A Bromine Adduct of 2,3,6,7,14,15-Hexamethyl-9,10-distibatriptycene. The First Stibonium–Stiborate Zwitterion

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2,3,6,7,14,15-Hexamethyl-9,10-distibatriptycene (**3**) reacted with bromine to give an adduct **4** with the composition of $\mathbf{3}\cdot 2Br_2$. X-ray structure analysis and ^{1}H NMR studies revealed that the bromine adduct **4** forms an intramolecular salt composed of a tetracoordinate bromostibonium ion moiety, R_3SbBr^+, and a hexacoordinate tribromostiborate ion moiety, $R_3SbBr_3^-$, both in the crystalline state and in solution.

Triptycene analogs with Group-15 elements (N, P, As, Sb, and Bi) at the two bridgehead positions have been reported in the literature, but their chemistry are hardly known because of the synthetic difficulty and the insolubility of reaction products.[1] 9,10-Distibatriptycene (**1**) was first synthesized in 1985 by the reaction of *o*-phenylenemercury with Sb powder,[2] but its reactivity has not been explored.

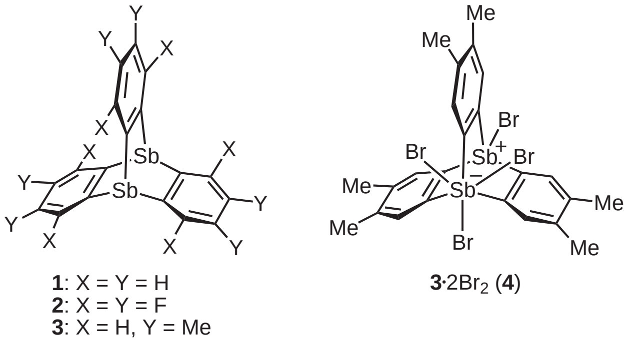
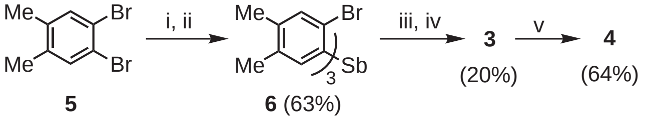


Chart 1.

The only reported reaction is the chlorination of perfluoro-9,10-distibatriptycene (**2**).[3] The authors claimed to have obtained an adduct $\mathbf{2}\cdot 2Cl_2$, but poorly elucidated the structure because of facile hydrolysis of the adduct. We have been interested in reactions, especially those with halogens, of **1** and its derivatives, and found that 2,3,6,7,14,15-hexamethyl-9,10-distibatriptycene (**3**) is a suitable target compound. We report here the synthesis of **3**, the bromination of **3** to give an adduct $\mathbf{3}\cdot 2Br_2$ (**4**), X-ray crystallography of **3** and **4**, and dynamic behavior of **4** in solution.



Reagents and conditions: i) *n*-BuLi (1.0 equiv.), THF–Et_2O (1:1), −110 °C, ii) $SbCl_3$ (0.33 equiv.), iii) *t*-BuLi (6.0 equiv.), THF, −78 °C, iv) $SbBr_3$ (1.0 equiv.), v) Br_2 (2.2 equiv.), CH_2Cl_2, 0 °C.

Scheme 1.

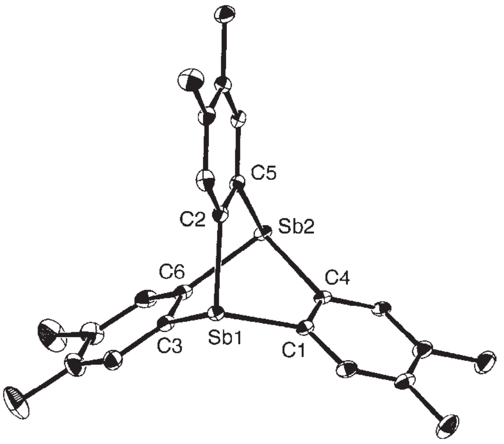


Figure 1. ORTEP drawing of **3**. Hydrogen atoms and C_6F_6 are omitted for clarity. Selected bond lengths (Å) and angles (°): Sb1–C1, 2.151(2); Sb1–C2, 2.149(2); Sb1–C3, 2.156(3); C1–Sb1–C2, 95.4(1); C1–Sb1–C3, 93.6(1); C2–Sb1–C3, 94.1(1); C4–C1–Sb1, 121.7(2); C5–C2–Sb1, 122.3(2); C6–C3–Sb1, 122.0(2); Sb2–C4, 2.154(3); Sb2–C5, 2.150(2); Sb2–C6, 2.151(2); C4–Sb2–C5, 93.7(1); C4–Sb2–C6, 94.0(1); C5–Sb2–C6, 94.6(1); C1–C4–Sb2, 122.5(2); C2–C5–Sb2, 122.2(2); C3–C6–Sb2, 122.7(2); Sb1···Sb2, 3.692.

The synthetic procedures are shown in Scheme 1. The reaction of 4,5-dibromo-*o*-xylene (**5**)[4] with *n*-BuLi at −110 °C and then with $SbCl_3$ gave tris(2-bromo-4,5-dimethylphenyl)stibine (**6**).[5] Compound **6** was treated with *t*-BuLi and then with $SbBr_3$ to afford the 9,10-distibatriptycene **3**[6] in 20% yield.

The X-ray molecular structure of **3** crystallized from C_6F_6 is shown in Figure 1.[7] The molecule has a nearly D_{3h} geometry. The Sb–C bond lengths and C–Sb–C angles are 2.152 Å and 94.2°, respectively, in average.

Treatment of **3** with bromine gave an adduct **4** with the composition of $\mathbf{3}\cdot 2Br_2$. The adduct **4** showed good solubility in common organic solvents and high stability toward air and moisture.[8]

The X-ray molecular structure of **4** recrystallized from $CHCl_3$–mesitylene (1:5) is shown in Figure 2.[9] One of the antimony atoms, Sb1, bonds to three Br atoms, constituting a hexacoordinate tribromostiborate ion structure. The average C–Sb1–C and *trans*-C–Sb1–Br angles are 94.9° and 173.4° respectively, indicating that Sb1 has a slightly distorted octahedral geometry. It is noted that the pyramidality around Sb1 atom is almost the same as that observed in **3**. The other antimony atom, Sb2, bonds to one Br atom, resulting in a tetracoordinate bromostibonium ion structure with a slightly distorted tetrahedral geometry. The average C–Sb2–C and C–Sb2–Br angles are 103.7° and 111.2°, respectively. The Sb2 moiety forms a flatter pyramid

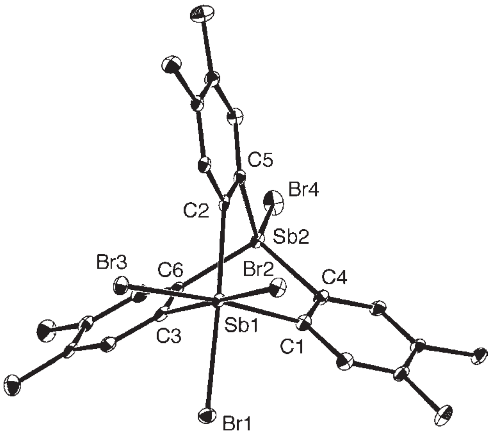
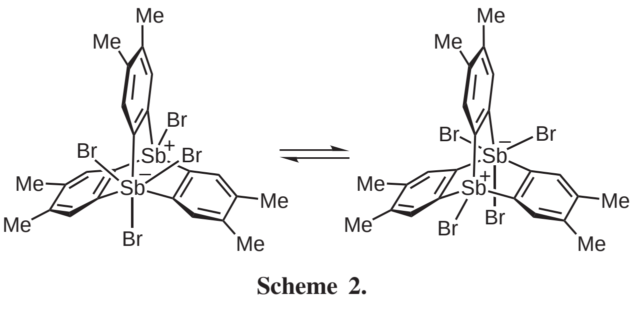


Figure 2. ORTEP drawing of **4**. Hydrogen atoms and $CHCl_3$ are omitted for clarity. Selected bond lengths (Å) and angles (°): Sb1–C1, 2.190(3); Sb1–C2, 2.213(3); Sb1–C3, 2.200(3); Sb1–Br1, 2.6691(4); Sb1–Br2, 2.6339(4); Sb1–Br3, 2.6359(4); C1–Sb1–Br1, 173.6(1); C2–Sb1–Br2, 172.0(1); C3–Sb1–Br3, 174.6(1); C1–Sb1–C2, 92.9(1); C1–Sb1–C3, 95.6(1); C2–Sb1–C3, 96.3(1); C4–C1–Sb1, 121.5(2); C5–C2–Sb1, 123.1(2); C6–C3–Sb1, 121.5(2); Sb2–Br4, 2.4066(4); Sb2–C4, 2.096(3); Sb2–C5, 2.086(3); Sb2–C6, 2.080(3); C4–Sb2–C5, 100.5(1); C4–Sb2–C6, 105.0(1); C5–Sb2–C6, 105.7(1); C4–Sb2–Br4, 108.4(1); C5–Sb2–Br4, 116.8(1); C6–Sb2–Br4, 108.4(1); C1–C4–Sb2, 114.8(2); C2–C5–Sb2, 113.2(2); C3–C6–Sb2, 113.4(2); Sb1···Sb2, 3.426.

than in **3** to result in the smaller Sb···Sb distance in **4** (3.43 Å) than in **3** (3.69 Å).

The Sb2–Br bond (2.407 Å) is considerably smaller than the Sb1–Br bonds (2.65 Å in average), reflecting the onium character in the tetracoordinate moiety: The Sb1–Br bond length is comparable with that of dibromotriphenylstiborane (2.63–2.64 Å),[10] where the bromine atoms are in the apical positions of a pentacoordinate trigonalbipyramid structure.

^1H NMR spectra of **4** in CD_2Cl_2 at 27 °C showed two singlets at δ 2.34 and 7.87 in a 3:1 ratio assigned to the methyl and aromatic protons, respectively. Upon lowering the temperature, each singlet broadened and split into two equally intense singlets. At −93 °C, the methyl signals appeared at δ 2.20 and 2.29, and the aromatic signals at δ 7.20 and 8.35. This lineshape change could be most reasonably explained in terms of the interchange between the two topomeric structures as shown in Scheme 2. The topomerization rate depended on the concentration of **4**,[11] indicating the intermolecularity of the bromide ion shifts, though the detailed mechanism awaits further study.



Scheme 2.

Compound **4** is the first example of a tetracoordinate bromostibonium ion observed in the crystalline state, and also of a stibonium–stiborate zwitterion. Studies on reactions of **3** with other halogens are in progress.

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References and Notes

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5 Tris(2-bromo-4,5-dimethylphenyl)stibine (**6**): white solids (from AcOEt), mp 251–252 °C (dec). Anal. Found: C, 42.74; H, 3.80%. Calcd for $C_{24}H_{24}Br_3Sb$: C, 42.77; H, 3.59%, ^1H NMR (300 MHz, $CDCl_3$) δ 2.05 (9H, s), 2.23 (9H, s), 6.77 (3H, s), 7.36 (3H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.4, 19.5, 129.4, 132.8, 136.5, 138.2, 139.8, 139.9. MS (70 eV) m/z 670 (M^+, 100%).
6 2,3,6,7,14,15-Hexamethyl-9,10-distibatriptycene (**3**); white solids (from benzene), mp 285–290 °C (dec). Anal. Found: C, 52.00; H, 4.46%. Calcd for $C_{24}H_{24}Sb_2$: C, 51.85; H, 4.35%. ^1H NMR (300 MHz, $CDCl_3$) δ 2.18 (18H, s), 7.81 (6H, s). ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.4, 136.8, 137.6, 146.0. MS (70 eV) m/z 554 (M^+, 13%), 226 (100%).
7 Crystal data of **3**: $C_{24}H_{24}Sb_2\cdot 0.5C_6F_6$, fw 648.96, monoclinic, $C2/c$, $a = 26.4096(10)$ Å, $b = 10.1131(1)$ Å, $c = 20.5028(9)$ Å, $\beta = 116.9319(5)°$, $V = 4882.1(3)$ Å^3, $Z = 8$, $D_{calcd} = 1.766\ g\cdot cm^{-3}$, Temp = −160 °C, $R1 = 0.0273$ for all data, $wR2 = 0.0660$ for all 5283 unique reflections (295 parameters), GOF = 1.081. CCDC No. 269390.
8 The bromine adduct **4**: yellow solids (washing with hexane), mp 203–204 °C (dec). Anal. Found: C, 33.20; H, 3.02%. Calcd for $C_{24}H_{24}Br_4Sb_2$: C, 32.92; H, 2.76%. ^1H NMR (300 MHz, CD_2Cl_2, 27 °C) δ 2.34 (18H, s), 7.87 (6H, s); ^{13}C NMR (75 MHz, CD_2Cl_2, 27 °C) δ 20.0, 134.5, 138.1, 142.3. MS (70 eV) m/z 795 (M − Br, 80%), 312 ($(C_6H_2(CH_3)_2)_3$, 100%).
9 Crystal data of **4**: $C_{24}H_{24}Br_4Sb_2\cdot CHCl_3$, fw 994.94, monoclinic, $P2_1/n$, $a = 11.0798(4)$ Å, $b = 18.9219(7)$ Å, $c = 14.3459(8)$ Å, $\beta = 100.1844(8)°$, $V = 2960.2(2)$ Å^3, $Z = 4$, $D_{calcd} = 2.232\ g\cdot cm^{-3}$, Temp = −160 °C, $R1 = 0.0271$ for all data, $wR2 = 0.0755$ for all 5973 unique reflections (313 parameters), GOF = 1.063. CCDC No. 269391.
10 M. J. Begley and D. B. Sowerby, *Acta Crystallogr.*, **C49**, 1044 (1993); M. Weber, *Acta Crystallogr.*, **C54**, 570 (1998).
11 The rate constants obtained by lineshape analysis (DNMR3[12]) in CD_2Cl_2 at −83 °C are 52, 83, and 113 s^{-1} for 2.63, 5.72, 10.8 M solutions, respectively. The $\Delta G^{\ddagger}$ values are 9.47, 9.29, and 9.17 kcal mol^{-1}, respectively.
12 D. A. Kleier and G. Binsch, QCPE Program No. 165.