 363, 362, 361, 360 ($M^+ - C_4H_9$, ^{130}Te), 260 ($[C_6H_4(Te)CH{=}NCHMe]^+$), 232 ($[C_6H_4(Te)CH{=}N]^+$), 220 ($[C_6H_4(Te)CH]^+$), 205 ($[C_6H_4Te]^+$), 149 ($[C_6H_5CHOHCHMeN]^+$), 135 $[C_6H_5CHOHCHMe]^+$, 100%). $[\alpha]_D{}^{25} = +22.0$ (*c* = 3.6%, $CHCl_3$).

Synthesis of [(((*R*)-Methylbenzylamino)methinyl)-phenyl]tellurium(IV) Tribromide (12). To a solution of *o*-[((*R*)-(+)-(methylbenzylamino)methinyl]phenyl butyl telluride (**10**; 0.6 g, 1.53 mmol) in chloroform (50 mL) at 0 °C was added bromine (0.49 g, 3.1 mmol) dropwise, and the reaction mixture was stirred for 2 h. The solvent was reduced to 20 mL, after which the tribromide **12** precipitated on cooling as a bright yellow solid. Recrystallization from chloroform afforded yellow prisms of **12**: yield 0.67 g, 76%; mp 216−218 °C. Anal. Calcd for $C_{15}H_{14}NTeBr_3$: C, 31.30; H, 2.45; N, 2.43. Found: C, 31.0; H, 2.4; N, 2.4. ^1H NMR ($CDCl_3$): δ 8.45 (s, 1H, azomethine H), 8.73−7.44 (m, 9H, aromatic H), 5.4 (dq, *J* = 7.5 Hz, 3 Hz, 1H, C*H*Me), 2.08 (d, *J* = 9 Hz, 3H, C*H*$_3$CH).

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Table 1. Crystallographic Data and Measurements for 7, 13a, and 13b

	7	**13a**	**13b**
Crystal Data			
empirical formula	$C_{14}H_{10}O_2Te_2$	$C_{18}H_{19}Br_3ON_2Te$	$C_{17}H_{17.5}Br_{3O}N_{1.5}Te$
cryst color; habit	yellow needles	yellow needles	yellow plates
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$P2_12_12_1$	$C2$
unit cell dimens			
a (Å)	7.964(2)	7.36(1)	12.000(2)
b (Å)	17.689(3)	12.76(1)	8.587(1)
c (Å)	20.167(2)	23.13(1)	18.876(2)
β (deg)	93.58(2)		93.174(8)
V (Å^3)	2835.3(9)	2169.0(2)	1942.1(4)
Z	8	4	4
fw	465.42	646.65	626.16
calcd density (g/cm^3)	2.18	1.98	2.14
measd density (g/cm^3)	2.15	1.93	2.12
abs coeff (mm^{-1})	4.11	6.77	7.71
F(000)	1712	1224	1180
Measurement of Intensity Data			
temp (K)	293(2)	296(2)	293(2)
θ range for data collcn (deg)	2.02−24.99	2− 25	2.16−30
index ranges	$-9 \le h \le 9$, $0 \le k \le 21$, $0 \le l \le 23$	$0 \le h \le 8$, $0 \le k \le 15$, $0 \le l \le 27$	$0 \le h \le 16$, $0 \le k \le 12$, $-26 \le l \le 26$
no of rflns collcd	4967	2047	3085
no of indpt rflns	3226 ($I > 2\sigma(I)$)	1455 ($I > 3\sigma(I)$)	2951 ($I > 2\sigma(I)$)
abs cor	empirical	empirical	empirical SHELXA
max and min transmissn	1.292/0.732	0.999/0.684	0.576/0.226
refinement method	full-matrix least squares on F^2	full-matrix least squares on F	full-matrix least squares on F^2
no. of data/restraints/params	3226/0/325	1455/-/196	2951/1/198
final R indices	R1 = 0.051, wR2 = 0.123	R1 = 0.066, wR2 = 0.084	R1 = 0.034, wR2 = 0.083
abs structure param		0.05(5)	0.003(13)
largest diff peak and hole (e/Å^{-3})	+0.893, −0.982	+1.67, −3.25	+1.278, −1.271

^{125}Te NMR ($CDCl_3$): δ +362 (relative to $Te(S_2CNEt_2)_2$). IR (KBr): 1620 cm^{-1} (ν(C═N)). MS (EI) *m/e* 500, 499, 498, 497, 496 (m), 495, 494, 493, 492, 491, 490 ($M^+ - Br$), 417 ($M^+ - Br_2$), 336 ($M^+ - Br_3$), 312 ($[C_6H_4(TeBr)CH{=}N]^+$, 233 ($[C_6H_4(Te)CH{=}N]^+$), 206 ($[C_6H_4Te]^+/M^+ - TeBr_3$), 105 ($[C_6H_5\text{-}CHMe]^+$, 100%). $[\alpha]_D{}^{27}$ = 40.0 (c = 1%, $CHCl_3$).

Synthesis of [*o*-((((1*S*,2*R*)-2-Hydroxy-2-phenyl-1-methylethyl)amino)methinyl)phenyl]tellurium(IV) Tribromide (13). *o*-[(((1*S*,2*R*)-2-hydroxy-2-phenyl-1-methylethyl)-amino)methinyl]phenyl butyl telluride (**11**; 1.72 g, 4.1 mmol) was brominated with bromine (1.3 g, 8.13 mmol) to give **13** by following the procedure as described for **12**. The product was recrystallized from chloroform /acetonitrile (1:1) to give **13** as yellow needles and plates yield 2.3 g, 93.4%; mp 206 °C. Anal. Calcd for $C_{16}H_{16}NTeBr_3O$: C, 31.73; H, 2.66; N, 2.31. Found: C, 31.99; H, 2.66; N, 2.34. ^{1}H NMR ($CDCl_3$): δ 8.79 (s, 1H, azomethine H), 8.81−7.33 (m, 9H, aromatic H), 5.48 (dd, J = 4.49, 2.1 Hz, 1H, C*H*OH), 4,27 (dq, J = 6.6, 2.1 Hz, 1H, C*H*Me), 2.98 (dd, J = 4.49, 0.9 Hz, 1H, O*H*), 1.48 (d, J = 6.4 Hz, 3H, C*H*$_3$CH). ^{13}C NMR (CD_3COCD_3): δ 170.2 (azomethine C), 145.1, 141.9, 136.8, 135.0, 133.9, 132.8, 131.5, 129.3, 128.6, 127.0 (aromatic C), 73.8 (*C*HOH), 70.2 (*C*HMe), 15.5 (*C*H$_3$CH). ^{125}Te NMR ($CDCl_3$): δ +387 (relative to $Te(S_2CNEt_2)_2$). IR (KBr): 3418 (ν(OH), s), 1635.1 cm^{-1} (ν(C═N)). $[\alpha]_D{}^{27}$ = 31.0 (c = 1%, CH_3CN).

Crystal Structure Determination of 7 and 13a,b. Diffraction-quality single crystals of **7** were obtained by allowing a saturated solution of **7** in chloroform to evaporate slowly at room temperature. The tribromide **13** crystallizes from acetonitrile or a chloroform−acetonitrile (1:1) mixture in two pseudopolymorphic forms, yellow needles (**13a**) and yellow plates (**13b**). All diffraction measurements for **7**, **13a**,**13b** were performed at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å) employing the $\omega-2\theta$ scan technique. The unit cell was determined from 25 randomly selected reflections using the automatic search, index, and least-squares routines. The data were corrected for Lorentz and polarization effects. For **7** and **13a** an empirical absorption correction was applied to the data by measuring the intensities of eight reflections with χ near 90° for different ψ values (0° < ψ < 360°, every 10°) and using the EAC program from the Enraf-Nonius Package.[13] For **13b**, however, an empirical absorption correction was applied using the SHELXA program.[14] The structures of **7** and **13b** were solved by routine heavy-atom/Fourier methods (using SHELXL 93/SHELX 86)[15,16] and refined by full-matrix least squares with the non-hydrogen atoms anisotropic. The structure of **13a** was refined in a similar manner using the SHELX 76 program,[17] keeping the temperature factor of the nitrogen atom of the solvent molecule fixed at 0.05 Å^2. The hydrogen atom bonded to the hydroxyl oxygen was located from the difference map, whereas the others were placed at calculated positions with fixed isotropic temperature factors of 0.07 Å^2. The weighting scheme employed for **13a** was of the form $w = K/[|\sigma^2(F_o)| + g(F_o)^2]$, where K and g were refined at convergence to 0.8764 and 0.007 465, respectively. For structures **7** and **13b**, however, the weighting scheme is as employed in the SHELXL 93 program. The scattering factors for tellurium (corrected for f' and f'') were taken from ref 18, while, those for the remaining atoms were as incorporated in the SHELX 76 program.[17] The absolute configurations of **13a** and **13b** were ascertained from the value of the Flack parameter (0.05(5) and 0.003(13), respectively) as determined from the SHELXL 93 program.[19] The relevant crystal data along with the refinement details are given in Table 1.

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(13) Enraf-Nonius Structure Determination Package; Enraf-Nonius, Delft, The Netherlands, 1983.

(14) Sheldrick, G. M. SHELXA: Program for Empirical Absorption Correction; University of Gottingen, Gottingen, Germany, 1993.

(15) Sheldrick, G. M. SHELXL 93: Program for the Refinement of Crystal Structure; University of Gottingen, Gottingen, Germany, 1993.

(16) Sheldrick, G. M. SHELX 86: Program for Solution of Crystal Structures; University of Gottingen, Gottingen, Germany, 1986.

(17) Sheldrick, G. M. SHELX 76, Program for Crystal Structure Determination: University of Cambridge, Cambridge, England, 1976.

(18) Cromer, D. T.; Waber, T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingharm, England, 1974; Vol. IV.

(19) Flack, H. *Acta Crystallogr. Sect. A* **1983**, *39*, 876.

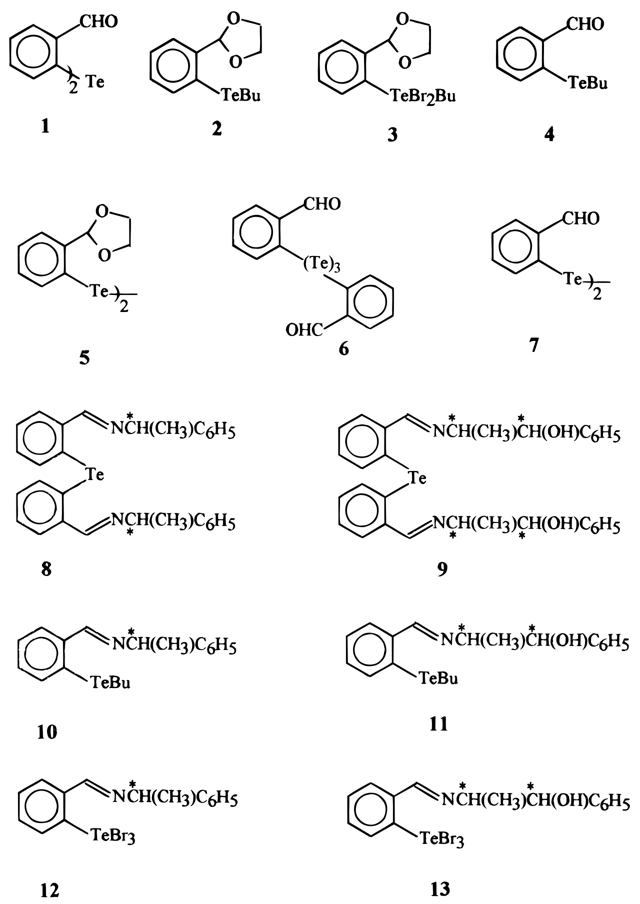

Figure 1.

Results and Discussion

The tellurium-containing precursor aldehydes, *i.e.*, bis(*o*-formylphenyl) telluride[11] (**1**; Figure 1) and *o*-(butyltelluro)benzaldehyde[12,9c] (**4**), were prepared by modification of the reported procedure. In the preparation of **1**, easily available and inexpensive *o*-bromotoluene was the starting material, instead of the *o*-iodotoluene used in the original preparation.[11] The transformation of *o*-bromotoluene to *o*-bromobenzaldehyde ethylene acetal proceeded as reported earlier. However, in the next step, i.e., the lithium−halogen exchange reaction, relatively more forcing conditions had to be used and the reaction of *o*-lithiobenzaldehyde ethylene acetal with TeI_2 followed by deprotection afforded **1** in good yield.

Of particular interest is the preparation of *o*-(butyltelluro)benzaldehyde acetal **2**. Though the preparation is well-established,[9c,12] in our hands it did not proceed exactly as reported. Interestingly, the reaction afforded the ditelluride acetal **5** and the benzaldehyde acetal (by TLC and NMR) in addition to the desired product **2**. The reported preparative sequence of reactions, *i.e.* lithiation of *o*-bromobenzaldehyde acetal and telluration followed by oxidative workup, gave a reddish, viscous liquid from which an orange solid precipitated. This was characterized after purification as the ditelluride acetal **5** as the major product. The crude acetal, however, on hydrolysis was found to contain the tritelluride **6** and ditelluride **7**. The mother liquor was found to contain the desired product **2** in addition to the benzaldehyde acetal.

The separation of **2** from the mother liquor proved to be quite difficult by either column chromatography or vacuum distillation. Hence, it was separated by making a tellurium(IV) derivative. The mixture, obtained from the mother liquor of the reaction, was brominated using bromine in chloroform. The yellow precipitate of *o*-(butyldibromotelluro)benzaldehyde ethylene acetal (**3**) thus obtained was reduced back to **2** by shaking a dichloromethane solution of **3** with $Na_2S{\cdot}9H_2O$. The aldehyde group was deprotected by the reported procedure, and the resulting *o*-(butyltelluro)benzaldehyde (**4**) was purified by flash column chromatography over silica gel.

Systematic workup of the crude solid (**5**) was effective. The crude acetal on hydrolysis afforded an orange precipitate whose ^1H NMR spectrum showed two aldehyde peaks at 10.1 and 10.6 ppm. This indicated the presence of two compounds with aldehyde groups. Separation of these compounds was achieved by crystallization of the crude product from acetic acid. Red needles (7%) with a melting point of 115 °C separated out first, and these exhibited the aldehyde peak at 10.6 ppm in the ^1H NMR spectrum and a strong IR band at 1584 cm^{-1}. The mass spectrum (EI) showed *m*/*e* values corresponding to the tritelluride **6**. The crystal structure of **6** could not be obtained, since all the crystals examined appear to be twinned. Evaporation of the mother liquor, followed by column chromatography over neutral alumina, afforded a yellow crystalline solid of bis(*o*-formylphenyl) ditelluride (**7**). Although **7** had been synthesized earlier by two different methods, (a) by *ortho*-lithiation of *o*-iodobenzaldehyde acetal using lithium metal followed by tellurium insertion and hydrolysis[12] and (b) by the reduction of *o*-(butyldichlorotelluro)benzaldehyde with pyridine,[12] the direct method has not been reported. The ditelluride was unambiguously characterized by single-crystal X-ray diffraction studies (*vide infra*).

The optically active bi- and multidentate tellurium azomethines **8**−**11** were obtained by the condensation reaction of bis(*o*-formylphenyl) telluride or *o*-(butyltelluro)benzaldehyde with (*R*)-(+)-(1-phenylethyl)amine and (1*R*,2S)-(−)-norephedrine. The preparative procedure involved separation of water formed from the reaction by using a Dean−Stark trap. The reaction rate was considerably increased with the addition of a catalytic amount of acetic acid. Out of the four Schiff bases **8**−**11** synthesized, the Schiff bases derived from phenylethylamine (**8** and **10**) were found to be liquid, whereas **9** was a low-melting solid. Compound **11** solidified after standing for a long time. Unfortunately, purification of the Schiff bases proved to be quite difficult, as the column chromatography and recrystallization from different solvents led to the hydrolysis of the Schiff bases. However, samples of reasonable purity (300 MHz NMR) could be obtained by washing the Schiff bases with petroleum ether. Compounds **10** and **11** were further characterized by derivatizing with Br_2 to yield the tribromides **12** and **13** with the loss of a butyl group. Similar halogenolysis attempts for **8** and **9** with sulfuryl chloride, chlorine gas, and bromine liquid were unsuccessful.

Compounds **8** and **9** showed molecular ion peaks at *m*/*e* 546 (^{130}Te) and 604 (^{128}Te), respectively; **10** and **11** failed to show the molecular ion peaks, the highest mass peaks observed being at *m*/*e* 336 and 368, respectively, with the loss of the butyl group. Vibrational frequencies of the azomethine bond (ν(C=N)) in the Te compounds were observed in the range 1654−1620 cm^{-1}.

In ^{1}H NMR spectra, the azomethine signals were observed at 8.49−8.7 ppm as a sharp singlet. The ^{13}C NMR spectra are characteristic, and the *ipso* carbon shifts are in the range 125.33−120.5 ppm. The ^{1}H NMR spectra of **12** and **13** in $CDCl_3$ exhibited the expected peak pattern for the CH_3 and CH protons. However, when the spectra were recorded in DMSO-d_6, three to four sets of signals for CH_3 and CH protons were observed in varying intensity. The peak positions of one set are close to those of the parent molecule. A similar pattern has been observed in the ^{13}C and ^{125}Te NMR spectra; *i.e.*, whereas one signal was observed in the ^{125}Te NMR spectra in $CDCl_3$, three to four signals were observed in DMSO-d_6. The occurrence of three to four signals may presumably be due to the transformation of the parent compound to other structural forms in DMSO-d_6. These forms are in equilibrium with each other, and the equilibria are attained fairly rapidly. The strongly coordinating DMSO-d_6 displaces weak intramolecularly coordinating N from the coordination sphere of Te. A similar observation has been reported by Minkin *et al.*[9f] and Lobana *et al.*[20] To eliminate the possibility of fluxional behavior, a variable-temperature NMR study was undertaken and no significant changes in the peak pattern were observed with the variation in temperature. Also, no significant changes were found in a variable-time ^{1}H NMR study. This is probably due to the fast rate of transformation of **12** to other forms.

The IR and NMR (^{1}H, ^{13}C, ^{125}Te) spectra of **13** showed some interesting features. The solid-state IR spectral measurements (KBr) showed a very sharp absorption at 3415 cm^{-1} for the O−H group, with a significant shift toward lower wavenumber than that of normal “free” hydroxyl absorption (3600 cm^{-1}). The ^{1}H NMR of **13** in $CDCl_3$ showed the expected peak pattern with a sharp doublet of doublets for the O−H proton at ∼3 ppm. Although hydrogen-bonded hydroxyl bands are almost invariably quoted as being broader, the observation of a sharp signal in this case is presumably due to a heavily buttressed hydroxyl group.[21] Such interactions are characterized by the increased probability of observation of the hydroxyl proton multiplicity.[22] Assignments of the coupling constants ($J_{\mathrm{HO-CH}}$ = 4.5 Hz, $J_{\mathrm{HO-C-CH}}$ = 0.6 Hz) were unambiguously made by selective ^{1}H spin decoupling experiments. It is worth noting that ^{1}H NMR also showed the presence of cocrystallized CH_3CN at δ 2 ppm, which was further confirmed by X-ray studies (*vide infra*).

To further establish the nature of hydrogen bonding in $CDCl_3$, titration with the aggressive hydrogen bond acceptor solvent DMSO was undertaken. Incremental addition of 5 μL of DMSO-d_6 to a $CDCl_3$ solution of **13** resulted in significant deshielding of the hydroxyl signal with concomitant simplification of the C*H*−OH signal. Accordingly, rupture of the hydrogen bond is evident on hydrogen bonding of the hydroxyl group with DMSO. The resultant relief of the hydroxyl group from its fixed position affects the observed coupling pattern. In contrast, 4-fold dilution of the $CDCl_3$ solution of **13** did not simplify the coupling patterns of C*H*−OH. Very poor solubility of **13** in $CHCl_3$ (∼1% on saturation) and CCl_4 coupled with the coordination of DMSO to tellurium in DMSO solution prevented us from extensive dilution studies by IR and multinuclear NMR spectroscopy. In order to establish the nature of hydrogen bonding in the solid state, single-crystal X-ray crystallographic studies have been carried out.

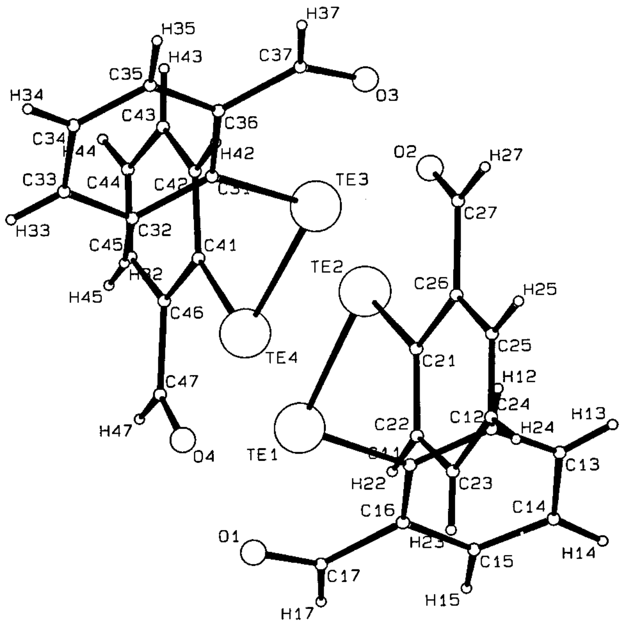

Figure 2. Molecular structure of bis(*o*-formylphenyl) ditelluride (**7**).

Optical purity of the chiral compounds was determined by recording ^{1}H NMR spectra in the presence of various mole ratios of the chiral shift reagent, and it was estimated to be 85−90%. Since the Schiff base preparation was carried out using optically pure amines and the chiral centers are expected to be unaffected by Schiff base formation, all the chiral Schiff bases are expected to be optically pure. This is further confirmed by the single-crystal diffraction studies of **13a**,**b** which were optically pure, as shown by the refined value of the Flack parameters, which were 0.00 within experimental error and thus showed the presence of only one optical isomer. However, the observation of both enantiomers in solution might be due to some racemization taking place due to the presence of traces of acid in $CDCl_3$ or due to some other impurity in the chiral shift reagent.

Crystal and Molecular Structure of 7. A PLUTO[23] view of **7** is shown in Figure 2, and the bond lengths and bond angles are given in Table 2. The asymmetric unit consists of the two crystallographically independent molecules A and B. The unit cell contains eight molecules. The Te(1)−Te(2) distances (2.714(1) Å) in molecule A and Te(3)−Te(4) (2.711(1) Å) in molecule B are slightly less than the sum of the Pauling single-bond covalent radii (2.74 Å)[24] but are comparable to values reported for the crystal structures of a number of analogous compounds ranging between 2.697 and 2.718

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Table 2. Bond Lengths (A) and Angles (deg) for 7 with Esd's in Parentheses

Te(1)−C(11)	2.145(8)	C(22)−C(23)	1.37(2)
Te(1)−Te(2)	2.7143(10)	C(23)−C(24)	1.39(2)
Te(2)−C(21)	2.117(10)	C(24)−C(25)	1.33(2)
Te(3)−C(31)	2.088(10)	C(25)−C(26)	1.36(2)
Te(3)−Te(4)	2.7108(11)	C(26)−C(27)	1.50(2)
Te(4)−C(41)	2.148(10)	C(31)−C(32)	1.402(13)
O(1)−C(17)	1.232(13)	C(31)−C(36)	1.40(2)
O(2)−C(27)	1.09(2)	C(32)−C(33)	1.42(2)
O(3)−C(37)	1.203(11)	C(33)−C(34)	1.38(2)
O(4)−C(47)	1.22(2)	C(34)−C(35)	1.35(2)
C(11)−C(16)	1.325(13)	C(35)−C(36)	1.39(2)
C(11)−C(12)	1.394(13)	C(36)−C(37)	1.46(2)
C(12)−C(13)	1.36(2)	C(41)−C(42)	1.36(2)
C(13)−C(14)	1.40(2)	C(41)−C(46)	1.408(14)
C(14)−C(15)	1.36(2)	C(42)−C(43)	1.33(2)
C(15)−C(16)	1.384(14)	C(43)−C(44)	1.39(2)
C(16)−C(17)	1.456(14)	C(44)−C(45)	1.37(2)
C(21)−C(22)	1.39(2)	C(45)−C(46)	1.35(2)
C(21)−C(26)	1.46(2)	C(46)−C(47)	1.50(2)

C(11)−Te(1)−Te(2)	100.6(3)	O(2)−C(27)−C(26)	126.3(12)
C(21)−Te(2)−Te(1)	100.1(4)	C(32)−C(31)−C(36)	116.0(9)
C(31)−Te(3)−Te(4)	99.9(2)	C(32)−C(31)−Te(3)	123.3(7)
C(41)−Te(4)−Te(3)	97.5(3)	C(36)−C(31)−Te(3)	120.7(7)
C(16)−C(11)−C(12)	118.6(9)	C(31)−C(32)−C(33)	119.8(10)
C(16)−C(11)−Te(1)	121.5(7)	C(34)−C(33)−C(32)	121.7(11)
C(12)−C(11)−Te(1)	119.8(8)	C(35)−C(34)−C(33)	119.1(11)
C(13)−C(12)−C(11)	119.2(12)	C(34)−C(35)−C(36)	120.2(10)
C(12)−C(13)−C(14)	121.6(12)	C(35)−C(36)−C(31)	123.2(10)
C(15)−C(14)−C(13)	117.4(11)	C(35)−C(36)−C(37)	116.2(11)
C(14)−C(15)−C(16)	119.6(11)	C(31)−C(36)−C(37)	120.6(9)
C(11)−C(16)−C(15)	122.9(9)	O(3)−C(37)−C(36)	125.0(11)
C(11)−C(16)−C(17)	123.3(9)	C(42)−C(41)−C(46)	118.4(10)
C(15)−C(16)−C(17)	113.8(9)	C(42)−C(41)−Te(4)	124.2(9)
O(1)−C(17)−C(16)	123.5(10)	C(46)−C(41)−Te(4)	117.2(8)
C(22)−C(21)−C(26)	118.8(10)	C(43)−C(42)−C(41)	122.0(11)
C(22)−C(21)−Te(2)	124.1(9)	C(42)−C(43)−C(44)	119.5(12)
C(26)−C(21)−Te(2)	122.1(13)	C(45)−C(44)−C(43)	120.1(11)
C(22)−C(23)−C(24)	118(2)	C(44)−C(45)−C(46)	119.9(12)
C(25)−C(24)−C(23)	121.2(13)	C(45)−C(46)−C(41)	120.1(11)
C(24)−C(25)−C(26)	124(2)	C(45)−C(46)−C(47)	116.6(12)
C(25)−C(26)−C(21)	115.9(14)	C(41)−C(46)−C(47)	123.2(11)
C(25)−C(26)−C(27)	125.6(14)	O(4)−C(47)−C(46)	121.8(11)
C(21)−C(26)−C(27)	118.5(10)		

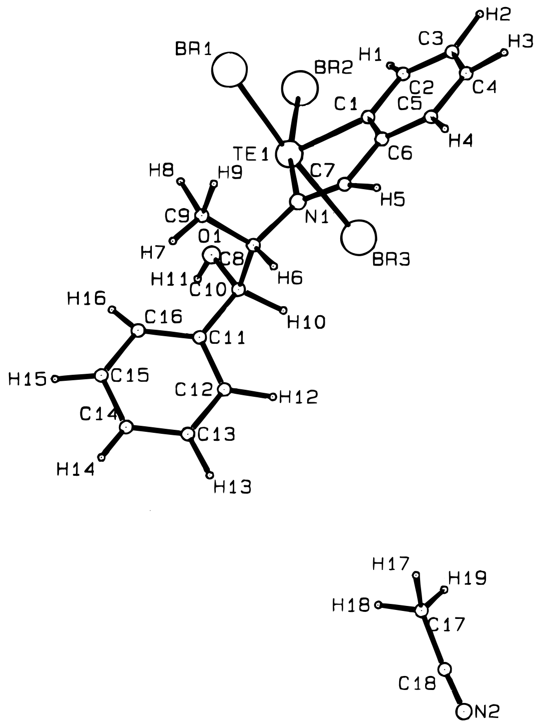

Figure 3. Molecular structure of [*o*-((((1*S*,2*R*)-2-hydroxy-2-phenyl-1-methylethyl)amino)methinyl)phenyl]tellurium(IV) tribromide (**13a**).

Å.[25−27] The Te(1)···O(1) (2.81(1) Å) and Te(2)···O(2) (2.70(1) Å) distances in molecule A and Te(3)···O(3) (2.78(1) Å) and Te(4)···O(4) (2.73(1) Å) in molecule B are much longer than the sum of the covalent radii (2.03 Å).[24] However, these are much less than the sum of the van der Waals radii (3.60 Å),[28] thus indicating a strong intramolecular interaction. Comparable Te···O(carbonyl) contacts have been reported in bis[2-(ethylcarboxy)benzenetellurenyl]selenide (2.658 Å).[29] Owing to this interaction, the geometry around tellurium may be considered as T-shaped. The distances C(11)−Te(1) (2.145(8) Å), C(21)−Te(2) (2.12(1) Å), C(31)−Te(3) (2.09(1) Å), and C(41)−Te(4) (2.15(1) Å) are in good agreement with the sum of the Pauling's single bond covalent radii of Te (1.37 Å)[24] and sp^2-hybridized carbon (0.74 Å) and with the values reported for the crystal structures of analogous compounds.[9c] The C(11)−Te(1)−Te(2)−C(21) and C(31)−Te(3)−Te(4)−C(41) torsion angles in the two moieties of the asymmetric unit are −89.7(5) and 91.5(5)°, respectively; these are marginally different and suggest a cisoid and transoid conformation, respectively. The pairs of torsion angles involving the −CHO group *viz*. C(21)−C(26)−C(27)−O(2) (1.7(5)°) and C(41)−C(46)−C(47)−O(4) (3.3(5)°), are significantly different in the two molecules A and B respectively while in the other pair, *viz*. C(11)−C(16)−C(17)−O(1) (2.6(5)°) and C(31)−C(36)−C(37)−O(3) (2.4(5)°), they are quite similar. The intermolecular distances between the tellurium atoms of the two molecules A and B in the asymmetric unit, *i.e.* Te(1)···Te(4), Te(2)···Te(3), and Te(1)···Te(3), are 4.167, 3.935, and 4.220 Å, respectively. These distances are close to the van der Waals distance of 4.12[28] or 4.40 Å[24] and thus suggest a normal interaction.

Crystal and Molecular Structures of 13a,b. The molecular structure of **13a** with atom numbering is shown in Figure 3. Table 3 contains the selected bond lengths and bond angles. The coordination around tellurium can be considered as essentially distorted pseudooctahedral with a lone pair of electrons occupying the fourth equatorial site: Br(1) and Br(3) lie 2.673(3) and 2.666(3) Å on either side of the Te(1), N(1), C(l), Br(2) plane. The distortion of the coordination geometry from ideal octahedral angles (90 and 180°), particularly N(1)−Te(1)−Br(2) (168.4(7)°), can be explained in terms of the lone pair of electrons occupying an equatorial position between N(1) and Br(2). The small value of the angle N(1)−Te(1)−C(1) (76.9(7)°) is due to the constraint of the five-membered chelate ring (N(1), Te(1), C(1), C(6), C(7)). The sum of the endocyclic torsion angles of the chelated ring is close to zero (0.1°) and suggests a planar conformation. The axial atoms are displaced from the lone-pair electrons, reducing the Br(3)−Te(1)−Br(1) angle to 173.34(4)° from the ideal angle of 180°. These values are analogous to those found in the crystal structure of [2-(2-pyridyl)phenyl]-

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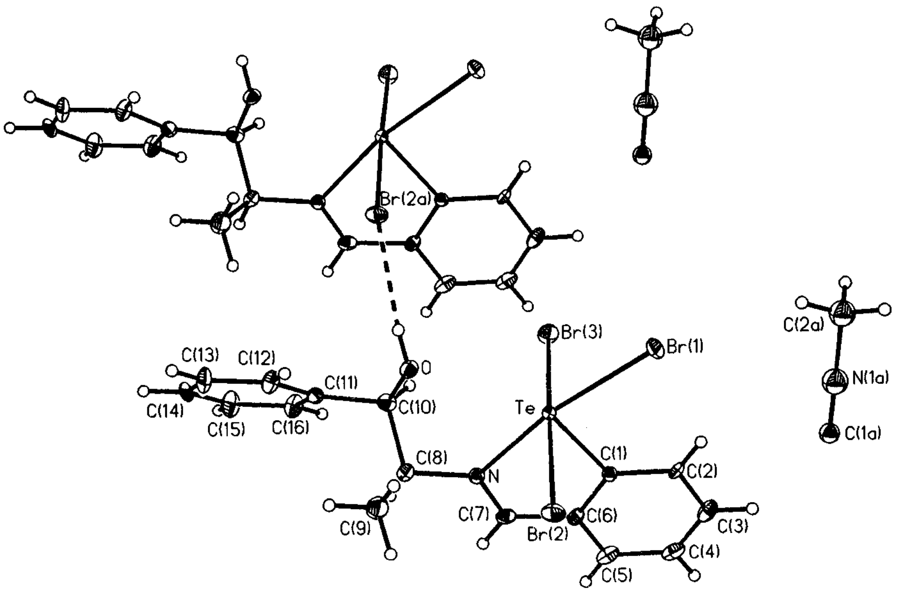

Figure 4. Molecular structure of [*o*-((((1*S*,2*R*)-2-hydroxy-2-phenyl-1-methylethyl)amino)methinyl)phenyl]tellurium(IV) tribromide (**13b**).

Table 3. Bond Lengths (Å) and Bond Angles (deg) for 13a with Esd's in Parentheses

Te(1)–Br(1)	2.671(3)	Te(1)–Br(2)	2.679(3)
Te(1)–Br(3)	2.666(3)	Te(1)–C(1)	2.10(1)
Te(1)–N(1)	2.28(2)	C(1)–C(2)	1.40(2)
C(2)–C(3)	1.40(2)	C(3)–C(4)	1.40(2)
C(4)–C(5)	1.40(2)	C(5)–C(6)	1.40(2)
C(1)–C(6)	1.40(2)	C(6)–C(7)	1.45(2)
C(7)–N(1)	1.29(3)	N(1)–C(8)	1.49(3)
C(8)–C(9)	1.50(3)	C(8)–C(10)	1.50(3)
C(10)–O(1)	1.42(3)	C(10)–C(11)	1.48(3)
C(11)–C(12)	1.40(2)	C(12)–C(13)	1.40(2)
C(13)–C(14)	1.40(2)	C(14)–C(15)	1.40(2)
C(15)–C(16)	1.40(2)	C(11)–C(16)	1.40(2)
Br(1)–Te(1)–Br(2)	91.7(1)	Br(1)–Te(1)–Br(3)	173.3(1)
Br(2)–Te(1)–Br(3)	91.4(1)	Br(1)–Te(1)–C(1)	87.2(3)
Br(2)–Te(1)–C(1)	91.6(4)	Br(3)–Te(1)–C(1)	86.8(3)
C(1)–Te(1)–N(1)	76.9(5)	N(1)–Te(1)–Br(3)	87.7(4)
N(1)–Te(1)–Br(1)	88.1(4)	N(1)–Te(1)–Br(2)	168.5(4)
Te(1)–C(1)–C(2)	126.4(9)	C(1)–C(2)–C(3)	120(1)
Te(1)–C(1)–C(6)	113.5(9)	C(1)–C(6)–C(5)	120(1)
Te(1)–N(1)–C(8)	125(1)	C(2)–C(3)–C(4)	120(1)
C(3)–C(4)–C(5)	120(1)	C(4)–C(5)–C(6)	120(1)
C(5)–C(6)–C(7)	120(1)	C(1)–C(6)–C(7)	120(1)
C(6)–C(7)–N(1)	117(2)	C(2)–C(1)–C(6)	120(1)
C(7)–N(1)–C(8)	122(2)	C(7)–N(1)–Te(1)	113(1)
N(1)–C(8)–C(9)	112(2)	N(1)–C(8)–C(10)	109(2)
C(8)–C(10)–C(11)	113(2)	O(1)–C(10)–C(8)	103(2)
C(9)–C(8)–C(10)	116(2)	O(1)–C(10)–C(11)	112(2)
C(10)–C(11)–C(12)	120(1)	C(10)–C(11)–C(16)	121(1)
C(11)–C(12)–C(13)	120(1)	C(12)–C(13)–C(14)	120(1)
C(13)–C(14)–C(15)	120(1)	C(14)–C(15)–C(16)	120(1)
C(15)–C(16)–C(11)	120(1)		

Table 4. Intra- and Intermolecular Interactions in 13a

bond	distance	symmetry code
Br(1)···H(8)	3.0(1)	*x*, *y*, *z*
Br(2)···H(1)	2.6(1)	*x*, *y*, *z*
N(1)···H(6)	2.1(1)	*x*, *y*, *z*
Br(1)···H(3)	2.9(1)	$1 - x, y - 0.5, 1.5 - z$
Br(2)···H(2)	2.8(1)	$-x, y - 0.5, 1.5 - z$
N(2)···H(11)	2.0(1)	$-x, 0.5 + y, 0.5 - z$

Table 5. Bond Lengths (Å) and Bond Angles (deg) for 13b with Esd's in Parentheses

Te–C(1)	2.116(7)	Te–N	2.289(6)
Te–Br(3)	2.5905(9)	Te–Br(1)	2.6387(9)
Te–Br(2)	2.7364(9)	O–C(10)	1.408(9)
N–C(7)	1.272(10)	N–C(8)	1.468(9)
C(1)–C(6)	1.372(10)	C(1)–C(2)	1.373(9)
C(2)–C(3)	1.390(10)	C(3)–C(4)	1.372(12)
C(4)–C(5)	1.390(12)	C(5)–C(6)	1.394(10)
C(6)–C(7)	1.461(10)	C(8)–C(10)	1.509(11)
C(8)–C(9)	1.519(11)	C(10)–C(11)	1.515(10)
C(11)–C(12)	1.377(10)	C(11)–C(16)	1.389(10)
C(12)–C(13)	1.381(11)	C(13)–C(14)	1.376(12)
C(14)–C(15)	1.366(12)	C(15)–C(16)	1.386(11)
N(1A)–C(1A)	1.13(2)	N(1A)–C(2A)	1.44(2)
C(1)–Te–N	76.3(2)	C(1)–Te–Br(3)	88.3(2)
N–Te–Br(3)	88.36(14)	C(1)–Te–Br(1)	92.7(2)
N–Te–Br(1)	169.0(2)	Br(3)–Te–Br(1)	90.85(3)
C(1)–Te–Br(2)	87.9(2)	N–Te–Br(2)	89.52(14)
Br(3)–Te–Br(2)	176.01(3)	Br(1)–Te–Br(2)	90.58(3)
C(7)–N–C(8)	121.4(6)	C(7)–N–Te	112.3(5)
C(8)–N–Te	126.3(5)	C(6)–C(1)–C(2)	121.2(6)
C(6)–C(1)–Te	114.4(5)	C(2)–C(1)–Te	124.3(5)
C(1)–C(2)–C(3)	118.4(7)	C(4)–C(3)–C(2)	120.9(7)
C(3)–C(4)–C(5)	120.7(7)	C(4)–C(5)–C(6)	118.0(8)
C(1)–C(6)–C(5)	120.7(7)	C(1)–C(6)–C(7)	118.4(7)
C(5)–C(6)–C(7)	120.8(7)	N–C(7)–C(6)	118.6(7)
N–C(8)–C(10)	108.1(6)	N–C(8)–C(9)	109.3(6)
C(10)–C(8)–C(9)	113.9(7)	O–C(10)–C(8)	107.2(6)
O–C(10)–C(11)	113.0(6)	C(8)–C(10)–C(11)	111.3(6)
C(12)–C(11)–C(16)	119.1(7)	C(12)–C(11)–C(10)	121.8(7)
C(16)–C(11)–C(10)	119.0(7)	C(11)–C(12)–C(13)	120.3(7)
C(14)–C(13)–C(12)	120.0(8)	C(15)–C(14)–C(13)	120.6(7)
C(14)–C(15)–C(16)	119.4(7)	C(15)–C(16)–C(11)	120.5(7)
C(1A)–N(1A)–C(2A)	180.0		

tellurium tribromide[30] (172.4(1)°) and [2-((*S*)-1-(dimethylamino)ethyl)phenyl]tellurium trichloride (175.4(1)°).[4]

The C(1)–Te(1) (2.1(1) Å) bond distance is in good agreement with the sum of the Pauling[24] single-bond covalent radii of Te–C(sp^2) of 2.11 Å and with the reported values.[9c] The Te(1)–N(1) distance of 2.29(2) Å is longer than the sum of the covalent radii (2.07 Å) but shorter than that previously reported for [2-(phenylazo)phenyl-C,N′]tellurium trichloride (2.414 Å)[31] and similar to that for [2-(2-pyridyl)phenyl]tellurium tribromide (2.244(14) Å),[30] thus indicating a much stronger interaction in this case. The Te(1)–Br(2) equatorial distance (2.679(3) Å) slightly deviates from the sum of

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[30] Al-Salim, N.; West, A. A.; McWhinnie, W. R.; Hamor, T. A. *J. Chem. Soc., Dalton Trans.* **1988**, 2363.

the covalent radii (equatorial Te−Br 2.51 Å). However, the Te(1)−Br axial distances (2.673(3), 2.666(3) Å) are in good agreement with those commonly found in Te−Br covalent compounds (2.67 Å).

An interesting feature of the molecular structure is the short Te(1)···O(1) distance of 2.90(2) Å in addition to the intramolecular Te···N interaction. This distance is less than the sum of the van der Waals distances (3.6 Å)[28] and indicates a weak Te···O interaction. Another interesting structural factor is that the Br(2) atom is intramolecularly hydrogen bonded to the hydrogen (H(1)) of the phenyl carbon C(2) (H(1)···Br(2) = 2.6(1) Å). A three-dimensional network of hydrogen bonds involving the bromines and the hydrogen atoms of the neighboring molecules, as detailed in Table 4, stabilizes the crystal packing. The hydrogen atom of the hydroxyl group, H(11), is intermolecularly linked to the nitrogen of the acetonitrile solvent (H(11)···N(2) = 2.04(1) Å).

An ORTEP[32] view of **13b** with atom numbering is shown in Figure 4, and the bond lengths and bond angles are given in Table 5. This compound crystallizes in a monoclinic space group, in contrast to the orthorhombic space group of **13a**. Compound **13b** contains half a molecule of acetonitrile as the solvent of crystallization lying along the 2-fold axis, whereas **13a** contains one molecule of acetonitrile. The coordination environment around tellurium can be considered as essentially distorted pseudooctahedral and is quite similar to **13a**. The angles N(1)−Te(1)−Br(1) and N(1)−Te(1)−C(1) are comparable to the corresponding angles in **13a**. The distances C(1)−Te(1) and Te(1)···N(1) are also comparable. The unique feature of the molecular structure is the short interatomic distance between hydroxyl hydrogen and bromine of the next molecule (OH···Br(2) = 2.453 Å). The O···Br(2) distance is 3.268 Å ($^1/_2 + x$, $y - {}^1/_2$, z), and the O−H···Br(2) angle is 172.4°.

Conclusions

A series of potential multidentate tellurium-containing chiral Schiff base ligands has been synthesized. Interesting side products, *viz*. bis(*o*-formylphenyl) tritelluride and bis(*o*-formylphenyl) ditelluride, have been isolated during the course of starting material preparation. Pseudopolymorphism exhibited by the tribromide derivative of one of the Schiff bases has been investigated by single-crystal X-ray diffraction studies.

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Supporting Information Available: Tables of atomic coordinates and anisotropic thermal parameters for **7** and **13a**,**b**, a table of torsion angles for **13a**, and two figures giving reaction schemes (12 pages). Ordering information is given on any current masthead page.

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