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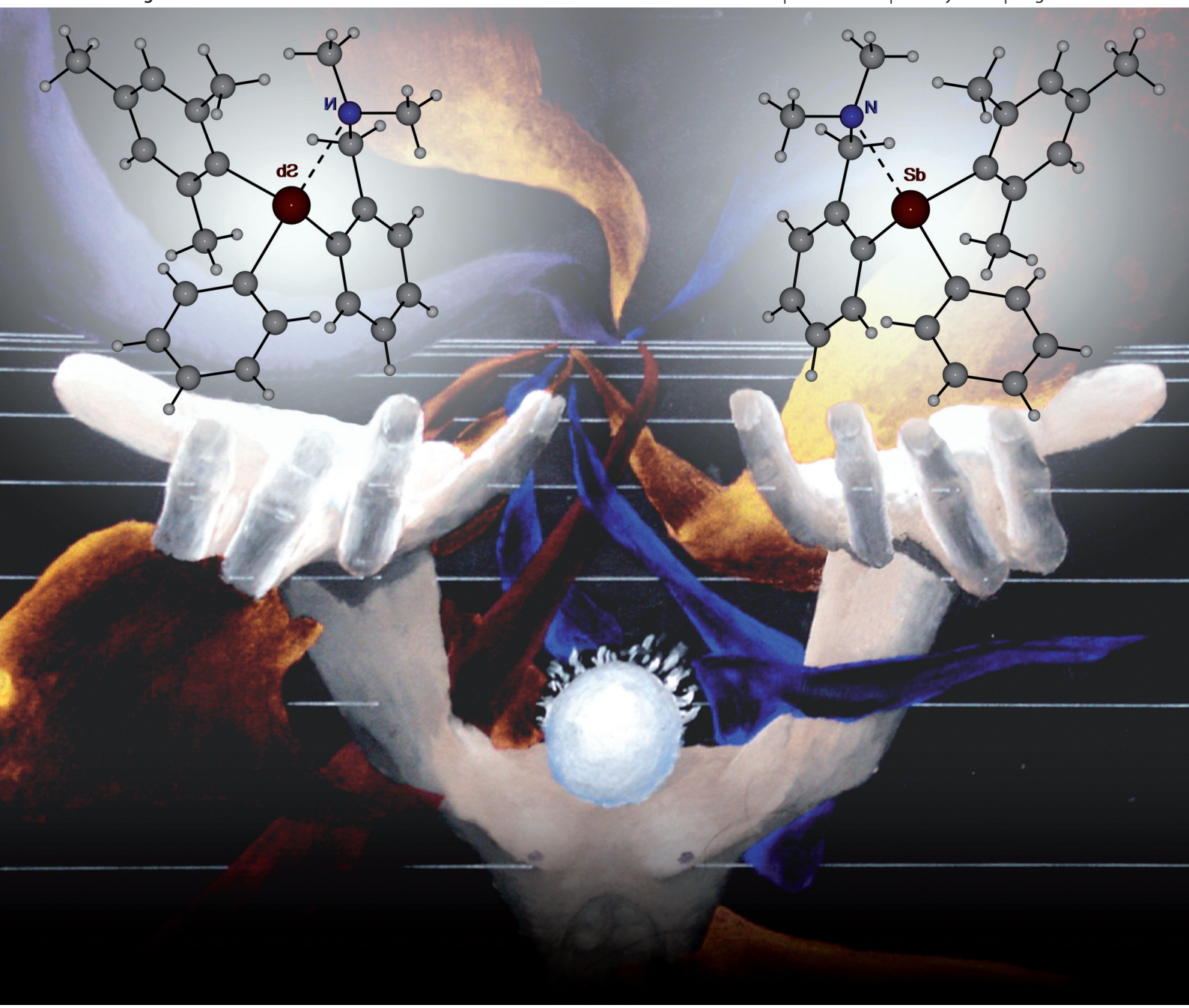

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New chiral organoantimony(III) compounds containing intramolecular N → Sb interactions – solution behaviour and solid state structures†

Dana Copolovici,[a] Vilma R. Bojan,[a] Ciprian I. Raţ,[a] Anca Silvestru,[a] Hans J. Breunig[b] and Cristian Silvestru*[a]

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Hypervalent organoantimony(III) compounds of the type [2-(Me_2NCH_2)C_6H_4]PhSbCl (**1**), [2-(Me_2NCH_2)C_6H_4]MesSbBr (**7**) and [2-(Me_2NCH_2)C_6H_4]$_n$$Ar_{3-n}$Sb [$n$ = 1, Ar = Ph (**4**), Mes (**9**); n = 2, Ar = Ph (**5**), Mes (**10**)] were prepared *via* salt elimination reactions between [2-(Me_2NCH_2)C_6H_4]Li and MesMgBr and Ph_nSbCl_{3-n}, [2-(Me_2NCH_2)C_6H_4]$SbBr_2$ or [2-(Me_2NCH_2)C_6H_4]$_n$$SbCl_{3-n}$ (n = 1, 2), in appropriate molar ratios. Halogen exchange reactions with aqueous KBr or KI gave [2-(Me_2NCH_2)C_6H_4]ArSbX [Ar = Ph, X = Br (**2**), I (**3**); Ar = Mes, X = I (**8**)]. Metathesis reaction between **1** and MesMgBr affords [2-(Me_2NCH_2)C_6H_4]PhMesSb (**6**). Compounds **1–10** were investigated by means of NMR (^{1}H, ^{13}C) in solution and by mass spectrometry. The investigation of the molecular structures of **2–8** by single-crystal X-ray diffraction revealed that the nitrogen atoms of the pendant CH_2NMe_2 arms are strongly coordinated to the antimony atoms. All compounds exhibit chirality and crystallize as racemic mixtures.

Introduction

Chiral organostibanes were obtained and their structures investigated in the last decade because they are of considerable interest as potential chiral sources for the inductive generation of optical activity.[1-14] One group of chiral organostibanes are compounds where three different substituents are bonded to antimony, *e.g.* compounds of the type RR′SbX (**Ia** and **Ib** in Fig. 1). These stibanes can be named "*Sb*-chiral" compounds. Other types of chirality occur with pendant arm ligands like the 2-(dimethylaminomethyl)phenyl group, which is able to coordinate not only through the carbon center but also through the pendant amino moiety (*C*,*N*-ligand). This intramolecular coordination of the nitrogen atom to antimony induces chirality at the Sb centre even when the other two substituents are the same ("chelate-induced-*Sb*-chiral" compounds, *e.g.* **IIa** and **IIb** in Fig. 1). A third type of chirality appears when one atom of the resulting chelate ring is out of the plane described by the remaining atoms [compounds with "chiral planarity", the C(1)–C(6) aromatic ring and the N(1) atom being the chiral plane and pilot atom, respectively] (**IIIa** and **IIIb** in Fig. 1).[15]

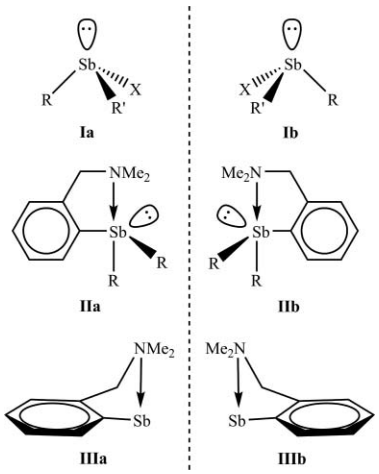


Fig. 1 Chirality in organoantimony(III) compounds.

Known examples of chiral antimony derivatives containing the 2-(dimethylaminomethyl)phenyl group [R] are: R[($Me_3Si)_2$CH]SbCl, R[($Me_3Si)_2$CH]SbH, R[($Me_3Si)_2$CH]Sb–Li·2THF (THF = tetrahydrofuran), R[($Me_3Si)_2$CH]Sb–Na·TMEDA (TMEDA = tetramethylethylenediamine),[10] R_2SbX (X = Cl,[2] Br, I[11]), $RSbX_2$ (X = Cl, Br, I),[11] $R_2SbI{\cdot}HI$,[11] *cyclo*-R_4Sb_4, $RSb[W(CO)_5]_2$, $(RSbCl)_2E$ [E = O, S], $(RSbI)_2O$, $(RSbBr)_2S$, *cyclo*-$(RSbE)_n$ [E = O, n = 3, E = S, n = 2],[12] and the ionic species $[R_3SbOH]^+[I_3]^-$.[11]

We report here the synthesis and characterisation of [2-(Me_2NCH_2)C_6H_4]ArSbX [Ar = Ph, X = Cl (**1**), Br (**2**), I (**3**); Ar = Mes, X = Br (**7**), I (**8**)], [2-(Me_2NCH_2)C_6H_4]$_n$$Ar_{3-n}$Sb [$n$ = 1, Ar = Ph (**4**), Mes (**9**); n = 2, Ar = Ph (**5**), Mes (**10**)] and [2-(Me_2NCH_2)C_6H_4]PhMesSb (**6**).

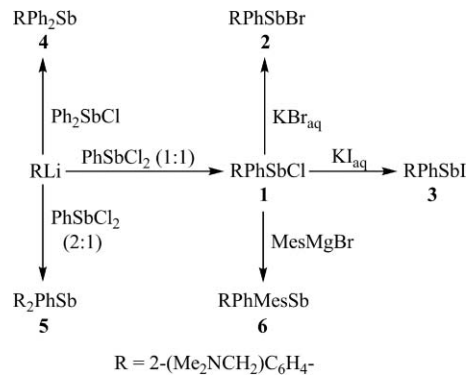
[a]*Facultatea de Chimie si Inginerie Chimica, Universitatea Babes-Bolyai, RO-400028, Cluj-Napoca, Romania. E-mail: cristi@chem.ubbcluj.ro; Fax: (+40) 264-590818; Tel: (+40) 264-593833*
[b]*Institut für Anorganische und Physikalische Chemie, Universität Bremen, D-28334, Bremen, Germany. E-mail: hbreunig@uni-bremen.de; Fax: (+49) 421-21862809; Tel: (+49) 421-21863150*

† Electronic supplementary information (ESI) available: X-ray crystallographic data in CIF format for **2–8**; figures representing the molecular structure and supramolecular architectures in the crystals of compounds **2–8**; variable temperature ^{1}H NMR data for compounds **1** (in C_6D_6, DMSO-d_6) and **7** (in DMSO-d_6); ^{1}H and ^{13}C NMR data for compound **9** (in C_6D_6). CCDC reference numbers 752088 (**2**), 752089 (**3**), 752092 (**4**), 752087 (**5**), 752091 (**6**), 752086 (**7**) and 752090 (**8**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c003318a

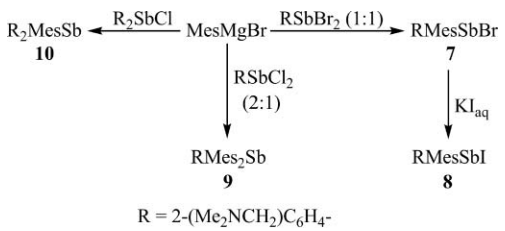
Results and discussion

Synthesis

The preparative pathways leading to compounds **1–10** are shown in Schemes 1 and 2. The chloride **1** and the heteroleptic stibines **4** and **5** were obtained by reacting stoichiometric amounts of $PhSbCl_2$ or Ph_2SbCl with [2-(Me_2NCH_2)C_6H_4]Li. Reaction of **1** with the organolithium reagent gave the stibine **6**. Similar reactions between $RSbCl_2$ or R_2SbCl [R = 2-(Me_2NCH_2)C_6H_4] and MesMgBr afforded the related mixed triarylstibines **9** and **10**. The bromide **7** was obtained from $RSbBr_2$ and MesMgBr. Attempts to prepare the corresponding chloride from $RSbCl_2$ and the Grignard reagent failed and only the same bromide **7** was isolated as result of *in situ* halogen scrambling with the inorganic magnesium salt. The halides **2**, **3** and **8** were prepared using exchange of the halogen in the presence of KBr or KI, according to similar published procedures.[11]



Scheme 1 Preparation of compounds **1–6**



Scheme 2 Preparation of compounds **7–10**

The compounds were obtained as air-stable, colourless and yellow (**3** and **8**) crystalline solids, which melt without decomposition. They are soluble in common organic solvents, such as chloroform, methylene chloride or benzene as well as in DMSO. MS and NMR data of **1–10** as well as elemental analytical data are consistent with the anticipated formulae. Characteristic ions, including the molecular ion except for the iodides **3** and **8**, are present in the mass spectra, which contain [RArSb$^+$] (for **1–4**, **6–9**) and [R_2Sb^+] (for **5** and **10**) (R = $Me_2NCH_2C_6H_4$; Ar = Ph, Mes) as the base peak.

Chiral diorganoantimony(III) halides, RR′SbX

Single crystals of the title halides, suitable for X-ray diffraction studies were obtained from $CHCl_3$–hexane (for **2** and **3**), slow evaporation of a hexane solution (for **7**) and CH_2Cl_2–hexane (for **8**). The molecular structures are shown in Fig. 2–4 (see also ESI†) and selected interatomic distances and angles are listed in Table 1.

Table 1 Selected bond distances (Å) and angles (°) for compounds **2**, **3**, **7** and **8**

	2	**3**	**7**	**8**
Sb(1)–C(1)	2.150(4)	2.152(4)	2.149(4)	2.156(4)
Sb(1)–C(10)	2.146(5)	2.154(4)	2.167(4)	2.166(4)
Sb(1)–X(1)	2.6977(6)	2.9870(4)	2.7016(6)	2.9496(5)
Sb(1)–N(1)	2.444(4)	2.426(3)	2.468(4)	2.456(4)
C(1)–Sb(1)–C(10)	96.90(17)	97.28(14)	105.55(15)	103.44(17)
C(1)–Sb(1)–X(1)	93.47(12)	93.00(10)	93.35(12)	93.88(12)
C(10)–Sb(1)–X(1)	90.46(12)	88.67(10)	89.69(10)	91.70(12)
N(1)–Sb(1)–C(1)	75.57(15)	75.15(13)	74.79(15)	74.31(14)
N(1)–Sb(1)–C(10)	88.88(15)	86.75(13)	88.06(14)	87.42(15)
N(1)–Sb(1)–X(1)	168.85(9)	166.62(8)	166.82(10)	167.57(9)
C(7)–N(1)–C(8)	110.8(5)	111.0(3)	110.1(4)	110.8(4)
C(7)–N(1)–C(9)	112.2(5)	111.2(3)	111.5(5)	110.7(4)
C(8)–N(1)–C(9)	108.5(5)	109.1(4)	109.6(4)	109.5(4)
Sb(1)–N(1)–C(7)	106.3(3)	104.9(2)	104.2(3)	103.4(3)
Sb(1)–N(1)–C(8)	102.8(3)	105.6(3)	105.2(3)	106.2(3)
Sb(1)–N(1)–C(9)	115.8(3)	115.0(3)	115.9(3)	116.1(3)

X = Br for **2** and **7**, and I for **3** and **8**.

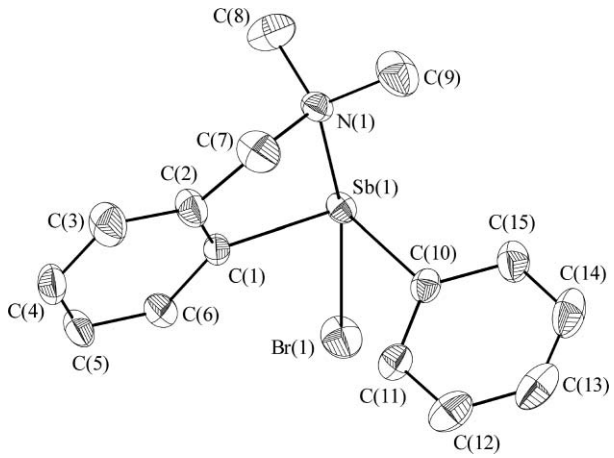


Fig. 2 ORTEP representation at 30% probability and atom numbering scheme for (S_N,C_{Sb})-**2** isomer. Hydrogen atoms are omitted.

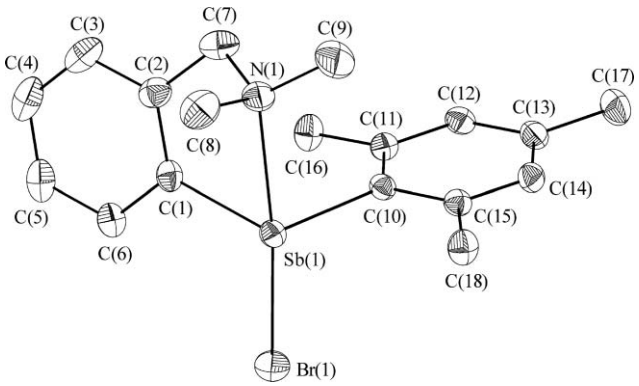


Fig. 3 ORTEP representation at 30% probability and atom numbering scheme for (R_N,C_{Sb})-**7** isomer. Hydrogen atoms are omitted.

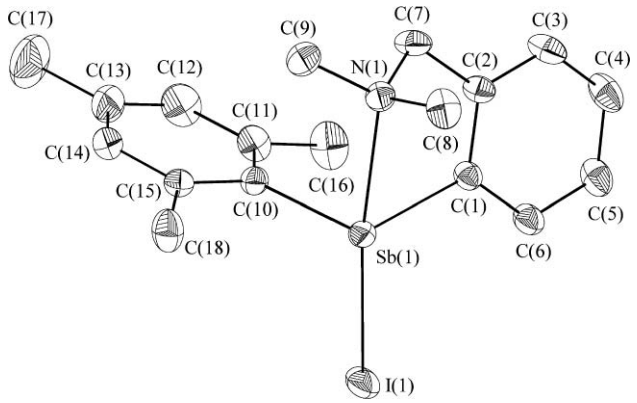


Fig. 4 ORTEP representation at 30% probability and atom numbering scheme for (S_N,A_{Sb})-**8** isomer. Hydrogen atoms are omitted.

The crystals of the halides **2**, **3**, **7** and **8** contain discrete monomers, with no unusual intermolecular distances shorter than the sum of the van der Waals radii between heavy atoms. In all these molecules the nitrogen atoms of the pendant arm are strongly coordinated to the metal *trans* to the halogen atom [N(1)–Sb(1)–X(1) 168.85(9), 166.62(8), 166.82(10) and 167.57(9)° for **2**, **3**, **7** and **8**, respectively]. The value of Sb(1)–N(1) distance [Sb(1)–N(1) 2.444(4), 2.426(3), 2.468(4) and 2.456(4) Å for **2**, **3**, **7** and **8**, respectively] is of the same magnitude as the Sb–N distances in the *trans*-N–Sb–X system of the monohalides $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbX$ [2.423(3) and 2.417(3) Å for X = Br and I, respectively].[11]

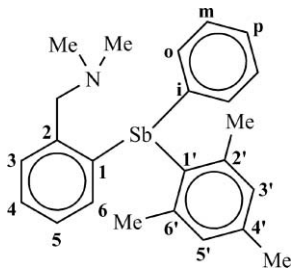
The Sb–halogen bond distances [Sb(1)–Br(1) 2.6977(6) and 2.7016(6) Å for **2** and **7**; Sb(1)–I(1) 2.9870(4) and 2.9496(5) Å for **3** and **8**, respectively] are significantly shorter compared to those found in $[2\text{-}(Me_2NCH_2)C_6H_4]_2SbX$ [Sb(1)–Br(1) 2.7775(8) Å; Sb(1)–I(1) 3.0105(5) Å].[11] However, as expected for a σ*-orbital bonding model,[2,10] the Sb–halogen bonds in **2**, **3**, **7** and **8** are considerably elongated with respect to those observed for the related monomeric Ph_2SbX [Sb–Br 2.553(1) Å;[16] Sb–I 2.771(1) Å[17]].

The antimony centre in all four halides achieves a distorted *pseudo*-trigonal-bipyramidal environment [$SbC(C,N)X$ core], with two carbon atoms in the equatorial sites, while the halogen and the nitrogen atoms are in the axial positions. The compounds can be described as hypervalent 10-Sb-4 species.[18,19]

Since three different substituents are attached to the metal centre these halides belong to the "*Sb*-chiral" class of compounds (see Fig. 1). The five-membered SbC_3N ring formed through intramolecular coordination of the nitrogen atom is folded along the $Sb\cdots C_{methylene}$ axis, with the nitrogen atom lying out of the best plane defined by the residual SbC_3 fragment. This folding induces planar chirality (with the aromatic ring and the nitrogen atom as chiral plane and pilot atom, respectively; isomers given as S_N and R_N).[15] Taking into account this intramolecular N → Sb coordination the chirality at the antimony atom in the *pseudo*-trigonal bipyramidal environment can be described in term of C_{Sb} and A_{Sb} isomers.[20] This description was preferred instead of R_{Sb}/S_{Sb} isomers for better comparison with the situation observed for the chiral triarylantimony(III) described in the subsequent discussion. The title halides crystallize as 1 : 1 mixtures of (R_N,A_{Sb}) and (S_N,C_{Sb}) isomers for **2** and **3**, and (R_N,C_{Sb}) and (S_N,A_{Sb}) isomers for **7** and **8**.

A closer check of the crystal packing of the halides **2**, **3**, **7** and **8** revealed several halogen–hydrogen contacts shorter than the sum of the corresponding van der Waals radii [*cf.* $\sum r_{vdW}$(Br,H) 3.15 Å, $\sum r_{vdW}$(I,H) 3.35 Å][21] as well as C–H$\cdots\pi$ ($Ph_{centroid}$) distances shorter than 3.10 Å which suggest some π interaction between a hydrogen atom and an aromatic ring. These result in supramolecular architectures, *i.e.* layer of alternating chain polymers built from (S_N,C_{Sb})-**2** and (R_N,A_{Sb})-**2** isomers, respectively, with no further contacts between parallel layers; chain polymer association of alternating (S_N,C_{Sb})-**3** and (R_N,A_{Sb})-**3** isomers with no further contacts between parallel chains; columnar polymer association of the $(R_N,C_{Sb})/(S_N,A_{Sb})$-**7** dimer units, or a 3D structure built from alternating chain polymers of (R_N,C_{Sb})-**8** and (S_N,A_{Sb})-**8** isomers, respectively (for details, see ESI†).

The solution behaviour of the halides **1–3**, **7** and **8** was investigated by NMR spectroscopy. The assignment of the signals in ^1H and ^{13}C NMR spectra was based on the 2D NMR spectra according to the numbering scheme shown in Scheme 3.



Scheme 3 Numbering scheme for NMR resonance assignments

For all compounds the ^1H NMR spectra at room temperature in $CDCl_3$ exhibit two sharp singlet resonances for the NMe_2 and an AB system for the CH_2 protons of the pendant arm. This indicates a similar structure as observed in the solid state by X-ray diffraction, *i.e.* the nitrogen atoms are coordinated to antimony and the configurations at Sb are stable at room temperature in $CDCl_3$ solution.

In order to study dynamic processes variable temperature NMR study was performed for chloride **1** in various solvents. While the AB system for the CH_2 protons remained unaffected, the two singlets for the methyl protons of the dimethylamino group showed coalescence at 65 °C in C_6D_6 solution (calculated $\Delta G‡ =$ 16.6 kcal mol^{-1}).[22] This process corresponds to the dissociation–recoordination between the nitrogen and the antimony atoms, with inversion at a three-coordinated nitrogen atom and rotation of the $(H_2)C$–N bond.

The inversion barrier upon the Sb atom was reported to be diminished by nucleophilic solvents.[23] The room-temperature ^1H spectrum of **1** in DMSO-d_6 exhibits the same pattern of the aliphatic region as observed in $CDCl_3$ or in C_6D_6 solutions, thus suggesting a similar structure, regardless of the nature of the solvent. However, by raising the temperature, coalescence of both systems was observed at different temperatures. Thus, the two singlet resonances for the NMe_2 group showed coalescence at 50 °C (calculated $\Delta G‡ = 15.7$ kcal mol^{-1}), while the coalescence of the AB system for the CH_2 protons was achieved at 78 °C (calculated $\Delta G‡ = 17.1$ kcal mol^{-1}).

For halides **7** and **8**, the NMR data indicate an additional dynamic process due to replacement of the phenyl group on

antimony by the bulkier mesityl moiety. The ^{1}H spectra in $CDCl_3$, at room temperature, exhibit (*i*) two broad resonances for the methyl groups from positions 2′ and 6′ of the mesityl ligand (*ortho*-CH_3) in the alkyl region, in addition to the resonances for the pendant arm protons; (*ii*) a broad resonance for the protons in positions 3′ and 5′ of the mesityl group in the aromatic region. This behaviour suggests that the free rotation of the mesityl group around the Sb–$C_{mesityl}$ bond is blocked due to the coordination of the nitrogen atom from the pendant arm to antimony. This process is even better observed in the ^{1}H spectrum of **7** when recorded in DMSO-d_6. At room temperature there are five well resolved resonances in the 1 : 1 : 1 : 1 : 1 ratio of intensities for the NMe_2 groups and the three Me groups of the mesityl moiety. Moreover, in the aromatic region two singlet resonances are observed for the protons of the mesityl group. At 45 °C the coalescence of the resonances for these aromatic protons was achieved (calculated $\Delta G^{\ddagger} = 15.7$ kcal mol^{-1}), while the resonances for the pendant arm protons remain basically unchanged (see ESI†), thus suggesting a higher degree of free rotation of the mesityl group around the Sb–$C_{mesityl}$ bond.

Chiral triorganoantimony(III) compounds, RR′$_2$Sb and RR′R″Sb

Single crystals suitable for X-ray diffraction studies were obtained from hot hexane solution (for **4** and **6**) or CH_2Cl_2–hexane (for **5**). Two independent, very similar molecules **5a** and **5b** are present in the unit cell of **5** and in the subsequent discussion we will refer only to molecule **5a**. The molecular structures are shown in Fig. 5–7 (see also ESI†) and selected interatomic distances and angles are listed in Table 2.

The molecules of the triarylstibines **4–6** feature a common structural aspect, *i.e.* the nitrogen atom of a pendant arm coordinated

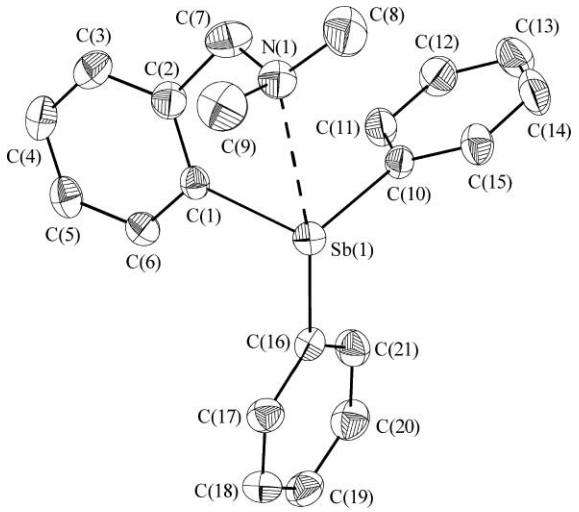


Fig. 5 ORTEP representation at 30% probability and atom numbering scheme for (R_N,C_{Sb})-**4** isomer. Hydrogen atoms are omitted.

to the metal is *trans* to the *ipso* carbon of the phenyl group attached to antimony [N(1)–Sb(1)–C(16) 163.40(12)° for **4**; N(1)–Sb(1)–C(19) 161.85(14)° for **5a**; N(1)–Sb(1)–C(19) 165.6(3)° for **6**, respectively]. These Sb(1)–N(1) distances [Sb(1)–N(1) 2.848(4), 2.920(3) and 2.923(9) Å for **4**, **5a** and **6**, respectively] are, as expected, longer than in the related monohalides. For compound **5** the molecules contain an additional longer intramolecular Sb(1)–N(2) distance [3.042(3) Å for **5a**] of the same magnitude as in [2-(Me_2NCH_2)C_6H_4]$_3$Sb [av. 3.03 Å][1] [*cf.* the sum of the corresponding covalent, $\sum r_{cov}$(Sb,N) 2.11 Å, and van der Waals radii, $\sum r_{vdW}$(Sb,N) 3.74 Å, respectively].[21] The Sb(1)–N(2) vector lies approximately *trans* to the C(1) atom of the first pendant

Table 2 Selected bond distances (Å) and angles (°) for compounds **4–6**

4		**5a**		**5b**		**6**	
Sb(1)–C(1)	2.166(4)	Sb(1)–C(1)	2.177(4)	Sb(2)–C(25)	2.184(4)	Sb(1)–C(1)	2.166(8)
Sb(1)–C(10)	2.152(4)	Sb(1)–C(10)	2.155(4)	Sb(2)–C(34)	2.158(4)	Sb(1)–C(10)	2.149(5)
Sb(1)–C(16)	2.172(4)	Sb(1)–C(19)	2.169(4)	Sb(2)–C(43)	2.157(4)	Sb(1)–C(19)	2.165(8)
Sb(1)–N(1)	2.848(4)	Sb(1)–N(1)	2.920(3)	Sb(2)–N(3)	2.948(3)	Sb(1)–N(1)	2.923(9)
		Sb(1)–N(2)	3.042(3)	Sb(2)–N(4)	3.059(3)		
C(1)–Sb(1)–C(10)	97.62(14)	C(1)–Sb(1)–C(10)	96.09(14)	C(25)–Sb(2)–C(34)	95.99(14)	C(1)–Sb(1)–C(10)	102.8(3)
C(1)–Sb(1)–C(16)	94.33(14)	C(1)–Sb(1)–C(19)	93.76(15)	C(25)–Sb(2)–C(43)	93.23(15)	C(1)–Sb(1)–C(19)	98.2(3)
C(10)–Sb(1)–C(16)	96.29(15)	C(10)–Sb(1)–C(19)	97.64(16)	C(34)–Sb(2)–C(43)	98.48(15)	C(10)–Sb(1)–C(19)	96.5(3)
N(1)–Sb(1)–C(1)	70.04(12)	N(1)–Sb(1)–C(1)	68.96(11)	N(3)–Sb(2)–C(25)	68.85(12)	N(1)–Sb(1)–C(1)	69.9(3)
N(1)–Sb(1)–C(10)	80.87(12)	N(1)–Sb(1)–C(10)	79.46(11)	N(3)–Sb(2)–C(34)	79.22(11)	N(1)–Sb(1)–C(10)	78.9(2)
N(1)–Sb(1)–C(16)	163.40(12)	N(1)–Sb(1)–C(19)	161.85(14)	N(3)–Sb(2)–C(43)	161.40(11)	N(1)–Sb(1)–C(19)	165.6(3)
		N(2)–Sb(1)–C(1)	161.16(11)	N(4)–Sb(2)–C(25)	159.60(11)		
		N(2)–Sb(1)–C(10)	67.10(10)	N(4)–Sb(2)–C(34)	66.75(10)		
		N(2)–Sb(1)–C(19)	80.78(14)	N(4)–Sb(2)–C(43)	79.37(13)		
		N(1)–Sb(1)–N(2)	113.77(9)	N(3)–Sb(2)–N(4)	115.70(9)		
C(7)–N(1)–C(8)	115.9(5)	C(7)–N(1)–C(8)	111.2(4)	C(31)–N(3)–C(32)	111.4(4)	C(7)–N(1)–C(8)	110.6(9)
C(7)–N(1)–C(9)	110.9(4)	C(7)–N(1)–C(9)	111.9(4)	C(31)–N(3)–C(33)	112.2(4)	C(7)–N(1)–C(9)	113.1(10)
C(8)–N(1)–C(9)	107.0(5)	C(8)–N(1)–C(9)	111.2(4)	C(32)–N(3)–C(33)	111.4(4)	C(8)–N(1)–C(9)	109.0(10)
Sb(1)–N(1)–C(7)	100.6(3)	Sb(1)–N(1)–C(7)	91.4(2)	Sb(2)–N(3)–C(31)	90.5(2)	Sb(1)–N(1)–C(7)	97.1(7)
Sb(1)–N(1)–C(8)	120.5(3)	Sb(1)–N(1)–C(8)	120.9(3)	Sb(2)–N(3)–C(32)	121.5(3)	Sb(1)–N(1)–C(8)	100.9(5)
Sb(1)–N(1)–C(9)	100.9(3)	Sb(1)–N(1)–C(9)	108.7(3)	Sb(2)–N(3)–C(33)	108.3(3)	Sb(1)–N(1)–C(9)	124.8(6)
		C(16)–N(2)–C(17)	111.1(4)	C(40)–N(4)–C(41)	112.1(4)		
		C(16)–N(2)–C(18)	111.4(4)	C(40)–N(4)–C(42)	110.9(4)		
		C(17)–N(2)–C(18)	110.9(4)	C(41)–N(4)–C(42)	110.9(4)		
		Sb(1)–N(2)–C(16)	86.1(2)	Sb(2)–N(4)–C(40)	85.4(2)		
		Sb(1)–N(2)–C(17)	112.3(3)	Sb(2)–N(4)–C(41)	110.9(3)		
		Sb(1)–N(2)–C(18)	122.4(3)	Sb(2)–N(4)–C(42)	123.8(3)		

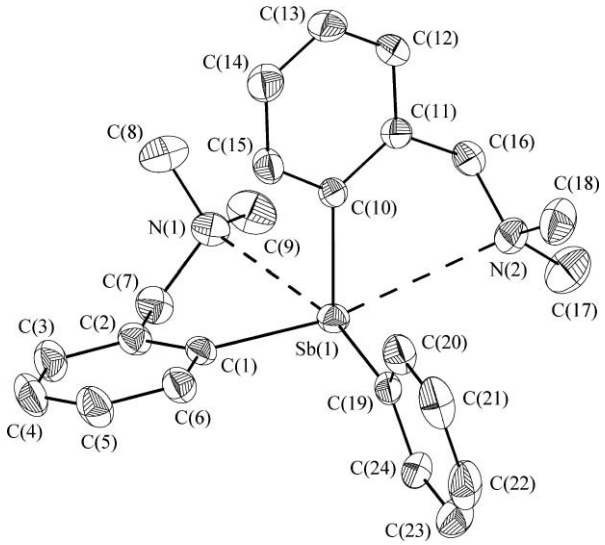


Fig. 6 ORTEP representation at 30% probability and atom numbering scheme for (R_{N1},R_{N2},A_{Sb})-**5a** isomer. Hydrogen atoms are omitted.

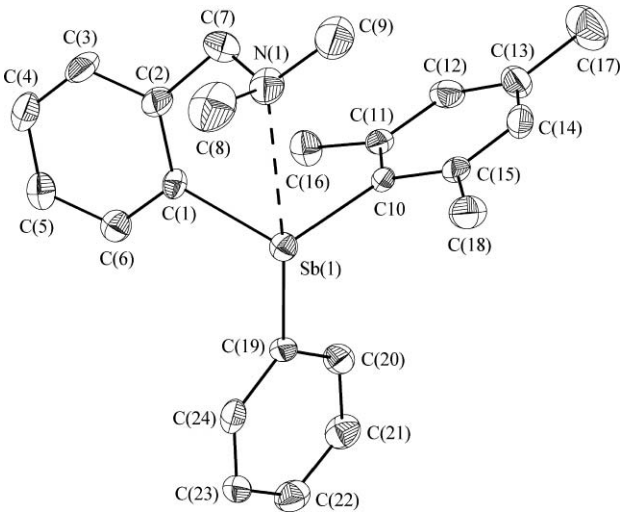


Fig. 7 ORTEP representation at 30% probability and atom numbering scheme for (R_N,A_{Sb})-**6** isomer. Hydrogen atoms are omitted.

arm ligand. A difference which should be noted is the significant increase of the C–Sb–C bond angles in the trigonal pyramidal SbC_3 skeleton when a bulky mesityl group is attached to antimony, *i.e.* in the chiral stibine **6** (see Table 2)

As in the title chiral halides, the antimony centre in **4** and **6** achieves a distorted *pseudo*-trigonal-bipyramidal environment [$SbC_2(C,N)$ core, hypervalent 10-Sb-4 species[18,19]], with two carbon atoms in the equatorial sites, and a carbon and nitrogen atom in the axial ones. In **5a**, if both intramolecular N → Sb interactions are taken into account, the overall coordination geometry around antimony can be described as distorted square pyramidal [$SbC(C,N)_2$ core; hypervalent 12-Sb-5 species[18,19]], with a carbon atom in the apical position and the nitrogen atoms in *cis* positions of the base.

The conformation of the five-membered SbC_3N rings in the triarylstibines **4–6** induces planar chirality,[15] as observed for the halides **2**, **3**, **7** and **8**. Moreover, chirality at the antimony centre of **4** and **5** is also induced, at least in solid state, since the same organic groups attached to the metal become non-equivalent as a result of the intramolecular N → Sb interactions. Thus, in **4** one phenyl group is in the equatorial position, while the other is in the axial position of the *pseudo*-trigonal-bipyramidal $SbC_2(C,N)$ core, *trans* to the nitrogen atom. The two organic ligands bearing the pendant arm are also non-equivalent in the molecule of **5a**: the aryl moiety of one ligand is placed in the apical position of the square pyramidal $SbC(C,N)_2$ core and its nitrogen atom is coordinated in the basal plane *trans* the Sb–C bond established by the other 2-$(Me_2NCH_2)C_6H_4$ group, which, subsequently, has both its carbon atom attached to the metal and its nitrogen atom in the basal plane, coordinated *trans* to the Sb–C bond established by the remaining phenyl group. Indeed, the title stibines crystallize as 1 : 1 mixtures of (R_N,C_{Sb}) and (S_N,A_{Sb}) isomers for **4**, (R_{N1},R_{N2},A_{Sb1})/(S_{N1},S_{N2},C_{Sb1})-**5a** and (R_{N3},R_{N4},A_{Sb2})/(S_{N3},S_{N4},C_{Sb2})-**5b** isomers [(with respect to the two chelate rings at a metal centre)] for **5**, and (R_N,A_{Sb}) and (S_N,C_{Sb}) isomers for **6**.

The crystal packing check for the title triarylstibines **4–6** revealed several C–H···π ($Ph_{centroid}$) distances shorter than 3.10 Å which result in supramolecular architectures, *i.e.* layers of (R_N,C_{Sb})-**4** and (S_N,A_{Sb})-**4** isomers, respectively, with no further contacts between parallel layers; chain polymer association of alternating (R_{N1},R_{N2},A_{Sb1})-**5a**/(S_{N3},S_{N4},C_{Sb2})-**5b** isomers and (S_{N1},S_{N2},C_{Sb1})-**5a**/(R_{N3},R_{N4},A_{Sb2})-**5b** isomers, respectively, with no further contacts between parallel chains; double-layer association between layers of (R_N,A_{Sb}) and (S_N,C_{Sb})-**6** isomers, respectively (for details, see ESI†).

The solution behaviour of the stibines **4–6**, **9** and **10** was investigated by NMR spectroscopy in $CDCl_3$. The assignment of the signals in ^1H and ^{13}C NMR spectra was based on the 2D NMR spectra according to the numbering scheme shown in Scheme 3.

For all these stibines the ^1H NMR spectra at room temperature in $CDCl_3$ exhibit a sharp singlet resonance for the NMe_2 protons. The spectra of compounds **4** and **9** exhibit a sharp singlet, while for compounds **5**, **6** and **10** an AB system was observed for the CH_2 protons signal of the pendant arm. The spectra exhibit only one set of ^1H or ^{13}C resonances, respectively, for the two organic groups of the same type (phenyl, mesityl or pendant arm ligand) attached to antimony in compounds **4**, **5**, **9** and **10**. Variable temperature ^1H spectra (–60 up to 45 °C) for compounds **5** and **6** in $CDCl_3$ solutions show no changes in the pattern of the signals. This suggests that dissociation of the bond between the nitrogen and antimony atoms is very fast even at this temperature. This behaviour is also supported by the presence of only one resonance for the methyl groups from positions 2′ and 6′ of the mesityl moiety (*ortho*-CH_3) in compounds **6**, **9** and **10**, indicating that free rotation around the Sb–$C_{mesityl}$ bond is allowed in these triarylstibines.

No significant changes were observed when the spectra were recorded in C_6D_6 for compounds **5** (at r.t. and 45 °C) and **9** (at r.t.) (see ESI†) in comparison with the spectra recorded in $CDCl_3$.

Conclusions

New chiral diorganoantimony(III) halides and triorganoantimony(III) compounds were prepared and characterized both in solid state and in solution. In solid state the intramolecular N → Sb interaction induces chirality at the metal centre in compounds containing two organic groups of the same type attached to

antimony. All compounds crystallize as racemates. NMR studies provided evidence for the presence of the intramolecular N → Sb interaction in the chiral halides, in solution, at room temperature. This resulted in hindered rotation around the Sb–C bond in the mesityl-containing derivatives due to steric impediments. Variable-temperature experiments revealed several dynamic processes which include the intramolecular coordination–decoordination of the nitrogen atom, configuration inversion at the metal centre and free rotation around the Sb–C bond. For the triorganostibines the NMR data suggest that dissociation of the bond between the nitrogen and antimony atoms is very fast at room temperature.

Experimental

General procedures

NMR spectra were recorded in dried solvents on BRUKER DPX 200, BRUKER Avance 300 or BRUKER AVANCE DRX 400 instruments. ^{1}H and ^{13}C chemical shifts are reported in δ units (ppm) relative to the residual peak of solvent (ref. $CHCl_3$: ^{1}H 7.26, ^{13}C 77.0 ppm; C_6H_6: ^{1}H 7.16, ^{13}C 128.06 ppm; DMSO-d_6: ^{1}H 2.50, ^{13}C 39.43 ppm). Mass spectra were recorded with FINNIGAN MAT 8200 and microOTOF-Q-Bruker spectrometers. Melting points were measured on an Electrothermal 9200 apparatus and are not corrected. Elemental analyses were performed by Facultatea de Farmacie, Universitatea de Medicina si Farmacie "Iuliu Hatieganu", Cluj-Napoca (Romania). All manipulations were carried out under an inert atmosphere of argon using Schlenk techniques. Solvents were dried and freshly distilled under argon prior to use. N,N-Dimethylbenzylamine, mesityl bromide and butyllithium (15% in hexane) were commercially available. [2-(Me_2NCH_2)C_6H_4]Li,[24] $PhSbCl_2$, Ph_2SbCl,[25] [2-(Me_2NCH_2)C_6H_4]$SbBr_2$ and [2-(Me_2NCH_2)C_6H_4]$_2$SbCl,[11] were prepared according to published methods.

Synthesis of [2-(Me_2NCH_2)C_6H_4]PhSbCl (1). [2-(Me_2NCH_2)-C_6H_4]Li (3.36 g, 24 mmol) in hexane (90 mL) was added to a cold solution (–78 °C) of $PhSbCl_2$ (6.44 g, 24 mmol) in hexane (250 mL). The reaction mixture was stirred at –78 °C for 2 h, then allowed to warm to room temperature and stirred for a further 72 h. The solvent was removed in vacuum and the remaining solid was extracted with benzene. The yellowish solution was filtered and removal of the solvent gave 6.47 g (74%) of the title compound as a white solid, mp 115 °C. Anal. Calcd. for $C_{15}H_{17}ClNSb$ (368.51): C, 48.89; H, 4.65; N, 3.80. Found: C, 48.54; H, 4.25; N, 3.72%. ^{1}H NMR (400 MHz, 20 °C, $CDCl_3$): δ 2.07 [3 H, s, $N(CH_3)_2$ (A)], 2.42 [3 H, s, $N(CH_3)_2$ (B)], AB spin system with A at 3.56 and B at 3.61 ppm (2 H, CH_2, $^{2}J_{HH}$ 14.4 Hz), 7.22 (1 H, d, H-3, C_6H_4, $^{3}J_{HH}$ 7.4 Hz), 7.31 (3 H, m, H-*meta* + *para*, C_6H_5), 7.41 (1 H, ddd, H-4, C_6H_4, $^{3}J_{HH}$ 7.4, $^{4}J_{HH}$ 1.4 Hz), 7.48 (1 H, ddd, H-5, C_6H_4, $^{3}J_{HH}$ 7.4, $^{4}J_{HH}$ 1.1 Hz), 7.52 (2 H, m, H-*ortho*, C_6H_5), 8.50 (1 H, dd, H-6, C_6H_4, $^{3}J_{HH}$ 7.5, $^{4}J_{HH}$ 1.0 Hz). ^{13}C-NMR (100.6 MHz, 20 °C, $CDCl_3$): δ 45.32 [s, $N(CH_3)_2$ (B)], 45.47 [s, $N(CH_3)_2$ (A)], 65.60 (s, CH_2), 126.37 (s, C-3), 128.51 (s, C-4), 128.95 (s, C-*meta*), 129.28 (s, C-5 or C-*para*), 129.37 (s, C-*para* or C-5), 134.57 (s, C-*ortho*), 137.06 (s, C-6), 143.00 (s, C-2), 144.34 (s, C-1), 144.61 (s, C-*ipso*). MS (CI, NH_3), *m*/*z* (%), neg.: 404 (100) [M^- + Cl], 369 (11) [M^-]; pos.: 370 (2) [M^+ + H], 332 (100) [M^+ – Cl], 292 (10) [M^+ – Ph].

Synthesis of [2-(Me_2NCH_2)C_6H_4]PhSbBr (2). A solution of KBr (1.07 g, 9 mmol) in distilled water (15 mL) was added to a clear, colorless solution of **1** (1.11 g, 3 mmol) in CH_2Cl_2 (25 mL). The mixture was stirred vigorously for 3 days at room temperature, then the organic layer was separated. The aqueous phase was washed with CH_2Cl_2 (4 × 10 mL) and the unified organic phases were dried over anhydrous $CaCl_2$. After filtration and removal of the solvent under reduced pressure, compound **2** was obtained as a white solid (1.12 g, 90%), mp 140 °C. Anal. Calcd. for $C_{15}H_{17}BrNSb$ (412.96): C, 43.63; H, 4.15; N, 3.39. Found: C, 43.25; H, 4.06; N, 3.12%. ^{1}H NMR (300 MHz, 20 °C, $CDCl_3$): δ 2.11 [3 H, s, $N(CH_3)_2$ (A)], 2.42 [3 H, s, $N(CH_3)_2$ (B)], AB spin system with A at 3.55 and B at 3.62 ppm (2 H, CH_2, $^{2}J_{HH}$ 14.2 Hz), 7.22 (1 H, d, H-3, C_6H_4, $^{3}J_{HH}$ 6.9 Hz), 7.30 (3 H, m, H-*meta* + *para*, C_6H_5), 7.42 (1 H, ddd, H-4, C_6H_4, $^{3}J_{HH}$ 7.4, $^{4}J_{HH}$ 1.5 Hz), 7.47 (1 H, ddd, H-5, C_6H_4, $^{3}J_{HH}$ 7.1, $^{4}J_{HH}$ 1.4 Hz), 7.51 (2 H, m, H-*ortho*, C_6H_5), 8.59 (1 H, dd, H-6, C_6H_4, $^{3}J_{HH}$ 7.1, $^{4}J_{HH}$ 1.6 Hz). ^{13}C-NMR (75.4 MHz, 20 °C, $CDCl_3$): δ 45.30 [s, $N(CH_3)_2$ (B)], 45.57 [s, $N(CH_3)_2$ (A)], 65.55 (s, CH_2), 126.34 (s, C-3), 128.57 (s, C-4), 128.94 (s, C-*meta*), 129.36 (s, C-5 or C-*para*), 129.38 (s, C-*para* or C-5), 134.63 (s, C-*ortho*), 138.57 (s, C-6), 142.02 (s, C-2), 142.83 (s, C-1), 142.93 (s, C-*ipso*). MS (EI, 70 eV, 200 °C), *m*/*z* (%): 412 (2) [M^+], 332 (100) [M^+ – Br], 134 (24) [R^+] [R = 2-(Me_2NCH_2)C_6H_4].

Synthesis of [2-(Me_2NCH_2)C_6H_4]PhSbI (3). A mixture of KI (1.07 g, 9 mmol) and **1** (0.72 g, 1.95 mmol) in acetone (60 mL) was stirred vigorously for 12 h, at room temperature. The reaction mixture was filtered off and the solvent was removed under vacuum. The title compound was obtained as a yellow solid (0.87 g, 97%), mp 149 °C. Anal. Calcd. for $C_{15}H_{17}INSb$ (459.96): C, 39.17; H, 3.73; N, 3.05. Found: C, 39.42; H, 3.92; N, 2.97%. ^{1}H NMR (300 MHz, 20 °C, $CDCl_3$): δ 2.14 [3 H, s, $N(CH_3)_2$ (A)], 2.42 [3 H, s, $N(CH_3)_2$ (B)], AB spin system with A at 3.53 and B at 3.61 ppm (2 H, CH_2, $^{2}J_{HH}$ 14.2 Hz), 7.20 (1 H, m, H-3, C_6H_4), 7.29 (3 H, m, H-*meta* + *para*, C_6H_5), 7.44 (2 H, m, H-4,5, C_6H_4), 7.52 (2 H, m, H-*ortho*, C_6H_5), 8.69 (1 H, m, H-6, C_6H_4). ^{13}C-NMR (75.4 MHz, 20 °C, $CDCl_3$): δ 45.22 [s, $N(CH_3)_2$ (B)], 45.73 [s, $N(CH_3)_2$ (A)], 65.43 (s, CH_2), 126.38 (s, C-3), 128.72 (s, C-4), 128.90 (s, C-*meta*), 129.35 (s, C-5 or C-*para*), 129.46 (s, C-*para* or C-5), 134.88 (s, C-*ortho*), 138.20 (s, C-2), 139.89 (s, C-*ipso*), 141.60 (s, C-6), 142.89 (s, C-1). MS (EI, 70 eV, 200 °C), *m*/*z* (%): 382 (3) [M^+ – Ph], 332 (100) [M^+ – I], 134 (17) [R^+] [R = 2-(Me_2NCH_2)C_6H_4].

Synthesis of [2-(Me_2NCH_2)C_6H_4]Ph_2Sb (4). [2-(Me_2NCH_2)-C_6H_4]Li (3.4 g, 24 mmol) in hexane (80 mL) was added to a cold solution (–78 °C) of Ph_2SbCl (7.51 g, 24 mmol) in hexane (200 mL). The reaction mixture was stirred at –78 °C for 2 h, then allowed to warm to room temperature and stirred for further 72 h. The solvent was removed in vacuum and the remaining solid was extracted with benzene. The yellowish solution was filtered and removal of the solvent gave 8.0 g (81%) of the title compound as a white solid, mp 89 °C. Anal. Calcd. for $C_{21}H_{22}NSb$ (410.16): C, 61.50; H, 5.41; N, 3.41. Found: C, 61.24; H, 5.77; N, 3.54%. ^{1}H NMR (400 MHz, 20 °C, $CDCl_3$): δ 1.89 [6 H, s, $N(CH_3)_2$], 3.46 (2 H, s, CH_2), 7.14 (2 H, m, H-3,4, C_6H_4), 7.26 (8 H, m, H-5,6, C_6H_4, and H-*meta* + *para*, C_6H_5), 7.46 (4 H, m, H-*ortho*, C_6H_5). ^{13}C-NMR (100.6 MHz, 20 °C, $CDCl_3$): δ 43.81 [s, $N(CH_3)_2$], 65.26 (s, CH_2), 127.54 (s, C-3), 127.67 (s, C-*para*), 128.04 (s, C-4), 128.22 (s, C-5), 128.32 (s, C-*meta*), 136.17 (s, C-*ortho*), 137.15 (s, C-6),

140.55 (s, C-2), 142.19 (s, C-*ipso*), 144.62 (s, C-1). MS (CI, NH_3), *m/z* (%), pos.: 410 (28) [M^+ + H], 332 (100) [M^+ – Ph], 136 (45) [R^+ + 2H] [R = 2-(Me_2NCH_2)C_6H_4].

Synthesis of [2-(Me_2NCH_2)C_6H_4]$_2$PhSb (5). [2-(Me_2NCH_2)-C_6H_4]Li (2.35 g, 16.7 mmol) in hexane (80 mL) was added to a cold solution (–78 °C) of Ph_2SbCl (2.25 g, 8.3 mmol) in hexane (80 mL). The reaction mixture was stirred at –78 °C for 2 h, then allowed to warm to room temperature. The yellowish solution was filtered and the solvent was removed in vacuum to yield 3.51 g (90%) of the title compound as a white solid, mp 100 °C. Anal. Calcd. for $C_{24}H_{29}N_2Sb$ (467.26): C, 61.69; H, 6.26; N, 6.00. Found: C, 61.34; H, 5.98; N, 5.84%. ^{1}H NMR (300 MHz, 20 °C, $CDCl_3$): δ 1.88 [12 H, s, $N(CH_3)_2$], AB spin system with A at 3.35 and B at 3.59 ppm (4 H, CH_2, $^2J_{HH}$ 12.9 Hz), 7.09 (2 H, m, H-4, C_6H_4), 7.21 (9 H, m, H-3,5,6, C_6H_4, and H-*meta* + *para*, C_6H_5), 7.45 (2 H, m, H-*ortho*, C_6H_5). ^{13}C-NMR (75.4 MHz, 20 °C, $CDCl_3$): δ 44.00 [s, $N(CH_3)_2$], 65.74 (s, CH_2), 126.93 (s, C-*para*), 127.02 (s, C-4), 127.24 (s, C-5), 127.82 (s, C-3), 128.10 (s, C-*meta*), 136.28 (s, C-*ortho*), 137.21 (s, C-6), 143.76 (s, C-2), 144.52 (s, C-1), 145.23 (s, C-*ipso*). MS (EI, 70 eV, 200 °C): *m/z* (%): 466 (1) [M^+], 389 (100) [M^+ – Ph], 332 (76) [M^+ – R], 134 (23) [R^+] [R = 2-(Me_2NCH_2)C_6H_4].

Synthesis of [2-(Me_2NCH_2)C_6H_4]PhMesSb (6). MesBr (1.32 g, 1.0 mL, ρ 1.301 g cm^{-3}, 6.6 mmol) in THF (20 mL) was added dropwise, under stirring, to the Mg filings (0.159 g, 6.6 mmol). The mixture starts to warm up and results in a yellow solution after 2 h. Solid **1** (2.44 g, 6.6 mmol) was added to the resulted solution of MesMgBr and the reaction mixture was left to stirr over night at ambient temperature. The solvent was removed under vacuum and the white oily residue was extracted with hexane. The hexane solution was filtered off and removal of the solvent gave 1.83 g (61%) of the title compound as a white, crystalline solid, mp 94–95 °C. Anal. Calcd. for $C_{24}H_{28}NSb$ (452.24): C, 63.74; H, 6.24; N, 3.10. Found: C, 63.71; H, 5.93; N, 3.23%. ^{1}H NMR (300 MHz, 20 °C, $CDCl_3$): δ 2.00 [6 H, s, $N(CH_3)_2$], 2.38 (3 H, s, *para*-CH_3), 2.41 (6 H, s, *ortho*-CH_3), AB spin system with A at 3.44 and B at 3.57 ppm (2 H, CH_2, $^2J_{HH}$ 13.2 Hz), 6.97 (2 H, s, H-3′,5′, C_6H_2), 7.20 (2 H, m, H-3,5, C_6H_4), 7.30 (1 H, ddd, H-4, C_6H_4, $^3J_{HH}$ 7.2, $^4J_{HH}$ 1.4 Hz), 7.40 (3 H, m, H-*meta* + *para*, C_6H_5), 7.63 (2 H, m, H-*ortho*, C_6H_5), 7.73 (1 H, dd, H-6, C_6H_4, $^3J_{HH}$ 7.2, $^4J_{HH}$ 1.7 Hz). ^{13}C-NMR (75.4 MHz, 20 °C, $CDCl_3$): δ 21.02 (s, *para*-CH_3), 26.39 (s,br, *ortho*-CH_3), 44.01 [s, $N(CH_3)_2$], 65.30 (s, CH_2), 127.33 (s, C-*para*), 127.42 (s, C-3), 127.65 (s, C-4), 128.18 (s, C-5), 128.31 (s, C-*meta* or C-3′,5′), 128.32 (s, C-3′,5′ or C-*meta*), 136.01 (s, C-6), 136.56 (s, C-*ortho*), 136.95 (s, C-1′), 137.62 (s, C-4′), 139.88 (s, C-1), 142.35 (s, C-*ipso*), 144.16 (s, C-2), 145.00 (s, C-2′,6′). MS (ES), *m/z* (%), pos.: 453 (25) [M^+ + H], 332 (100) [M^+ – Mes] [R = 2-(Me_2NCH_2)C_6H_4].

Synthesis of [2-(Me_2NCH_2)C_6H_4]MesSbBr (7). MesMgBr was prepared from MesBr (2.73 g, 2.1 mL, d 1.301 g cm^{-3}, 13.7 mmol) and magnesium filings (0.33 g, 13.7 mmol) in anhydrous diethyl ether (60 mL). The solution of the Grignard reagent was added dropwise to a stirred solution of [2-(Me_2NCH_2)C_6H_4]$SbBr_2$ (5.72 g, 13.7 mmol) in THF (60 mL) cooled to 0 °C. The reaction mixture was allowed to warm to room temperature and then stirred for 48 h. The solvents were removed under vacuum and the remaining grey residue was extracted with toluene (3 × 50 mL). The clear toluene solution was concentrated and stored at –28 °C when a white solid formed and was filtered off. Recrystallization from acetone gave 2.9 g (47%) of the title compound as colourless crystals, mp 170 °C. Anal. Calcd. for $C_{18}H_{23}BrNSb$ (455.04): C, 47.51; H, 5.09; N, 3.08. Found: C, 47.24; H, 4.83; N, 3.25%. ^{1}H NMR (300 MHz, 20 °C, $CDCl_3$): δ 1.93 (3 H, s,br, *ortho*-CH_3), 2.14 [3 H, s, $N(CH_3)_2$ (A)], 2.23 (3 H, s, *para*-CH_3), 2.36 [3 H, s, $N(CH_3)_2$ (B)], 2.74 (3 H, s,br, *ortho*-CH_3), AB spin system with A at 3.43 and B at 3.73 ppm (2 H, CH_2, $^2J_{HH}$ 13.9 Hz), 6.82 (2 H, s,br, H-3′,5′, C_6H_2), 7.16 (1 H, d, H-3, C_6H_4, $^3J_{HH}$ 7.1 Hz), 7.34 (1 H, ddd, H-4, C_6H_4, $^3J_{HH}$ 7.4, $^4J_{HH}$ 1.4 Hz), 7.40 (1 H, ddd, H-5, C_6H_4, $^3J_{HH}$ 7.3, $^4J_{HH}$ 0.7 Hz), 8.58 (1 H, dd, H-6, C_6H_4, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1.4 Hz). ^{13}C-NMR (75.4 MHz, 20 °C, $CDCl_3$): δ 20.96 (s, *para*-CH_3), 25.08 (s,br, *ortho*-CH_3), 45.45 [s, $N(CH_3)_2$], 66.27 (s, CH_2), 125.99 (s, C-3), 128.66 (s, C-5), 128.89 (s, C-4), 129.08 (s,br, C-3′,5′), 137.72 (s, C-6), 139.05 (s, C-4′), 139.85 (s, C-1′), 142.46 (s, C-1 and C-2′,6′), 143.40 (s, C-2). MS (CI, NH_3), *m/z* (%), neg.: 534 (63) [M^- + Br], 374 (58) [M^- – Br^-], 79 (100) [Br^-] [*R* = 2-(Me_2NCH_2)C_6H_4]; pos.: 456 (3) [M^+ + H], 374 (100) [M^+ – Br], 336 (9) [M^+ – Mes].

Synthesis of [2-(Me_2NCH_2)C_6H_4]MesSbI (8). A mixture of KI (0.28 g, 1.69 mmol) and **7** (0.53 g, 1.16 mmol) in acetone (60 mL) was stirred vigorously for 12 h, at room temperature. The reaction mixture was filtered off and the solvent was removed under vacuum. The solid residue was recrystallized from CH_2Cl_2 to afford the title compound as yellow crystals (0.40 g, 69%), mp 180 °C. Anal. Calcd. for $C_{18}H_{23}INSb$ (502.04): C, 43.06; H, 4.62; N, 2.79. Found: C, 42.82; H, 4.33; N, 2.64%. ^{1}H NMR (300 MHz, 20 °C, $CDCl_3$): δ 1.92 (3 H, s,br, *ortho*-CH_3), 2.15 [3 H, s, $N(CH_3)_2$ (A)], 2.23 (3 H, s, *para*-CH_3), 2.35 [3 H, s, $N(CH_3)_2$ (B)], 2.71 (3 H, s,br, *ortho*-CH_3), AB spin system with A at 3.42 and B at 3.71 ppm (2 H, CH_2, $^2J_{HH}$ 13.9 Hz), 6.82 (2 H, s,br, H-3′,5′, C_6H_2), 7.14 (1 H, m, H-3, C_6H_4), 7.36 (2 H, m, H-4,5, C_6H_4), 8.68 (1 H, m, H-6, C_6H_4). ^{13}C-NMR (75.4 MHz, 20 °C, $CDCl_3$): δ 20.93 (s, *para*-CH_3), 24.99 (s,br, *ortho*-CH_3), 45.29 [s, $N(CH_3)_2$ (B)], 45.55 [s, $N(CH_3)_2$ (A)], 66.09 (s, CH_2), 126.08 (s, C-3), 128.75 (s, C-4), 128.89 (s,br, C-3′,5′–partially overlapped by the resonance of C-5 carbon), 128.99 (s, C-5), 137.24 (s, C-1′), 139.01 (s, C-4′), 139.59 (s, C-2), 140.22 (s, C-6), 142.51 (s, C-1 and C-2′,6′). MS (EI, 70 eV, 200 °C), *m/z* (%): 374 (100) [M^+ – I], 255 (10) [RSb^+], 240 (15) [$MesSb^+$], 134 (30) [R^+] [R = 2-(Me_2NCH_2)C_6H_4].

Synthesis of [2-(Me_2NCH_2)C_6H_4]Mes_2Sb (9). A solution of MesMgBr [prepared from MesBr (0.84 g, 0.65 mL, ρ 1.301 g cm^{-3}, 4.2 mmol) and magnesium filings (0.10 g, 4.2 mmol) in anhydrous THF (20 mL)] was added dropwise to a stirred solution of [2-(Me_2NCH_2)C_6H_4]$SbCl_2$ (0.69 g, 2.1 mmol) in THF (20 mL) cooled to 0 °C. The reaction mixture was allowed to warm to room temperature and then stirred over night. The solvent was removed under vacuum and the remaining residue was extracted with hexane. The clear hexane solution was evaporated to dryness to give 0.86 g (83%) of the title compound as a white crystalline solid, mp 102 °C. Anal. Calcd. for $C_{27}H_{34}NSb$ (494.31): C, 65.60; H, 6.93; N, 2.83. Found: C, 64.93; H, 7.37; N, 2.92%. ^{1}H NMR (300 MHz, 20 °C, $CDCl_3$): δ 1.92 [6 H, s, $N(CH_3)_2$], 2.27 (12 H, s, *ortho*-CH_3), 2.28 (6 H, s, *para*-CH_3), 3.48 (2 H, s, CH_2), 6.83 (4 H, s, H-3′,5′, C_6H_2), 7.07 (1 H, ddd, H-5, C_6H_4, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1.9 Hz), 7.18 (1 H, dd, H-3, C_6H_4, $^3J_{HH}$ 7.4, $^4J_{HH}$ 1.7 Hz), 7.23 (1 H, ddd, H-4, C_6H_4, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.3 Hz), 7.61 (1 H, dd, H-6, C_6H_4, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.0 Hz). ^{13}C-NMR (75.4 MHz, 20 °C, $CDCl_3$):

Table 3 Crystallographic data for compounds **2–8**

	2	**3**	**4**	**5**	**6**	**7**	**8**
Empirical formula	$C_{15}H_{17}BrNSb$	$C_{15}H_{17}INSb$	$C_{21}H_{22}NSb$	$C_{24}H_{29}N_2Sb$	$C_{24}H_{28}NSb$	$C_{18}H_{23}BrNSb$	$C_{18}H_{23}INSb$
M	412.96	459.95	410.15	467.24	452.22	557.28	502.02
T	297(2)	297(2)	297(2)	297(2)	297(2)	297(2)	297(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/Å	25.7685(17)	13.2997(9)	8.452(3)	8.7366(6)	8.4829(17)	8.8931(5)	9.8671(6)
b/Å	7.9478(5)	12.2869(8)	35.081(12)	16.1565(11)	37.717(8)	9.5876(6)	15.2192(9)
c/Å	15.3568(10)	10.4529(7)	6.335(2)	16.1689(11)	6.7885(14)	21.2914(13)	13.3666(8)
α/°	90	90	90	88.276(1)	90	90	90
β/°	103.259(1)	111.129(1)	95.200(6)	89.618(1)	98.986(3)	99.265(1)	104.159(1)
γ/°	90	90	90	82.723(1)	90	90	90
V/Å^3	3061.3(3)	1593.29(18)	1870.7(11)	2262.9(3)	2145.3(8)	1791.70(19)	1946.3(2)
Z	8	4	4	4	4	4	4
No. of reflections collected	11 854	12 446	14 969	22 113	15 307	13 934	15 379
No. of independent reflections	3115 ($R_{int} = 0.0303$)	3248 ($R_{int} = 0.0295$)	3817 ($R_{int} = 0.0298$)	7962 ($R_{int} = 0.0463$)	3758 ($R_{int} = 0.0510$)	3656 ($R_{int} = 0.0280$)	3976 ($R_{int} = 0.0369$)
Absorption correction	Multi-Scan[26]	Multi-Scan[26]	Multi-Scan[26]	Multi-Scan[26]	Multi-Scan[26]	Multi-Scan[26]	Multi-Scan[26]
μ(Mo-Kα)/mm^{-1}	4.396	3.653	1.474	1.229	1.293	3.764	2.999
R_1 [$I > 2\sigma(I)$]	0.0395	0.0327	0.0421	0.0442	0.0871	0.0367	0.0392
wR_2	0.0886	0.0638	0.0914	0.0838	0.1500	0.0872	0.0818
GOF on F^2	1.177	1.213	1.157	1.085	1.376	1.154	1.113

δ 20.90 (s, *para*-CH_3), 25.82 (s, *ortho*-CH_3), 44.36 [s, $N(CH_3)_2$], 65.87 (s, CH_2), 127.05 (s, C-5), 127.69 (s, C-4), 128.38 (s, C-3), 128.54 (s, C-3′,5′), 137.25 (s, C-1′), 137.68 (s, C-6), 138.89 (s, C-4′), 139.42 (s, C-1), 144.76 (s, C-2′,6′), 144.81 (s, C-2). MS (CI, NH_3), m/z (%), neg.: 492 (7) [M^- − H], 374 (68) [M^- − Mes], 359 (17) [M^- − R], 134 (8) [R^-] [R = 2-$(Me_2NCH_2)C_6H_4$]; pos.: 494 (5) [M^+ + H], 374 (100) [M^+ − Mes], 256 (9) [RSb^+ + H], 134 (9) [R^+].

Synthesis of [2-$(Me_2NCH_2)C_6H_4]_2$MesSb (10). A solution of MesMgBr [prepared from MesBr (0.33 g, 0.25 mL, ρ 1.301 g cm^{-3}, 1.7 mmol) and magnesium filings (0.04 g, 1.7 mmol) in anhydrous THF (20 mL)] was added dropwise to a stirred solution of [2-$(Me_2NCH_2)C_6H_4]_2$SbCl (0.72 g, 1.7 mmol) in THF (20 mL) cooled to 0 °C. The reaction mixture was allowed to warm to room temperature and then stirred over night. The solvent was removed under vacuum and the remaining yellowish oily residue was extracted with hexane. The clear hexane solution was evaporated to dryness to give 0.47 g (54%) of the title compound as a white crystalline solid, mp 83–85 °C. Anal. Calcd. for $C_{27}H_{35}N_2Sb$ (509.34): C, 63.67; H, 6.93; N, 5.50. Found: C, 63.23; H, 6.77; N, 5.34%. ^{1}H NMR (300 MHz, 20 °C, $CDCl_3$): δ 1.92 [12 H, s, $N(CH_3)_2$], 2.26 (3 H, s, *para*-CH_3), 2.28 (6 H, s, *ortho*-CH_3), AB spin system with A at 3.33 and B at 3.65 ppm (4 H, CH_2, $^2J_{HH}$ 13.2 Hz), 6.80 (2 H, s, H-3′,5′, C_6H_2), 7.05 (2 H, m, H-5, C_6H_4), 7.21 (4 H, m, H-3,4, C_6H_4), 7.45 (2 H, d, H-6, C_6H_4, $^3J_{HH}$ 7.2 Hz). ^{13}C-NMR (75.4 MHz, 20 °C, $CDCl_3$): δ 20.98 (s, *para*-CH_3), 26.32 (s, *ortho*-CH_3), 44.33 [s, $N(CH_3)_2$], 65.62 (s, CH_2), 126.86 (s, C-5), 127.32 (s, C-3), 128.18 (s, C-4, and C-3′,5′), 136.88 (s, C-1′), 137.63 (s, C-6), 140.73 (s, C-1), 142.12 (s, C-4′), 144.77 (s, C-2′,6′), 145.05 (s, C-2). MS (EI, 70 eV, 200 °C), m/z (%): 508 (2) [M^+], 389 (100) [M^+ − Mes], 374 (15) [M^+ − R], 240 (8) [M^+ − 2R], 134 (21) [R^+] (R = $Me_2NCH_2C_6H_4$).

Crystal structures†

The details of the crystal structure determination and refinement for compounds **2–8** are given in Table 3. The crystals were attached with epoxy glue on cryoloops. Data were collected at room temperature (297 K) on a Bruker SMART APEX diffractometer, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). Scan type ω and ϕ. Absorption corrections: multi-scan.[26] The structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a riding model and a mutual isotropic thermal parameter. For structure solving and refinement the software package SHELX-97 was used.[27] The drawings were created with the Diamond program.[28]

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