

Supporting information

Monoorganobismuth(III) dihalides containing the new pincer 2,6-{MeN(CH₂CH₂)₂NCH₂}₂C₆H₃ ligand: solution NMR, vibrational and single-crystal X-ray studies

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[2,6-{MeN(CH₂CH₂)₂N}CH₂]₂C₆H₃]BiCl₂ (**2**)

- the crystal contains a 1:1 mixture of (*S*_{N1},*S*_{N3}) and (*R*_{N1},*R*_{N3}) isomers
 - intramolecular distances
- | | | |
|--------------|--------|-----------------------------|
| Cl(1)⋯H(7A) | 2.96 Å | $\sum r_{vdw}(Cl,H)$ 3.01 Å |
| Cl(1)⋯H(12B) | 2.85 Å | |
| Cl(1)⋯H(16B) | 2.87 Å | |
| Cl(2)⋯H(8A) | 2.85 Å | |
| Cl(2)⋯H(10B) | 2.86 Å | |
| Cl(2)⋯H(14B) | 2.95 Å | |

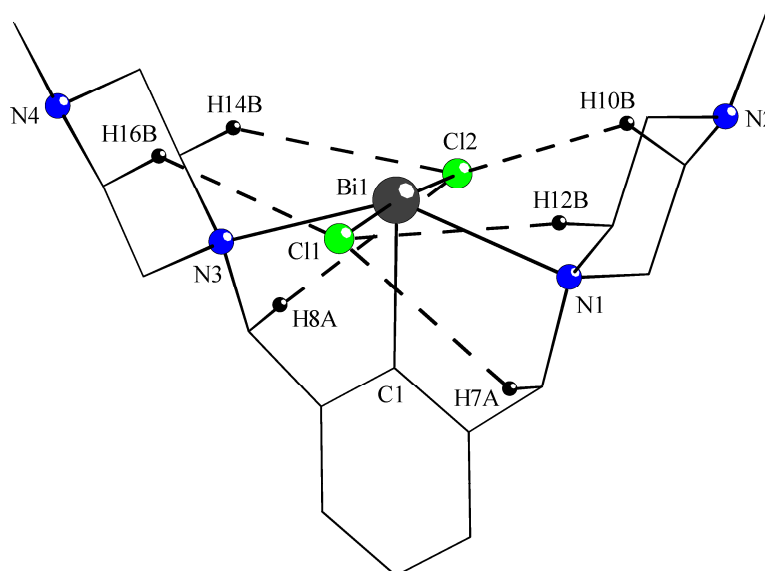


Figure S1. Intramolecular chlorine-hydrogen contacts in the molecule of (*R*_{N1},*R*_{N3})-**2** isomer (only hydrogens involved in intramolecular interactions are shown).

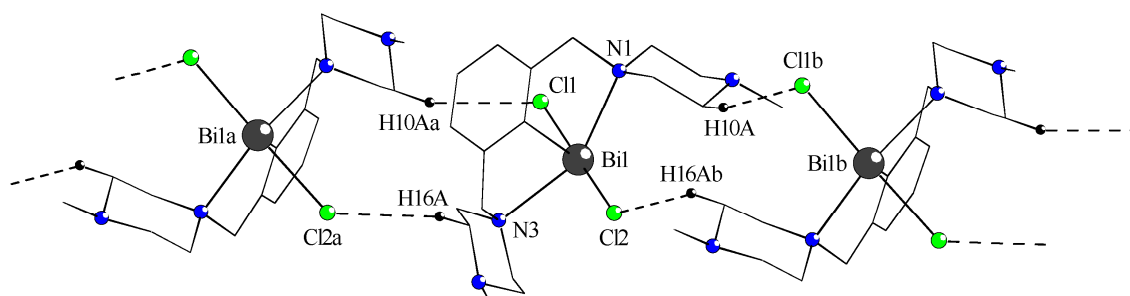


Figure S2. View of the chain polymer of alternating (*S*_{N1},*S*_{N3}) and (*R*_{N1},*R*_{N3}) isomers in the crystal of **2** (only hydrogens involved in intermolecular interactions are shown). Symmetry equivalent positions: Bi(1a) (*0.5+x*, *1.5-y*, *0.5+z*); Bi(1b) (*-0.5+x*, *1.5-y*, *-0.5+z*). Intermolecular contacts within a chain: Cl(1)⋯H(10Aa)_{N-methylene-ring} 2.85 Å; Cl(2)⋯H(16Ab)_{N-methylene-ring} 2.87 Å. No further inter-chain contacts.

[2,6-{MeN(CH₂CH₂)₂N}CH₂]₂C₆H₃]BiBr₂ (**3**)

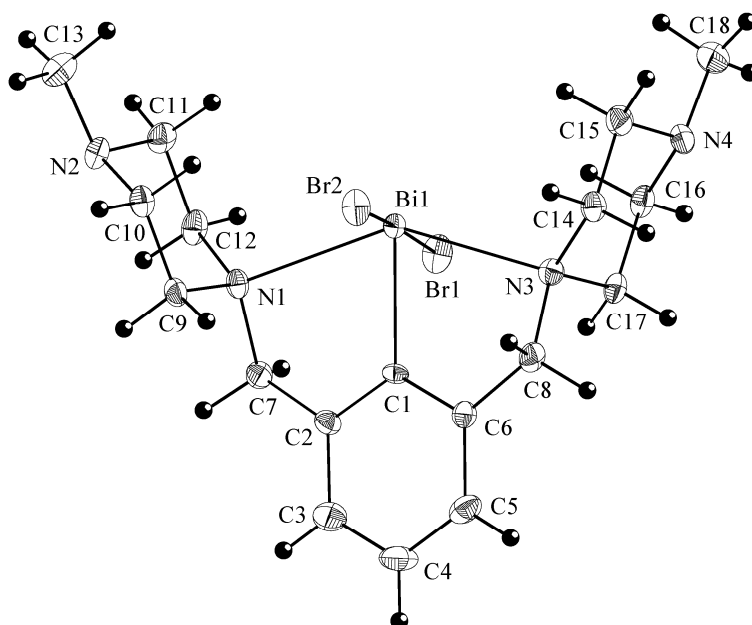


Figure S3. Molecular structure of the (*R*_{N1},*R*_{N3}) isomer of **3** (ORTEP drawing with 20% probability ellipsoids) with the labeling scheme for the atom positions.

- the crystal contains a 1:1 mixture of (*S*_{N1},*S*_{N3}) and (*R*_{N1},*R*_{N3}) isomers
- intramolecular distances
Br(1)⋯H(7A) 2.92 Å
Br(1)⋯H(12B) 3.00 Å
Br(1)⋯H(17A) 3.10 Å
Br(1)⋯H(16B) 2.94 Å
Br(2)⋯H(10B) 2.93 Å
Br(2)⋯H(8A) 3.03 Å
Br(2)⋯H(14B) 2.90 Å
 $\sum r_{\text{vdW}}(\text{Br},\text{H})$ 3.15 Å

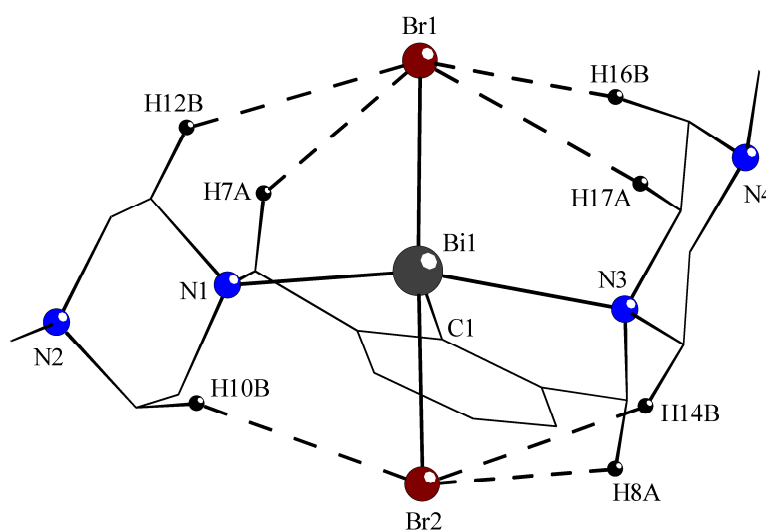


Figure S4. Intramolecular bromine-hydrogen contacts in the molecule of (*R*_{N1},*R*_{N3})-**3** isomer (only hydrogens involved in intramolecular interactions are shown).

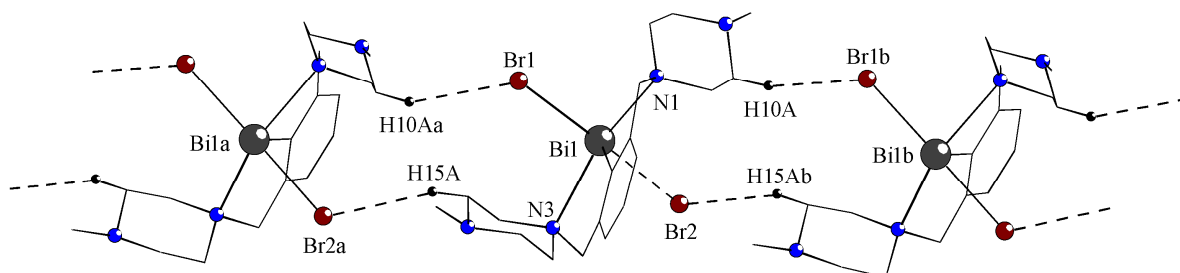


Figure S5. View of the chain polymer of alternating (S_{N1}, S_{N3}) and (R_{N1}, R_{N3}) isomers in the crystal of **3** (only hydrogens involved in intermolecular interactions are shown). Symmetry equivalent positions: Bi(1a) ($-0.5+x, 0.5-y, -0.5+z$); Bi(1b) ($0.5+x, 0.5-y, 0.5+z$). Intermolecular contacts within a chain: Br(1) \cdots H(10Aa)_{N-methylene-ring} 2.94 Å; Br(2) \cdots H(16Ab)_{N-methylene-ring} 2.96 Å.

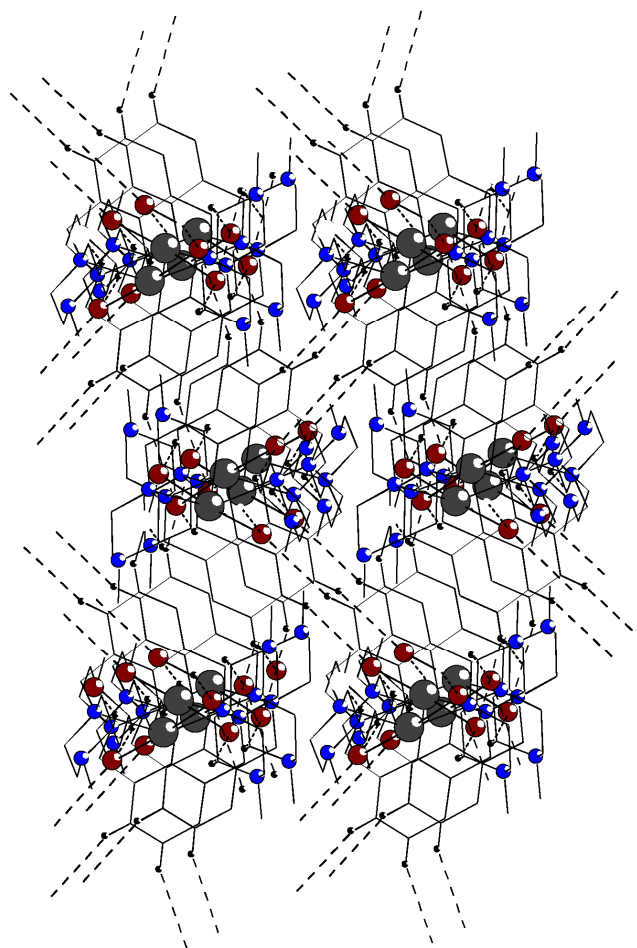


Figure S6. View of the tridimensional network built from columnar chain polymers in the crystal of **3**, through weak bromine-hydrogen inter-chain contacts (only hydrogens involved in hydrogen contacts are shown). Symmetry equivalent positions: Bi(1c) ($1.5-x, -0.5+y, 0.5-z$); Bi(1d) ($0.5-x, -0.5+y, 0.5-z$); Bi(1e) ($0.5-x, 0.5+y, 0.5-z$); Bi(1f) ($1.5-x, 0.5+y, 0.5-z$). Inter-chain contacts: Br(1) \cdots H(4e)_{aryl} 3.11 Å; Br(2) \cdots H(5f)_{aryl} 3.14 Å.

[2,6-{MeN(CH₂CH₂)₂N}CH₂]₂C₆H₃]BiI₂ (4)

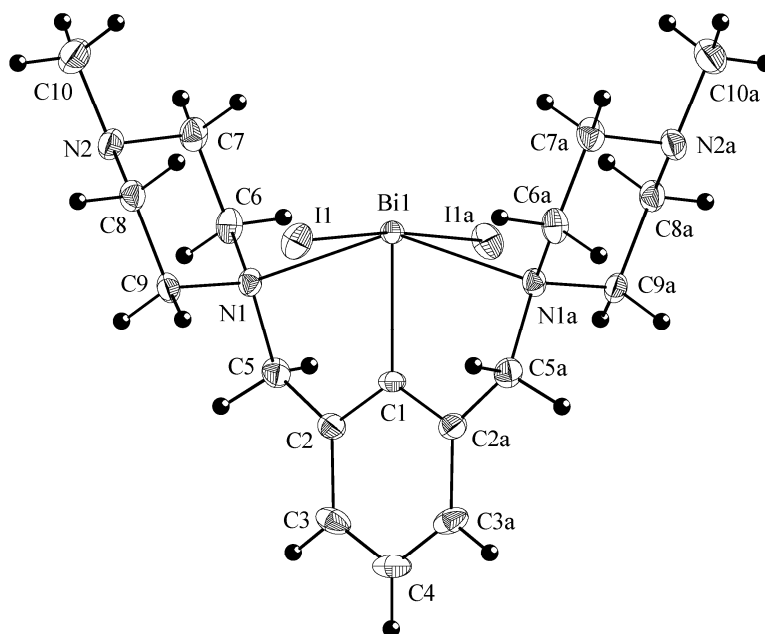


Figure S7. Molecular structure of the (*R*_{N1},*R*_{N1a}) isomer of **4** (ORTEP drawing with 20% probability ellipsoids) with the labeling scheme for the atom positions.

- the crystal contains a 1:1 mixture of (*S*_{N1},*S*_{N1a}) and (*R*_{N1},*R*_{N1a}) isomers
- intramolecular distances
I(1)⋯H(5Aa) 3.21 Å
I(1)⋯H(6Ba) 3.04 Å
I(1)⋯H(8B) 3.18 Å
I(1)⋯H(9A) 3.16 Å
 $\sum r_{\text{vdW}}(\text{I},\text{H})$ 3.35 Å

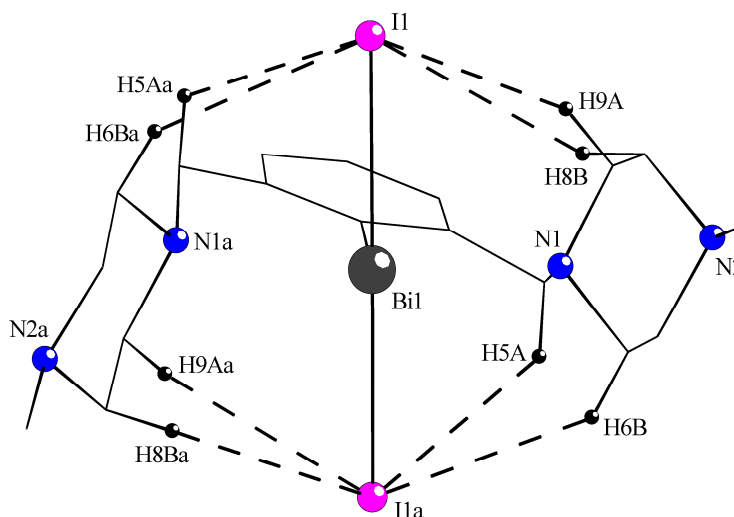


Figure S8. Intramolecular iodine-hydrogen contacts in the molecule of (*R*_{N1},*R*_{N3})-**4** isomer (only hydrogens involved in intramolecular interactions are shown). No further intermolecular contacts.

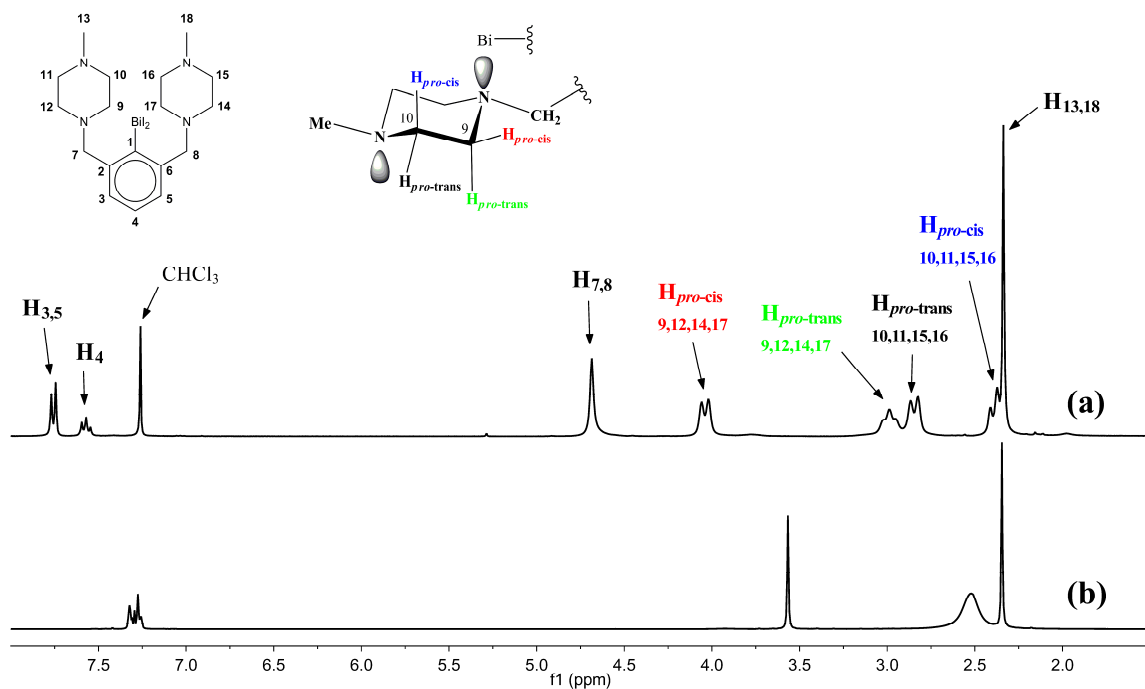
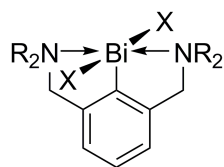


Figure S9. ^1H NMR (CDCl_3 , 400 MHz) spectra of (a) diiodide **4**, and (b) the free organic ligand **1**.



R = H X = Cl (**5a**); Br (**6a**); I (**7a**)
 R = Me X = Cl (**5**); Br (**6**); I (**7**)

Table S1. Selected optimized^{a,b} and experimental^c bond lengths (Å) and angles (°) for the dihalides **5a–7a** and **5–7**.

Compound	R	X	Bi-X	Bi-C	Bi-N	X-Bi-X	N-Bi-N	τ^d
5a	H	Cl	^a 2.683	2.214	2.510	175.69	144.18	80.03
			^b 2.657	2.206	2.490	173.81	143.86	79.40
6a	H	Br	^a 2.860	2.215	2.512	177.97	144.23	80.24
			^b 2.828	2.207	2.490	175.79	143.99	79.53
7a	H	I	^a 3.079	2.215	2.512	179.91	144.53	80.78
			^b 3.039	2.208	2.493	177.57	144.12	80.00
5	Me	Cl	^a 2.692	2.204	2.590	179.94	144.84	70.80
			^b 2.667	2.196	2.556	178.09	144.67	70.01
			^c 2.704	2.224	2.566	173.73	144.18	70.89
6	Me	Br	^a 2.875	2.206	2.601	176.81	144.64	71.09
			^b 2.843	2.198	2.567	178.92	144.47	70.39
			^c 2.840	2.194	2.565	175.86	144.34	71.33
7	Me	I	^a 3.105	2.209	2.616	187.66	144.12	71.08
			^b 3.064	2.201	2.583	185.22	143.99	70.26
			^c 3.082	2.215	2.589	180.30	143.65	70.42

^a Calculated with the B3LYP functional; ^b calculated with the mPW1PWfunctional; ^c structural experimental mean values; ^d dihedral angle between the CBiX₂ plane and that containing the phenyl ring.

Table S2. Selected NBO charges Q (e) and Wiberg bond indexes calculated for dihalides **5a–7a** and **5–7**.

Compound	R	X		Q(Bi)	Q(X)	Q(N)	W(Bi-C)	W(Bi-X)	W(Bi-N)
5a	H	Cl	^a	1.499	-0.663	-0.895	0.709	0.476	0.264
			^b	1.502	-0.662	-0.907	0.704	0.477	0.262
6a	H	Br	^a	1.376	-0.608	-0.892	0.718	0.518	0.268
			^b	1.378	-0.605	-0.904	0.713	0.521	0.267
7a	H	I	^a	1.251	-0.55	-0.891	0.728	0.548	0.273
			^b	1.249	-0.546	-0.902	0.722	0.553	0.271
5	Me	Cl	^a	1.522	-0.657	-0.582	0.699	0.477	0.238
			^b	1.532	-0.655	-0.593	0.691	0.478	0.233
6	Me	Br	^a	1.398	-0.601	-0.578	0.707	0.522	0.243
			^b	1.405	-0.597	-0.588	0.700	0.525	0.238
7	Me	I	^a	1.270	-0.542	-0.573	0.715	0.554	0.246
			^b	1.275	-0.535	-0.585	0.709	0.559	0.242

^a Calculated with the B3LYP functional; ^b calculated with the mPW1PWfunctional.

Table S3. Experimental FT-Raman and FT-IR spectra in the low frequency region (500 –50 cm⁻¹) of **5-7**.

Compound	FT-Raman	FT-IR
5	473 (1.6), 449 (1.8), 371 (3), 230 (1.3), 215 (1.3), 202 (1), 164 (1.8), 109 (10)	480m, 454br s, 372m, 358m, 279m, 270m, 227m, 196br m, 173br s, 140br m, 105br s
6	473 (1.4), 451 (1.4), 370 (5), 334 (2), 205 (3), 161 (4), 134 (7.6), 122 (2), 92 (10)	480w, 456m, 438s, 420m, 386s, 352m, 326m, 303m, 280s, 267m, 227m, 203m, 140br m, 128 br m, 120br m
7	473 (1.1), 450 (1.3), 368 (2.2), 205 (1.3), 162 (2.9), 119 (1.5), 103 (10), 85 (4.5)	404br s, 392 m, 352m, 325s, 302s, 290m, 280s, 227w, 144w, 101br m