Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

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

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[2-(Me_2NCH_2)C_6H_4]PhSbCl (1)

Coalescence of the NMe_2 resonances in C_6D_6

^{1}H NMR (200 MHz, 20 °C, C_6D_6): δ 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, $^2J_{HH}$ 14.2 Hz), 6.82 (1 H, d, H-3, C_6H_4, $^3J_{HH}$ 7.4 Hz), 7.02 (3 H, m, H-*meta*+*para*, C_6H_5), 7.15 (1 H, m, H-4, C_6H_4, partially overlapped by residual solvent resonance), 7.30 (1 H, dd, H-5, C_6H_4, $^3J_{HH}$ 7.4 Hz), 7.51 (2 H, m, H-*ortho*, C_6H_5), 8.99 (1 H, dd, H-6, C_6H_4, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.1 Hz).

^{1}H NMR (200 MHz, 65 °C, C_6D_6): δ 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, $^2J_{HH}$ 14.1 Hz), 6.84 (1 H, d, H-3, C_6H_4, $^3J_{HH}$ 7.4 Hz), 7.04 (3 H, m, H-*meta*+*para*, C_6H_5), 7.14 (1 H, m, H-4, C_6H_4, partially overlapped by residual solvent resonance), 7.30 (1 H, dd, H-5, C_6H_4, $^3J_{HH}$ 7.4 Hz), 7.51 (2 H, m, H-*ortho*, C_6H_5), 8.88 (1 H, d, H-6, C_6H_4, $^3J_{HH}$ 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): δ 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, $^2J_{HH}$ 14.6 Hz), 7.35 (4 H, m, H-3, C_6H_4, and H-*meta*+*para*, C_6H_5), 7.47 (4 H, m, H-4,5, C_6H_4, and H-*ortho*, C_6H_5), 8.30 (1 H, m, H-6, C_6H_4).

^{1}H NMR (200 MHz, 50 °C, DMSO-d_6): δ 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, $^2J_{HH}$ 14.2 Hz), 7.35 (4 H, m, H-3, C_6H_4, and H-*meta*+*para*, C_6H_5), 7.47 (4 H, m, H-4,5, C_6H_4, and H-*ortho*, C_6H_5), 8.32 (1 H, m, H-6, C_6H_4).

^{1}H NMR (200 MHz, 78 °C, DMSO-d_6): δ 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_6H_4, and H-*meta*+*para*, C_6H_5), 7.48 (4 H, m, H-4,5, C_6H_4, and H-*ortho*, C_6H_5), 8.34 (1 H, m, H-6, C_6H_4).

[2-(Me$_2$NCH$_2$)C$_6$H$_4$]PhSbBr (2)

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

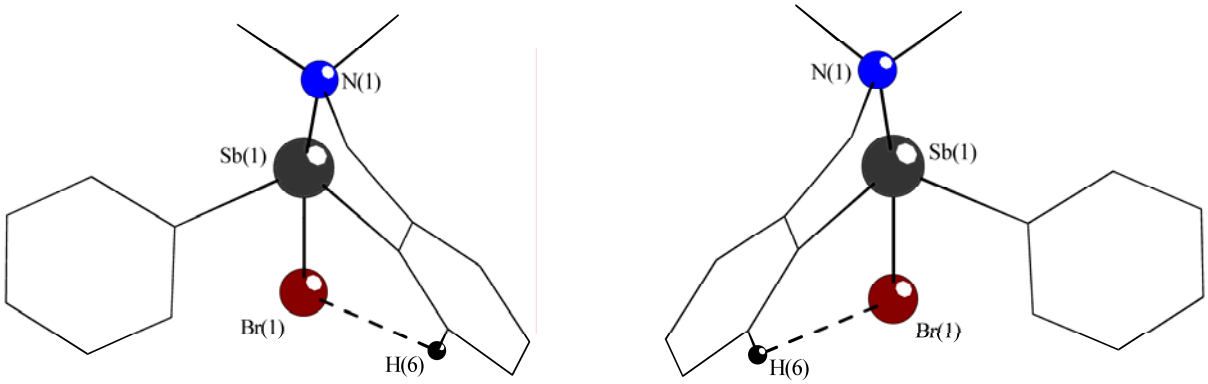


Figure S1. Molecular structure of (R_N,A_{Sb})-**2** isomer (*left*) and (S_N,C_{Sb})-**2** isomer (*right*) in the crystal of **2**, showing the intramolecular bromine-hydrogen contact (only hydrogen atoms involved in intramolecular contacts are shown).

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

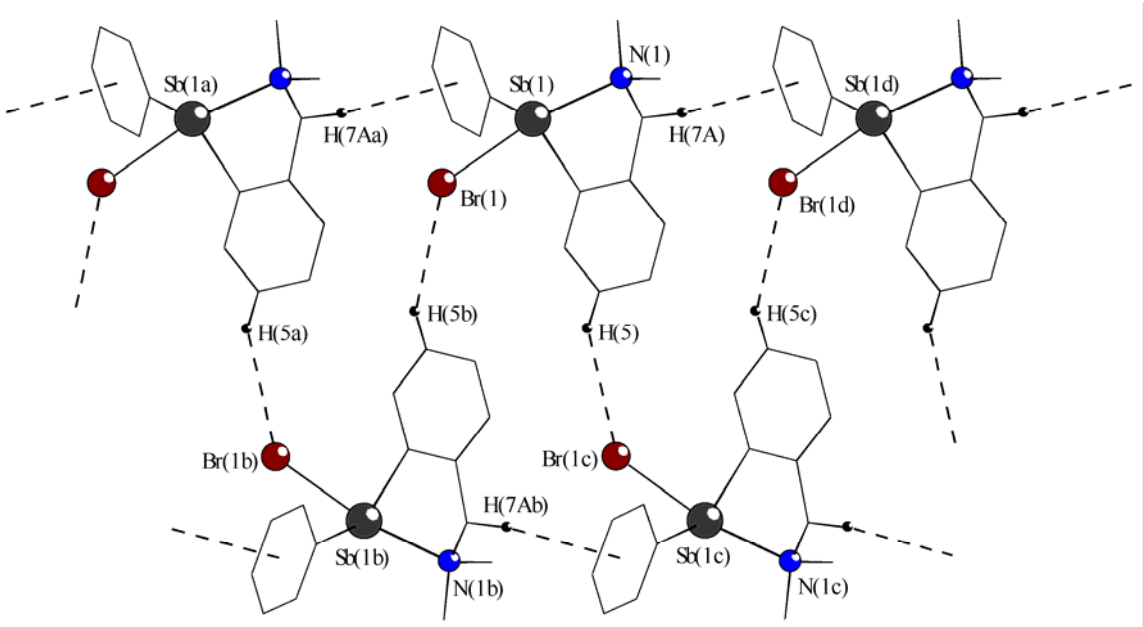


Figure S2. View of a chain polymer based on Br···H$_{aryl}$ and C-H$_{methylene}$···π (Ph$_{centroid}$) contacts between (S_N,C_{Sb})-**2** isomers in the crystal of **2** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (x, $-1 + y$, z), ($0.5 - x$, $-0.5 + y$, $0.5 - z$), ($0.5 - x$, $0.5 + y$, $0.5 - z$) and ($0.5 - x$, $0.5 + y$, $0.5 - z$) are given by ''a'', ''b'', ''c'' and ''d'', respectively].

- intermolecular distance Br(1)···H(5a) 3.12 Å
  C(7)-H(7A)···π (Ph$_{centroid}$) 2.95 Å

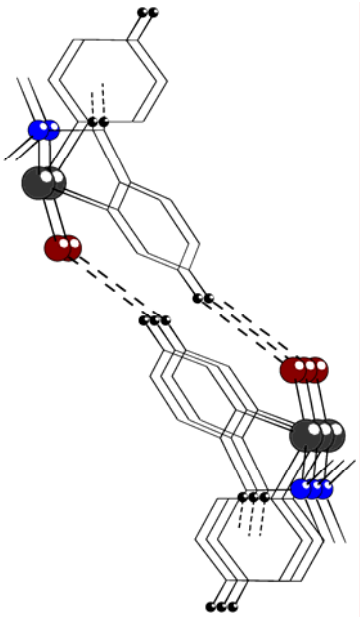


Figure S3. View along *b* axis of a chain polymer built from (S_N,C_{Sb})-**2** isomers in the crystal of **2** through Br···H_{aryl} and C-$H_{methylene}$···π ($Ph_{centroid}$) contacts.

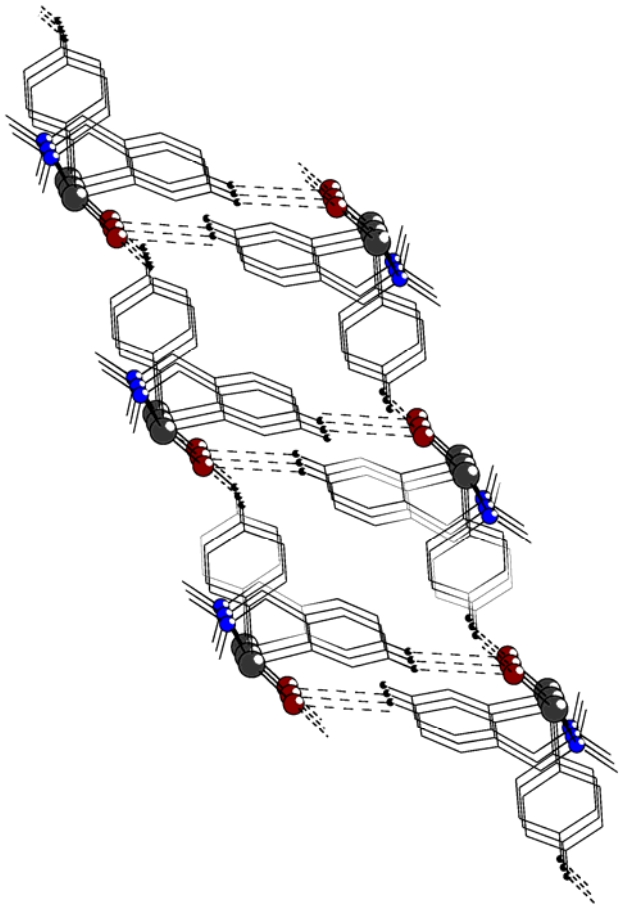


Figure S4. View of a layer with inter-chain Br···H_{aryl} contacts between alternating chain polymers built from (S_N,C_{Sb})-**2** and (R_N,A_{Sb})-**2** isomers, respectively, in the crystal of **2**.

- inter-chain distance Br(1)···H(13) 3.14 Å $\sum r_{vdW}$(Br,H) 3.15 Å

[2-(Me$_2$NCH$_2$)C$_6$H$_4$]PhSbI (3)

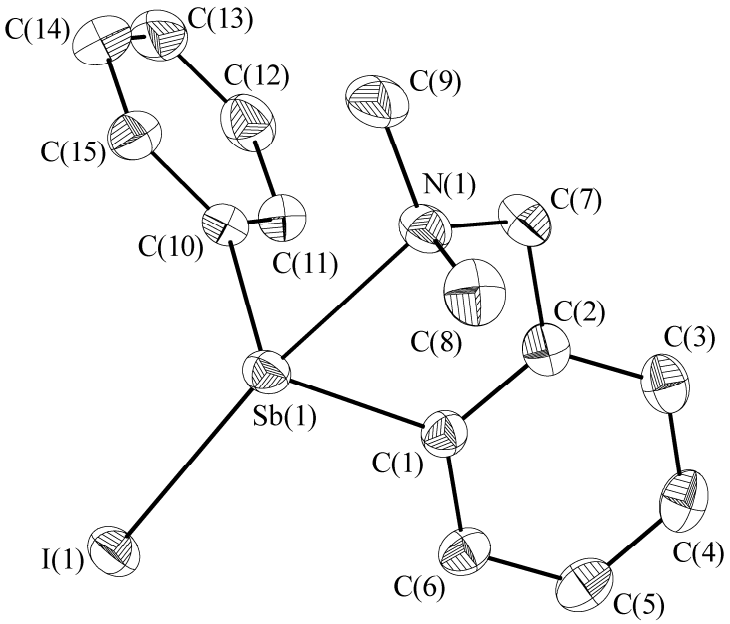


Figure S5. ORTEP representation at 30% probability and atom numbering scheme for (S_N,C_{Sb})-**3** isomer. Hydrogen atoms are omitted.

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

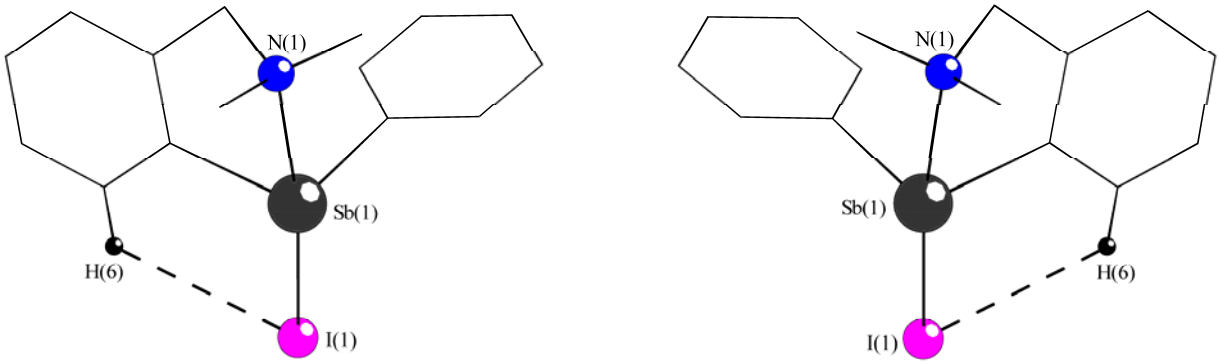


Figure S6. Molecular structure of (R_N,A_{Sb})-**3** isomer (*left*) and (S_N,C_{Sb})-**3** isomer (*right*) in the crystal of **3**, showing the intramolecular iodine-hydrogen contact (only hydrogen atoms involved in intramolecular contacts are shown).

- intramolecular distance I(1)···H(6) 3.04 Å $\sum r_{vdW}$(I,H) 3.35 Å

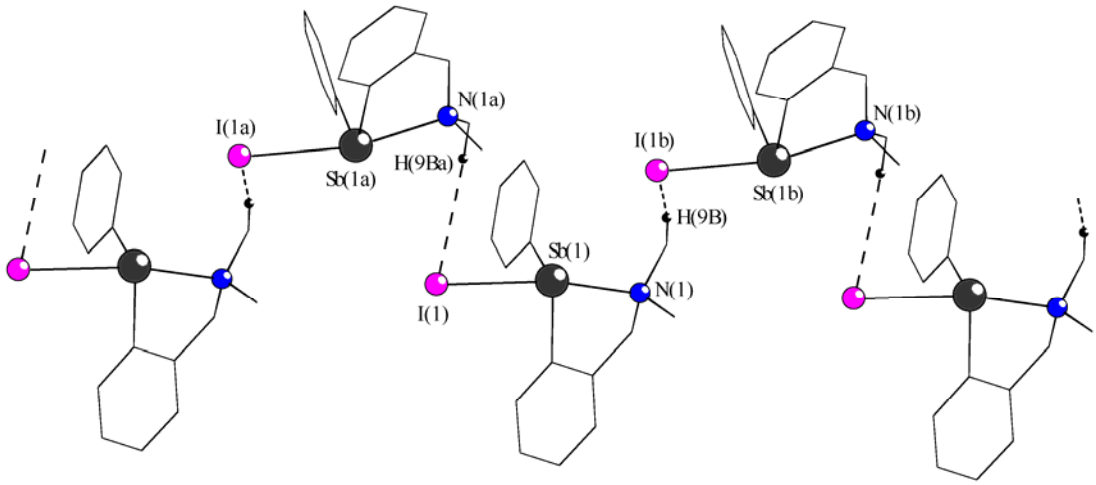


Figure S7. View of a chain polymer based on I···H_{methyl} contacts between alternating (S_N,C_{Sb})-**3** and (R_N,A_{Sb})-**3** isomers in the crystal of **3** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (x, 0.5 – y, 0.5 + z) and (x, 0.5 – y, –0.5 + z) are given by ‘‘a’’ and ‘‘b’’, respectively].

- intermolecular distance I(1)···H(9B) 3.22 Å $\sum r_{vdW}$(I,H) 3.35 Å

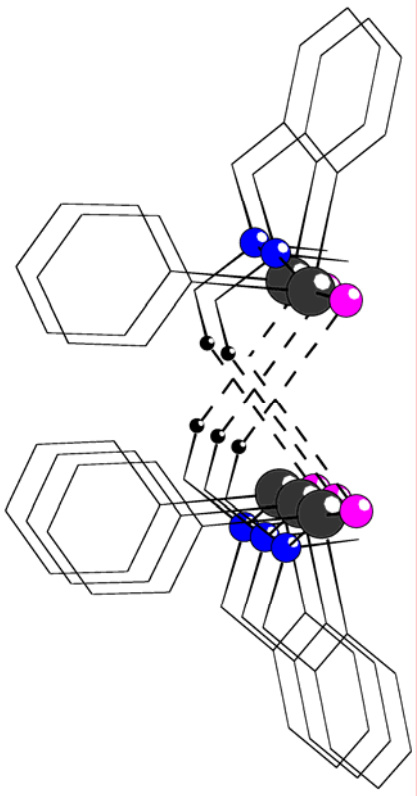


Figure S8. View along c axis of a chain polymer in the crystal of **3**.

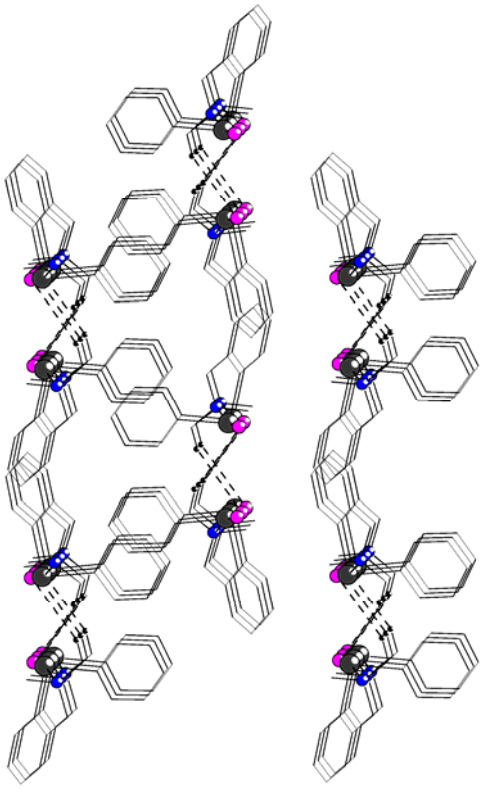


Figure S9. View along *c* axis of parallel chain polymers in the crystal of **3**.

- no further I···H contacts between parallel chains.

[2-(Me$_2$NCH$_2$)C$_6$H$_4$]Ph$_2$Sb (4)

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

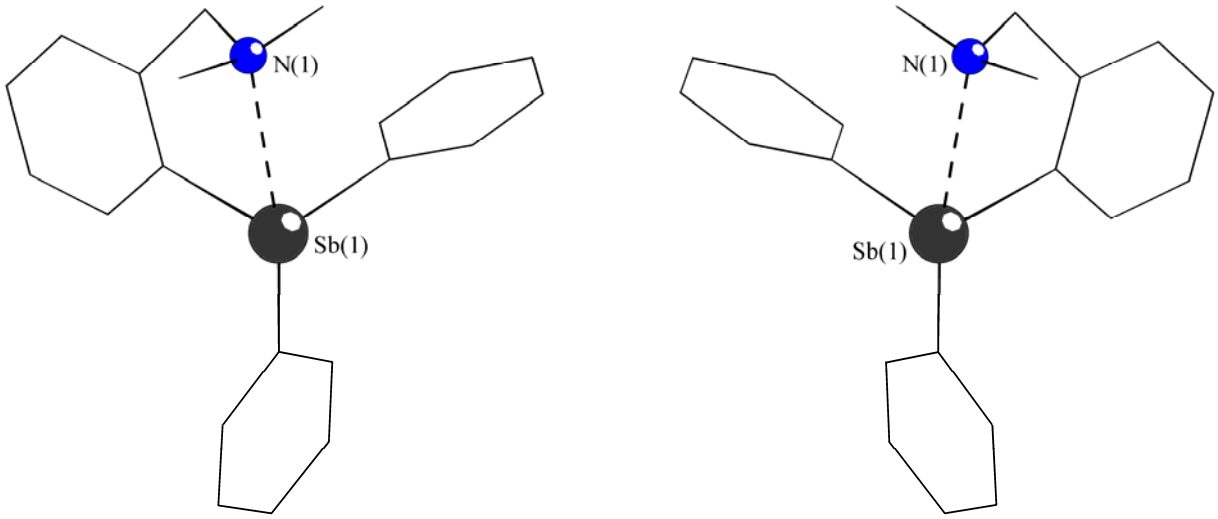


Figure S10. Molecular structure of (R_N,C_{Sb})-**4** isomer (*left*) and (S_N,A_{Sb})-**4** isomer (*right*) in the crystal of **4**.

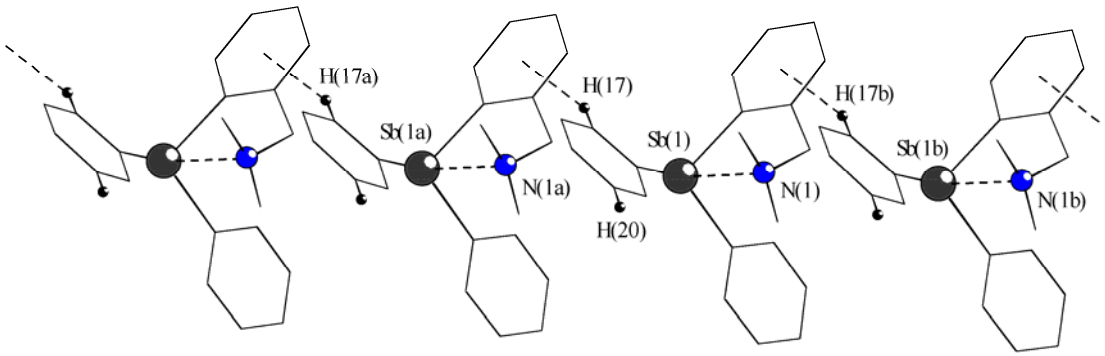


Figure S11. View of a chain polymer based on C-H$_{aryl}$···π (Ph$_{centroid}$) contacts between (R_N,C_{Sb})-**4** isomers in the crystal of **4** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (x, y, –1 + z) and (x, y, 1 + z) are given by ‘‘a’’ and ‘‘b’’,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

- intra-chain distance C(17)-H(17)···π (Ph$_{centroid}$) 2.80 Å

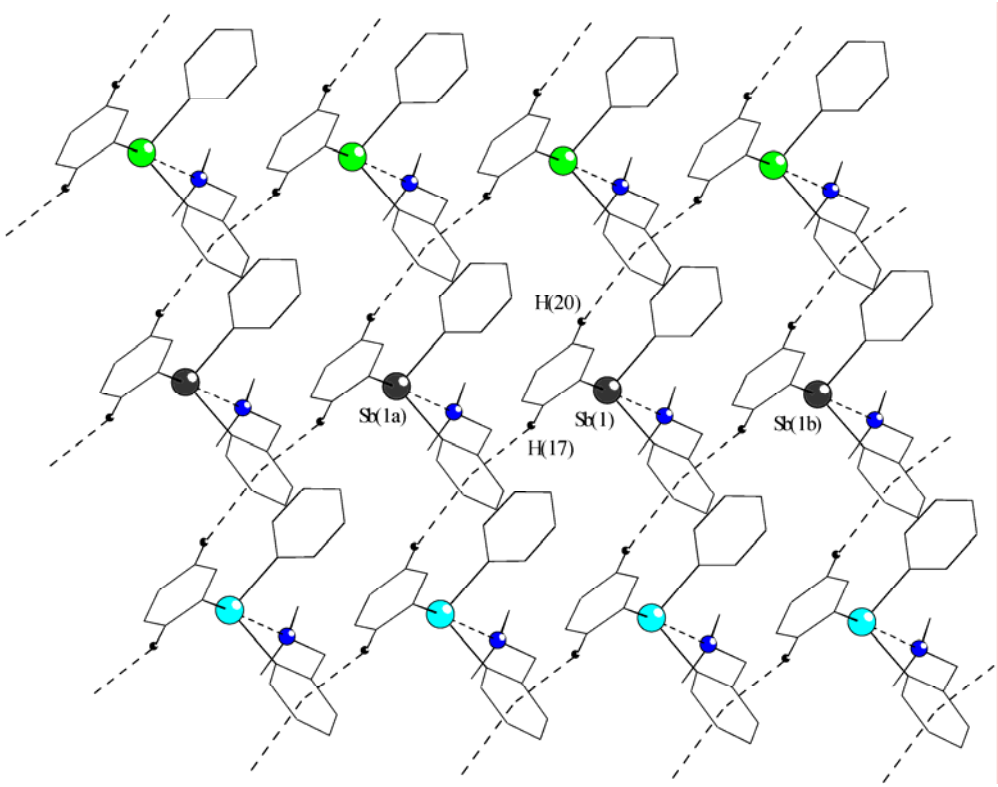


Figure S12. View of a layer of (R_N,C_{Sb})-**4** isomers based on C-H_{aryl}···π ($Ph_{centroid}$) contacts in the crystal of **4** (only hydrogen atoms involved in intermolecular contacts are shown).

- 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.

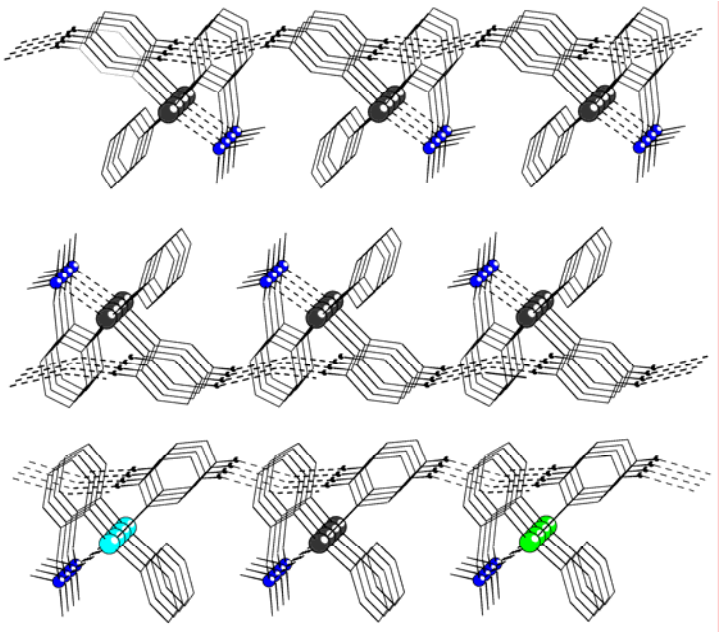


Figure S13. View along *c* axis of alternative layers of (R_N,C_{Sb}) and (S_N,A_{Sb}) isomers, respectively, in the crystal of **4**.

[2-(Me$_2$NCH$_2$)C$_6$H$_4$]$_2$PhSb (5)

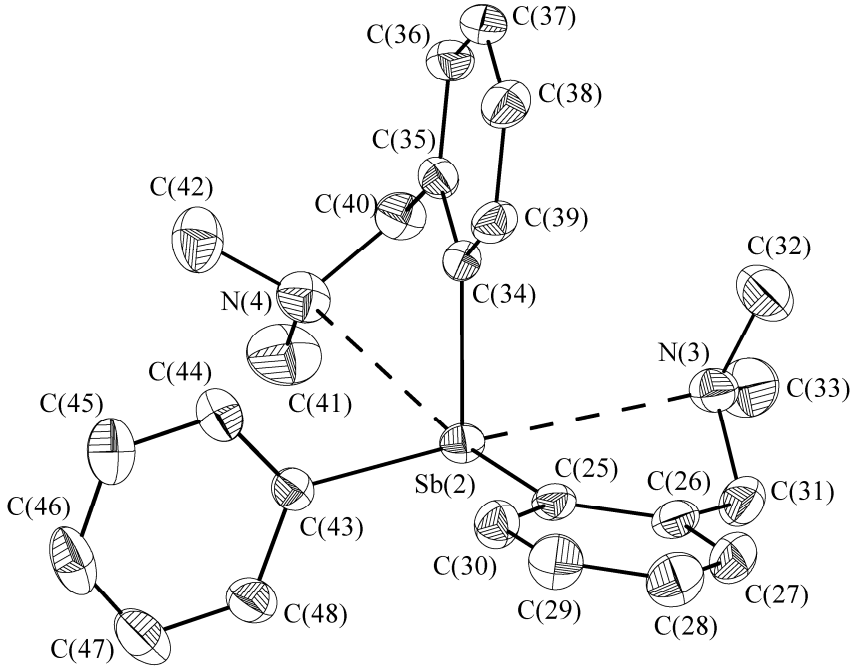
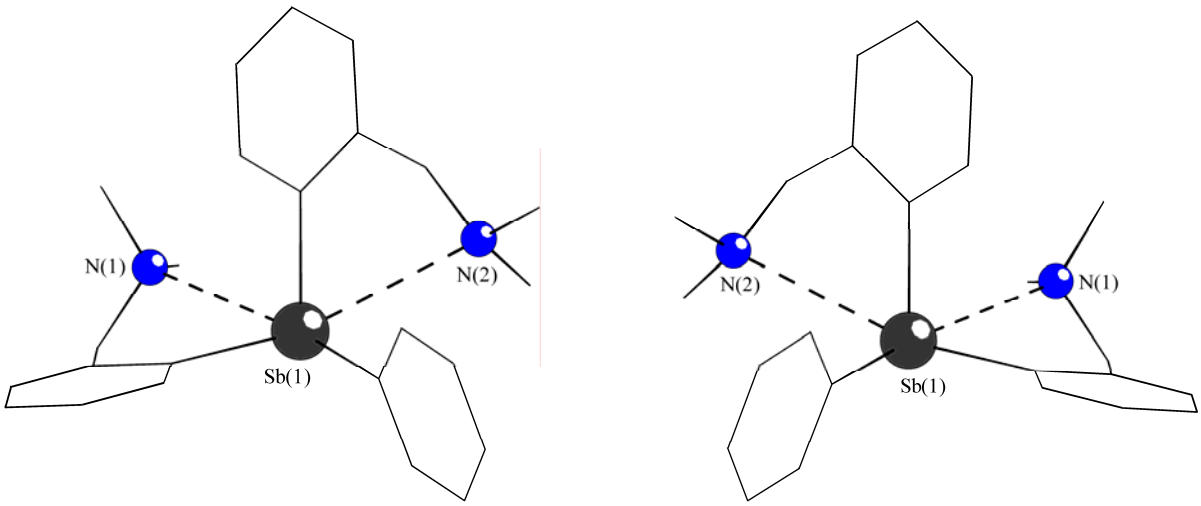
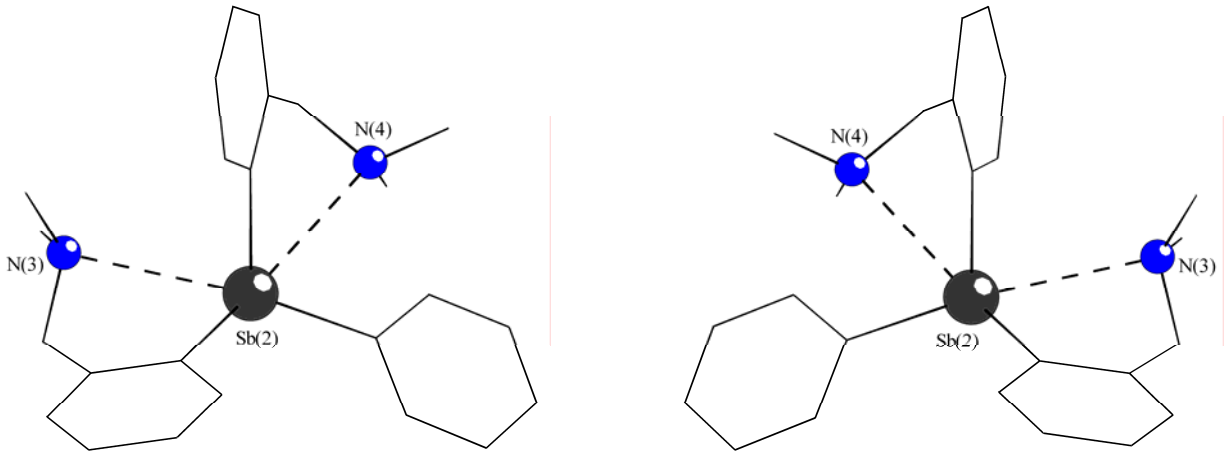


Figure S14. ORTEP representation at 30% probability and atom numbering scheme for (S_{N3},S_{N4},C_{Sb2})-**5b** isomer. Hydrogen atoms are omitted.

- 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



(a)



(b)

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**.

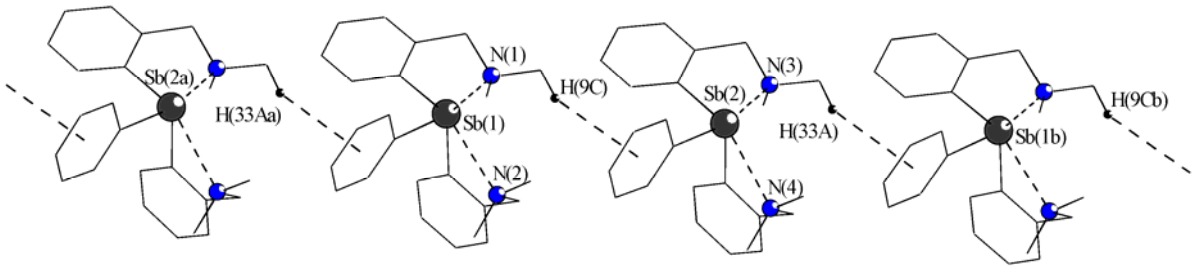


Figure S16. View along axis *a* of a chain polymer based on C-H_{methyl}···π ($Ph_{centroid}$) contacts between alternating (R_{N1},R_{N2},A_{Sb1})-**5a** and (S_{N3},S_{N4},C_{Sb2})-**5b** isomers in the crystal of **5** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (x, y, 1 + z) and (x, y, –1 + z) are given by ''a'' and ''b'', respectively].

- intra chain distance C(17)-H(17)···π ($Ph_{centroid}$) 3.06 Å

- no further contacts between parallel chains.

[2-(Me_2NCH_2)C_6H_4]PhMesSb (6)

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

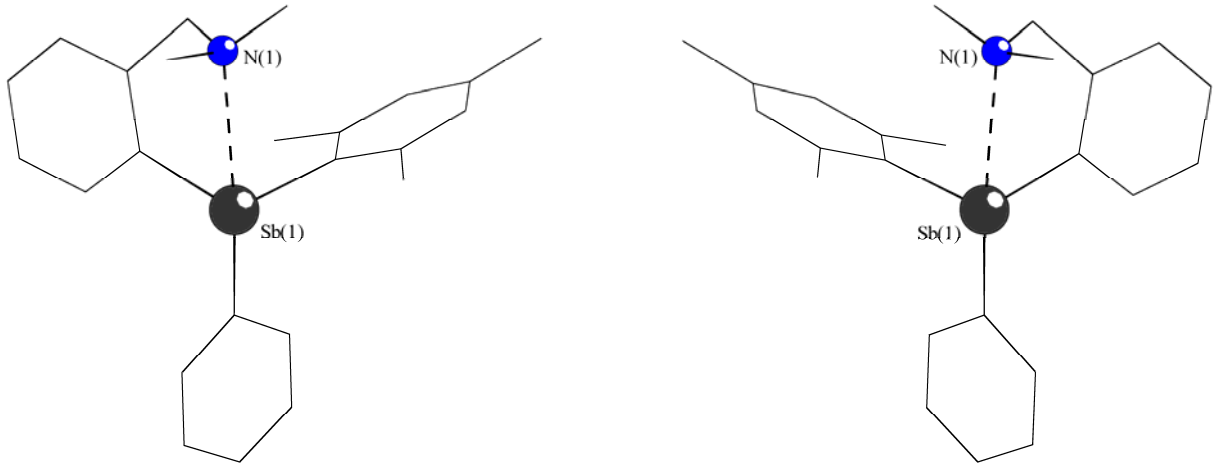


Figure S17. Molecular structure of (R_N,A_{Sb})-**6** isomer (*left*) and (S_N,C_{Sb})-**4** isomer (*right*) in the crystal of **6**.

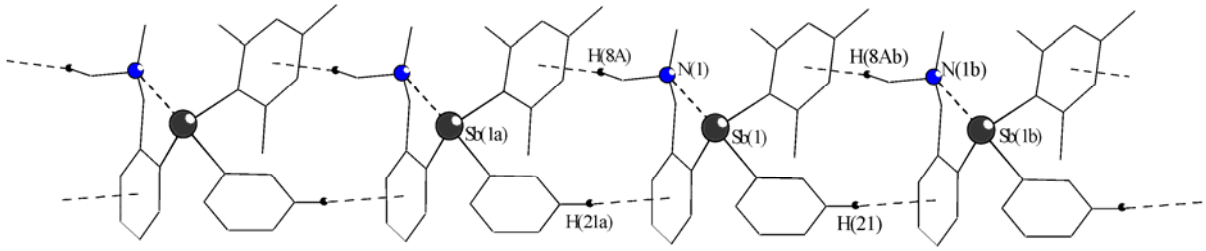


Figure S18. View of a chain polymer based on C-H_{aryl}···π and C-H_{methyl}···π ($Ph_{centroid}$) contacts between (R_N,A_{Sb})-**6** isomers in the crystal of **6** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (–1 + *x*, *y*, *z*) and (1 + *x*, *y*, *z*) are given by ‘‘a’’ and ‘‘b’’, respectively].

- intra chain distance
  - C(21)-H(21)···π ($Ph_{centroid}$) 2.90 Å
  - C(8)-H(8A)···π ($Ph_{centroid}$) 2.94 Å

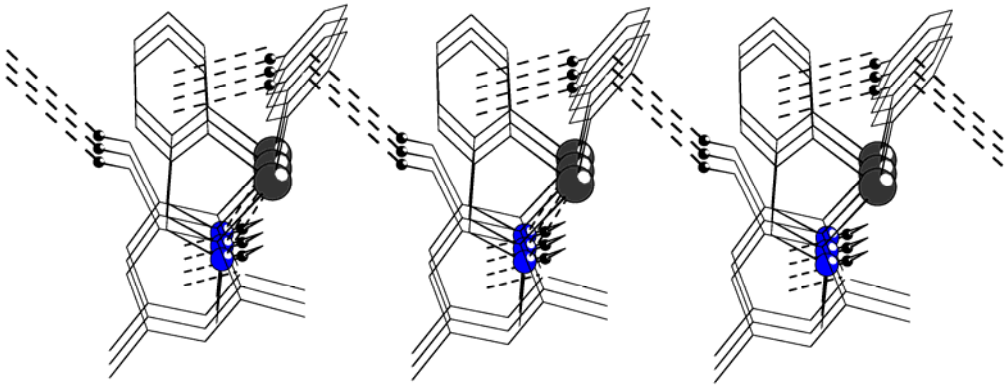


Figure S19. View of a layer of (R_N,A_{Sb})-**6** isomers based on C-H_{methyl}···π ($Ph_{centroid}$) contacts in the crystal of **6** (only hydrogen atoms involved in intermolecular contacts are shown).

- inter-chain distance C(16)-H(16B)···π ($Ph_{centroid}$) 2.97 Å

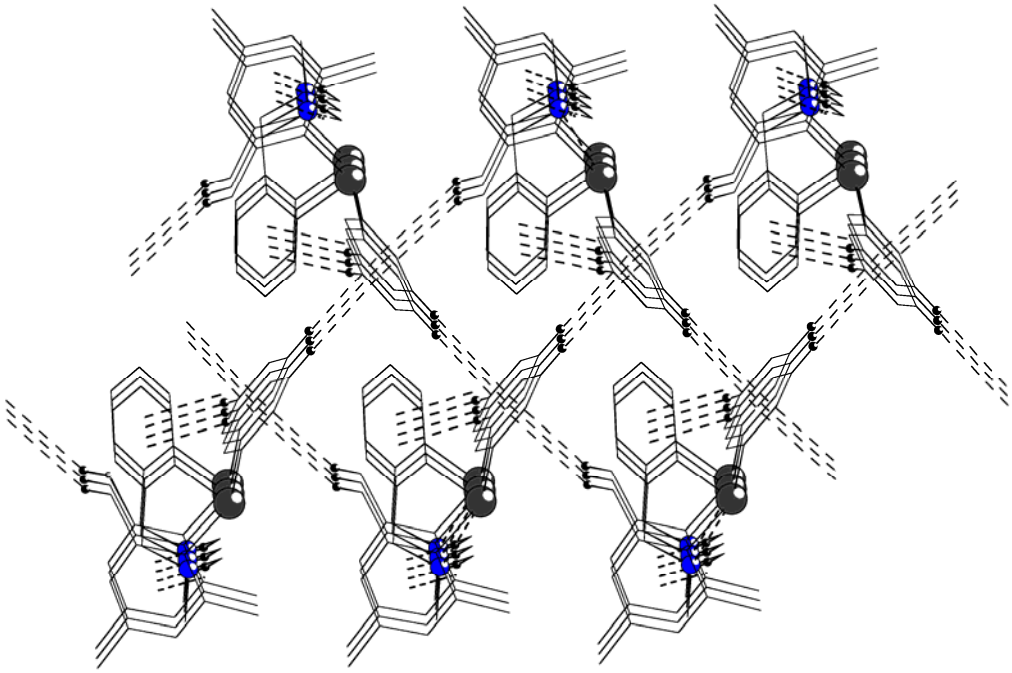


Figure S20. View of a double-layer association between layers of (R_N,A_{Sb}) and (S_N,C_{Sb}) isomers, respectively, in the crystal of **6**.

- inter-layer distance C(23)-H(23)···π ($Ph_{centroid}$) 2.98 Å

[2-(Me$_2$NCH$_2$)C$_6$H$_4$]MesSbBr (7)

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

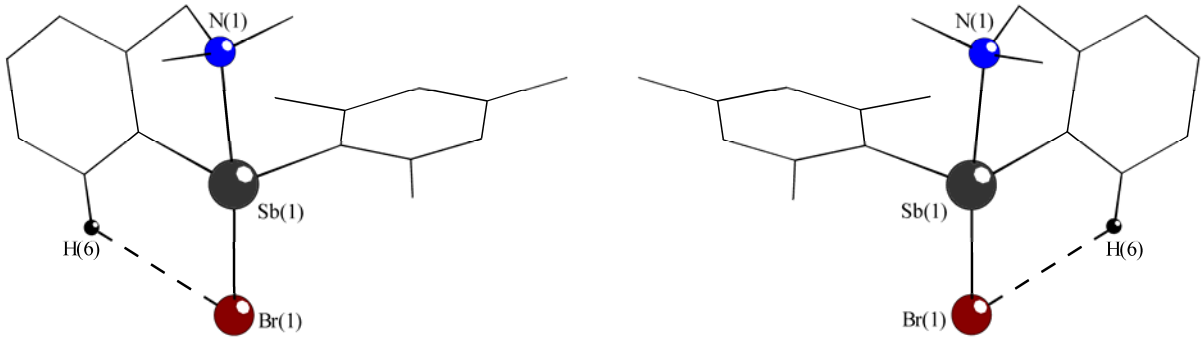


Figure S21. Molecular structure of (R_N,C_{Sb})-**7** isomer (*left*) and (S_N,A_{Sb})-**7** isomer (*right*) in the crystal of **7**, showing the intramolecular bromine-hydrogen contact (only hydrogen atoms involved in intramolecular contacts are shown).

- intramolecular distance Br(1)···H(6) 2.86 Å $\sum r_{vdW}$(Br,H) 3.15 Å

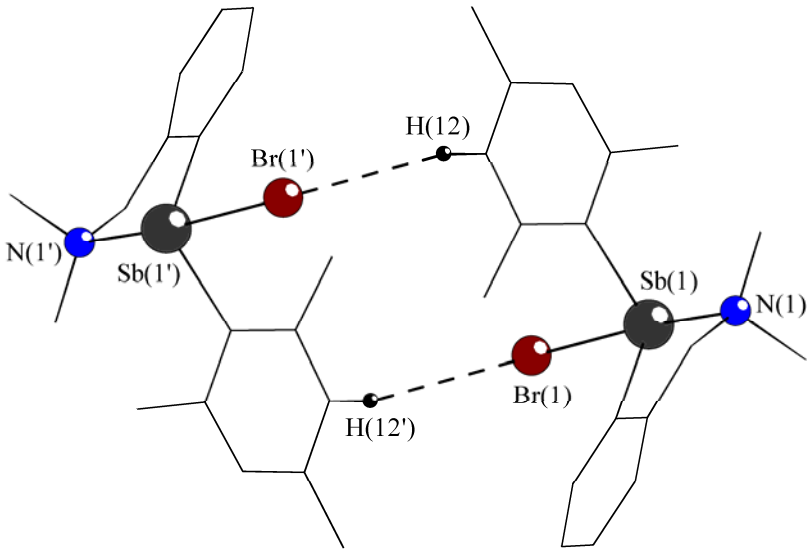


Figure S22. View of a dimer based on Br···H$_{aryl}$ contacts between (R_N,C_{Sb}) and (S_N,A_{Sb})-**7** isomers in the crystal of **7** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (1 – x, 1 – y, –z) are given by ‘‘prime’’].

- intermolecular distance Br(1)···H(12a) 3.07 Å

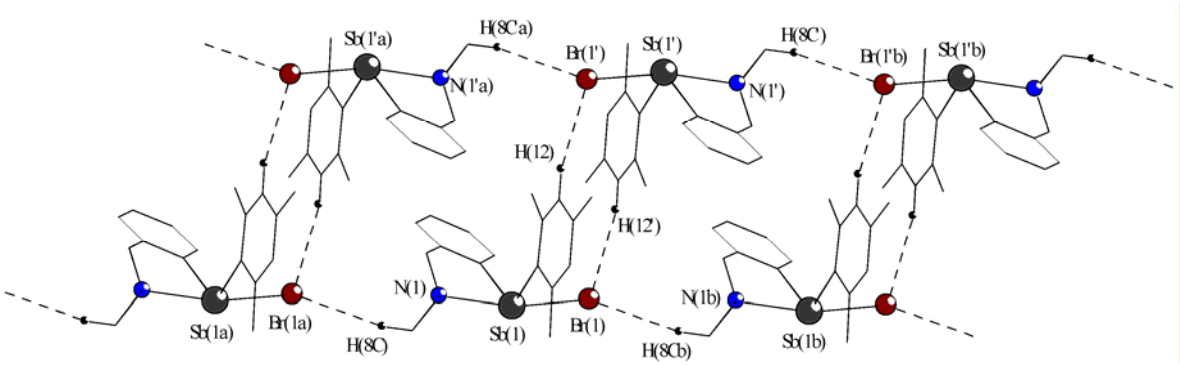


Figure S23. View of a columnar polymer of (R_N,C_{Sb}) / (S_N,A_{Sb})-**7** dimer units based on Br···H_{methyl} contacts in the crystal of **7** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (1 – *x*, 1 – *y*, –*z*), (*x*, 1 – *y*, *z*), (1 – *x*, – *y*, –*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 Br(1)···H(8Cb) 3.10 Å

[2-(Me_2NCH_2)C_6H_4]MesSbBr (7)

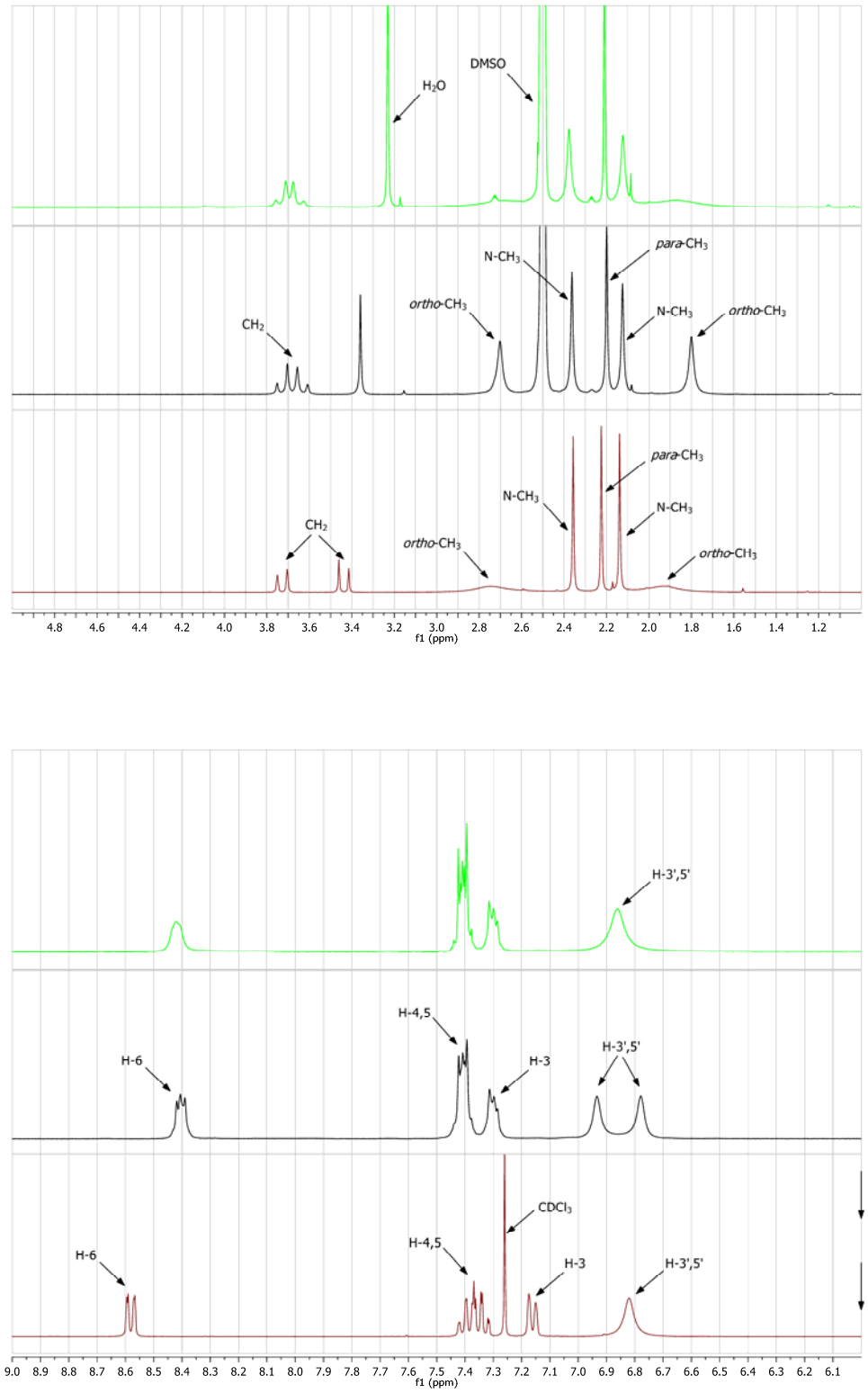


Figure S23a. ^{1}H NMR spectra of **7**: (*up*) aliphatic region, and (*down)* aromatic region [*violet* - in $CDCl_3$, at r.t.; *black* - in DMSO-d_6, at 20 °C; *green* - in DMSO-d_6, at 45 °C].

Coalescence of resonances for the aromatic protons of mesityl group in DMSO-d_6

^{1}H NMR (300 MHz, 20 °C, DMSO-d_6): δ 1.80 (3 H, s, *ortho*-CH_3), 2.12 [3 H, s, $N(CH_3)_2$ (A)], 2.20 (3 H, s, *para*-CH_3), 2.36 [3 H, s, $N(CH_3)_2$ (B)], 2.70 (3 H, s, *ortho*-CH_3), AB spin system with A at 3.633 and B at 3.728 ppm (2 H, CH_2, $^2J_{HH}$ 14.40 Hz), 6.78 (1 H, s,br, H-3',5', C_6H_2), 6.93 (1 H, s,br, H-3',5', C_6H_2), 7.30 (1 H, m, H-3, C_6H_4), 7.41 (2 H, ddd, H-4,5, C_6H_4), 8.40 (1 H, m, H-6, C_6H_4).

^{1}H NMR (300 MHz, 45 °C, DMSO-d_6): δ 1.87 (3 H, s,br, *ortho*-CH_3), 2.12 [3 H, s, $N(CH_3)_2$ (A)], 2.21 (3 H, s, *para*-CH_3), 2.38 [3 H, s, $N(CH_3)_2$ (B)], 2.68 (3 H, s,br, *ortho*-CH_3), AB spin system with A at 3.651 and B at 3.734 ppm (2 H, CH_2, $^2J_{HH}$ 14.20 Hz), 6.86 (2 H, s,br, H-3',5', C_6H_2), 7.30 (1 H, m, H-3, C_6H_4), 7.41 (2 H, ddd, H-4,5, C_6H_4), 8.42 (1 H, m, H-6, C_6H_4).

[2-(Me$_2$NCH$_2$)C$_6$H$_4$]MesSbI (8)

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

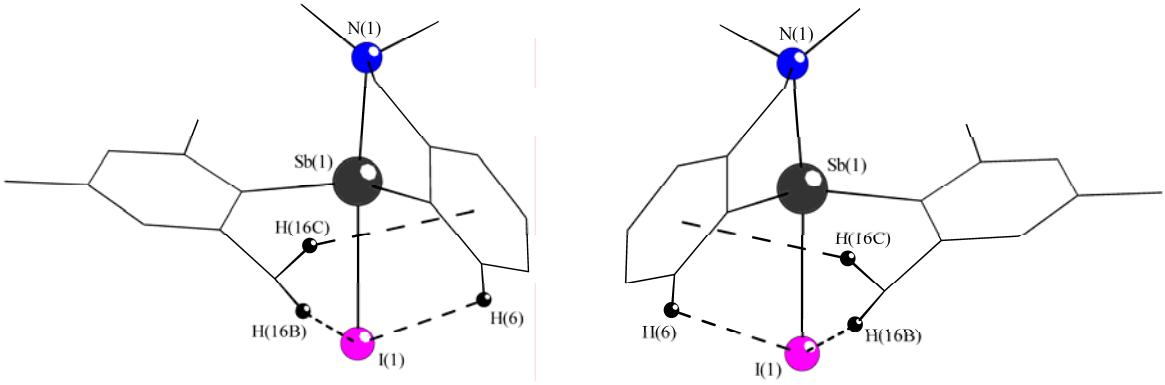


Figure S24. Molecular structure of (R_N,C_{Sb})-**8** isomer (*left*) and (S_N,A_{Sb})-**8** isomer (*right*) in the crystal of **8**, showing the intramolecular iodine-hydrogen and C-H$_{methyl}$···π (Ph$_{centroid}$) contacts (only hydrogen atoms involved in intramolecular interactions are shown).

- intramolecular distance	I(1)···H(6)	3.06 Å	$\sum r_{vdW}$(I,H) 3.35 Å
	I(1)···H(16B)	3.23 Å	
	C(16)-H(16C)···π (Ph$_{centroid}$)	3.02 Å	

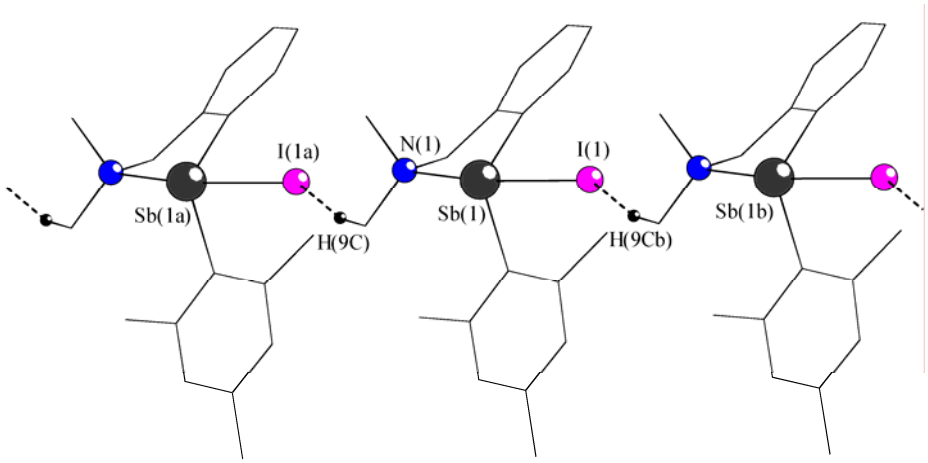


Figure S25. View of a chain polymer association based on I···H$_{methyl}$ contacts between (S_N,A_{Sb})-**8** isomers in the crystal of **8** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (–1 + *x*, *y*, *z*) and (1 + *x*, *y*, *z*) are given by ‘‘a’’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

- intermolecular distance I(1)···H(9Cb) 3.17 Å

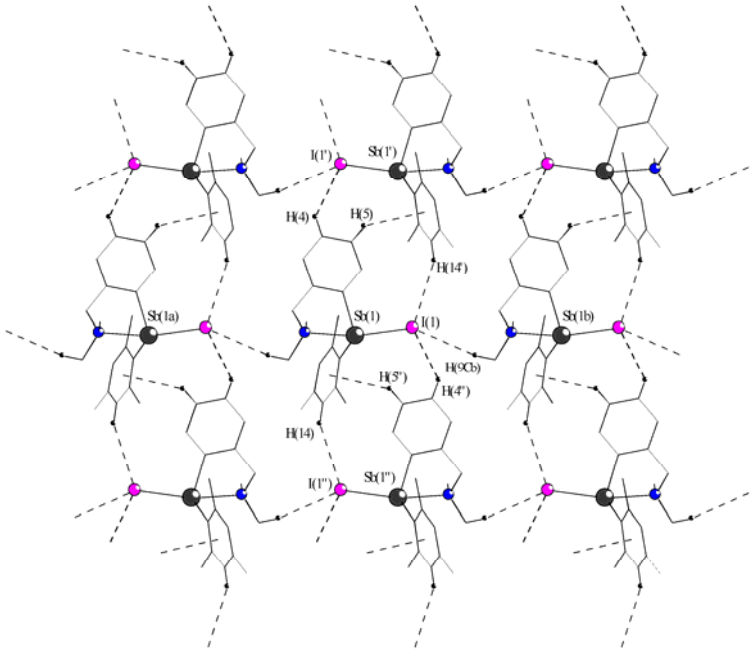


Figure S26. View along axis *c* of a layer of (S_N,A_{Sb})-**8** isomers based on I···H_{methyl}, I···H_{aryl} and C-H_{aryl}···π ($Ph_{centroid}$) contacts in the crystal of **8** (only hydrogen atoms involved in intermolecular contacts are shown) [symmetry equivalent atoms (2 – *x*, 0.5 + *y*, 0.5 – *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

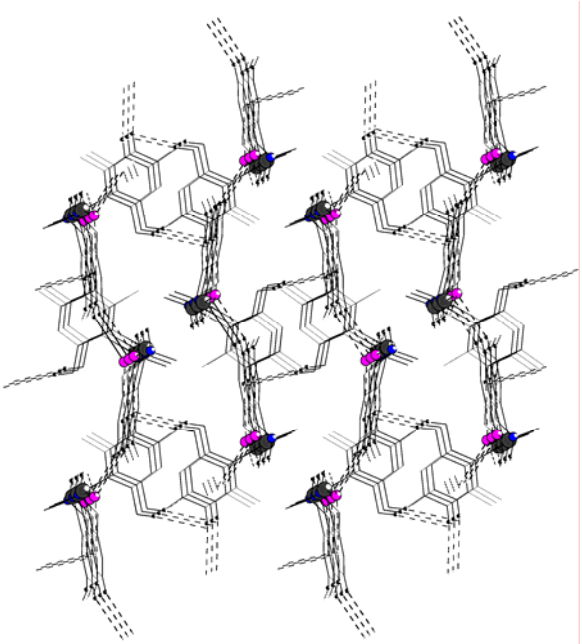


Figure S27. View along axis *a* of the 3D structure built from alternating layers of (R_N,C_{Sb})-**8** and (S_N,A_{Sb})-**8** isomers based on C-H_{methyl}···π ($Ph_{centroid}$) contacts in the crystal of **8** (only hydrogen atoms involved in intermolecular contacts are shown).

-	intermolecular distance	C(16)-H(16A)···π ($Ph_{centroid}$)	2.99 Å

$[2\text{-}(Me_2NCH_2)C_6H_4]Mes_2Sb$ (9)

^{1}H NMR (200 MHz, 20 °C, C_6D_6): δ 1.79 [6 H, s, $N(CH_3)_2$], 2.13 (6 H, s, *para*-CH_3), 2.40 (12 H, s, *ortho*-CH_3), 3.35 (2 H, s, CH_2), 6.77 (4 H, s, H-3',5', C_6H_2), 6.91 (1 H, m, H-5, C_6H_4), 7.03 (2 H, m, H-3,4, C_6H_4), 7.91 (1 H, d, H-6, C_6H_4, $^3J_{HH}$ 7.2 Hz).

^{13}C-NMR (50 MHz, 20 °C, C_6D_6): 20.98 (s, *para*-CH_3), 26.16 (s, *ortho*-CH_3), 44.31 [s, $N(CH_3)_2$], 66.21 (s, CH_2), 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).