Synthesis and characterization of chiral (-)-menthyltin(IV) compounds containing potentially C,N-chelating ligands. X-ray structure of (RSn)-[8-(dimethylamino)naphthyl]-(-)-menthylmethyltin bromide

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Synthesis and Characterization of Chiral (–)-Menthyltin(IV) Compounds Containing Potentially C,N-Chelating Ligands. X-ray Structure of (R_{Sn})-[8-(Dimethylamino)naphthyl]-(–)-menthylmethyltin Bromide

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Starting from (–)-menthyltrimethyltin, Sn–chiral (–)-menthyltin(IV) derivatives bearing potentially bidentate (dimethylamino)organo ligands of different flexibility have been synthesized and characterized. (–)-Menthylmethyltin dibromide (1), obtained by dihalogenation, is monoalkylated by the respective lithium reagent to give [3-(dimethylamino)propyl]-, [2-[(dimethylamino)methyl]phenyl]-, and [8-(dimethylamino)naphthyl]-(–)-menthylmethyltin bromide (2–4). Reduction yields the corresponding tin hydrides (5–7). For comparison, the nondonor-atom substituted (–)-menthylmethylnaphthyltin bromide (8) and hydride (9) have been prepared accordingly. Polarimetric and multinuclear NMR investigations show the structure and configurational stability of 2–7 in solution reflecting the increasing rigidity of their potentially C,N-chelating ligands: The tin center in 2–4 is rendered pentacoordinate as a result of intramolecular Sn–N coordination. The stability of the five-membered chelate ring with regard to a Sn–N dissociation/association process taking place and the configurational stability of the tin center increase likewise. While an epimerization process of 2 occurs fast on the NMR time scale, slow inversion of the configuration at the tin atom can be observed on a freshly prepared solution of crystalline, diastereomerically pure 3 or 4. The Lewis acidity of the tin center in 5–7 is too low for effecting Sn–N coordination. The geometric constraint of the aminoorgano ligand in 6 and 7, however, causes a distortion of the tetrahedral structure into a beginning trigonal bipyramidal structure. The epimer ratios of the "doubly chiral" organotin compounds in solution are found to differ from 1. The X-ray structural investigation of 4 reveals an absolute configuration of R_{Sn} for both molecules in the asymmetric unit: 4 crystallizes monoclinically, space group $P2_1$, with a = 9.259(5) Å, b = 20.615(9) Å, c = 12.964(7) Å, β = 105.40(5)°, and Z = 4. The structure was solved from 3498 reflections with $I > 2\sigma(I)$ and refined to a final R factor of 0.044, showing a distorted trigonal bipyramidal coordination geometry at the tin center.

Introduction

In organotin chemistry, the concept of hypervalency caused by intramolecular Sn–N coordination has created a series of five- and six-coordinate organotin(IV) halides[1-23] as well as some five- or six-coordinate tetraorganotin[9,24-27] and hexaorganoditin[28] compounds. Recently, we extended this concept to triorganotin hydrides. In connection with

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our investigations on chiral (−)-menthyltin(IV) compounds,[29,30] we synthesized *tert*-butyl[8-(dimethylamino)-naphthyl]-(−)-menthyltin hydride, an X-ray structural characterization of which revealed a weak Sn–N interaction.[31]

With the optically pure ligand bound to an asymmetric tin atom, these (−)-menthyltin derivatives feature a chiral label[4–6,8] for monitoring a configurational instability of the tin center. In this paper, we describe our studies on the influence of C,N-chelating ligands of different flexibility on the structure and configurational stability of the corresponding asymmetric (−)-menthyltin compounds. The potentially bidentate ligands 3-(dimethylamino)-propyl, 2-[(dimethylamino)methyl]phenyl, and 8-(dimethylamino)naphthyl have been used for the syntheses of the respective [(dimethylamino)organo]-(−)-menthylmethyltin bromides and hydrides. A description of the preparation of these new, fully characterized compounds will be given; the results of polarimetric and multinuclear NMR investigations will be discussed, and the X-ray crystal structure determination of the diastereomerically pure [8-(dimethylamino)naphthyl]-(−)-menthylmethyltin bromide (4) will be presented.

Experimental Section

All reactions were carried out in an atmosphere of dry, oxygen-free argon. CHN analyses were performed on a Perkin-Elmer 240 C elemental analyzer; Sn contents were determined using a Perkin-Elmer 2380 atomic absorption spectrophotometer. Optical rotations were measured on a Schmidt + Haensch Polartronic-D polarimeter (200-mm cell). IR spectra were recorded on a Perkin-Elmer 457 grating infrared spectrophotometer. Mass spectra (electron impact ionization) were obtained on the instruments Varian MAT 311 A (70 eV) and Hewlett Packard 5985 (70 or 12 eV). NMR spectra were recorded on the spectrometers Bruker WH 270 (^{1}H NMR at 270 MHz and ^{13}C{^{1}H} NMR at 67.93 MHz, 5-mm tubes) or Bruker WP 80 SY (^{117}Sn{^{1}H inverse gated} NMR at 28.552 MHz, 10 mm-tubes); chemical shifts are referenced to $(CH_3)_4Si$ (^{1}H, ^{13}C NMR) or $(CH_3)_4Sn$ (^{117}Sn NMR), with positive shifts referring to lower field.

(−)-Menthyltrimethyltin was prepared according to the procedure reported earlier.[31]

(−)-Menthylmethyltin Dibromide (1). A vigorously stirred emulsion of 100 g (330 mmol) of (−)-menthyltrimethyltin in 1200 mL of methanol was slowly treated with 116 g (726 mmol) of bromine at 0 °C under exclusion of light. After the dark orange reaction mixture was stirred for 50 h, the solvent was removed in vacuo to leave a reddish brown residue. The crude product, an orange liquid, was distilled off. Fractionated redistillation yielded 103 g (72%) of **1** as a colorless liquid, which crystallized upon cooling; bp 99 °C/0.04 mbar, mp 35 °C. $[\alpha]^{20}_D$ −35.7° (c 1.78, benzene). MS (70 eV, 30 °C): *m/z* (%) 295 (4) $[M - C_{10}H_{19}]^+$, 199 (4) $[SnBr]^+$, 139 (100) $[C_{10}H_{19}]^+$, 97 (33) $[C_7H_{13}]^+$, 95 (18) $[C_7H_{11}]^+$, 83 (93) $[C_6H_{11}]^+$, 81 (35) $[C_6H_9]^+$, 69 (63) $[C_5H_9]^+$, 67 (9) $[C_5H_7]^+$, 57 (54) $[C_4H_9]^+$, 55 (44) $[C_4H_7]^+$, 43 (22) $[C_3H_7]^+$, 41 (36) $[C_3H_5]^+$. Anal. Calcd for $C_{11}H_{22}Br_2Sn$: C, 30.53; H, 5.12; Sn, 27.43. Found: C, 30.75; H, 5.08; Sn, 26.97.

[3-(Dimethylamino)propyl]-(−)-menthylmethyltin Bromide (2). A solution of 6.02 g (64.7 mmol) of [3-(dimethylamino)-propyl]lithium[32] in 450 mL of diethyl ether was added dropwise over a period of 4 h to a stirred solution of 28.0 g (64.7 mmol) of **1** in 150 mL of diethyl ether at 5 °C. After the reaction mixture was stirred for 24 h at room temperature, the solvent was removed in vacuo, and the white, oily residue was extracted with boiling pentane. The resulting solution was concentrated and cooled to 5 °C. A total of 15.1 g (53%) of **2** formed as colorless crystals; mp 97 °C. $[\alpha]^{20}_D$ −37.7° (c 1.00, benzene). MS (12 eV, 30 °C): *m/z* (%) 424 (3) $[M - CH_3]^+$, 360 (10) $[M - Br]^+$, 300 (76) $[M - C_{10}H_{19}]^+$, 139 (1) $[C_{10}H_{19}]^+$, 86 (2) $[C_5H_{12}N]^+$, 83 (2) $[C_6H_{11}]^+$, 58 (100) $[C_3H_8N]^+$. MS (70 eV, 106 °C): *m/z* (%) 424 (11) $[M - CH_3]^+$, 360 (1) $[M - Br]^+$, 300 (6) $[M - C_{10}H_{19}]^+$, 286 (7) $[MH - CH_3 - C_{10}H_{19}]^+$, 206 (10) $[SnC_5H_{12}N]^+$, 199 (3) $[SnBr]^+$, 139 (4) $[C_{10}H_{19}]^+$, 135 (1) $[SnCH_3]^+$, 97 (4) $[C_7H_{13}]^+$, 95 (2) $[C_7H_{11}]^+$, 86 (24) $[C_5H_{12}N]^+$, 84 (17) $[C_5H_{10}N]^+$, 83 (17) $[C_6H_{11}]^+$, 81 (4) $[C_6H_9]^+$, 69 (8) $[C_5H_9]^+$, 67 (2) $[C_5H_7]^+$, 58 (100) $[C_3H_8N]^+$, 57 (10) $[C_4H_9]^+$, 56 (2) $[C_3H_6N]^+$, 55 (12) $[C_4H_7]^+$. Anal. Calcd for $C_{16}H_{34}BrNSn$: C, 43.77; H, 7.81; N, 3.19; Sn, 27.04. Found: C, 43.55; H, 7.96; N, 3.25; Sn, 26.94.

[2-[(Dimethylamino)methyl]phenyl]-(−)-menthylmethyltin Bromide (3). [2-[(Dimethylamino)methyl]phenyl]lithium[33,34] (7.34 g, 52.0 mmol), suspended in 350 mL of diethyl ether, and 22.5 g (52.0 mmol) of **1**, dissolved in 125 mL of diethyl ether, were reacted as described for the preparation of **2**. After removal of the solvent, extraction of the beige, oily residue with boiling pentane, and concentration of the resulting solution, a precipitate formed. Recrystallization from a toluene/pentane mixture yielded 18.5 g (73%) of **3** as a white, crystalline solid; mp 90 °C. $[\alpha]^{20}_D$ −14.8° to −41.5° (over 2.5 days) (c 1.15, benzene). MS (70 eV, 105 °C): *m/z* (%) 408 (25) $[M - Br]^+$, 348 (75) $[M - C_{10}H_{19}]^+$, 254 (33) $[SnC_6H_4CH_2NMe_2]^+$, 199 (10) $[SnBr]^+$, 134 (75) $[C_6H_4CH_2NMe_2]^+$, 91 (100) $[C_7H_7]^+$, 86 (10) $[C_5H_{12}N]^+$, 83 (28) $[C_6H_{11}]^+$, 81 (12) $[C_6H_9]^+$, 76 (21) $[C_6H_4]^+$, 69 (14) $[C_5H_9]^+$, 67 (10) $[C_5H_7]^+$, 58 (42) $[C_3H_8N]^+$, 57 (49) $[C_4H_9]^+$, 56 (16) $[C_3H_6N]^+$, 55 (34) $[C_4H_7]^+$. Anal. Calcd for $C_{20}H_{34}BrNSn$: C, 49.32; H, 7.04; N, 2.88; Sn, 24.37. Found: C, 49.23; H, 7.23; N, 3.14; Sn, 24.42.

[8-(Dimethylamino)naphthyl]-(−)-menthylmethyltin Bromide (4). [8-(Dimethylamino)naphthyl]lithium etherate[35] (15.4 g, 61.2 mmol), suspended in 330 mL of diethyl ether, and 26.5 g (61.2 mmol) of **1**, dissolved in 150 mL of diethyl ether, were reacted as described for the preparation of **2**. Afterward, the solvent was removed and the residue extracted with hot benzene. Removal of the solvent from the benzene filtrate afforded a yellowish oil, which was crystallized from a toluene/pentane mixture. Recrystallization from pentane yielded 20.8 g (65%) of **4** as colorless crystals; mp 127 °C. $[\alpha]^{20}_D$ +2.9° to −37.9° (over 5 days) (c 1.24, benzene). MS (12 eV, 30 °C): *m/z* (%) 508 (4) $[M - CH_3]^+$, 444 (8) $[M - Br]^+$, 384 (100) $[M - C_{10}H_{19}]^+$, 290 (2) $[SnC_{10}H_6NMe_2]^+$, 170 (3) $[C_{10}H_6NMe_2]^+$. MS (70 eV, 132 ° C): *m/z* (%) 508 (2) $[M - CH_3]^+$, 444 (7) $[M - Br]^+$, 384 (100) $[M - C_{10}H_{19}]^+$, 369 (32) $[M - C_{10}H_{19} - CH_3]^+$, 354 (2) $[M - C_{10}H_{19} - 2\,CH_3]^+$, 290 (17) $[SnC_{10}H_6NMe_2]^+$, 275 (25) $[SnC_{10}H_6NMe]^+$, 274 (24) $[M - C_{10}H_6NMe_2 - Br]^+$, 199 (8) $[SnBr]^+$, 170 (36) $[C_{10}H_6NMe_2]^+$, 154 (40) $[C_{11}H_8N]^+$, 139 (3) $[C_{10}H_{19}]^+$, 135 (2) $[SnCH_3]^+$, 127 (31) $[C_{10}H_7]^+$, 120 (6) $[Sn]^+$, 97 (5) $[C_7H_{13}]^+$, 95 (5) $[C_7H_{11}]^+$, 91 (2) $[C_7H_7]^+$, 84 (2) $[C_5H_{10}N]^+$, 83 (26) $[C_6H_{11}]^+$, 81 (9) $[C_6H_9]^+$, 77 (6) $[C_6H_5]^+$, 69 (13) $[C_5H_9]^+$, 67 (9) $[C_5H_7]^+$, 57 (5) $[C_4H_9]^+$, 56 (2) $[C_3H_6N]^+$, 55 (34) $[C_4H_7]^+$. Anal. Calcd for $C_{23}H_{34}BrNSn$: C, 52.81; H, 6.55; N, 2.68; Sn, 22.69. Found: C, 53.22; H, 6.50; N, 3.14; Sn, 23.10.

[3-(Dimethylamino)propyl]-(-)-menthylmethyltin Hydride (5). A solution of 8.55 g (19.5 mmol) of **2** in 100 mL of diethyl ether and 15 mL of benzene was slowly added to a stirred suspension of 0.74 g (19.5 mmol) of lithium aluminum hydride in 30 mL of diethyl ether at 0 °C. After the reaction mixture was

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stirred for 6 h at room temperature, 1.4 mL (78.0 mmol) of water in 5.0 mL of dioxane was added dropwise at 0 °C, and the mixture was stirred for another 15 min at room temperature. Subsequently, the solution was filtered off and the residue washed with diethyl ether. The combined filtrate was dried over anhydrous sodium sulfate, and the solvents were removed in vacuo. Extraction of the residue with pentane at −30 °C and renewed removal of the solvent in vacuo gave 5.4 g (77 %) of **5** as a colorless, viscous liquid. $[\alpha]^{20}{}_{D}$ −36.2° (c 0.67, benzene). IR: ν(Sn–H) 1793 (s) cm^{-1}. MS (70 eV, 25 °C): *m/z* (%) 360 (2) $[M - H]^+$, 346 (2) $[M - CH_3]^+$, 222 (15) $[M - C_{10}H_{19}]^+$, 206 (4) $[SnC_5H_{12}N]^+$, 139 (6) $[C_{10}H_{19}]^+$, 135 (12) $[SnCH_3]^+$, 120 (11) $[Sn]^+$, 97 (14) $[C_7H_{13}]^+$, 95 (16) $[C_7H_{11}]^+$, 91 (7) $[C_7H_7]^+$, 86 (74) $[C_5H_{12}N]^+$, 84 (21) $[C_5H_{10}N]^+$, 83 (24) $[C_6H_{11}]^+$, 81 (25) $[C_6H_9]^+$, 77 (6) $[C_6H_5]^+$, 69 (20) $[C_5H_9]^+$, 67 (13) $[C_5H_7]^+$, 58 (100) $[C_3H_8N]^+$, 57 (22) $[C_4H_9]^+$, 56 (6) $[C_3H_6N]^+$, 55 (48) $[C_4H_7]^+$. Anal. Calcd for $C_{16}H_{35}NSn$: C, 53.36; H, 9.79; N, 3.89; Sn, 32.96. Found: C, 52.96; H, 9.60; N, 4.17; Sn, 33.44.

[2-[(Dimethylamino)methyl]phenyl]-(−)-menthylmethyltin Hydride (6). **3** (12.2 g, 25.0 mmol) in 70 mL of diethyl ether was reacted with 0.95 g (25.0 mmol) of lithium aluminum hydride in 40 mL of diethyl ether as described for the preparation of **5**. The workup was done accordingly using 1.8 mL (100 mmol) of water in 6.4 mL of dioxane. Removal of the pentane from the extraction solution yielded 9.0 g (88%) of **6** as a colorless oil. $[\alpha]^{20}{}_{D}$ −52.1° (c 0.70, benzene). IR: ν(Sn–H) 1799 (s) cm^{-1}. MS (70 eV, 25 °C): *m/z* (%) 409 (1) $[M]^+$, 408 (3) $[M - H]^+$, 351 (24) $[M - C_3H_8N]^+$, 270 (15) $[M - C_{10}H_{19}]^+$, 254 (9) $[SnC_6H_4CH_2NMe_2]^+$, 197 (15) $[SnC_6H_5]^+$, 134 (100) $[C_6H_4CH_2NMe_2]^+$, 120 (20) $[Sn]^+$, 97 (13) $[C_7H_{13}]^+$, 95 (19) $[C_7H_{11}]^+$, 91 (53) $[C_7H_7]^+$, 84 (4) $[C_5H_{10}N]^+$, 83 (15) $[C_6H_{11}]^+$, 81 (24) $[C_6H_9]^+$, 77 (14) $[C_6H_5]^+$, 69 (31) $[C_5H_9]^+$, 67 (18) $[C_5H_7]^+$, 58 (37) $[C_3H_8N]^+$, 57 (28) $[C_4H_9]^+$, 56 (6) $[C_3H_6N]^+$, 55 (40) $[C_4H_7]^+$, 44 (22) $[C_2H_6N]^+$, 43 (44) $[C_3H_7]^+$, 42 (12) $[C_2H_4N]^+$, 41 (31) $[C_3H_5]^+$. Anal. Calcd for $C_{20}H_{35}NSn$: C, 58.85; H, 8.64; N, 3.43; Sn, 29.08. Found: C, 58.64; H, 8.42; N, 3.66; Sn, 28.68.

[8-(Dimethylamino)naphthyl]-(−)-menthylmethyltin Hydride (7). **4** (14.3 g, 27.3 mmol) in 100 mL of diethyl ether and 10 mL of benzene was reacted with 1.04 g (27.3 mmol) of lithium aluminum hydride in 50 mL of diethyl ether, and the reaction mixture was worked up using 2.0 mL (109 mmol) of water in 7.0 mL of dioxane as described for the preparation of **5**. After removal of the pentane from the extraction solution, 10.9 g (90 %) of **7** remained as a colorless oil. $[\alpha]^{20}{}_{D}$ −38.9° (c 0.60, benzene). IR: ν(Sn–H) 1801 (s) cm^{-1}. MS (70 eV, 80 °C): *m/z* (%) 445 (1) $[M]^+$, 444 (5) $[M - H]^+$, 430 (22) $[M - CH_3]^+$, 306 (93) $[M - C_{10}H_{19}]^+$, 290 (29) $[SnC_{10}H_6NMe_2]^+$, 275 (29) $[SnC_{10}H_6NMe]^+$, 259 (6) $[SnC_{10}H_{19}]^+$, 170 (100) $[C_{10}H_6NMe_2]^+$, 154 (27) $[C_{11}H_8N]^+$, 139 (3) $[C_{10}H_{19}]^+$, 135 (8) $[SnCH_3]^+$, 127 (17) $[C_{10}H_7]^+$, 120 (7) $[Sn]^+$, 97 (19) $[C_7H_{13}]^+$, 95 (6) $[C_7H_{11}]^+$, 91 (2) $[C_7H_7]^+$, 86 (2) $[C_5H_{12}N]^+$, 84 (2) $[C_5H_{10}N]^+$, 83 (16) $[C_6H_{11}]^+$, 81 (17) $[C_6H_9]^+$, 77 (6) $[C_6H_5]^+$, 69 (17) $[C_5H_9]^+$, 67 (11) $[C_5H_7]^+$, 57 (10) $[C_4H_9]^+$, 56 (6) $[C_3H_6N]^+$, 55 (78) $[C_4H_7]^+$, 44 (3) $[C_2H_6N]^+$, 43 (25) $[C_3H_7]^+$, 42 (50) $[C_2H_4N]^+$, 41 (52) $[C_3H_5]^+$. Anal. Calcd for $C_{23}H_{35}NSn$: C, 62.18; H, 7.94; N, 3.15; Sn, 26.72. Found: C, 61.98; H, 7.80; N, 3.44; Sn, 26.75.

(−)-Menthylmethylnaphthyltin Bromide (8). A solution of 1-naphthyllithium prepared from 6.22 g (30.0 mmol) of 1-bromonaphthalene and n-butyllithium (1.6 M in hexane, 18.8 mL, 30.0 mmol) in 170 mL of diethyl ether[36] was added dropwise over a period of 4 h to a stirred solution of 13.0 g (30.0 mmol) of **1** in 90 mL of diethyl ether at 0 °C. Stirring was continued for 24 h at room temperature. After removal of the solvents in vacuo, the residue was extracted with hot benzene. The benzene filtrate was concentrated to leave a yellow oil, which was prepurified by distillation. The fraction with the boiling range of 160–185 °C/0.01 mbar was dissolved in pentane; upon cooling to −30 °C, a white precipitate formed. Recrystallization from pentane yielded 4.2 g (29%) of **8** as a white, crystalline solid; mp 67 °C. $[\alpha]^{20}{}_{D}$ −29.3° to −47.1° (over 20 h) (c 0.97, benzene). MS (70 eV, 105 °C): *m/z* (%) 352 (4) $[M - C_{10}H_8]^+$, 341 (17) $[M - C_{10}H_{19}]^+$, 262 (3) $[M - C_{10}H_{19} - Br]^+$, 247 (4) $[SnC_{10}H_7]^+$, 199 (11) $[SnBr]^+$, 139 (22) $[C_{10}H_{19}]^+$, 135 (5) $[SnCH_3]^+$, 120 (2) $[Sn]^+$, 97 (18) $[C_7H_{13}]^+$, 95 (6) $[C_7H_{11}]^+$, 83 (100) $[C_6H_{11}]^+$, 81 (13) $[C_6H_9]^+$, 77 (2) $[C_6H_5]^+$, 69 (30) $[C_5H_9]^+$, 67 (5) $[C_5H_7]^+$, 57 (29) $[C_4H_9]^+$, 55 (18) $[C_4H_7]^+$, 43 (13) $[C_3H_7]^+$, 41 (12) $[C_3H_5]^+$. Anal. Calcd for $C_{21}H_{29}BrSn$: C, 52.54; H, 6.09; Sn, 24.73. Found: C, 52.49; H, 6.16; Sn, 24.60.

Table I. Crystal and Data Collection Parameters for 4[a]

formula	$C_{23}H_{34}BrNSn$
fw	523.14
cryst size, mm	0.3 × 0.3 × 0.5
cryst syst	monoclinic
space group	$P2_1$ (No. 4)
Z	4
a, Å	9.259(5)
b, Å	20.615(9)
c, Å	12.964(7)
β, deg	105.40(5)
V, Å^3	2385.7
d_c, g/cm^3	1.46
radiation; λ, Å	Mo Kα; 0.71073
μ_c, cm^{-1}	27.4
$2\theta_{max}$, deg	55
hkl range	$-10 \le h \le 10, 0 \le k \le 24, 0 \le l \le 15$
scan type	ω-scan
scan speed, θ, deg/min	min 1.0, max 29.3
no. of data measd	4620
no. of unique data	3498 $I > 2\sigma(I)$
R	0.044 (unit weights)
res electr dens, e Å^{-3}	−0.61/0.76
abspn corrn	empirical, min/max corrections 0.783/1.131

[a] Estimated standard deviations are given in parentheses.

(−)-Menthylmethylnaphthyltin Hydride (9). In analogy to the preparation of **5**, **8** (2.7 g, 5.6 mmol) in 18 mL of diethyl ether was reacted with 0.21 g (5.6 mmol) of lithium aluminum hydride in 10 mL of diethyl ether, and the mixture was worked up using 0.40 mL (22.4 mmol) of water in 1.4 mL of dioxane. Concentration of the pentane extraction solution afforded 1.9 g (84 %) of **9** as a colorless, viscous liquid. $[\alpha]^{20}{}_{D}$ −37.6° (c 0.48, benzene). IR: ν(Sn–H) 1806 (s) cm^{-1}. MS (70 eV, 75 °C): *m/z* (%) 387 (3) $[M - CH_3]^+$, 274 (29) $[M - H - C_{10}H_7]^+$, 263 (53) $[M - C_{10}H_{19}]^+$, 262 (37) $[M - H - C_{10}H_{19}]^+$, 259 (32) $[SnC_{10}H_{19}]^+$, 247 (100) $[SnC_{10}H_7]^+$, 139 (54) $[C_{10}H_{19}]^+$, 135 (52) $[SnCH_3]^+$, 128 (65) $[C_{10}H_8]^+$, 120 (40) $[Sn]^+$, 97 (18) $[C_7H_{13}]^+$, 95 (22) $[C_7H_{11}]^+$, 83 (69) $[C_6H_{11}]^+$, 81 (29) $[C_6H_9]^+$, 77 (9) $[C_6H_5]^+$, 69 (33) $[C_5H_9]^+$, 67 (21) $[C_5H_7]^+$, 57 (20) $[C_4H_9]^+$, 55 (71) $[C_4H_7]^+$, 43 (26) $[C_3H_7]^+$, 41 (37) $[C_3H_5]^+$. Anal. Calcd for $C_{21}H_{30}Sn$: C, 62.87; H, 7.54; Sn, 29.59. Found: C, 63.29; H, 7.37; Sn, 29.80.

X-ray Structure Analysis of 4. Suitable crystals of **4** were grown from a concentrated diethyl ether/pentane solution at room temperature. The compound is monoclinic, space group $P2_1$, $Z = 4$. The asymmetric unit contains two crystallographically independent molecules of identical configuration and conformation. The unit cell parameters and intensities were measured at room temperature by use of a Syntex $P2_1$ four circle diffractometer; empirical absorption correction was done using DIFABS.[37] Important crystal and data collection details are listed in Table I. The structure was solved by the heavy atom method and refined by blocked least-squares; programs used were SHELXS-86[38] and SHELX-76,[39] respectively. The non-hydrogen atoms were refined anisotropically; H atom coordinates were calculated geometrically, and their contribution was included in the last stages of the refinement. The final discrepancy factor

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(36) Weisemann, C.; Schmidtberg, G.; Brune, H.-A. *J. Organomet. Chem.* **1989**, *361*, 299.

(37) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

(38) Sheldrick, G. M. *SHELXS-86, Crystal Structure Solution Program*; Universität Göttingen: Göttingen, Germany, 1986.

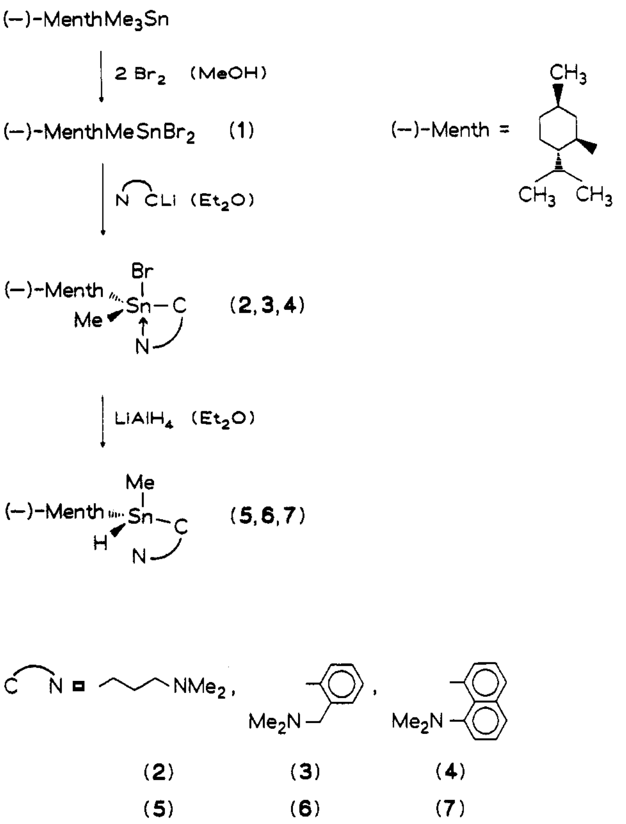
(39) Sheldrick, G. M. *SHELX-76, A Program for Crystal Structure Solution*; Cambridge University: Cambridge, England, 1976.

Table II. Atom Positions and B_{eq} Values for 4[a]

atom	x	y	z	B_{eq},[b] Å^2
Sn1	0.5511(1)	0.8710(0)	0.5253(1)	4.09
Sn2	0.1072(1)	0.5005(0)	−0.0698(1)	4.13
Br1	0.5022(2)	0.9425(1)	0.3504(1)	6.93
Br2	0.1130(2)	0.4419(1)	0.1115(1)	7.55
C11	0.7921(12)	0.8592(5)	0.5454(9)	4.09
C12	0.8363(13)	0.8413(6)	0.4440(9)	4.73
C13	0.0078(14)	0.8396(7)	0.4723(10)	5.43
C14	0.0725(13)	0.9065(8)	0.5052(11)	6.20
C15	0.0292(15)	0.9319(7)	0.6066(10)	5.73
C16	0.8547(13)	0.9281(6)	0.5813(9)	4.56
C17	0.0873(16)	0.9979(8)	0.6372(12)	7.08
C18	0.7684(14)	0.7741(7)	0.3996(12)	6.02
C19	0.7962(18)	0.7612(8)	0.2913(10)	6.84
C110	0.8162(21)	0.7163(7)	0.4733(14)	8.13
C111	0.5087(15)	0.9458(8)	0.6238(12)	6.80
C112	0.4987(18)	0.7299(7)	0.6152(14)	6.32
C113	0.5244(25)	0.6708(11)	0.6581(23)	11.13
C114	0.4683(34)	0.6176(13)	0.6055(29)	14.89
C115	0.3709(32)	0.6209(14)	0.5022(32)	16.87
C116	0.3437(24)	0.6801(10)	0.4561(26)	10.19
C117	0.2564(29)	0.6861(14)	0.3500(27)	12.40
C118	0.2362(21)	0.7422(13)	0.3008(18)	9.87
C119	0.3127(14)	0.7980(8)	0.3514(12)	6.57
C120	0.4009(13)	0.7960(6)	0.4521(11)	4.93
C121	0.4154(15)	0.7390(7)	0.5067(14)	6.36
C122	0.6874(18)	0.7852(12)	0.7599(14)	9.69
C123	0.4311(18)	0.8110(9)	0.7250(13)	7.65
C21	0.3451(11)	0.4931(6)	−0.0532(9)	4.58
C22	0.4450(12)	0.5234(6)	0.0547(10)	4.68
C23	0.6125(13)	0.5104(8)	0.0605(11)	5.96
C24	0.6428(14)	0.4388(8)	0.0508(11)	6.39
C25	0.5525(16)	0.4114(8)	−0.0530(12)	6.17
C26	0.3846(14)	0.4236(6)	−0.0666(10)	5.08
C27	0.5779(22)	0.3398(9)	−0.0660(16)	8.88
C28	0.4155(17)	0.5943(8)	0.0717(13)	7.09
C29	0.4529(20)	0.6406(8)	−0.0075(18)	9.07
C210	0.4866(21)	0.6130(10)	0.1865(15)	9.15
C211	−0.0164(17)	0.4246(7)	−0.1646(11)	6.34
C212	0.0674(13)	0.6374(6)	−0.1927(10)	4.78
C213	0.1052(17)	0.6915(10)	−0.2426(14)	7.68
C214	0.0941(24)	0.7539(11)	−0.1993(22)	9.76
C215	0.0421(22)	0.7601(8)	−0.1078(23)	9.48
C216	0.0051(16)	0.7081(8)	−0.0559(16)	7.36
C217	−0.0507(18)	0.7103(9)	0.0412(16)	7.36
C218	−0.0751(21)	0.6580(11)	0.0861(17)	9.22
C219	−0.0381(15)	0.5956(9)	0.0592(13)	7.15
C220	0.0076(12)	0.5910(6)	−0.0347(9)	4.59
C221	0.0267(14)	0.6424(6)	−0.0927(11)	4.95
C222	0.1571(17)	0.5602(9)	−0.3057(11)	7.11
C223	−0.0998(15)	0.5601(8)	−0.2974(11)	6.12
N1	0.5460(12)	0.7912(7)	0.6750(9)	6.54
N2	0.0602(11)	0.5719(6)	−0.2361(8)	5.34

[a] Estimated standard deviations are given in parentheses. [b] $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\mathbf{a}_j$.

Scheme I



Scheme II

$$\begin{tikzcd}
\underset{(1)}{(-)\text{-MenthMeSnBr}_2} \arrow[r, "\text{NaphLi}", "(\text{Et}_2\text{O})"'] & (-)\text{-MenthMeNaphSnBr}\ (8) \arrow[d, "\text{LiAlH}_4\ (\text{Et}_2\text{O})"] \\
 & (-)\text{-MenthMeNaphSnH}\ (9)
\end{tikzcd}$$

was R = 0.044. The absolute configuration of 4 was deduced from the molecular geometry of the (−)-menthyl ligand—the stereochemistry of its carbon atoms C2 and C5 could not have changed during the reaction—and was confirmed by refining the structure with a set of inverted atomic coordinates, which resulted in a significantly higher R value. Atom positions and isotropic equivalent thermal parameters are listed in Table II.

Results and Discussion

Synthesis. The starting organotin compound containing the optically pure (−)-menthyl ligand, (−)-menthyltrimethyltin, was obtained, as described earlier,[31] by stereospecific reaction of trimethyltin chloride with the Grignard reagent derived from (−)-menthyl chloride.

Dihalogenation of (−)-menthyltrimethyltin carried out with 2 equiv of bromine in methanol[40] yields 1 as a colorless, distillable liquid, which crystallizes in the form of low melting needles. Subsequent monoalkylation of the diorganotin dibromide creates the center of asymmetry at the tin atom: The slow 1/1 addition of highly diluted [3-(dimethylamino)propyl]lithium,[32] [2-[(dimethylamino)methyl]phenyl]lithium,[33,34] or [8-(dimethylamino)-naphthyl]lithium etherate[35,41] to 1 affords the crystalline [(dimethylamino)organo]-(−)-menthylmethyltin bromides 2, 3, or 4, respectively. The isolated crystals of 3 and 4 are diastereomerically pure; in solution an equilibrium mixture of both epimers differing in the absolute configuration at the tin center in a ratio of 47:53 or 46:54, respectively, is formed slowly. A determination of the diastereomer composition of 2 was not possible due to its very high configurational instability.

The corresponding [(dimethylamino)organo]-(−)-menthylmethyltin hydrides 5–7 are obtained by the reduction with lithium aluminum hydride. The thermally sensitive compounds, colorless oils, show constant diastereomer ratios of 49:51, 46:54, and 38:62.

For the purpose of comparison, the (−)-menthylmethylorganotin bromide and hydride 8 and 9 without amino functionality have been synthesized analogously: 1 reacts with 1-naphthyllithium[36] to give 8; a solution of the crystalline solid reaches a diastereomer ratio of 48:52 at

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[40] Sisido, K.; Miyanisi, T.; Isida, T.; Kozima, S. *J. Organomet. Chem.* **1970**, *23*, 117.

[41] Jastrzebski, J. T. B. H.; van Koten, G.; Goubitz, K.; Arlen, C.; Pfeffer, M. *J. Organomet. Chem.* **1983**, *246*, C75.

equilibrium. Reduction with lithium aluminum hydride affords **9**, a viscous liquid, showing a constant diastereomer ratio of 48:52.

Polarimetry. The optical rotations of the compounds synthesized have been measured in benzene solution. With the "doubly chiral" organotin compounds bearing an optically active ligand linked to an asymmetric tin center, the observation of a constant optical rotation indicates a constant ratio of diastereomers, while a rotation changing with time illustrates a slow stereoisomerization process taking place.

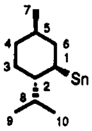
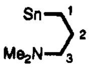
Two out of the three [(dimethylamino)organo]-(–)-menthylmethyltin bromides show nonconstant optical rotation values. A freshly prepared 0.024 M solution of crystalline **3** features a specific rotation $[\alpha]^{20}_{D}$ changing from –14.8° to a final –41.5° within 2.5 days; a freshly prepared solution of crystalline **4** of the same molar concentration changes its specific rotation $[\alpha]^{20}_{D}$ from +2.9° to a final –37.9° within 5 days. Since the asymmetric tin atom is the only configurationally labile center of chirality in these compounds,[42] the changes observed indicate epimerizations involving inversion of configuration at the tin center. As verified by NMR spectroscopy (see below), the crystalline (aminoaryl)-(–)-menthylmethyltin bromides **3** and **4** exist as pure diastereomers; in solution slow epimerization occurs to give an equilibrium mixture of both diastereomers differing in the absolute configuration at the tin atom. The crystalline aminoalkyl derivative **2**, on the other hand, shows a constant optical rotation instantaneously after dissolving, corresponding to the equilibrium concentration of its diastereomers; NMR spectroscopy points to a stereoisomerization process that occurs fast on the NMR time scale (see below). Comparison of the respective time necessary for reaching equilibrium reveals a strongly increasing kinetic stabilization of the configuration at the tin center with decreasing flexibility of the potentially bidentate ligand. The remarkably high configurational stability of the 8-(dimethylamino)naphthyl derivative **4** has to be ascribed to the dimethylamino group, which is directed toward the tin atom by the rigid aromatic ring system.[43] The analogue lacking the N-donor site shows a much lower stability of its stereocenter at tin: A solution of crystalline **8** of comparable concentration already reaches a constant equilibrium value of its optical rotation within 20 h after preparation.

The initial positive value $[\alpha]^{20}_{D}$ observed for **4** relates to the diastereomer with the absolute configuration R_{Sn} as an X-ray structural investigation reveals (see below). The negative contribution of the (–)-menthyl ligand entails a positive contribution of this *R* configurated chiral tin center to the total optical rotation.

The triorganotin hydrides **5–7** and **9** all show constant optical rotation values, indicating a constant ratio of diastereomers most likely stable toward interconversion.[44]

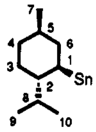
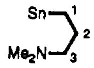
NMR Spectroscopy. The NMR spectra of the compounds synthesized, recorded in benzene-d_6, give an insight into the coordination behavior of the amino ligands, which are capable of an intramolecular N–Sn donor–acceptor interaction. The broad-band-decoupled $^{13}C\{^1H\}$ NMR spectra show distinguishable peaks with Sn satellite lines surrounding the signals for carbons separated from tin by up to four bonds. The ^1H NMR spectra, which reveal Sn satellites only for intense, well-separated signals, and the $^{117}Sn\{^1H\}$ NMR spectra supplement the information obtained from the ^{13}C NMR spectra. In addition, the inverse-gated broad-band-decoupled $^{117}Sn\{^1H\}$ NMR spectra allow the quantitative determination of the epimers formed by integration of the two single resonances observed. The spectral data for **1–9** are given in Tables III–VIII. Assignment of the respective menthyl resonances has been done by comparison with those of (–)-menthyltrimethyltin, the analysis of which determined the configuration and conformation of the optically pure ligand bound to tin as has been described earlier.[31]

Table III. $^{13}C\{^1H\}$ **NMR (67.93-MHz) Chemical Shifts**[a] **and** ^{13}C–$^{117/119}Sn$ **Coupling Constants**[b,c] **of the [3-(Dimethylamino)propyl]-(–)-menthylmethyltin Compounds 2 and 5**[d]

		2	**5**
	δ C$_1$ ($\lvert{}^1J\rvert$)	39.4 (480.3/502.6)	32.2 (384.8/402.8)
			32.0 (386.0/404.0)
	δ C$_2$ ($\lvert{}^2J\rvert$)	44.6 (22.4)	47.3 (15.6)
			47.2 (14.8)
	δ C$_3$ ($\lvert{}^3J_{trans}\rvert$)	26.5 (78.0/81.6)	26.9 (60.8)
	δ C$_4$ ($\lvert{}^4J\rvert$)	35.35 (9.7)	35.9
	δ C$_5$ ($\lvert{}^3J_{trans}\rvert$)	35.4 (82.8/86.6)	35.62 (65.7)
			35.58 (66.0)
	δ C$_6$ ($\lvert{}^2J\rvert$)	40.2 (26.8)	42.2 (17.1)
			41.9 (17.0)
	δ C$_7$ ($\lvert{}^4J\rvert$)	22.8 (5.7)	22.9
	δ C$_8$ ($\lvert{}^3J_{gauche}\rvert$)	32.6 (22.7)	33.7 (20.6)
			33.6 (20.5)
	δ C$_9$	22.1	22.3
	δ C$_{10}$	15.9	15.8
Sn–CH$_3$	δ CH$_3$ ($\lvert{}^1J\rvert$)	2.8 [broad]	–13.3 (283.8/297.0)
			–13.4 (283.9/297.1)
	δ C$_1$ ($\lvert{}^1J\rvert$)	18.0 [broad]	7.3 (335.7/351.3)
			6.8 (337.5/353.2)
	δ C$_2$ ($\lvert{}^2J\rvert$)	22.7 (27.9)	25.7 (22.4)
			25.6 (22.6)
	δ C$_3$ ($\lvert{}^3J\rvert$)	62.0 (42.7)	63.3 (46.8)
	δ CH$_3$	46.2	45.8

[a] δ in ppm. [b] $\lvert{}^nJ\rvert$ in Hz. [c] A single value quoted means unresolved $^{117/119}Sn$ satellites. [d] In C_6D_6.

Table IV. ^1H **NMR (270-MHz) and** $^{117}Sn\{^1H$ **Inverse Gated} NMR (28.552-MHz) Chemical Shifts**[a] **and** ^1H–$^{117/119}Sn$ **Coupling Constants**[b] **of the [3-(Dimethylamino)propyl]-(–)-menthylmethyltin Compounds 2 and 5**[c]

		2	**5**
	δ H–C$_7$	0.89 d[d]	0.83 d[d]
	δ H–C$_9$	1.05 d[e]	0.88 d[e]
	δ H–C$_{10}$	0.77 d[e]	0.73 d[e]
	δ other H	2.15–0.90 m	2.25–0.85 m
Sn–CH$_3$	δ CH$_3$ ($\lvert{}^2J\rvert$)	0.70 s (53.1/55.6)	0.09 d[f] (48.5/50.8)
			0.08 d[f] (48.2/50.4)
Sn–H	δ H ($\lvert{}^1J\rvert$)		4.98 q[f] (1543.8/ 1615.7)
			4.96 q[f] (1543.0/ 1614.7)
	δ CH$_2$	1.80–1.25 m	2.15–1.20 m
	δ CH$_3$	1.67 s	2.05 s
	δ Sn	–3.7 [broad]	–88.8 –92.1 (49:51)[g]

[a] δ in ppm. [b] $\lvert{}^nJ\rvert$ in Hz. [c] In C_6D_6. [d] $\lvert{}^3J(^1H^1H)\rvert \approx 6$ Hz. [e] $\lvert{}^3J(^1H^1H)\rvert \approx 7$ Hz. [f] $\lvert{}^3J(^1H^1H)\rvert \approx 2$ Hz. [g] Relative integral ratio.

The $^{13}C\{^1H\}$ NMR spectrum of the tin bromide **2**, featuring 15 signals, presents magnetically equivalent amine methyl groups. The equivalence reflects a fast exchange of the environments of the two methyls and

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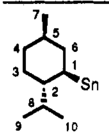
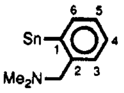
(42) Gielen, M.; Simon, S.; Tondeur, Y.; van de Steen, M.; Hoogzand, C.; van den Eynde, I. *Isr. J. Chem.* **1976/1977**, *15*, 74.

(43) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681.

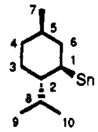
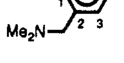
(44) Gielen, M. *Pure Appl. Chem.* **1980**, *52*, 657.

Table V. $^{13}C\{^1H\}$ NMR (67.93-MHz) Chemical Shifts[a] and $^{13}C-^{117/119}Sn$ Coupling Constants[b,c] of the [2-[(Dimethylamino)methyl]phenyl]-(–)-menthylmethyltin Compounds 3 and 6[d]

		3	6
	δ C_1 ($\lvert ^1J \rvert$)	41.0 (536.0/560.7)	35.0 (455.0/476.1)
		39.9 (525.6/549.9)	34.2 (458.9/480.1)
	δ C_2 ($\lvert ^2J \rvert$)	44.9 (21.9)	47.0 (14.7)
		44.6 (23.0)	46.8 (13.6)
	δ C_3 ($\lvert ^3J_{\mathrm{trans}} \rvert$)	26.7 (83.9/87.8)	27.0 (68.9)
		26.4 (86.0/90.0)	
	δ C_4 ($\lvert ^4J \rvert$)	35.4 (9.8)	36.1
		35.3 (9.2)	36.0
	δ C_5 ($\lvert ^3J_{\mathrm{trans}} \rvert$)	35.6 (89.9/94.1)	35.9 (74.0)
		35.3 (87.9/92.0)	35.7 (73.8)
	δ C_6 ($\lvert ^2J \rvert$)	40.3 (26.4)	42.7 (17.9)
		40.0 (30.8)	41.3 (19.3)
	δ C_7	22.8	23.1
		22.5	23.0
	δ C_8 ($\lvert ^3J_{\mathrm{gauche}} \rvert$)	33.2 (24.0)	33.6 (21.5)
		32.7 (25.8)	33.3 (24.5)
	δ C_9	22.0	22.5
			22.45
	δ C_{10}	16.0	16.0
		15.8	
Sn–CH_3	δ CH_3 ($\lvert ^1J \rvert$)	3.8 (407.6/426.4)	–10.6 (280.8/293.8)
		0.2 (437.6/457.8)	–12.2 (281.1/294.1)
	δ C_1 ($\lvert ^1J \rvert$)	142.6 (582.5/609.7)	142.4 (474.4/496.4)
		141.0 (576.3/603.0)	141.8 (481.0/503.3)
	δ C_2 ($\lvert ^2J \rvert$)	142.9 (33.3)	145.6 (23.8)
		142.2 (36.1)	145.5 (24.3)
	δ C_3 ($\lvert ^3J \rvert$)	128.4 (59.5/62.3)	128.54 (40.6)
		128.1 (58.5/61.2)	128.52 (41.2)
	δ C_4 ($\lvert ^4J \rvert$)	129.3 (11.8)	128.3 (10.7)
	δ C_5 ($\lvert ^3J \rvert$)	127.0 (52.5)	127.2 (52.3)
		126.8 (52.6)	127.1 (50.7)
	δ C_6 ($\lvert ^2J \rvert$)	139.6 (36.7)	137.9 (37.2)
		138.5 (40.0)	137.6 (38.6)
	δ CH_2 ($\lvert ^3J \rvert$)	65.17 (20.8)	66.3 (19.8)
		65.12 (23.5)	
	δ CH_3	45.2	44.9
			44.8

[a] δ in ppm. [b] $\lvert ^nJ \rvert$ in Hz. [c] A single value quoted means unresolved $^{117/119}Sn$ satellites. [d] In C_6D_6.

Table VI. ^1H NMR (270-MHz) and $^{117}Sn\{^1H$ Inverse Gated$\}$ NMR (28.552-MHz) Chemical Shifts[a] and $^1H-^{117/119}Sn$ Coupling Constants[b,c] of the [2-[(Dimethylamino)methyl]phenyl]-(–)-menthylmethyltin Compounds 3 and 6[d]

		3	6
	δ H–C_7	*0.91 $d^{e,m}$	0.89 d^f
		0.70 d^e	0.83 d^f
	δ H–C_9	1.10 d^g	0.99 d^g
		*1.04 d^g	0.83 d^g
	δ H–C_{10}	0.81 d^g	0.98 d^g
		*0.51 d^g	0.68 d^g
	δ other H	2.35–0.95 m	2.20–0.85 m
Sn–CH_3	δ CH_3 ($\lvert ^2J \rvert$)	0.81 s (57.0/59.7)	0.33 d^h (45.3)
		*0.70 s (56.4/59.0)	0.28 d^h (45.0)
Sn–H	δ H ($\lvert ^1J \rvert$)		5.73 q^h (1668.0/1745.5)
			5.59 q^h (1647.6/1724.2)
	δ H–C_3	6.81 $dd^{g,i}$	7.05 m
		*6.79 $dd^{g,i}$	
	δ H–C_4	7.09 $ddd^{g,g,i}$	
		*7.07 $ddd^{g,g,i}$	
	δ H–C_5	7.18 $ddd^{g,g,i}$	
	δ H–C_6 ($\lvert ^3J \rvert$)	*8.72 $dd^{g,i}$ (61.9)	7.62 m
		8.71 $dd^{g,i}$ (59.6)	
	δ CH_2	*3.08 d^j and *2.91 d^j	3.49 d^k and 3.09 d^k
		3.04 d^j and 2.77 d^j	3.40 d^k and 3.21 d^k
	δ CH_3	1.72 s	2.08 s
		*1.69 s	
	[δ other H]		7.25–7.10 m
	δ Sn	–49.4 –50.4 (53:47)[l]	–119.1 –137.0 (46:54)[l]

[a] δ in ppm. [b] $\lvert ^nJ \rvert$ in Hz. [c] A single value quoted means unresolved $^{117/119}Sn$ satellites. [d] In C_6D_6. [e] $\lvert ^3J(^1H^1H) \rvert \approx 6$ Hz. [f] $\lvert ^3J(^1H^1H) \rvert \approx 5$ Hz. [g] $\lvert ^3J(^1H^1H) \rvert \approx 7$ Hz. [h] $\lvert ^3J(^1H^1H) \rvert \approx 2$ Hz. [i] $\lvert ^4J(^1H^1H) \rvert \approx 1$ Hz. [j] $\lvert ^2J_{AB}(^1H^1H) \rvert \approx 14$ Hz. [k] $\lvert ^2J_{AB}(^1H^1H) \rvert \approx 13$ Hz. [l] Relative integral ratio. [m] Values marked with an asterisk refer to the crystallized diastereomer.

precludes a permanent formation of a $\overline{\mathrm{Sn(CH_2)_3N}}$ chelate ring. An equilibrium between both epimers differing in the configuration at the asymmetric tin center and between an Sn–N coordinated and uncoordinated mode with interconversion rates that are fast on the NMR time scale is in agreement with the observation of just one signal for each carbon atom present in the molecule. A strong, resonance frequency dependent broadening of the signals of the Sn-bound propyl and methyl carbon atoms confirms the existence of a dynamic process. This uncomplete coalescence of the Sn-bound carbons is due to especially large separations $\Delta\delta$ for these carbon atoms in the equilibrating stereoisomers. The coupling constant $\lvert ^1J(^{13}C^{117/119}Sn) \rvert$ observable for the menthyl C_1 indicates an average increase in coordination number at the tin to larger than 4:[45] The value of 480.3/502.6 Hz is clearly larger than that to be estimated for the corresponding coupling constant of the unknown (–)-menthylmethyl-*n*-propyltin bromide, the analogue with a four-coordinate tin atom. According to Bent's theory of isovalent rehybridization,[46] $\lvert ^1J(^{13}C^{117/119}Sn)_{\mathrm{menthyl}} \rvert$ of the latter compound amounts to a value between those observed for (–)-menthyldimethyltin bromide (415.6/435.0 Hz)[31] and (–)-menthylmethylisopropyltin bromide (353.9/370.5 Hz).[29,47,48] Likewise, the ^1H NMR spectrum of 2 indicates a coordination number of larger than 4 with the coupling constant $\lvert ^2J(^1H^{117/119}Sn) \rvert$ observable for the Sn-bound methyl group; its amount (53.1/55.6 Hz) is larger than the corresponding one of the analogous unsubstituted *n*-propyl derivative, which ranges between 48.4/50.6 Hz observed for (–)-menthyldimethyltin bromide[31] and 42.7/44.7 Hz for (–)-menthylmethylisopropyltin bromide.[29,47] In a low-temperature 80-MHz ^1H NMR experiment, a freezing of the molecular dynamics was not possible. Neither a diastereotopic nonequivalence of the amine methyl groups nor doubled signals due to a just slow interconversion of the diastereomers could be observed. At –60 °C, the lowest temperature studied, solely a broadening of the signals of the Sn-bound methyl group and the dimethylamino group occurred. The one broad $^{117}Sn\{^1H\}$ resonance of 2 at –3.7 ppm—upfield[49,50] of (–)-menthyldimethyltin bromide (124.7 ppm)[31] and of (–)-menthylmethylisopropyltin bromide (129.7 and 127.2 ppm)[29,47]— corroborates the above results.

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(45) Nadvornik, M.; Holecek, J.; Handlir, K.; Lycka, A. *J. Organomet. Chem.* **1984**, *275*, 43.

(46) Mitchell, T. N.; Walter, G. *J. Organomet. Chem.* **1976**, *121*, 177.

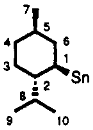
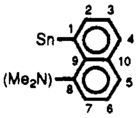
(47) Wassermann, B. C. Dissertation, Technische Universität Berlin, Berlin, Germany, 1992.

(48) The tin coupling constants of corresponding signals of the two diastereomers differ in magnitude. The mean value has been cited in the text.

(49) Otera, J. *J. Organomet. Chem.* **1981**, *221*, 57.

(50) Mügge, C.; Pepermans, H.; Gielen, M.; Willem, R.; Tzschach, A.; Jurkschat, K. *Z. Anorg. Allg. Chem.* **1988**, *567*, 122.

Table VII. $^{13}C\{^1H\}$ NMR (67.93-MHz) Chemical Shifts[a] and ^{13}C–$^{117/119}Sn$ Coupling Constants[b,c] of 1 and of the [8-(Dimethylamino)naphthyl]-(–)-menthylmethyltin Compounds 4 and 7 and Their Unsubstituted Analogues, the (–)-Menthylmethylnaphthyltin Compounds 8 and 9[d]

		1	4	8	7	9
	$\delta\,C_1$ ($\lvert ^1J \rvert$)	48.4 (453.1/474.2)	40.8 (519.6/543.8) 40.3 (513.4/537.3)	41.5 (420.7/440.2) 41.1 (421.4/441.0)	34.3 (455.9/477.1) 33.1 (454.3/475.5)	34.0 (411.1/430.2) 33.7 (410.3/429.4)
	$\delta\,C_2$ ($\lvert ^2J \rvert$)	45.9 (25.5)	44.9 (22.3) 44.7 (24.8)	46.5 (18.4) 46.4 (19.1)	46.8 (13.4) 46.7 (13.2)	47.3 (16.7) 47.2 (16.6)
	$\delta\,C_3$ ($\lvert ^3J_{trans} \rvert$)	26.4 (108.8/113.8)	26.44 (82.5/86.3) 26.41 (87.3/91.4)	26.7 (80.8/84.6)	26.9 (66.4) 26.8 (69.5)	26.9 (65.9)
	$\delta\,C_4$ ($\lvert ^4J \rvert$)	34.7 (13.4)	35.3	35.2 35.1	35.9	35.7 35.65
	$\delta\,C_5$ ($\lvert ^3J_{trans} \rvert$)	34.9 (104.0/108.8)	35.4 (89.7/93.9) 35.1 (87.0/91.0)	35.23 (83.6) 35.21 (83.2)	35.8 (76.6) 35.5 (72.3)	35.6 (68.8/72.0) 35.5 (68.7/71.9)
	$\delta\,C_6$ ($\lvert ^2J \rvert$)	39.0 (38.3)	40.3 (24.5) 39.6 (30.8)	40.3 (24.6) 40.1 (23.5)	42.9 (15.2) 40.8 (19.3)	42.0 (18.0) 41.7 (17.9)
	$\delta\,C_7$ ($\lvert ^4J \rvert$)	22.4 (9.7)	22.9 22.5	22.5 22.45	23.0 22.7	22.7
	$\delta\,C_8$ ($\lvert ^3J_{gauche} \rvert$)	34.8 (34.3)	32.6 (24.8) 32.5 (24.0)	34.3 (25.8)	33.2 (27.3) 33.0 (25.8)	33.8 (21.1)
	$\delta\,C_9$	21.8	22.0 21.9	21.8	22.2 22.1	22.1
	$\delta\,C_{10}$	15.5	16.0 15.0	15.7	16.0 15.1	15.7
Sn–CH$_3$	$\delta\,CH_3$ ($\lvert ^1J \rvert$)	8.4 (301.3/315.3)	6.1 (404.2/422.9) 1.8 (433.8/454.0)	–1.0 (297.8/311.7) –1.3 (296.6/310.4)	–10.6 (261.9/274.1) –10.9 (273.8/286.5)	–11.5 (309.8/324.3) –12.1 (311.7/326.3)
	$\delta\,C_1$ ($\lvert ^1J \rvert$)		138.0 (583.1/610.5) 135.5 (580.6/607.6)	141.2 (427.5/447.1) 141.1 (424.3/444.1)	138.0 (496.7/519.7) 136.3 (506.2/529.7)	141.5 (416.7/436.0) 141.2 (417.6/436.9)
	$\delta\,C_2$ ($\lvert ^2J \rvert$)		138.9 (33.6) 137.5 (35.9)	135.8 (33.7) 135.7 (33.8)	136.8 (35.3) 135.9 (36.2)	136.3 (31.2)
	$\delta\,C_3$ ($\lvert ^3J \rvert$)		127.4 (48.4) 127.1 (46.2)	126.1 (57.7)	126.4 (58.3) 126.3 (57.9)	125.8 (49.6)
	$\delta\,C_4$ ($\lvert ^4J \rvert$)		129.4 (13.7) 129.3 (14.8)	130.3 (12.6)	129.3 (10.3) 129.2 (12.5)	129.3 (11.1)
	$\delta\,C_5$ ($\lvert ^4J \rvert$)		127.5 127.3	129.6 (7.8)	126.4 126.1	129.4
	$\delta\,C_6$		125.95 125.88	126.7 126.6	125.60 125.58	126.2
	$\delta\,C_7$		116.8 116.3	126.1	117.0 116.6	125.8
	$\delta\,C_8$ ($\lvert ^3J \rvert$)		150.1 (20.0) 149.8 (23.0)	129.1 (41.3) 129.0 (40.5)	152.2 (18.3) 152.1 (18.3)	130.6 (32.9)
	$\delta\,C_9$ ($\lvert ^2J \rvert$)		134.4 (38.2) 133.9 (40.8)	134.5 (38.3/40.1)	135.2 (26.3) 134.9 (27.3)	139.4 (31.1)
	$\delta\,C_{10}$ ($\lvert ^3J \rvert$)		134.6 (43.3) 134.5 (45.0)	138.0 (46.5/48.7) 137.95 (45.4/47.5)	135.3 (35.3)	134.5 (32.5) 134.2 (32.1)
	$\delta\,CH_3$		50.2 48.9 48.6 46.3		49.2 48.6 46.5 45.1	

[a] δ in ppm. [b] $\lvert ^nJ \rvert$ in Hz. [c] A single value quoted means unresolved $^{117/119}Sn$ satellites. [d] In C_6D_6.

The $^{13}C\{^1H\}$ NMR spectrum of equilibrated 3, showing 16 out of 19 signals doubled, represents a superposition of the two different spectra of two diastereomers that interconvert slowly. With the separation of corresponding signals $\Delta\delta$ (maximum 3.6 ppm) decreasing as the distance between the respective carbon and the asymmetric tin atom increases, just the menthyl C_9 in the δ trans position, the benzene C_4 in the para position to tin, and the dimethylamino group show the same resonances for both diastereomers. A coordination number of higher than 4 at the metal center of the tin bromide[45] is suggested by the enlarged coupling constants $\lvert ^1J(^{13}C^{117/119}Sn) \rvert$ of the Sn-bound methyl and menthyl carbons as compared to those couplings observed for the similar compound bearing an unsubstituted aromatic ligand, 8. The ^1H NMR spectrum of 3 shows a correspondingly enlarged coupling constant $\lvert ^2J(^1H^{117/119}Sn) \rvert$ of the methyl group and, moreover, evidences a pentacoordinate structure by the significant downfield shift of the resonance of the phenyl C_6 proton (8.72 and 8.71 ppm) in comparison to the corresponding resonance of four-coordinate dimethylphenyltin bromide ($\delta[H_{phenyl}]$ = 7.44–7.10 ppm):[51] A trigonal bipyramidal arrangement around tin—as a result of intramolecular Sn–N coordination—with the electronegative nitrogen and bromine in axial positions[1,4] places the phenyl C_6 proton near the bromine.[52] The magnetic equivalence of the amine methyl groups indicates Sn–N bond dissociation followed by inversion at nitrogen with concomitant 180° rotation around the CH_2–N bond and renewed formation of the Sn–N bond,[2,3] occurring fast on the NMR time scale—a process which can be frozen, however: A low-temperature 80-MHz ^1H NMR experiment allows the observation of diastereotopic amine methyl groups below 0 °C. The epimerization process involving inversion of configuration at the tin takes place on the laboratory time scale and can be observed NMR spectroscopically on a freshly prepared solution of crystalline 3: In addition to the original resonances of the crystallized diastereomer, the resonances due to the second diastereomer appear with

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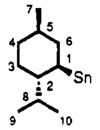
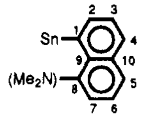
(51) Baldwin Frech, C. Dissertation, The University of Oklahoma, Norman, OK, 1987.

(52) van Koten, G.; Schaap, C. A.; Noltes, J. G. *J. Organomet. Chem.* 1975, *99*, 157.

Table VIII. ^{1}H NMR (270-MHz) and ^{117}Sn{^{1}H Inverse Gated} NMR (28.552-MHz) Chemical Shifts^{a} and ^{1}H–$^{117/119}$Sn Coupling Constants^{b,c} of 1 and of the [8-(Dimethylamino)naphthyl]-(−)-menthylmethyltin Compounds 4 and 7 and Their Unsubstituted Analogues, the (−)-Menthylmethylnaphthyltin Compounds 8 and 9^{d}

		1	4	8	7	9
	δ H–C$_1$	1.90 ddd^{e,e,f}				
	δ H–C$_5$			1.13 m		
	δ H$_e$–C$_6$	1.98 dddd^{g,f,f,h}				
	δ H$_a$–C$_6$			1.37 ddd^{e,e,g} 1.35 ddd^{e,e,g}		
	δ H–C$_7$	0.75 d^{j}	0.87 d^{j} *0.84 d^{j,p}	0.73 d^{i}	0.88 d^{l} 0.60 d^{i}	0.740 d^{l} 0.738 d^{l}
	δ H–C$_9$	0.81 d^{j}	1.12 d^{j} *0.93 d^{j}	0.75 d^{j}	0.95 d^{j} 0.75 d^{j}	0.83 d^{j} 0.82 d^{j}
	δ H–C$_{10}$	0.62 d^{j}	0.53 d^{i} *−0.10 d^{j}	0.60 d^{j} 0.57 d^{j}	0.80 d^{j} 0.11 d^{j}	0.69 d^{j} 0.66 d^{j}
	δ other H	1.60–0.85 m	2.35–0.85 m	2.20–0.80 m	2.30–0.85 m	2.05–0.85 m
Sn–CH$_3$	δ CH$_3$ (|^2J|)	0.94 s (50.2/52.5)	0.91 s (57.4/60.1) *0.88 s (57.0/59.6)	0.84 s (48.1/50.3) 0.82 s (48.1/50.3)	0.42 d^{k} (42.8/44.8) 0.40 d^{k} (42.9/44.9)	0.46 d^{k} (50.3/52.6) 0.44 d^{k} (50.4/52.7)
Sn–H	δ H (|^1J|)				6.25 q^{k} (1751.8/1833.2) 6.10 q^{k} (1763.8/1845.8)	5.98 q^{k} (1617.1/1692.2) 5.93 q^{k} (1614.6/1689.7)
	δ H–C$_2$ (|^3J|)		9.09 dd^{j,l} (69.4) *9.01 dd^{j,l} (71.6)	8.03 dd^{j,l} (60.7/63.5) 7.99 dd^{j,l} (60.9/63.7)	7.90 dd^{j,l} (60.7) 7.89 dd^{j,l} (61.0)	7.70 dd^{j,l} (53.0) 7.69 dd^{j,l} (53.4)
	δ H–C$_3$		7.40 dd^{j,m} *7.38 dd^{j,m}	7.26 m	7.34 dd^{j,m} 7.33 dd^{j,m}	
	δ H–C$_4$		7.57 dd^{l,m} *7.55 dd^{l,m}	7.61 d^{m}	7.64 d^{m}	7.63 d^{m}
	δ H–C$_5$		7.47 dd^{l,m} *7.45 dd^{l,m}	7.61 d^{m}	7.50 dd^{l,m} 7.49 dd^{l,m}	7.63 d^{m}
	δ H–C$_6$		7.14 dd^{j,m} *7.13 dd^{j,m}	7.34 m	7.24 dd^{m,m} 7.23 dd^{m,m}	
	δ H–C$_7$		6.81 dd^{j,l} *6.76 dd^{j,l}	7.26 m	7.06 dd^{l,m} 7.03 dd^{l,m}	
	δ H–C$_8$			7.92 d^{n} 7.89 d^{n}		8.02 d^{m} 8.01 d^{m}
	δ CH$_3$		*2.24 s 2.22 s 2.04 s *1.90 s		2.51 s 2.49 s 2.38 s 2.35 s	
	[δ other H]					7.40–7.20 m
	δ Sn	80.2	−35.0 −38.7 (46:54)^{o}	68.9 68.4 (48:52)^{o}	−108.5 −125.4 (62:38)^{o}	−117.0 −121.6 (48:52)^{o}

^{a} δ in ppm. ^{b} \|^nJ\| in Hz. ^{c} A single value quoted means unresolved $^{117/119}$Sn satellites. ^{d} In C_6D_6. ^{e} \|$^3J(^1H^1H)$\| ≈ 12 Hz. ^{f} \|$^3J(^1H^1H)$\| ≈ 3 Hz. ^{g} \|$^2J(^1H^1H)$\| ≈ 12 Hz. ^{h} \|$^4J(^1H^1H)$\| ≈ 3 Hz. ^{i} \|$^3J(^1H^1H)$\| ≈ 6 Hz. ^{j} \|$^3J(^1H^1H)$\| ≈ 7 Hz. ^{k} \|$^3J(^1H^1H)$\| ≈ 2 Hz. ^{l} \|$^4J(^1H^1H)$\| ≈ 1 Hz. ^{m} \|$^3J(^1H^1H)$\| ≈ 8 Hz. ^{n} \|$^3J(^1H^1H)$\| ≈ 9 Hz. ^{o} Relative integral ratio. ^{p} Values marked with an asterisk refer to the crystallized diastereomer.

increasing intensity until equilibrium is reached (see Figure 1). The length of time necessary for reaching equilibrium increases from several hours to several days with decreasing concentration of the solution investigated. The relative integral ratio of the two ^{117}Sn{^{1}H} resonances of 3 at equilibrium was determined to be 47:53. An upfield shift of the resonances at −49.4 and −50.4 ppm as compared to 8 (δ ^{117}Sn = 68.9 and 68.4 ppm) and to dimethylphenyltin bromide (δ ^{119}Sn = 62.6 ppm)[51] corresponds to pentacoordination.[49,53]

A comparison of the NMR spectra of 4 with those of 8 is especially fruitful, determining the influence of the donor atom, with 8 being the exact analogue of 4 without the amino functionality. Each illustrating two slowly interconverting diastereomers of the tin bromide, the ^{13}C{^{1}H} NMR spectrum of equilibrated 4 has 22 out of 23 signals doubled with separations Δδ up to 4.3 ppm, whereas the ^{13}C{^{1}H} NMR spectrum of equilibrated 8 shows only 12 out of 21 signals doubled with considerably smaller separations of maximum 0.4 ppm. The coupling constants |$^1J(^{13}C^{117/119}Sn)$| of the methyl C and menthyl C$_1$, which feature an increase by an average of about 30% for 4 in comparison with 8, evidence the pentacoordinate structure of 4,[45] as does the coupling constant |$^2J(^1H^{117/119}Sn)$| of the methyl protons accordingly. The ^{1}H resonances of the naphthyl C$_2$ proton of 4 (9.09 and 9.01 ppm) appear significantly downfield of those of 8 (8.03 and 7.99 ppm) due to the trigonal bipyramidal structure involving intramolecular Sn–N coordination,[9] which places the naphthyl C$_2$ proton in the proximity of the axial bromine.[35] A fixed Sn–N coordination renders the two amine methyl groups diastereotopic; 4 causes four dimethylamino resonances, two for each diastereomer. Also in a high-temperature 80-MHz ^{1}H NMR experiment, there is no coalescence observable up to 105 °C, the highest temperature studied. NMR investigation of a freshly prepared solution of 4 allows the observation of the epimerization process occurring on the laboratory time scale: While a ^{1}H NMR spectrum recorded immediately after dissolving the crystalline compound exclusively shows the resonances of one diastereomer (see Figure 2a)—the R_{Sn} diastereomer according to X-ray structural characterization—following

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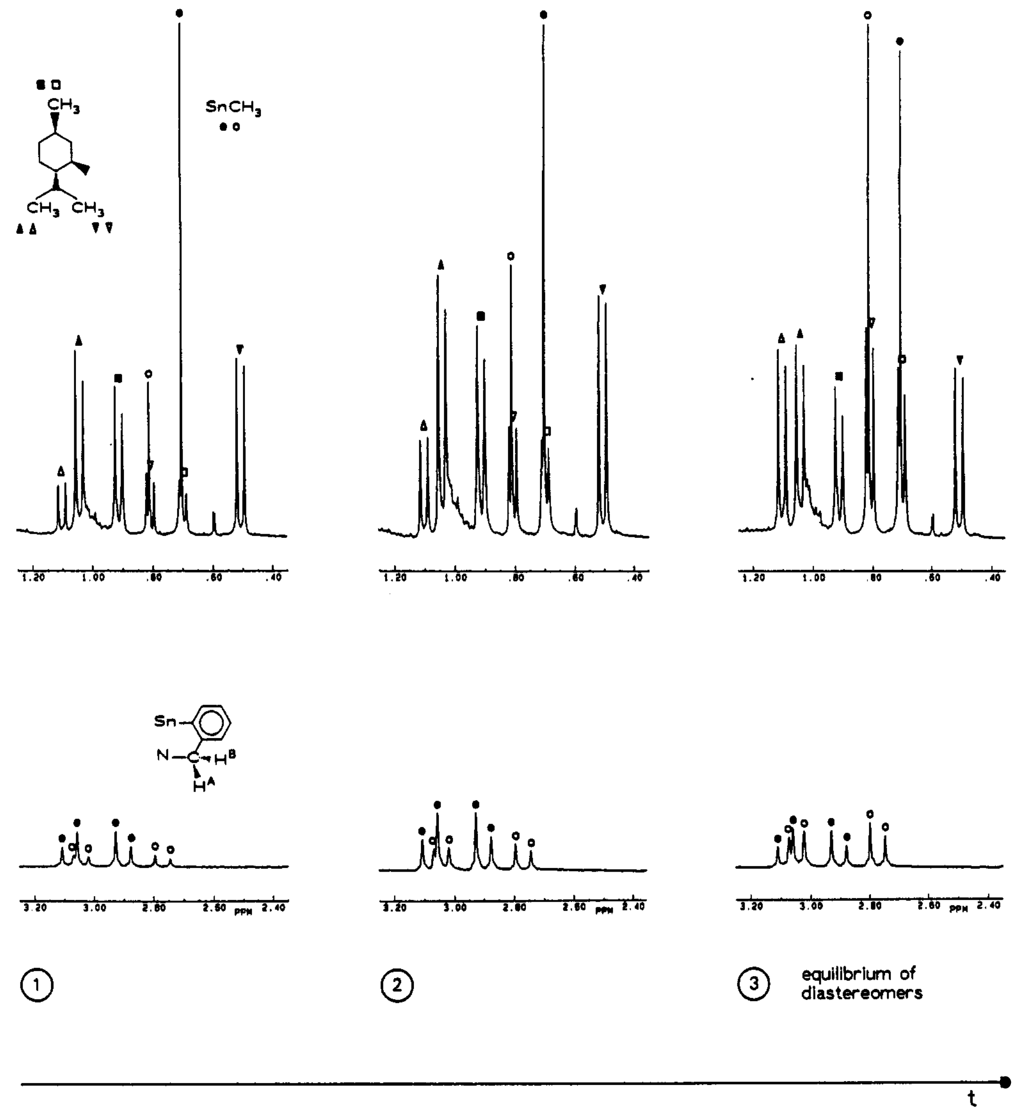


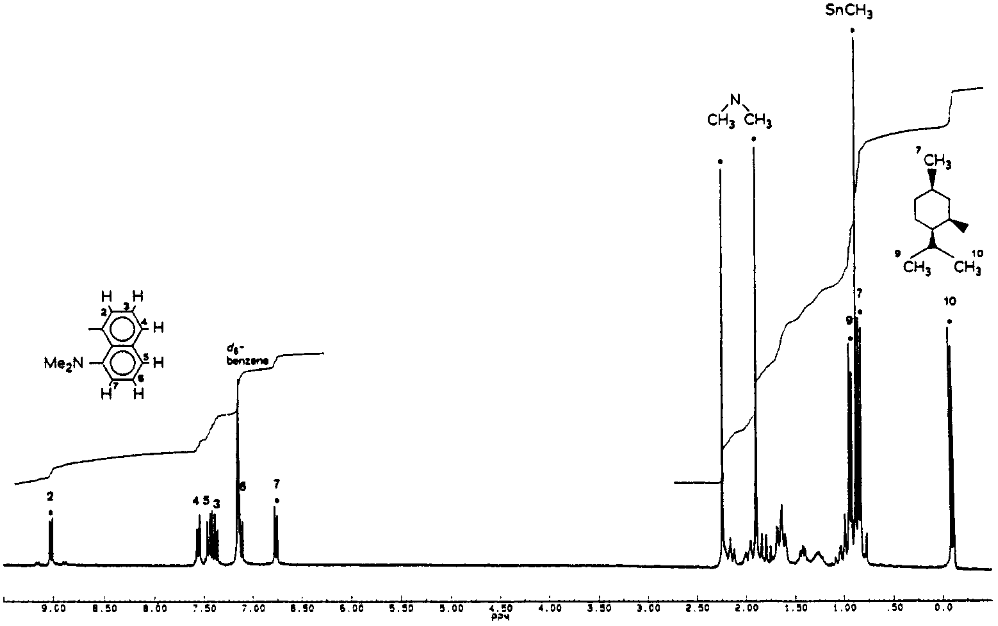
Figure 1. Details of the ^{1}H NMR spectra (270 MHz) of [2-[(dimethylamino)methyl]phenyl]-(−)-menthylmethyltin bromide (**3**) in C_6D_6 illustrating the epimerization process.

measurements of the sample produce spectra with additional resonances of increasing intensity due to the second diastereomer. Finally, after 5 days a constant diastereomer ratio is reached; the spectrum of the equilibrated solution identifies the prevalent diastereomer as the one crystallized originally (see Figure 2b). The two ^{117}Sn{^{1}H} resonances of **4** at −35.0 and −38.7 ppm are shifted upfield of those of **8** by about 100 ppm as expected for pentacoordination versus tetracoordination at the tin atom.[49,53] Integration reveals a diastereomer ratio at equilibrium of 46:54 for **4** and of 48:52 for **8**.

The NMR spectral data of **5** indicate a coordination sphere of the dimethylamino substituted organotin hydride similar to that of an unsubstituted tin hydride. The ^{13}C{^{1}H} NMR spectrum, having 8 out of 15 signals doubled with separations $\Delta\delta$ of maximum only 0.5 ppm, corresponds to two diastereomers, the interconversion of which is inert on the NMR time scale or—most likely[44]—completely blocked. The Lewis acidity of the metal center in **5**—contrary to the corresponding tin bromide **2**—seems to be too low for effecting a coordination of the amino group: The magnetic equivalence of the amine methyl groups together with the tin couplings $|^1J|$ and $|^2J|$ reflect a four-coordinate tin center with a dangling (dimethylamino)propyl ligand. The coupling constants $|^1J(^{13}C^{117/119}Sn)|$ for the methyl C (283.9/297.1 Hz)[48] and the menthyl C_1 (385.4/403.4 Hz)[48] of **5** lie in size exactly between the respective couplings of (−)-menthyldimethyltin hydride ($|^1J(^{13}C^{117/119}Sn)_{methyl}|$ = 300.1/314.0 Hz, $|^1J(^{13}C^{117/119}Sn)_{menthyl}|$ = 405.1/423.8 Hz)[29,47] and (−)-menthylmethylisopropyltin hydride ($|^1J(^{13}C^{117/119}Sn)_{methyl}|$ = 269.0/281.5 Hz, $|^1J(^{13}C^{117/119}Sn)_{menthyl}|$ = 366.8/383.9Hz)[29,47,48] and, therefore,[46] correspond to those of the unknown (−)-menthylmethyl-*n*-propyltin hydride, the unsubstituted analogue. The coupling constants $|^2J(^1H^{117/119}Sn)|$ for the methyl protons (48.4/50.6 Hz)[48] and $|^1J(^1H^{117/119}Sn)|$ for the Sn-bound hydrogen (1543.4/1615.2 Hz)[48] compare accordingly with those of (−)-menthyldimethyltin hydride ($|^2J(^1H^{117/119}Sn)_{methyl}|$ = 50.4/52.7 Hz, $|^1J(^1H^{117/119}Sn)|$ = 1570.9/1644.0 Hz)[29] and (−)-menthylmethylisopropyltin hydride ($|^2J(^1H^{117/119}Sn)_{methyl}|$ = 47.0/49.1 Hz, $|^1J(^1H^{117/119}Sn)|$ = 1486.4/1555.5 Hz).[29,48] The two ^{117}Sn{^{1}H} resonances, the integral ratio of which is 49:51, are found at −88.8 and −92.1 ppm in the region of the resonances of the likewise tetrahedrally coordinated tin in (−)-menthyldimethyltin hydride (−96.8 ppm) and (−)-menthylmethylisopropyltin hydride (−68.8 and −70.2 ppm).[29]

The ^{13}C{^{1}H} NMR spectrum of the tin hydride **6** shows 15 out of its 19 signals doubled with separations $\Delta\delta$ of 1.6

a) R_{Sn} diastereomer



b) equilibrium of diastereomers (R_{Sn}/S_{Sn} = 54:46)

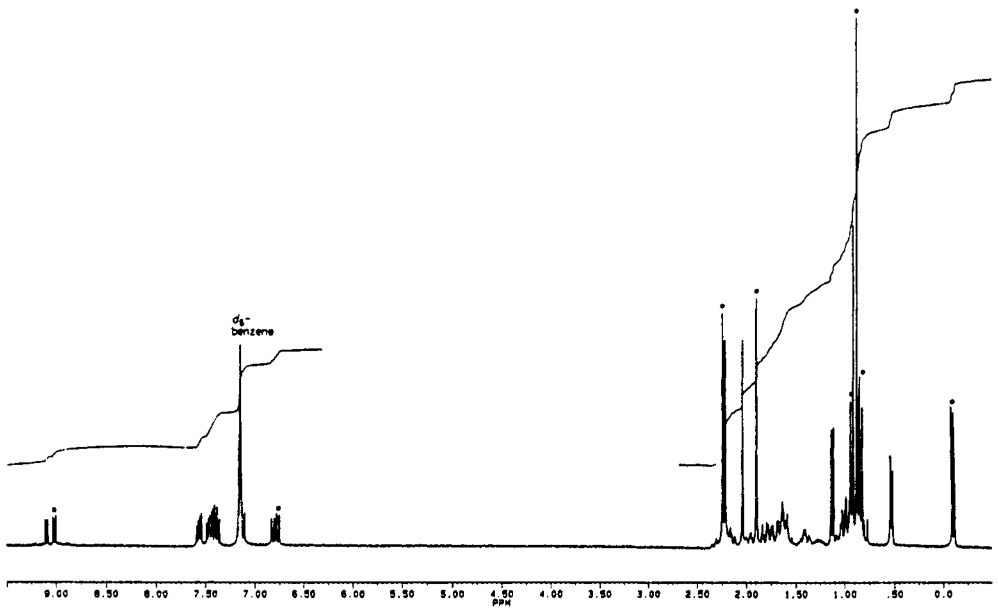


Figure 2. ^{1}H NMR spectra (270 MHz) of [8-(dimethylamino)naphthyl]-(−)-menthylmethyltin bromide (4) in C_6D_6.

ppm and smaller, again representing two diastereomers that are most likely configurationally stable.[44] Analysis of the relevant coupling constants suggests a distortion of the tetrahedral coordination geometry around tin toward a trigonal bipyramidal one. For comparison, the similar tin hydride with an unsubstituted aromatic ligand, 9, featuring the tetrahedral structure is used: The menthyl coupling constant $|^1J(^{13}C^{117/119}Sn)|$ in 6 is increased, and the methyl coupling constants $|^1J(^{13}C^{117/119}Sn)|$ and $|^2J(^1H^{117/119}Sn)|$ are decreased. While an enlarged tin coupling indicates an increased s orbital participation in a shortened, equatorial Sn–C bond in a trigonal bipyramidal structure—as observed for the pentacoordinate organotin bromides with nitrogen and bromine in the axial positions—a diminished tin coupling accordingly indicates a decreased s orbital participation in a lengthened, axial Sn–C bond.[24] This points to a structure of 6 in which the dimethylamino group approaches the tin from the site opposite to the methyl group, with the aminobenzyl ligand spanning a quasi-equatorial (C) and a quasi-axial site (N) of a beginning trigonal bipyramidal arrangement. The approach of the donor atom—bearing magnetically equivalent methyl groups—does not result in a strong Sn–N interaction as suggested by the low Lewis acidity of the metal center in the tin hydride and by the two $^{117}Sn\{^1H\}$ resonances at −119.1 and −137.0 ppm (relative integral ratio 46:54), which show up in the region of those for unsubstituted 9 (δ ^{117}Sn = −117.0 and −121.6 ppm). The nitrogen functionality in 6 is brought into the proximity of the tin mainly for steric reasons—due to the ortho disubstituted phenyl group.

Comparison of the separations $\Delta\delta$ of doubled signals in the $^{13}C\{^1H\}$ NMR spectra of the tin hydride 7 and of its exact analogue without amino functionality, 9—both consisting of two most likely configurationally stable diastereomers[44]—illustrates the influence of the dimethylamino group in the former with clearly larger values Δδ of up to 2.1 ppm for the 21 out of its 23 signals doubled as compared to a maximum of 0.3 ppm for the 8 out of 21 signals doubled of the latter. The tin couplings $|^1J|$ and $|^2J|$ reflect the distortion of the tetrahedral coordination geometry around tin caused by the dimethylamino group in **7**. The increase of the menthyl and the decrease of the methyl coupling constants $|^1J(^{13}C^{117/119}Sn)|$ of **7** as compared to **9**—with respective differences less than half as large as the increases that correspond to the change in coordination number from 4 to 5 for the organotin bromides—indicate a beginning change from tetrahedral into trigonal bipyramidal structure. The menthyl group occupies a quasi-equatorial position; the methyl group, a quasi-axial position. The hydrogen atom bound to tin, featuring an enlarged coupling constant $|^1J(^1H^{117/119}Sn)|$ with respect to **9**, resides in another quasi-equatorial position. The (dimethylamino)naphthyl ligand spans the remaining quasi-equatorial and -axial sites, with the electronegative nitrogen approaching the tin from the latter site. A similar solid-state structure has been established for *tert*-butyl[8-(dimethylamino)naphthyl]-(−)-menthyltin hydride.[31] For the two amine methyls in **7**, there are four resonances observable; this diastereotopicity reflects a blocked exchange of the N-bound groups, i.e., a fixed orientation of the nitrogen lone pair of electrons toward the tin atom. Yet, mainly steric reasons are responsible for this positioning, with the rigid, peri disubstituted naphthalene ring system connecting tin and nitrogen.[31] There is no significant donor–acceptor interaction as suggested by the absence of an upfield shift of the two $^{117}Sn\{^1H\}$ resonances of **7** at −108.5 and −125.4 ppm in comparison with those of unsubstituted **9**. The relative integral ratios were determined to be 38:62 for **7**, yet only 48:52 for **9**.

The different potentially bidentate ligands 3-(dimethylamino)propyl, 2-[(dimethylamino)methyl]phenyl, and 8-(dimethylamino)naphthyl influence the structure, configurational stability, and optical induction in the organotin bromides and hydrides quite differently—due to the increasing rigidity of their three-membered carbon chain that connects tin and nitrogen. Comparison of the [(dimethylamino)organo]-(−)-menthylmethyltin bromides **2**–**4**, which feature pentacoordinate tin centers as a result of intramolecular Sn–N coordination, reveals a clearly increasing stability of the $\overline{\text{Sn–C–C–C–N}}$ chelate ring formed with regard to a Sn–N dissociation/association process occurring. The equally increasing configurational stability of the tin center in **2**–**4** may be explained with the steric crowding around tin, e.g. in the four-coordinate transition state during an irregular inversion process:[54] While the aminopropyl ligand in its nonchelating mode does not hinder the intermolecular nucleophilic attack at the tin, which leads to inversion of its configuration,[55] the (aminomethyl)phenyl ligand and the aminonaphthyl ligand crowd the coordination sphere of the tin atom regardless of their coordination mode (see Figure 3), thus hindering the inversion process. The instability of the Sn–N coordination observed for **2** and **3** supports a dissociative mechanism. For the stereoisomerization of **4**, however, a regular inversion process with conservation of the pentacoordination,[54] e.g. a series of Berry pseudorotations—an energetically unfavorable process[4]—seems to be likely. The concentration independence of the epimerization of **4** precludes a stereoisomerization route involving hexacoordinate intermediates formed by association of two intramolecularly Sn–N coordinated molecules.[4,56] The [(dimethylamino)organo]-(−)-menthylmethyltin hydrides **5**–**7**, in which the tin centers show too low a Lewis acidity for Sn–N coordination, reflect the decreasing flexibility of their amino ligands in the distortion of the tetrahedral structure observed for **6** and **7**. The diastereomer ratios of the "doubly chiral" organotin compounds being unequal to 1 reveal an optical induction from the (−)-menthyl ligand to the asymmetric tin center. This optical control of the configuration at the tin atom by the optically active ligand increases as the rigidity of the potentially bidentate ligand increases.

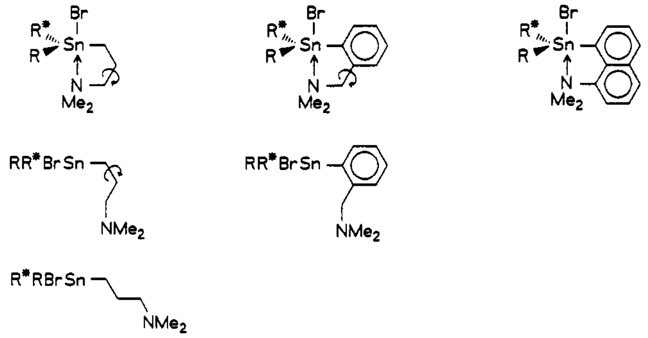


Figure 3. Comparison of the flexibilities of the 3-(dimethylamino)propyl, 2-[(dimethylamino)methyl]phenyl, and 8-(dimethylamino)naphthyl ligands.

Crystal Structure of 4. The single-crystal X-ray diffraction study of **4**[30] reveals a crystal structure which consists of discrete mononuclear molecules. The asymmetric unit contains two independent molecules of identical conformation. The absolute configuration of the stereocenter at the tin atom is assigned to R_{Sn} for both molecules while confirming the 1*R*,2*S*,5*R* configuration of their (−)-menthyl ligand. ORTEP[57] drawings of the two molecules 1 and 2 (different perspectives) in the asymmetric unit are shown in Figure 4 along with the adopted numbering scheme (the first digit of the atom numbering refers to the respective molecule and will be omitted in the following discussion). Selected bond distances and angles are summarized in Table IX.

The molecular structure of **4** shows the solid-state structure of the organotin bromide matching with the structure determined in solution. In a distorted trigonal bipyramidal coordination geometry, the pentacoordinate tin atom is surrounded by the carbon atoms of the organo ligands in the equatorial positions and by the bromine and nitrogen atoms in the axial positions. The flat, bidentate aminonaphthyl ligand forms a five-membered chelate ring, which bridges an equatorial and an axial coordination site. Its bite angle N–Sn–C20 of 74.3(4)° [72.3(4)°] (molecule 1 [molecule 2]) differs widely from the angle in an ideal trigonal bipyramidal array (90°). Likewise, the N–Sn–Br arrangement deviates from linearity, featuring an angle N–Sn–Br of 168.1(2)° [168.1(3)°]. With a sum of the three equatorial C–Sn–C angles

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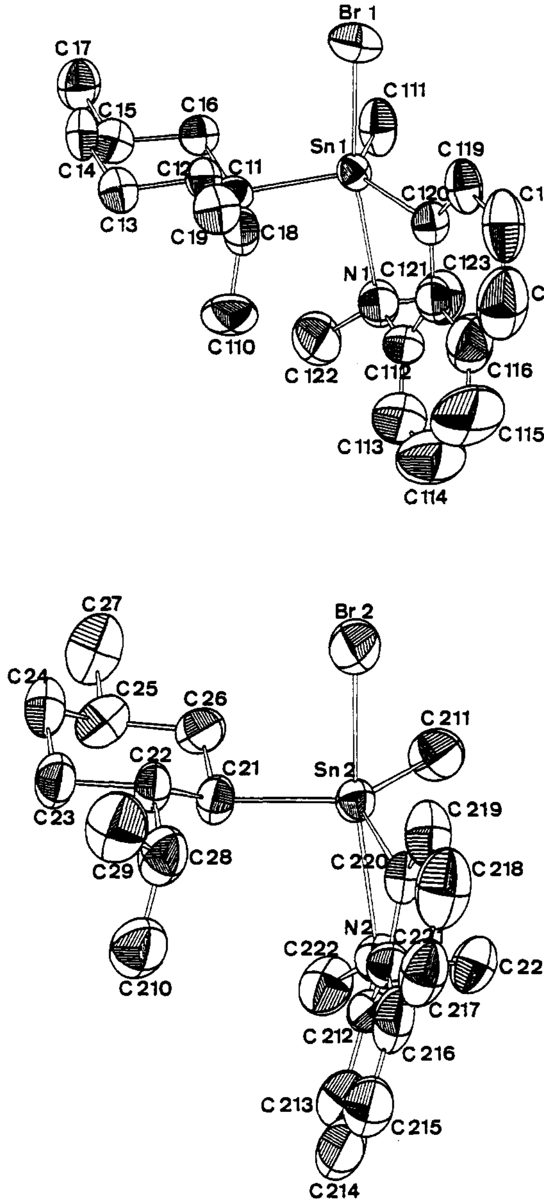

Figure 4. ORTEP drawings of [8-(dimethylamino)naphthyl]-(−)-menthylmethyltin bromide (4) (upper molecule 1, lower molecule 2). Hydrogen atoms are omitted for clarity.

Table IX. Selected Bond Distances and Bond Angles for 4[a,b]

	molecule 1	molecule 2
	Bond Distances, Å	
Sn–N	2.55(1)	2.55(1)
Sn–C1	2.19(1)	2.16(1)
Sn–C11	2.11(2)	2.13(1)
Sn–C20	2.13(1)	2.18(1)
Sn–Br	2.641(2)	2.630(2)
	Bond Angles, deg	
N–Sn–C1	93.6(4)	93.8(4)
N–Sn–C11	88.1(5)	89.5(5)
N–Sn–C20	74.3(4)	72.3(4)
N–Sn–Br	168.1(2)	168.1(3)
C1–Sn–C11	110.9(5)	112.6(6)
C1–Sn–C20	119.8(5)	121.0(4)
C1–Sn–Br	95.8(3)	95.7(3)
C11–Sn–C20	126.7(5)	123.9(5)
C11–Sn–Br	95.4(4)	93.4(4)
C20–Sn–Br	94.6(4)	96.6(3)
Sn–C20–C19	125(1)	119(1)
Sn–C20–C21	115.7(9)	116(1)
C19–C20–C21	119(1)	124(1)
N–C12–C21	114(1)	115(1)
N–C12–C13	124(2)	124(1)
C21–C12–C13	121(2)	121(1)

[a] Estimated standard deviations are given in parentheses. [b] Sn is Sn1 for molecule 1 and Sn2 for molecule 2, C1 is C11 for molecule 1 and C21 for molecule 2, etc.; see Figure 4.

of 357.4° [357.5°], the SnC_3 unit does not show planarity. The tin atom is displaced by 0.19 Å [0.21 Å] out of the equatorial plane toward the bromine, onto the side opposite the attacking nitrogen atom. This geometry corresponds to an intermediate stage of the S_N2 reaction pathway of a nucleophilicly attacked triorganotin halide during its passage from a monocapped tetrahedron to an ideal trigonal bipyramid as deduced by Britton and Dunitz from crystallographic evidence.[58]

The Sn–N distance is 2.55(1) Å [2.55(1) Å]. It is longer than the sum of the covalent radii of tin and nitrogen (2.15 Å),[59] yet short enough—significantly shorter than the sum of their van der Waals radii (3.75 Å)[59]—to indicate a substantial bonding interaction. This donor–acceptor interaction between the nitrogen and tin atoms is also reflected in the geometry of the 1,8-disubstituted naphthyl system. Showing angles Sn–C20–C19 and Sn–C20–C21 of 125(1)° [119(1)°] and 115.7(9)° [116(1)°] and angles N–C12–C21 and N–C12–C13 of 114(1)° [115(1)°] and 124(2)° [124(1)°], the exocyclic C–Sn and C–N bonds are bent toward each other.

The Sn–Br distance of 2.641(2) Å [2.630(2) Å] is longer than that found in gaseous, four-coordinate trimethyltin bromide (2.49(3) Å)[60] or in (4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)dimethyltin bromide (2.504(5) Å), which features just beginning pentacoordination.[61] This lengthening of the bond trans to the coordinating nitrogen atom is in agreement with the structural correlation derived by Britton and Dunitz for *trans*-SnC_3XY ensembles: the shorter the Sn–Y distance, the longer the Sn–X distance.[58]

Occupying an equatorial position in the trigonal bipyramidal arrangement of the ligands, the methyl group shows a slightly shortened Sn–C distance of 2.11(2) Å [2.13(1) Å] as compared to trimethyltin bromide (2.17(5) Å)[60] or (4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)dimethyltin bromide (2.150(22) and 2.195(24) Å).[61] The Sn–C distances of the menthyl and naphthyl ligands were determined to be 2.19(1) Å [2.16(1) Å] and 2.13(1) Å [2.18(1) Å].

The geometry of the structure of 4 compares well with those of related triorganotin bromides featuring an intramolecular Sn–N coordination. Yet, the distorted trigonal bipyramidal molecule structures found for [8-(Me_2NCH_2)-5-$(MeO)C_{10}H_5$]MePhSnBr (d_{Sn-N} = 2.401(4) Å),[13] [2-$(Me_2NCH_2)C_6H_4$]Ph_2SnBr (d_{Sn-N} = 2.511(12) Å),[1] [2-$(Me_2NCHMe)C_6H_4$]MePhSnBr (d_{Sn-N} = 2.476(7) Å),[4] [2-$(Me_2NCH^tBu)C_6H_4$]MePhSnBr (d_{Sn-N} = 2.482(5) Å [2.552(5) Å]),[6] [2-$(Me_2N)C_6H_4CH(SiMe_3)$]MePhSnBr (d_{Sn-N} = 2.492(3) Å),[8] and [8-$(Me_2N)C_{10}H_6$]MePhSnBr (d_{Sn-N} = 2.496(6) Å)[9] almost all show shorter Sn–N distances. In the 8-[(dimethylamino)methyl]naphthyl derivative the formation of a puckered six-membered chelate ring enables the tin and nitrogen atoms to come especially close. The 2-[(dimethylamino)methyl]phenyl, [2-(dimethylamino)phenyl]methyl, and 8-(dimethylami-

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no)naphthyl derivatives form puckered or planar five-membered chelate rings with Sn–N distances in the upper range of which the distance observed for 4 was found—presumably due to the bulkiness of the menthyl ligand. A diastereomeric purity, as observed for crystalline 4, has also been described for the C,Sn-chiral [2-[1-(*S*)-(dimethylamino)ethyl]phenyl]methylphenyltin bromide, crystallization of which results in resolution of its S_{Sn} diastereomer.[4]

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Supplementary Material Available: Tables listing all bond distances and angles, anisotropic thermal parameters, and hydrogen positions of both molecules of 4 in the asymmetric unit (6 pages). Ordering information is given on any current masthead page.

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