Electronic Supplementary Information

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

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Coalescence of the NMe$_2$ resonances in C$_6$D$_6$

$^1$H NMR (200 MHz, 20 °C, C$_6$D$_6$): $\delta$ 1.33 [3 H, s, N(CH$_3$)$_2$ (A)], 1.62 [3 H, s, N(CH$_3$)$_2$ (B)], AB spin system with A at 2.76 and B at 2.96 ppm (2 H, CH$_2$, $^2$$J_{HH}$ 14.2 Hz), 6.82 (1 H, d, H-3, C$_6$H$_4$, $^3$$J_{HH}$ 7.4 Hz), 7.02 (3 H, m, H-meta+para, C$_6$H$_3$), 7.15 (1 H, m, H-4, C$_6$H$_4$, partially overlapped by residual solvent resonance), 7.30 (1 H, dd, H-5, C$_6$H$_4$, $^3$$J_{HH}$ 7.4 Hz), 7.51 (2 H, m, H-ortho, C$_6$H$_3$), 8.99 (1 H, dd, H-6, C$_6$H$_4$, $^3$$J_{HH}$ 7.5, $^4$$J_{HH}$ 1.1 Hz).

$^1$H NMR (200 MHz, 65 °C, C$_6$D$_6$): $\delta$ 1.58 [6 H, s,br, N(CH$_3$)$_2$], AB spin system with A at 2.92 and B at 3.06 ppm (2 H, CH$_2$, $^2$$J_{HH}$ 14.1 Hz), 6.84 (1 H, d, H-3, C$_6$H$_4$, $^3$$J_{HH}$ 7.4 Hz), 7.04 (3 H, m, H-meta+para, C$_6$H$_3$), 7.14 (1 H, m, H-4, C$_6$H$_4$, partially overlapped by residual solvent resonance), 7.30 (1 H, dd, H-5, C$_6$H$_4$, $^3$$J_{HH}$ 7.4 Hz), 7.51 (2 H, m, H-ortho, C$_6$H$_3$), 8.88 (1 H, d, H-6, C$_6$H$_4$, $^3$$J_{HH}$ 7.4 Hz).

Coalescence of both NMe$_2$ resonances and methylene AB system, respectively, in DMSO-d$_6$

$^1$H NMR (200 MHz, 20 °C, DMSO-d$_6$): $\delta$ 2.01 [3 H, s, N(CH$_3$)$_2$ (A)], 2.41 [3 H, s, N(CH$_3$)$_2$ (B)], AB spin system with A at 3.48 (partially overlapped by water resonance) and B at 3.83 ppm (2 H, CH$_2$, $^2$$J_{HH}$ 14.6 Hz), 7.35 (4 H, m, H-3, C$_6$H$_4$, and H-meta+para, C$_6$H$_3$), 7.47 (4 H, m, H-4,5, C$_6$H$_4$, and H-ortho, C$_6$H$_3$), 8.30 (1 H, m, H-6, C$_6$H$_4$).

$^1$H NMR (200 MHz, 50 °C, DMSO-d$_6$): $\delta$ 2.22 [6 H, s,br, N(CH$_3$)$_2$], AB spin system with A at 3.51 and B at 3.83 ppm (2 H, CH$_2$, $^2$$J_{HH}$ 14.2 Hz), 7.35 (4 H, m, H-3, C$_6$H$_4$, and H-meta+para, C$_6$H$_3$), 7.47 (4 H, m, H-4,5, C$_6$H$_4$, and H-ortho, C$_6$H$_3$), 8.32 (1 H, m, H-6, C$_6$H$_4$).

$^1$H NMR (200 MHz, 78 °C, DMSO-d$_6$): $\delta$ 2.23 [6 H, s,br, N(CH$_3$)$_2$], 3.69 (2 H, s,br, CH$_2$), 7.34 (4 H, m, H-3, C$_6$H$_4$, and H-meta+para, C$_6$H$_3$), 7.48 (4 H, m, H-4,5, C$_6$H$_4$, and H-ortho, C$_6$H$_3$), 8.34 (1 H, m, H-6, C$_6$H$_4$).
[2-(Me₂NCH₂)C₆H₄]PhSbBr (2)

- the crystal contains a 1:1 mixture of \((R_N,A_{Sb})\) and \((S_N,C_{Sb})\) isomers

**Figure S1.** Molecular structure of \((R_N,A_{Sb})\)-2 isomer (left) and \((S_N,C_{Sb})\)-2 isomer (right) in the crystal of 2, showing the intramolecular bromine-hydrogen contact (only hydrogen atoms involved in intramolecular contacts are shown).

- intramolecular distance  \(\text{Br}(1)\ldots\text{H}(6) 2.81 \, \text{Å}\)
- \(\sum r_{\text{vdW}}(\text{Br},\text{H}) 3.15 \, \text{Å}\)

**Figure S2.** View of a chain polymer based on Br···Hₜₐₓ and C-Hmethylene···π (Phcentroid) contacts between \((S_N,C_{Sb})\)-2 isomers in the crystal of 2 (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms \((x, −1 + y, z), (0.5 − x, −0.5 + y, 0.5 − z), (0.5 − x, 0.5 + y, 0.5 − z)\) and \((0.5 − x, 0.5 + y, 0.5 − z)\) are given by ‘‘a’’, ‘‘b’’, ‘‘c’’ and ‘‘d’’, respectively].

- intermolecular distance  \(\text{Br}(1)\ldots\text{H}(5a) 3.12 \, \text{Å}\)
- \(\text{C}(7)\ldots\text{H}(7A)\ldots\pi (\text{Ph}_{\text{centroid}}) 2.95 \, \text{Å}\)
**Figure S3.** View along $b$ axis of a chain polymer built from ($S_N,C_{Sb}$)-2 isomers in the crystal of 2 through Br···H$_{aryl}$ and C-H$_{methylene}$···π (Ph$_{centroid}$) contacts.

**Figure S4.** View of a layer with inter-chain Br···H$_{aryl}$ contacts between alternating chain polymers built from ($S_N,C_{Sb}$)-2 and ($R_N,A_{Sb}$)-2 isomers, respectively, in the crystal of 2.

- inter-chain distance \( Br(1)\cdots H(13) \ 3.14 \ \text{Å} \)
- $\sum r_{vdW}(Br, H) \ 3.15 \ \text{Å}$
Figure S5. ORTEP representation at 30% probability and atom numbering scheme for \((S_N,Sb)\)-3 isomer. Hydrogen atoms are omitted.

- the crystal contains a 1:1 mixture of \((R_N,A_{Sb})\) and \((S_N,C_{Sb})\) isomers

Figure S6. Molecular structure of \((R_N,A_{Sb})\)-3 isomer (left) and \((S_N,C_{Sb})\)-3 isomer (right) in the crystal of 3, showing the intramolecular iodine-hydrogen contact (only hydrogen atoms involved in intramolecular contacts are shown).

- intramolecular distance \(I(1)\cdots H(6)\) 3.04 Å \(\sum r_{vdW}(I,H)\) 3.35 Å
**Figure S7.** View of a chain polymer based on I···H<sub>methyl</sub> contacts between alternating (S<sub>N</sub>,C<sub>Sb</sub>)-3 and (R<sub>N</sub>,A<sub>Sb</sub>)-3 isomers in the crystal of 3 (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (x, 0.5 − y, 0.5 + z) and (x, 0.5 − y, −0.5 + z) are given by “a” and “b”, respectively].

- intermolecular distance I(1)···H(9B) 3.22 Å
  \[ \sum_{\text{vdW(I,H)}} 3.35 \text{ Å} \]

**Figure S8.** View along c axis of a chain polymer in the crystal of 3.
Figure S9. View along \( c \) axis of parallel chain polymers in the crystal of 3.

- no further I···H contacts between parallel chains.
[2-(Me₂NCH₂)C₆H₄]Ph₂Sb (4)

- the crystal contains a 1:1 mixture of \((R_N, C_{Sb})\) and \((S_N, A_{Sb})\) isomers

![Diagram showing molecular structure of \((R_N, C_{Sb})-4\) isomer (left) and \((S_N, A_{Sb})-4\) isomer (right) in the crystal of 4.]

**Figure S10.** Molecular structure of \((R_N, C_{Sb})-4\) isomer (left) and \((S_N, A_{Sb})-4\) isomer (right) in the crystal of 4.

![Diagram showing view of a chain polymer based on C-H ᵃryl ---π (Ph centroid) contacts between \((R_N, C_{Sb})-4\) isomers in the crystal of 4 (only hydrogen atoms involved in intermolecular contacts are shown). Symmetry equivalent atoms \((x, y, -1 + z)\) and \((x, y, 1 + z)\) are given by “a” and “b”, respectively.]

**Figure S11.** View of a chain polymer based on C-Haryl ---π (Ph centroid) contacts between \((R_N, C_{Sb})-4\) isomers in the crystal of 4 (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms \((x, y, -1 + z)\) and \((x, y, 1 + z)\) are given by “a” and “b”, respectively].

- intra-chain distance \(C(17)-H(17) ---π (Ph centroid)\) 2.80 Å
Figure S12. View of a layer of $(R_N, C_{Sb})$-4 isomers based on C-H$_{aryl}$···π (Ph$_{centroid}$) contacts in the crystal of 4 (only hydrogen atoms involved in intermolecular contacts are shown).

- inter-chain distance $C(20)$-H(20)···π (Ph$_{centroid}$) 2.93 Å

- no further contacts between parallel, alternative layers of $(R_N, C_{Sb})$ and $(S_N, A_{Sb})$ isomers, respectively.

Figure S13. View along c axis of alternative layers of $(R_N, C_{Sb})$ and $(S_N, A_{Sb})$ isomers, respectively, in the crystal of 4.
**Figure S14.** ORTEP representation at 30% probability and atom numbering scheme for \((S_{N3},S_{N4},C_{Sb2})-5b\) isomer. Hydrogen atoms are omitted.

- the crystal contains a 1:1 mixture of \((R_{N1},R_{N2},A_{Sb1})/ (S_{N1},S_{N2},C_{Sb1})-5a\) and \((R_{N3},R_{N4},A_{Sb2})/ (S_{N3},S_{N4},C_{Sb2})-5b\) isomers
Figure S15. Molecular structure of (a) \((R_{N1},R_{N2},A_{Sb1})-5a\) (left) and \((S_{N1},S_{N2},C_{Sb1})-5a\) (right) isomers, and (b) \((R_{N3},R_{N4},A_{Sb2})-5b\) isomer (left) and \((S_{N3},S_{N4},C_{Sb2})-5b\) isomer (right), in the crystal of 5.

Figure S16. View along axis \(a\) of a chain polymer based on C-H\_methyl\(\cdots\pi\) (Ph\_centroid) contacts between alternating \((R_{N1},R_{N2},A_{Sb1})-5a\) and \((S_{N3},S_{N4},C_{Sb2})-5b\) isomers in the crystal of 5 (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms \((x, y, 1 + z)\) and \((x, y, -1 + z)\) are given by “a” and “b”, respectively].

- intra chain distance \(C(17)-H(17)\cdots\pi\) (Ph\_centroid) 3.06 Å
- no further contacts between parallel chains.
[2-(Me₂NCH₂)C₆H₄]PhMesSb (6)

- the crystal contains a 1:1 mixture of (R₅,A₅b) and (S₅,C₅b) isomers

**Figure S17.** Molecular structure of (R₅,A₅b)-6 isomer (*left*) and (S₅,C₅b)-4 isomer (*right*) in the crystal of 6.

**Figure S18.** View of a chain polymer based on C-Haryl···π and C-Hmethyl···π (Phcentroid) contacts between (R₅,A₅b)-6 isomers in the crystal of 6 (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (−1 + x, y, z) and (1 + x, y, z) are given by “a” and “b”, respectively].

- intra chain distance
  - C(21)-H(21)···π (Phcentroid) 2.90 Å
  - C(8)-H(8A)···π (Phcentroid) 2.94 Å
Figure S19. View of a layer of ($R_N,A_{Sb}$)-6 isomers based on C-H$_{methyl}$···π (Ph$_{centroid}$) contacts in the crystal of 6 (only hydrogen atoms involved in intermolecular contacts are shown).

- inter-chain distance  
  \[ C(16)-H(16B) \cdots \pi \text{(Ph$_{centroid}$)} \]  2.97 Å

Figure S20. View of a double-layer association between layers of ($R_N,A_{Sb}$) and ($S_N,C_{Sb}$) isomers, respectively, in the crystal of 6.

- inter-layer distance  
  \[ C(23)-H(23) \cdots \pi \text{(Ph$_{centroid}$)} \]  2.98 Å
[2-(Me₂NCH₂)C₆H₄]MesSbBr (7)
- the crystal contains a 1:1 mixture of (Rₐ,Cₛₐₐ) and (Sₐ,Aₛₐ) isomers

![Molecular structures](image)

**Figure S21.** Molecular structure of (Rₐ,Cₛₐₐ)-7 isomer (left) and (Sₐ,Aₛₐ)-7 isomer (right) in the crystal of 7, showing the intramolecular bromine-hydrogen contact (only hydrogen atoms involved in intramolecular contacts are shown).
- intramolecular distance  \( \text{Br(1)} \cdots \text{H(6)} \) 2.86 Å  \( \sum r_{\text{vdW}}(\text{Br,H}) \) 3.15 Å

![Dimer structure](image)

**Figure S22.** View of a dimer based on Br···Hₐryl contacts between (Rₐ,Cₛₐₐ) and (Sₐ,Aₛₐ)-7 isomers in the crystal of 7 (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms \((1-x, 1-y, -z)\) are given by “prime”].
- intermolecular distance  \( \text{Br(1)} \cdots \text{H(12a)} \) 3.07 Å
Figure S23. View of a columnar polymer of \((R_{N},C_{Sb}) / (S_{N},A_{Sb})\)-7 dimer units based on Br···Hmethyl contacts in the crystal of 7 (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms \((1-x,1-y,-z),(x,1-y,z),(1-x,-y,-z),\)

\((x,1+y,z)\) and \((1-x,2-y,-z)\) are given by ‘‘prime’’, ‘‘a’’, ‘‘prime a’’, ‘‘b’’ and ‘‘prime b’’, respectively].

- inter-dimer distance \(\text{Br}(1)\cdots\text{H}(8\text{Cb}) \text{ 3.10 Å}\)
Figure S23a. $^1$H NMR spectra of 7: (up) aliphatic region, and (down) aromatic region [violet - in CDCl$_3$, at r.t.; black - in DMSO-d$_6$, at 20 °C; green - in DMSO-d$_6$, at 45 °C].
Coalescence of resonances for the aromatic protons of mesityl group in DMSO-d₆

¹H NMR (300 MHz, 20 °C, DMSO-d₆): δ 1.80 (3 H, s, ortho-CH₃), 2.12 [3 H, s, N(CH₃)₂ (A)], 2.20 (3 H, s, para-CH₃), 2.36 [3 H, s, N(CH₃)₂ (B)], 2.70 (3 H, s, ortho-CH₃), AB spin system with A at 3.633 and B at 3.728 ppm (2 H, CH₂, ²JHH 14.40 Hz), 6.78 (1 H, s,br, H-3’,5’, C₆H₂), 6.93 (1 H, s,br, H-3’,5’, C₆H₂), 7.30 (1 H, m, H-3, C₆H₄), 7.41 (2 H, ddd, H-4,5, C₆H₄), 8.40 (1 H, m, H-6, C₆H₄).

¹H NMR (300 MHz, 45 °C, DMSO-d₆): δ 1.87 (3 H, s,br, ortho-CH₃), 2.12 [3 H, s, N(CH₃)₂ (A)], 2.21 (3 H, s, para-CH₃), 2.38 [3 H, s, N(CH₃)₂ (B)], 2.68 (3 H, s,br, ortho-CH₃), AB spin system with A at 3.651 and B at 3.734 ppm (2 H, CH₂, ²JHH 14.20 Hz), 6.86 (2 H, s,br, H-3’,5’, C₆H₂), 7.30 (1 H, m, H-3, C₆H₄), 7.41 (2 H, ddd, H-4,5, C₆H₄), 8.42 (1 H, m, H-6, C₆H₄).
[2-(Me₂NCH₂)C₆H₄]MesSbI (8)

- the crystal contains a 1:1 mixture of ($R_N$,C$_{Sb}$) and ($S_N$,A$_{Sb}$) isomers

Figure S24. Molecular structure of ($R_N$,C$_{Sb}$)-8 isomer (left) and ($S_N$,A$_{Sb}$)-8 isomer (right) in the crystal of 8, showing the intramolecular iodine-hydrogen and C-H$_{methyl}$···π (Ph$_{centroid}$) contacts (only hydrogen atoms involved in intramolecular interactions are shown).

- intramolecular distance
  - I(1)···H(6) 3.06 Å
  - I(1)···H(16B) 3.23 Å
  - C(16)-H(16C)···π (Ph$_{centroid}$) 3.02 Å

Figure S25. View of a chain polymer association based on I···H$_{methyl}$ contacts between ($S_N$,A$_{Sb}$)-8 isomers in the crystal of 8 (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (−1 + x, y, z) and (1 + x, y, z) are given by ‘a’ and ‘b’, respectively].

- intermolecular distance
  - I(1)···H(9Cb) 3.17 Å
**Figure S26.** View along axis $c$ of a layer of ($S_N,A_Sb$)-8 isomers based on I···H$_{methyl}$, I···H$_{aryl}$ and C-H$_{aryl}$···π (Ph$_{centroid}$) contacts in the crystal of 8 (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms $(2-x, 0.5+y, 0.5-z)$ and $(2-x, -0.5+y, 0.5-z)$ are given by ‘prime’ and ‘double prime’, respectively].

- intermolecular distance  
  I(1)···H(14')  3.31 Å  
  I(1)···H(4'')  3.34 Å  
  C(5)-H(5)···π (Ph$_{centroid}$)  3.00 Å

**Figure S27.** View along axis $a$ of the 3D structure built from alternating layers of ($R_N,C_{Sb}$)-8 and ($S_N,A_{Sb}$)-8 isomers based on C-H$_{methyl}$···π (Ph$_{centroid}$) contacts in the crystal of 8 (only hydrogen atoms involved in intermolecular contacts are shown).

- intermolecular distance  
  C(16)-H(16A)···π (Ph$_{centroid}$)  2.99 Å
[2-(Me2NCH2)C6H4]Mes2Sb (9)

1H NMR (200 MHz, 20 °C, C6D6): δ 1.79 [6 H, s, N(CH3)2], 2.13 (6 H, s, ortho-CH3), 2.40 (12 H, s, para-CH3), 3.35 (2 H, s, CH2), 6.77 (4 H, s, H-3’,5’, C6H2), 6.91 (1 H, m, H-5, C6H4), 7.03 (2 H, m, H-3,4, C6H4), 7.91 (1 H, d, H-6, C6H4, 3JHH 7.2 Hz).

13C-NMR (50 MHz, 20 °C, C6D6): 20.98 (s, para-CH3), 26.16 (s, ortho-CH3), 44.31 [s, N(CH3)2], 66.21 (s, CH2), 128.17 (s, C-5), 128.31 (s, C-4), 128.84 (s, C-3), 129.19 (s, C-3’,5’), 137.46 (s, C-1’), 138.20 (s, C-6), 139.43 (s, C-4’), 140.13 (s, C-1), 144.99 (s, C-2’,6’), 145.26 (s C-2).