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**[2-E(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>]<sub>n</sub>BiX<sub>3-n</sub> (E = O, NMe; X = Cl, Br, I; n = 1-3) and [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]BiBr<sub>2</sub> - new hypervalent organobismuth(III) compounds**

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**[2- $\{E(CH_2CH_2)_2NCH_2\}C_6H_4\}_nBiX_{3-n}$  (E = O, NMe; X = Cl, Br, I; n = 1-3) and [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]BiBr<sub>2</sub> – new hypervalent organobismuth(III) compounds**

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## ARTICLE

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[2- $\{E(CH_2CH_2)_2NCH_2\}C_6H_4\}_nBiX_{3-n}$  ( $E = O, NMe; X = Cl, Br, I; n = 1-3$ ) and [2-( $Me_2NCH_2$ ) $C_6H_4$ ]BiBr<sub>2</sub> – new hypervalent organobismuth(III) compoundsHans J. Breunig,<sup>\*,[a]</sup> Mihai G. Nema,<sup>[b]</sup> Cristian Silvestru,<sup>\*,[b]</sup> Albert Soran,<sup>[b]</sup> and Richard A. Varga<sup>[b]</sup>*To the Memory of Professor Dr. rer. nat. Herbert Schumann***Keywords:** Bismuth; Hypervalent; NMR studies; X-ray diffraction; Supramolecular

The homoleptic [2- $\{E(CH_2CH_2)_2NCH_2\}C_6H_4\}_3Bi$  [ $E = O$  (**1**), MeN (**2**)], the chlorides [2- $\{E(CH_2CH_2)_2NCH_2\}C_6H_4\}_2BiCl$  [ $E = O$  (**3**), MeN (**4**)] and the dichloride [2- $\{E(CH_2CH_2)_2NCH_2\}C_6H_4\}BiCl_2$  [ $E = O$  (**5**), MeN (**6**)] have been synthesized by reacting the corresponding *ortho*-lithium derivative with BiCl<sub>3</sub> in corresponding molar ratios. The dihalides [2- $\{E(CH_2CH_2)_2NCH_2\}C_6H_4\}BiX_2$  [ $X = Br, E = O$  (**7**), MeN (**9**);  $X = I, E = O$  (**8**), MeN (**10**)] as well as [2-( $Me_2NCH_2$ ) $C_6H_4$ ]BiBr<sub>2</sub> (**11**) were obtained by halide exchange reactions between RBiCl<sub>2</sub> and excess aqueous solution of KX. The compounds were characterized by multinuclear (<sup>1</sup>H, <sup>13</sup>C) NMR and MS. The crystal and molecular structures of **1–5** and **11** were determined by single-crystal X-ray diffraction. In all compounds the ( $C_6H_4CH_2$ )N atoms are coordinated to Bi. The crystals of **1** and **2**, as well as those of the chlorides **3** and **4**, contain discrete molecules. For R<sub>3</sub>Bi intramolecular N→Bi interactions of medium strength [Bi(1)–N(1) 3.170(7) Å for **1** and 3.211(5) Å for **2**] result in an overall distorted octahedral (*C,N*)<sub>3</sub>Bi core. In the

monochlorides one nitrogen is strongly coordinated to Bi [2.660(11) Å for **3** and 2.744(14) Å for **4**] *trans* to the halogen, while the second one is involved in a weaker intramolecular N→Bi interaction [3.095(11) Å for **3** and 3.061(14) Å for **4**] *trans* to a carbon atom. The overall (*C,N*)<sub>2</sub>BiCl core is distorted square-pyramidal. The crystals of the monohalides **5** and **11** contain discrete dimer units. The pendant arm nitrogen atom is strongly coordinated [2.548(9) Å for **5** and 2.485(13) Å for **11**] *trans* to the bridging halogen, thus resulting in an overall distorted square-pyramidal (*C,N*)BiX<sub>3</sub> ( $X = Cl, Br$ ) core. The six-membered morpholinyl and piperazinyl rings in **1–5** adopt the chair conformation which prevents intramolecular coordination of the O or N(Me) atoms to Bi. Supramolecular architectures based on intermolecular Bi⋯Br interactions, Cl⋯H and Br⋯H contacts are formed in the crystals of **3, 5** and **11**.

**Introduction**

The structural chemistry of organobismuth(III) halides reflects the Lewis amphoteric character of this class of compounds. There are Lewis acidic sites at the bismuth atoms and Lewis basic centres at the halogen atoms. For this reason, the compounds tend to form coordination polymers in the solid state, with *trans* bismuth-halogen bonds and ψ-trigonal bipyramidal coordination, which are poorly soluble in non-polar organic solvents, probably owing to the extended intermolecular association between the bismuth and halogen atoms in the solid state. The intermolecular

chains, and two- and three-dimensional structures [1-10]. In the case of monoorganobismuth(III) dihalides, it was observed that there is a tendency to form oligomers or polymers which involve one or both halogen atoms. Most of these compounds are insoluble in common solvents due to polymeric associations.

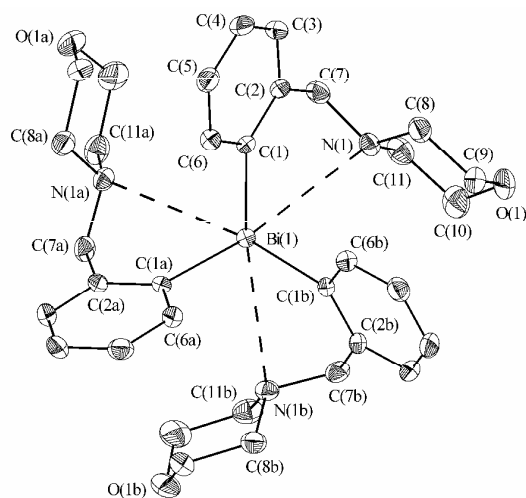
Recent developments show that the oligomerization of the organobismuth(III) halides can be overcome at least partially by two strategies. One is the use of bulky substituents which afford isolation of monomeric monohalide species, e.g. [2,4,6-(CF<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>]<sub>2</sub>BiCl [11], [(Me<sub>3</sub>Si)<sub>2</sub>CH]<sub>2</sub>BiCl [12], or [2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>BiCl [13]. Even with such bulky ligands the dihalides usually form at least dimers, e.g. [2,4,6-Ph<sub>3</sub>C<sub>6</sub>H<sub>2</sub>]<sub>2</sub>BiCl<sub>2</sub> [8] [14] or [2,6-Mes<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>BiX<sub>2</sub> ( $X = Cl$  [15], Br [16]). Another strategy is to use one pendant arm ligand such as 2-( $Me_2NCH_2$ ) $C_6H_4$  [9] and 2-(Et<sub>2</sub>NCH<sub>2</sub>) $C_6H_4$  [17], or “pincer” ligands like 2,6-( $Me_2NCH_2$ )<sub>2</sub> $C_6H_3$  [9,18] and 2,6-[MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]<sub>2</sub> $C_6H_3$  [18]. These ligands protect the bismuth atom not only sterically by increased coordination, but also reduce considerably the Lewis acidity and consequently the tendency for oligomerization. Indeed, the monohalides [2-( $Me_2NCH_2$ ) $C_6H_4$ ]<sub>2</sub>BiX ( $X = Cl$  [19], Br, I [9]), [2-(Et<sub>2</sub>NCH<sub>2</sub>) $C_6H_4$ ]<sub>2</sub>BiX [17] and [2,6-( $Me_2NCH_2$ )<sub>2</sub> $C_6H_3$ ]<sub>2</sub>BiCl [20] are monomeric. The corresponding dihalides usually exhibit low solubility in nonpolar solvents and for [2-( $Me_2NCH_2$ ) $C_6H_4$ ]BiCl<sub>2</sub> a dimer association was described in solid state [9]. Remarkably, the

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interactions involving bismuth play an important role in the construction of supramolecular compounds, e.g. polymeric



The molecular structure of **1** is depicted in Figure 1 and selected interatomic distances and angles for both **1** and **2** are listed in Table 1 (see Supporting information for the molecular structure of **2**).



**Figure 1.** The molecular structure of [2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>Bi (**1**) [*all-R<sub>N</sub>* isomer] (thermal ellipsoids are represented at 30% probability level; hydrogen atoms are omitted for clarity).

**Table 1.** Selected bond lengths /Å and angles /° for compounds **1** and **2** as determined by single-crystal X-ray diffraction.

	<b>1</b> <sup>[a]</sup>	<b>2</b> <sup>[a]</sup>
Bi(1)–C(1)	2.258(5)	2.252(4)
Bi(1)–N(1)	3.170(7)	3.211(5)
N(1)–C(7)	1.467(7)	1.462(6)
N(1)–C(8)	1.454(7)	1.454(6)
N(1)–C(11)	1.447(7)	1.460(6)
O(1)–C(9)	1.399(7)	
O(1)–C(10)	1.394(8)	
N(2)–C(9)		1.442(7)
N(2)–C(10)		1.452(6)
N(2)–C(12)		1.445(7)
C(1)–Bi(1)–C(1a)	94.20(17)	94.25(14)
N(1)–Bi(1)–C(1)	65.4(2)	64.6(1)
N(1)–Bi(1)–C(1a)	157.3(2)	156.3(1)
N(1)–Bi(1)–C(1b)	78.2(2)	77.9(1)
N(1)–Bi(1)–N(1a)	116.5(2)	117.1(1)
Bi(1)–N(1)–C(7)	82.9(3)	81.9(2)

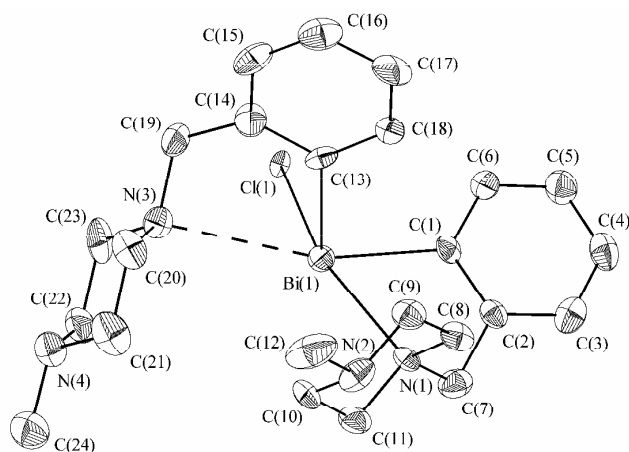
[a] Symmetry equivalent atoms are given by “a” ( $I - x + y, I - x, z$ ) and “b” ( $I - y, x - y, z$ ).

The crystals of both compounds belong to the *R*-3 rhombohedral system and contain highly symmetric discrete molecules, with no further intermolecular interactions between heavy atoms. In both molecules **1** and **2** the bismuth atom resides on a 3-fold axis which relates the three aryl substituents in a propeller-like conformation similar to that found in [2-(R<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>Bi (R = Me [23], Et [17]). The nitrogen atoms coordinate weakly to bismuth [Bi(1)–N(1) 3.170(7) Å for **1** and 3.211(5) Å for **2**, respectively; c.f. the

sum of covalent and van der Waals radii for nitrogen and bismuth;  $\Sigma r_{\text{cov}}(\text{Bi}, \text{N})$  2.27 Å and  $\Sigma r_{\text{vdw}}(\text{Bi}, \text{N})$  3.94 Å [24] almost *trans* to a Bi–C bond [N(1)–Bi(1)–C(1a) 157.3(2)° and 156.3(1)° for **1** and **2**, respectively]. The Bi–N bond lengths are considerably longer than those reported for [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>Bi [3.04(2)–3.11(3) Å] [23], a behaviour which could be attributed to combined electronic and steric effects of the morpholinyl / piperazinyl groups as was found for the related [2-(Et<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>Bi [3.214(7) Å] [17]. The coordination geometry at the bismuth atom, taking into account the intramolecular N→Bi interactions, is distorted octahedral [(C,N)<sub>3</sub>Bi core] and the compounds can be described as a hypervalent 14-Bi-6 species [25,26]. The morpholinyl and piperazinyl rings exhibit a *chair* conformation which prevents further intramolecular coordination to the bismuth atoms.

The nonplanarity of the five-membered BiC<sub>3</sub>N rings induces planar chirality (with the aromatic ring and the nitrogen atom as chiral plane and pilot atom, respectively; isomers given as *S<sub>N</sub>* and *R<sub>N</sub>*) [27] and the crystals of the triorganobismuthanes **1** and **2** contain a 1:1 mixture of *all-R<sub>N</sub>* and *all-S<sub>N</sub>* isomers (see Supporting information).

The crystals of monochlorides **3** and **4** contain one independent molecule in the asymmetric unit. The molecular structure of **4** is depicted in Figure 2 (see Supporting information for the molecular structure of **3**) and selected interatomic distances and angles are listed in Table 2.



**Figure 2.** The molecular structure of [2-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>BiCl (**4**) [(*R<sub>N1</sub>*,*S<sub>N2</sub>*-A<sub>Bi</sub>) isomer] (thermal ellipsoids are represented at 30% probability level; hydrogen atoms are omitted for clarity).

The molecules of both **3** and **4** show similar characteristics with respect to the coordination pattern of the nitrogen atoms, *i.e.* one nitrogen atom is strongly coordinated to the bismuth atom [Bi(1)–N(1) 2.660(11) Å for **3**, 2.744(14) Å for **4**] *trans* to the chlorine atom, while the second nitrogen atom displays a weaker interaction [Bi(1)–N(2) 3.095(11) Å for **3**, and Bi(1)–N(3) 3.061(14) Å for **4**] with its vector almost *trans* to a carbon atom. The interatomic distance for the N→Bi interaction *trans* to the halogen in **3** and **4**

**Table 2.** Selected bond lengths /Å and angles /° for compounds **3** and **4** as determined by single-crystal X-ray diffraction.<sup>[a]</sup>

	<b>3</b>	<b>4</b>
Bi(1)–C(1)	2.233(13)	2.250(16)
Bi(1)–X(1)	2.279(12)	2.235(16)

1			
2	Bi(1)–Cl(1)	2.623(4)	2.733(3)
3	Bi(1)–N(1)	2.660(11)	2.744(14)
4	Bi(1)–X(2)	3.095(11)	3.061(14)
5			
6	C(1)–Bi(1)–X(1)	91.3(5)	94.7(6)
7	C(1)–Bi(1)–Cl(1)	90.6(4)	92.5(4)
8	X(1)–Bi(1)–Cl(1)	93.5(3)	90.6(4)
9			
10	N(1)–Bi(1)–C(1)	70.4(4)	69.3(5)
11	N(1)–Bi(1)–X(1)	88.2(4)	98.1(5)
12	N(1)–Bi(1)–Cl(1)	161.0(2)	160.3(3)
13	N(1)–Bi(1)–X(2)	110.2(3)	115.7(4)
14			
15	X(2)–Bi(1)–C(1)	155.0(4)	162.7(5)
16	X(2)–Bi(1)–X(1)	63.9(4)	68.5(5)
17	X(2)–Bi(1)–Cl(1)	87.4(2)	83.9(3)
18			
19	Bi(1)–N(1)–C(7)	100.0(7)	92.9(10)
20	Bi(1)–X(2)–X(3)	88.6(7)	90.5(10)

[a] X(1), X(2) and X(3) are C(12), N(2) and C(18) for **3**, and C(13), N(3) and C(19) for **4**.

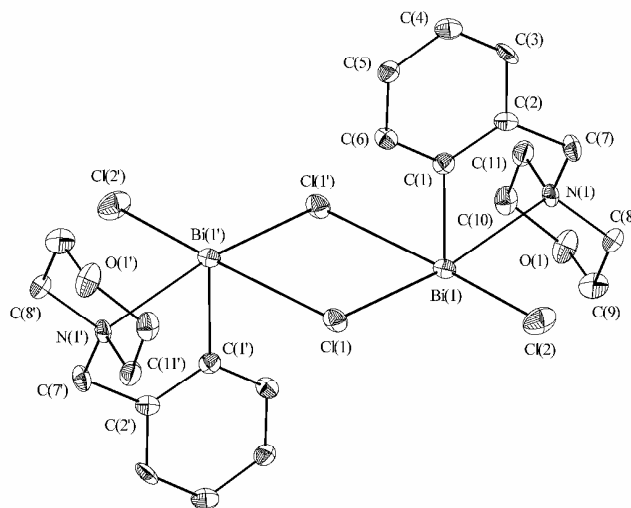
is longer than in [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>BiCl [2.570(5) Å] [19], but close to that observed for the ethyl analogue [2-(Et<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>BiCl [2.645(6) Å] [17]. The N→Bi interaction *trans* to the carbon atom is considerably shorter than in the related triorganobismuthanes (see Table 1), but of the same magnitude as in [2-(R<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>BiCl [3.047(5) Å for R = Me [19]; 3.056(7) Å for R = Et [17]]. The overall molecular structures of the monochlorides **3** and **4** are thus very similar to those reported for the related [2-(R<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>BiCl and, taking into account both intramolecular N→Bi interactions *per* metal atom, the coordination geometry features distorted square-pyramidal [(C,N)<sub>2</sub>BiCl cores; hypervalent 12-Bi-5 species [25,26]], with an aromatic carbon atom in apical position. The deviations of the bond angles at the metal atom from the ideal values are mainly due to the constraints imposed by the coordinated nitrogen atoms.

The bismuth-chlorine bond lengths are different in **3** [2.623(4) Å] and **4** [2.733(3) Å], but in the range observed for related compounds, *e.g.* [2-(R<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>BiCl [2.667(2) Å for R = Me [19]; 2.602(2) Å for R = Et [17)] or [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>](4-MeC<sub>6</sub>H<sub>4</sub>)BiCl [2.700(2) Å] [28]. The elongation of the Bi–Cl bond in these hypervalent species with respect to the values observed in tricoordinated monochlorides, *e.g.* [2,4,6-(CF<sub>3</sub>)C<sub>6</sub>H<sub>2</sub>]<sub>2</sub>BiCl [2.463(3) Å] [11], is apparently a consequence of the coordination of the amino group *trans* to the halogen atom.

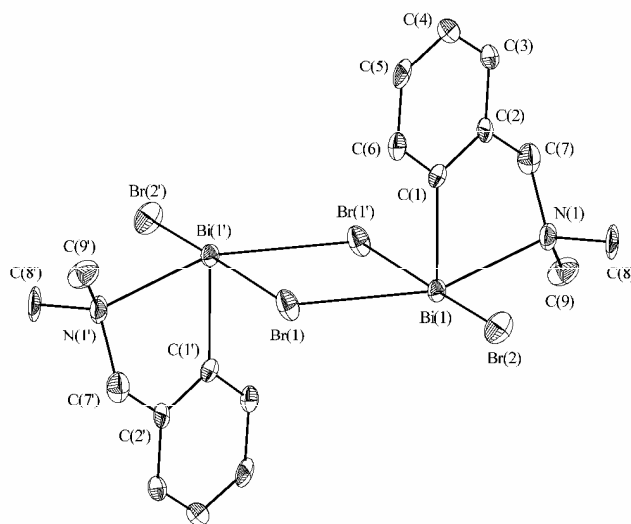
The molecules of **3** and **4** contain two five-membered BiC<sub>3</sub>N rings folded along the Bi⋯C<sub>methylene</sub> axis, with the nitrogen atom lying out of the best plane defined by the residual BiC<sub>3</sub> fragment. This induces planar chirality [27]. Moreover, chirality at the bismuth atom is also induced, at least in solid state, since the same organic groups attached to the metal become non-equivalent as result of the intramolecular N→Bi interactions: the aryl moiety of one ligand is placed in the apical position of the square pyramidal (C,N)<sub>2</sub>BiCl core and its nitrogen atom is coordinated in the basal plane *trans* the Bi–C bond established by the other pendant arm organic group, which, subsequently, has both its carbon atom attached to the metal and its nitrogen atom in the basal plane, coordinated *trans* to the chlorine atom. This “chelate-induced” chirality [29] at

the Bi atom in the square pyramidal environment can be described in term of C<sub>Bi</sub> and A<sub>Bi</sub> isomers [30]. Indeed, the crystals of **3** and **4** contain a 1:1 mixture of (R<sub>N1</sub>,S<sub>N2</sub>,C<sub>Bi</sub>) / (S<sub>N1</sub>,R<sub>N2</sub>,A<sub>Bi</sub>)-**3** isomers and (S<sub>N1</sub>,R<sub>N2</sub>,C<sub>Bi</sub>) / (R<sub>N1</sub>,S<sub>N2</sub>,A<sub>Bi</sub>)-**4** isomers (with respect to the two chelate rings at a metal atom), respectively.

The structures of the dihalides **5** and **11** are depicted in Figures 3 and 4. Relevant interatomic distances and angles are listed in Table 3.



**Figure 3.** Dimer association between (S<sub>N1</sub>,A<sub>Bi</sub>) and (R<sub>N1</sub>,C<sub>Bi</sub>) isomers in the crystal of [2-(O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]BiCl<sub>2</sub> (**5**) (thermal ellipsoids are represented at 30% probability level; hydrogen atoms are omitted for clarity).



**Figure 4.** Dimer association between (R<sub>N1</sub>,A<sub>Bi</sub>) and (S<sub>N1</sub>,C<sub>Bi</sub>) isomers in the crystal of [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]BiBr<sub>2</sub> (**11**) (thermal ellipsoids are represented at 30% probability level; hydrogen atoms are omitted for clarity).

**Table 3.** Selected bond lengths /Å and angles /° for compounds **5** and **11** as determined by single-crystal X-ray diffraction.<sup>[a]</sup>

	<b>5</b> <sup>[b]</sup>	<b>11</b> <sup>[b]</sup>
Bi(1)–C(1)	2.209(12)	2.214(15)
Bi(1)–X(1)	2.720(3)	2.9378(18)

1			
2	Bi(1)–X(2)	2.527(4)	2.720(2)
3	Bi(1)–N(1)	2.548(9)	2.485(13)
4	Bi(1)–X(1')	3.021(4)	3.0695(19)
5			
6	C(1)–Bi(1)–X(1)	91.4(3)	89.2(4)
7	C(1)–Bi(1)–X(2)	92.4(3)	89.2(4)
8	X(1)–Bi(1)–X(2)	90.91(12)	92.97(6)
9			
10	N(1)–Bi(1)–C(1)	73.5(4)	74.2(5)
11	N(1)–Bi(1)–X(1)	164.0(2)	160.7(3)
12	N(1)–Bi(1)–X(2)	84.6(2)	96.5(3)
13	N(1)–Bi(1)–X(1')	101.1(2)	85.6(3)
14			
15	X(1')–Bi(1)–C(1)	84.7(3)	87.3(4)
16	X(1')–Bi(1)–X(1)	82.29(10)	83.78(5)
17	X(1')–Bi(1)–X(2)	172.55(12)	175.26(6)
18			
19	Bi(1)–N(1)–C(7)	103.7(7)	104.4(9)
20			
21	Bi(1)–X(1)–Bi(1')	97.71(10)	96.22(5)

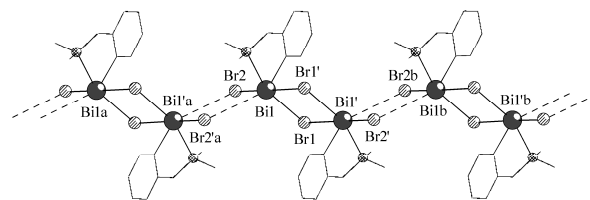
[a] X(1), X(2) and X(1') are Cl(1), Cl(2) and Cl(1') for **5**, Br(1), Br(2) and Br(1') for **11**. [b] Symmetry equivalent atoms are given by "prime":  $(-x, 1-y, -z)$  for **5**, and  $(1-x, -y, 2-z)$  for **11**.

The crystals of both compounds consist of centrosymmetric dimers in which  $(S_{N1}, A_{Bi1})$ - and  $(R_{N1}, C_{Bi1})$ -**5** isomers and  $(R_{N1}, A_{Bi1})$ - and  $(S_{N1}, C_{Bi1})$ -**11** isomers, respectively, are connected through bridging halogen atoms. Similar dimers were reported for the related  $[2-(\text{Me}_2\text{NCH}_2)_6\text{H}_4]\text{BiX}_2$  ( $X = \text{Cl}$  [9],  $\text{I}$  [19]). The nitrogen of the pendant arm is strongly coordinated to the metal [N(1)–Bi(1) 2.548(9) Å for **5** and 2.485(13) for **11**] in *trans* to the bridging halogen atom. The main difference resides in the extent of asymmetry of the Bi–X–Bi bridges, larger for the dichloride **5** [Bi(1)–Cl(1) 2.720(3) Å, Bi(1')–Cl(1) 3.021(4) Å] than for the dibromide **11** [Bi(1)–Br(1) 2.9378(18) Å, Bi(1')–Br(1) 3.0695(19) Å]. As expected, the Bi–X bonds in the planar  $\text{Bi}_2\text{X}_2$  fragment are considerably longer than the terminal bismuth-halogen bond [Bi(1)–Cl(2) 2.527(4) Å for **5** and Bi(1)–Br(2) 2.720(2) for **11**, respectively]. The geometry at bismuth is best described as distorted square-based pyramidal with the aryl group in the apical position and the three chlorides and the nitrogen atom of the amine arm in the basal plane [ $(C,N)\text{BiX}_3$  cores; hypervalent 12-Bi-5 species [25,26]].

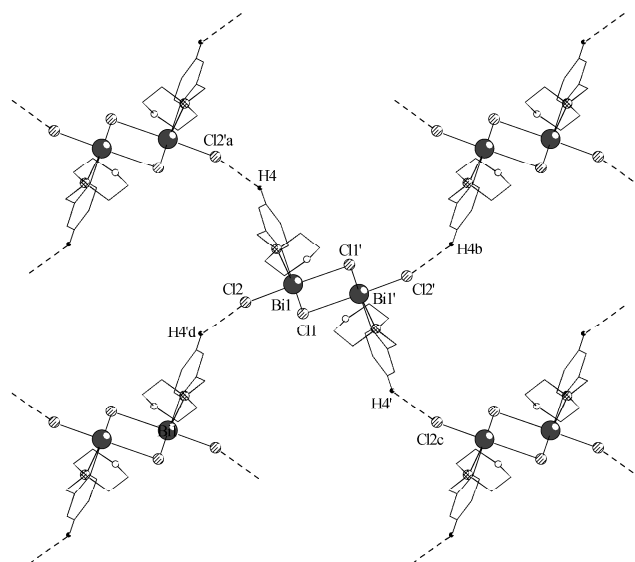
A closer check of the crystal packing revealed that for the triorganobismuthanes **1** and **2** and the monochloride **4** there are no intermolecular interactions. By contrast, for the monochloride **3** there are weak intermolecular Cl⋯H contacts close to the sum of corresponding van der Waals radii [ $\Sigma r_{\text{vdW}}(\text{Cl}, \text{H})$  ca. 3.0 Å] [24], which result in supramolecular architectures. Ribbon-like polymers of  $(R_{N1}, S_{N2}, C_{Bi})$ -**3** and  $(S_{N1}, R_{N2}, A_{Bi})$ -**3** isomers, respectively, are established through weak Cl⋯H<sub>aryl</sub> [Cl(1)⋯H(15b) 2.93 Å] and Cl⋯H<sub>morpholinyl</sub> [Cl(1)⋯H(10Aa) 2.95 Å] contacts. Additional weak Cl⋯H<sub>morpholinyl</sub> [Cl(1)⋯H(19Bb') 2.99 Å] contacts between parallel polymers extended along the *a* axis result in a waved layer. No further contacts are established between the layers (see Supporting information).

As described previously for the related  $[2-(\text{Me}_2\text{NCH}_2)_6\text{H}_4]\text{BiX}_2$  ( $X = \text{Cl}$  [9],  $\text{I}$  [19]), in the crystals of **11** the dimer units are further associated through weaker Bi(1)⋯Br(2'a) interactions [3.778(5) Å; c.f.  $\Sigma r_{\text{vdW}}(\text{Bi}, \text{Br})$  Table 4. X-ray crystallographic data for **1-5** and **11**.

4.35 Å] [24] into a ribbon-like polymer along the *a* axis. If these interactions are considered, the overall Bi coordination geometry in **11** is distorted octahedral (Figure 5). Further weak inter-chain Br⋯H contacts result in a 3D architecture (see Supporting information). By contrast, the metal atoms in the dimer of **5** are better sterically protected and no association through Bi⋯Cl interactions were observed. However, quite strong Cl⋯H<sub>aryl</sub> [Cl(2)⋯H(4b) 2.74 Å] interactions result in a layer structure, each dimer unit being connected to four other dimer fragments (Figure 6).



**Figure 5.** Ribbon-like polymer in the crystal of  $[2-(\text{Me}_2\text{NCH}_2)_6\text{H}_4]\text{BiBr}_2$  (**11**) [symmetry equivalent atoms  $(1-x, -y, 2-z)$ ,  $(-x, -y, 2-z)$  and  $(1+x, y, z)$  are given by "prime", "prime a" and "b", respectively].



**Figure 6.** View along *a* axis of a fragment from the layer of dimers in the crystal of  $[2-\{\text{O}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\}_6\text{H}_4]\text{BiCl}_2$  (**5**) [symmetry equivalent atoms  $(-x, 1-y, -z)$ ,  $(-x, 0.5+y, 0.5-z)$ ,  $(x, 1.5-y, -0.5+z)$ ,  $(x, 0.5-y, -0.5+z)$  and  $(-x, -0.5+y, 0.5-z)$  are given by "prime", "prime a", "b", "c" and "prime d", respectively].

## Conclusions

New bismuth compounds of the types  $[2-\{\text{E}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\}_6\text{H}_4]\text{Bi}$ ,  $[2-\{\text{E}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\}_6\text{H}_4]\text{BiCl}$  and  $[2-\{\text{E}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\}_6\text{H}_4]\text{BiX}_2$  ( $\text{E} = \text{O}, \text{MeN}; X = \text{Cl}, \text{Br}, \text{I}$ ), as well as  $[2-(\text{Me}_2\text{NCH}_2)_6\text{H}_4]\text{BiBr}_2$  were prepared and their structures were investigated both in solution and in

	1	2	3	4	5	11
Empirical formula	C <sub>33</sub> H <sub>42</sub> BiN <sub>5</sub> O <sub>3</sub>	C <sub>36</sub> H <sub>51</sub> BiN <sub>6</sub>	C <sub>22</sub> H <sub>28</sub> BiClN <sub>2</sub> O <sub>2</sub>	C <sub>24</sub> H <sub>34</sub> BiClN <sub>4</sub>	C <sub>22</sub> H <sub>28</sub> Bi <sub>2</sub> Cl <sub>4</sub> N <sub>2</sub> O <sub>2</sub>	C <sub>18</sub> H <sub>24</sub> Bi <sub>2</sub> Br <sub>4</sub> N <sub>2</sub>
Crystal system	Rhombohedral	Rhombohedral	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>R</i> -3	<i>R</i> -3	<i>Pbca</i>	<i>P2<sub>1</sub>/c</i>	<i>Pbca</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> /Å	19.067(2)	20.978(3)	9.397(2)	10.6424(10)	9.590(4)	9.1651(14)
<i>b</i> /Å	19.067(2)	20.978(3)	21.146(4)	9.5919(9)	14.568(6)	8.3800(12)
<i>c</i> /Å	14.530(3)	14.310(4)	22.313(4)	25.132(2)	19.042(8)	16.569(3)
<i>α</i> /°	90	90	90	90	90	90
<i>β</i> /°	90	90	90	102.016(2)	90	100.078(3)
<i>γ</i> /°	120	120	90	90	90	90
Volume /Å <sup>3</sup>	4574.8(12)	5453.6(19)	4433.8(15)	2509.3(4)	2660(2)	1253.0(3)
<i>Z</i>	6	6	8	4	4	2
Density (calcd.) /g·cm <sup>-3</sup>	1.607	1.419	1.788	1.649	2.278	2.666
Crystal size /mm <sup>3</sup>	0.46 x 0.45 x 0.34	0.35 x 0.28 x 0.26	0.70 x 0.60 x 0.50	0.30 x 0.29 x 0.20	0.20 x 0.18 x 0.14	0.27 x 0.11 x 0.10
Data collection temperature /K	297(2)	297(2)	173(2)	297(2)	297(2)	297(2)
Theta range /°	1.87–25.50	2.66–25.00	2.54–25.00	1.96–25.00	2.14–25.00	2.26–25.00
No. reflections collected	14874	13195	4943	17555	17929	6345
Independent reflections	1868 [ <i>R</i> (int) = 0.0604]	2134 [ <i>R</i> (int) = 0.0539]	3857 [ <i>R</i> (int) = 0.0444]	4416 [ <i>R</i> (int) = 0.0743]	2348 [ <i>R</i> (int) = 0.0834]	2190 [ <i>R</i> (int) = 0.0684]
Final <i>R</i> indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0348, <i>wR</i> <sub>2</sub> = 0.0650	<i>R</i> <sub>1</sub> = 0.0287, <i>wR</i> <sub>2</sub> = 0.0617	<i>R</i> <sub>1</sub> = 0.0577, <i>wR</i> <sub>2</sub> = 0.1277	<i>R</i> <sub>1</sub> = 0.0846, <i>wR</i> <sub>2</sub> = 0.2063	<i>R</i> <sub>1</sub> = 0.0614, <i>wR</i> <sub>2</sub> = 0.0938	<i>R</i> <sub>1</sub> = 0.0637, <i>wR</i> <sub>2</sub> = 0.1147
Largest difference peak and hole (e Å <sup>-3</sup> )	2.111 and -1.969	0.622 and -2.223	1.390 and -2.103	3.657 and -2.831	1.380 and -2.604	2.648 and -2.433

solid state. In all compounds intramolecular N→Bi interactions of different strength are established, resulting in (C,N)<sub>3</sub>Bi core for triorganobismuthanes, (C,N)<sub>2</sub>BiCl for diorganobismuth(III) chlorides, and (C,N)BiX<sub>3</sub> for dimeric organobismuth(III) dihalides. The room temperature <sup>1</sup>H NMR spectra provided evidence for the presence of internal nitrogen-bismuth coordination in solution for the dihalides, as observed in solid state. The bulkiness of the morpholinyl or piperazinyl substituents appears to not be sufficient to avoid the oligomerization of the organobismuth(III) dihalides. These new organobismuth(III) compounds are useful as starting materials for the preparation of further compounds and their potential use as ligands in transition metal coordination chemistry in order to obtain heterometallic species is under investigation.

## Experimental Section

All reactions were carried out under argon using standard Schlenk techniques under an atmosphere of argon. Solvents were dried by standard procedures and were freshly distilled prior to use. Bismuth(III) trichloride, *N,N*-dimethylbenzylamine, *N*-methylpiperazine, morpholine and butyllithium (15% in *n*-hexane) were commercially available. The other starting materials were prepared according to literature methods: 2-[O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br [21], 2-[MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br [31], [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]Li [32], and [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]BiCl<sub>2</sub> [19].

Room temperature <sup>1</sup>H, <sup>13</sup>C and 2D NMR spectra were recorded in dried CDCl<sub>3</sub> (1–4) or DMSO-*d*<sub>6</sub> (5–11), on Bruker Avance 300, Bruker Avance DPX 200 or Bruker Avance WB 360 instruments. The chemical shifts are reported in ppm relative to the residual peak of the solvent (ref. CHCl<sub>3</sub>: <sup>1</sup>H 7.26, <sup>13</sup>C 77.0 ppm; DMSO-*d*<sub>6</sub>: <sup>1</sup>H 2.50, <sup>13</sup>C 39.43 ppm). The NMR spectra were processed using

the *MestReC* and *MestReNova* software [33]. Mass spectra were recorded with Finnigan MAT 8200 instrument and were processed using the *MASPEC II* software [34].

The details of the crystal structure determination and refinement for compounds 1–5 and 11 are given in Table 4. Data were collected on Bruker SMART APEX (1, 2, 4, 5, 11) and Siemens P4 (3) diffractometers, using graphite-monochromated Mo-*K*α radiation (λ = 0.71073 Å). For this purpose the crystals were attached with epoxy glue on cryoloops and the data were collected at room temperature (297 K) and 173 K (cooled under a nitrogen stream), respectively. 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 [35]. The drawings were created with the Diamond program [36].

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 778940 - 778945. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax.: + 44-1223-336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

### Synthesis of [2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>Bi (I)

A solution of *n*-BuLi in *n*-hexane (14.64 mL 1.6 M, 23.43 mmol) was added dropwise to a stirred solution of 2-[O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br (6.0 g, 23.43 mmol) in 100 mL anhydrous *n*-hexane, at room temperature, under argon. The reaction mixture was stirred for 2 h. Evaporation of the solvent gave [2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]Li as a white compound. To the solid product suspended in 100 mL anhydrous diethyl ether was added, at -78 °C, a solution of BiCl<sub>3</sub> (2.45 g, 7.79 mmol) in 50 mL diethyl ether. The reaction temperature was maintained at -78 °C for 2 h, following which the reaction mixture was allowed to warm



slowly to ambient temperature. After being stirred for additional 12 h, the reaction mixture was filtered and the solvent was evaporated in vacuum to give **1** as a white-grey solid (4.09 g, 71% yield). M.p.: 239 °C. Anal. calcd. (found) for C<sub>33</sub>H<sub>42</sub>BiN<sub>3</sub>O<sub>3</sub>: C 53.73 (53.94) %; H 5.74 (5.65) %; N 5.70 (5.59) %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 2.26 (s,br, 12H, H-8,11), 3.00 (s,br, 12H, H-9,10), 3.58 (s,br, 6H, H-7), 7.08 (t, 3H, H-5, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz), 7.21 (t, 3H, H-4, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz), 7.26 (d, 3H, H-3, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz), 7.64 (d, 3H, H-6, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz): δ 53.42 (s, C-8,11), 66.23 (s, C-9,10), 67.90 (s, C-7), 126.73 (s, C-4), 129.67 (s, C-5), 129.99 (s, C-3), 139.81 (s, C-6), 142.90 (s, C-2), 163.53 (s, C-1). MS-EI 70 eV (200 °C) m/z (rel. int. %), 736 (5) [M]<sup>+</sup>, 561 (100) [R<sub>2</sub>Bi]<sup>+</sup>, 209 (5) [Bi]<sup>+</sup>, 176 (20) [R]<sup>+</sup> [R = 2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>].

### Synthesis of [2-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>Bi (**2**)

A solution of *n*-BuLi in *n*-hexane (5.66 mL 1.6 M, 9.18 mmol) was added dropwise to a stirred solution of 2-[MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br (2.47 g, 9.18 mmol) in 100 mL anhydrous *n*-hexane, at room temperature, under argon. After 30 minutes a white precipitate was formed. The reaction mixture was stirred for 4 h. Evaporation of the solvent gave [2-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]<sub>3</sub>Li as a white compound. To the suspension of the solid product in 100 mL anhydrous diethyl ether was added, at -78 °C, a solution of BiCl<sub>3</sub> (0.95 g, 3.02 mmol) in 50 mL diethyl ether. The reaction mixture was stirred for 1 h at -78 °C, then allowed to reach room temperature and filtered through a glass frit under argon atmosphere. The solution was evaporated under vacuum to give **2** as a white solid (1.0 g, 43% yield). M.p.: 205 °C. Anal. calcd. (found) for C<sub>36</sub>H<sub>51</sub>BiN<sub>6</sub>: C 55.66 (55.96) %; H 6.62 (6.44) %; N 10.82 (10.94) %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 1.95 (s, 9H, NCH<sub>3</sub>), 2.30 (s,br, 24H, H-8-11), 3.58 (s,br, 6H, H-7), 7.06 (t, 3H, H-5, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz), 7.19 (t, 3H, H-4, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz), 7.24 (m, 3H, H-3), 7.71 (d, 3H, H-6, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50.3 MHz): δ 45.93 (s, NCH<sub>3</sub>), 53.01 (s, C-9,10), 54.20 (s, C-8,11), 67.57 (s, C-7), 126.42 (s, C-4), 129.49 (s, C-5), 129.53 (s, C-3), 139.96 (s, C-6), 143.66 (s, C-2), 164.32 (s, C-1). MS-EI 70 eV (200 °C) m/z (rel. int. %), 587 (100) [R<sub>2</sub>Bi]<sup>+</sup>, 398 (10) [RBi]<sup>+</sup>, 209 (11) [Bi]<sup>+</sup>, 189 (28) [R]<sup>+</sup> [R = 2-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>].

### Synthesis of [2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>BiCl (**3**)

A suspension of [2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Li [obtained from *n*-BuLi in *n*-hexane (14.65 mL 1.6 M, 23.43 mmol) and 2-[O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br (6.0 g, 23.43 mmol)] in 100 mL anhydrous diethyl ether was added dropwise, at -78 °C, to a solution of BiCl<sub>3</sub> (3.69 g, 11.71 mmol) in 50 mL diethyl ether. The reaction mixture was allowed to reach room temperature over night and then filtered through a glass frit. The white solid retained on the frit was extracted with 2 x 50 mL of chloroform and evaporation of the clear solution gave **3** as a fade yellowish solid (4.61 g, 66% yield). M.p.: 195 °C. Anal. calcd. (found) for C<sub>22</sub>H<sub>28</sub>BiClN<sub>2</sub>O<sub>2</sub>: C 44.27 (44.11) %; H 4.73 (4.75) %; N 4.69 (4.66) %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 2.55 (s,br, 8H, H-8,11), 3.68 (s, 4H, H-7), 3.79 (s,br, 8H, H-9,10), 7.41 (m, 4H, H-4,5), 7.52 (d, 2H, H-3, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz), 8.57 (d, 2H, H-6, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75.5 MHz): δ 53.88 (s, C-8,11), 66.95 (s, C-9,10), 67.74 (s, C-7), 128.44 (s, C-4), 130.31 (s, C-3), 131.52 (s, C-5), 140.46 (s, C-6), 144.21 (s, C-2), 181.57 (s, C-1). MS-EI 70 eV (200 °C) m/z (rel. int. %), 561 (100) [M-Cl]<sup>+</sup>, 420 (20) [M-R]<sup>+</sup>, 385 (19) [RBi]<sup>+</sup>, 209 (28) [Bi]<sup>+</sup>, 176 (80) [R]<sup>+</sup> [R = 2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>].

### Synthesis of [2-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>BiCl (**4**)

A suspension of [2-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Li [obtained from *n*-BuLi in *n*-hexane (5.66 mL 1.6 M, 9.18 mmol) and 2-[MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br (2.47 g, 9.18 mmol)] in 100 mL anhydrous diethyl ether was added dropwise, at -78 °C, to a solution of BiCl<sub>3</sub> (1.42 g, 4.57 mmol) in 50 mL diethyl ether. The reaction mixture was stirred for 1 h at -78 °C, then 12 h to reach the room temperature. It was filtered under argon atmosphere and the solution was evaporated under vacuum to give **4** as a white-yellow solid (2.33 g, 82% yield). M.p.: 179 °C. Anal. calcd. (found) for C<sub>24</sub>H<sub>34</sub>BiClN<sub>4</sub>: C 46.27 (46.72) %; H 5.50 (5.72) %; N 8.99 (9.26) %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ 2.32 (s, 6H, NCH<sub>3</sub>), 2.56 (s,br, 16H, H-8-11), 3.69 (s,br, 4H, H-7), 7.39 (m, 4H, H-4,5), 7.51 (d, 2H, H-3, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz), 8.65 (d,br, 2H, H-6). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50.3 MHz): δ 46.01 (s, NCH<sub>3</sub>), 53.61 (s, C-9,10), 55.14 (s, C-8,11), 67.23 (s, C-7), 128.25 (s, C-4), 130.09 (s, C-3), 131.41 (s, C-5), 141.32 (s, C-6), 144.89 (s, C-2), 178.93 (s, C-1). MS-EI 70 eV (200 °C) m/z (rel. int. %), 586 (8) [M-Cl]<sup>+</sup>, 432 (27) [M-R]<sup>+</sup>, 209 (11) [Bi]<sup>+</sup>, 189 (30) [R]<sup>+</sup> [R = 2-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>].

### Synthesis of [2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>BiCl<sub>2</sub> (**5**)

A suspension of [2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Li [obtained from *n*-BuLi in *n*-hexane (7.32 mL 1.6 M, 11.71 mmol) and 2-[O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br (3.0 g, 11.71 mmol)] in 60 mL anhydrous diethyl ether was added dropwise, at -78 °C, to a solution of BiCl<sub>3</sub> (3.69 g, 11.71 mmol) in 30 mL diethyl ether. The reaction mixture was stirred for 2 h at -78 °C, then allowed to reach room temperature and filtered through a glass frit. The white solid retained on the frit was washed with 25 mL of *n*-hexane, then dried to give **5** as a white solid (3.99 g, 75% yield). M.p.: 145 °C (dec.). Anal. calcd. (found) for C<sub>11</sub>H<sub>14</sub>BiCl<sub>2</sub>NO: C 28.97 (28.67) %; H 3.09 (3.48) %; N 3.07 (3.03) %. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 360 MHz): δ 2.58 [t, 2H, H<sub>pro-trans</sub>-8,11, <sup>2</sup>J<sub>HH</sub> ≈ <sup>3</sup>J<sub>HH</sub> = 11.7 Hz], 3.26 [d, 2H, H<sub>pro-cis</sub>-8,11, <sup>2</sup>J<sub>HH</sub> = 12.1 Hz], 3.67 [t, 2H, H<sub>pro-trans</sub>-9,10, <sup>2</sup>J<sub>HH</sub> ≈ <sup>3</sup>J<sub>HH</sub> = 11 Hz], 3.79 [d, 2H, H<sub>pro-cis</sub>-9,10, <sup>2</sup>J<sub>HH</sub> = 12.2 Hz], 4.27 (s, 2H, H-7), 7.41 (t, 1H, H-4, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz), 7.67 (t, 1H, H-5, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz), 7.81 (d, 1H, H-3, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz), 9.16 (d, 1H, H-6, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 50.3 MHz): δ 53.76 (s, C-8,11), 66.91 (s, C-9,10), 68.10 (s, C-7), 127.77 (s, C-4), 129.73 (s, C-3), 131.08 (s, C-5), 139.51 (s, C-6), 148.38 (s, C-2), 211.47 (s, C-1). MS-EI 70 eV (200 °C) m/z (rel. int. %), 455 (20) [M]<sup>+</sup>, 420 (60) [M-Cl]<sup>+</sup>, 209 (24) [Bi]<sup>+</sup>, 176 (38) [R]<sup>+</sup> [R = 2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>].

### Synthesis of [2-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>BiCl<sub>2</sub> (**6**)

A suspension of [2-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]<sub>2</sub>Li [obtained from *n*-BuLi in *n*-hexane (12.50 mL 1.6 M, 20 mmol) and 2-[MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>]C<sub>6</sub>H<sub>4</sub>Br (5.38 g, 20 mmol)] in 50 mL anhydrous diethyl ether was added dropwise with stirring, at -78 °C, to a solution of BiCl<sub>3</sub> (6.31 g, 20 mmol) in 40 mL diethyl ether. The reaction mixture was stirred for 1 h at -78 °C, then over night to reach room temperature. It was filtered and the remaining white residue was washed with 25 mL *n*-hexane and dried under vacuum to give **6** as a white solid (8.44 g, 90% yield). M.p.: 195 °C (dec.). Anal. calcd. (found) for C<sub>12</sub>H<sub>17</sub>BiCl<sub>2</sub>N<sub>2</sub>: C 30.72 (30.36) %; H 3.65 (3.72) %; N 5.97 (5.56) %. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 360 MHz): δ 2.68 (s,br, 3H, NCH<sub>3</sub>), 3.41 (br, 8H, H-8-11), 4.27 (s, 2H, H-7), 7.42 (t, 1H, H-4, <sup>3</sup>J<sub>HH</sub> = 6.9 Hz), 7.69 (t, 1H, H-5, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz), 7.83 (d, 1H, H-3, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz), 9.18 (d, 1H, H-6, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 50.3 MHz): δ 42.14 (s, NCH<sub>3</sub>), 50.42 (s, C-9,10), 52.57 (s, C-8,11), 66.54 (s, C-7), 127.48 (s, C-4), 129.82 (s, C-3), 131.22 (s, C-5), 139.35 (s, C-6), 147.54 (s, C-2), 214.61 (s, C-1). MS-EI 70 eV (200 °C) m/z (rel. int. %), 434 (30) [M-Cl]<sup>+</sup>, 398

(10) [RBi]<sup>+</sup>, 209 (26) [Bi]<sup>+</sup>, 189 (18) [R]<sup>+</sup> [R = 2-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>].

#### Synthesis of [2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]BiBr<sub>2</sub> (7)

A suspension of **5** (0.50 g, 1.09 mmol) in 50 mL methylene chloride was vigorously stirred for 24 h with a solution of KBr (0.39 g, 3.28 mmol) in 25 mL distilled water. The reaction mixture was filtered off, the colorless organic phase was removed with a syringe and the aqueous phase was washed with methylene chloride (2 x 25 mL). The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed in vacuum to give **6** as a white powder (0.26 g, 45% yield). M.p.: 112 °C (dec.). Anal. calcd. (found) for C<sub>11</sub>H<sub>14</sub>BiBr<sub>2</sub>NO: C 24.24 (24.41) %; H 2.59 (2.13) %; N 2.57 (2.22) %. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 200 MHz): δ 2.73 [t, 2H, *H*<sub>pro-trans</sub>-8,11, <sup>2</sup>*J*<sub>HH</sub> ≈ <sup>3</sup>*J*<sub>HH</sub> = 11.6 Hz], 3.19 [d, 2H, *H*<sub>pro-cis</sub>-8,11, <sup>2</sup>*J*<sub>HH</sub> = 12.0 Hz], 3.67 [t, 2H, *H*<sub>pro-trans</sub>-9,10, <sup>2</sup>*J*<sub>HH</sub> ≈ <sup>3</sup>*J*<sub>HH</sub> = 11.0 Hz], 3.82 [d, 2H, *H*<sub>pro-cis</sub>-9,10, <sup>2</sup>*J*<sub>HH</sub> = 11.6 Hz], 4.34 (s, 2H, *H*-7), 7.51 (t, 1H, *H*-4, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz), 7.73 (t, 1H, *H*-5, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz), 7.94 (d, 1H, *H*-3, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz), 9.42 (d, 1H, *H*-6, <sup>3</sup>*J*<sub>HH</sub> = 7.0 Hz). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 50.3 MHz): δ 53.74 (s, C-8,11), 66.37 (s, C-9,10), 68.32 (s, C-7), 128.13 (s, C-4), 129.94 (s, C-3), 131.53 (s, C-5), 141.00 (s, C-6), 149.06 (s, C-2), 209.08 (s, C-1). MS-EI 70 eV (200 °C) m/z (rel. int. %), 466 (100) [M-Br]<sup>+</sup>, 385 (19) [RBi]<sup>+</sup>, 209 (40) [Bi]<sup>+</sup>, 176 (22) [R]<sup>+</sup> [R = 2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>].

#### Synthesis of [2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]BiI<sub>2</sub> (8)

Compound **8** was prepared similar to **7**, from a suspension of **5** (0.50 g, 1.09 mmol) in 50 mL methylene chloride and a solution of KI (0.54 g, 3.28 mmol) in 25 mL distilled water, as a yellow powder (0.45 g, 65% yield). M.p.: 101 °C (dec.). Anal. calcd. (found) for C<sub>11</sub>H<sub>14</sub>BiI<sub>2</sub>NO: C 20.67 (20.51) %; H 2.21 (2.24) %; N 2.19 (1.86) %. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 200 MHz): δ 2.76 [t, 2H, *H*<sub>pro-trans</sub>-8,11, <sup>2</sup>*J*<sub>HH</sub> ≈ <sup>3</sup>*J*<sub>HH</sub> = 10.2 Hz], 3.25 [d, 2H, *H*<sub>pro-cis</sub>-8,11, <sup>2</sup>*J*<sub>HH</sub> = 12.8 Hz], 3.65 [t, 2H, *H*<sub>pro-trans</sub>-9,10, <sup>2</sup>*J*<sub>HH</sub> ≈ <sup>3</sup>*J*<sub>HH</sub> = 11.2 Hz], 3.83 [d, 2H, *H*<sub>pro-cis</sub>-9,10, <sup>2</sup>*J*<sub>HH</sub> = 11.5 Hz], 4.38 (s, 2H, *H*-7), 7.57 (t, 1H, *H*-4, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz), 7.68 (t, 1H, *H*-5, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz), 7.93 (d, 1H, *H*-3, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz), 9.73 (d, 1H, *H*-6, <sup>3</sup>*J*<sub>HH</sub> = 6.5 Hz). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 50.3 MHz): δ 54.36 (s, C-8,11), 66.49 (s, C-9,10), 69.10 (s, C-7), 128.08 (s, C-4), 129.74 (s, C-3), 132.19 (s, C-5), 145.34 (s, C-6), 149.38 (s, C-2), 198.2 (s, C-1). MS-EI 70 eV (200 °C) m/z (rel. int. %), 512 (100) [M-I]<sup>+</sup>, 385 (22) [RBi]<sup>+</sup>, 209 (24) [Bi]<sup>+</sup>, 176 (22) [R]<sup>+</sup> [R = 2-{O(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>].

#### Synthesis of [2-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]BiBr<sub>2</sub> (9)

A suspension of **6** (0.50 g, 1.06 mmol) in 50 mL methylene chloride was vigorously stirred for 24 h with a solution of KBr (0.38 g, 3.19 mmol) in 25 mL distilled water. The reaction mixture was filtered off and the precipitate was dried in vacuum to give compound **9** as a white powder (0.38 g, 65% yield). M.p.: 205 °C (dec.). Anal. calcd. (found) for C<sub>12</sub>H<sub>17</sub>BiCl<sub>2</sub>N<sub>2</sub>: C 25.83 (25.36) %; H 3.07 (3.12) %; N 5.02 (5.26) %. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 200 MHz): δ 2.60 (s,br, 3H, NCH<sub>3</sub>), 2.75 [t, 2H, *H*<sub>pro-trans</sub>-8,11, <sup>2</sup>*J*<sub>HH</sub> ≈ <sup>3</sup>*J*<sub>HH</sub> = 12.4 Hz], 2.97 [t, 2H, *H*<sub>pro-trans</sub>-9,10, <sup>2</sup>*J*<sub>HH</sub> ≈ <sup>3</sup>*J*<sub>HH</sub> = 11.8 Hz], 3.23 [d, 2H, *H*<sub>pro-cis</sub>-9,10, <sup>2</sup>*J*<sub>HH</sub> = 11.6 Hz], 3.43 [d, 2H, *H*<sub>pro-cis</sub>-8,11, <sup>2</sup>*J*<sub>HH</sub> = 12.3 Hz], 4.34 (s, 2H, *H*-7), 7.48 (t, 1H, *H*-4, <sup>3</sup>*J*<sub>HH</sub> = 7.1 Hz), 7.71 (t, 1H, *H*-5, <sup>3</sup>*J*<sub>HH</sub> = 6.9 Hz), 7.91 (d, 1H, *H*-3, <sup>3</sup>*J*<sub>HH</sub> = 7.2 Hz), 9.47 (d, 1H, *H*-6, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 50.3 MHz): δ 42.56 (s, NCH<sub>3</sub>), 51.19 (s, C-9,10), 52.84 (s, C-8,11), 67.01 (s, C-7), 127.67 (s, C-4), 129.82 (s, C-3), 131.70 (s, C-5), 141.70 (s, C-6), 141.70 (s, C-2), 208.09 (s, C-1). MS-EI 70 eV (200 °C) m/z (rel.

int. %), 558 (20) [M]<sup>+</sup>, 477 (100) [M-Br]<sup>+</sup>, 268 (22) [RBr]<sup>+</sup>, 209 (44) [Bi]<sup>+</sup>, 189 (21) [R]<sup>+</sup> [R = 2-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>].

#### Synthesis of [2-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>]BiI<sub>2</sub> (10)

Compound **10** was prepared similar to **9**, from a suspension of **6** (0.50 g, 1.06 mmol) in 50 mL methylene chloride and a solution of KI (0.53 g, 3.19 mmol) in 25 mL distilled water, as an orange powder (0.54 g, 78% yield). M.p.: 156 °C (dec.). Anal. calcd. (found) for C<sub>12</sub>H<sub>17</sub>BiI<sub>2</sub>N<sub>2</sub>: C 22.10 (21.87) %; H 2.63 (2.42) %; N 4.30 (4.06) %. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 200 MHz): δ 2.80 (s,br, 3H, NCH<sub>3</sub>), 3.32 (br, 8H, *H*-8-11), 4.34 (s, 2H, *H*-7), 7.55 (t, 1H, *H*-4, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz), 7.70 (t, 1H, *H*-5, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz), 7.93 (d, 1H, *H*-3, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz), 9.68 (s,br, 1H, *H*-6). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 50.3 MHz): δ 41.99 (s, NCH<sub>3</sub>), 51.20 (s, C-9,10), 52.65 (s, C-8,11), 67.60 (s,br, C-7), 127.70 (s, C-4), 129.86 (s, C-3), 132.10 (s, C-5), 144.14 (s,br, C-6), 148.02 (s, C-2) (the resonance for the C-1 atom was not observed). MS-EI 70 eV (200 °C) m/z (rel. int. %), 525 (58) [M-I]<sup>+</sup>, 398 (10) [RBi]<sup>+</sup>, 209 (37) [Bi]<sup>+</sup>, 189 (38) [R]<sup>+</sup> [R = 2-{MeN(CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NCH<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>].

#### Synthesis of [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]BiBr<sub>2</sub> (11)

Compound **11** was prepared similar to **9**, from a suspension of [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]BiCl<sub>2</sub> (1.0 g, 2.41 mmol) in 50 mL methylene chloride and a solution of KBr (0.86 g, 7.23 mmol) in 25 mL distilled water, as a white powder (0.64 g, 53% yield). M.p.: 240 °C. Anal. calcd. (found) for C<sub>9</sub>H<sub>12</sub>BiBr<sub>2</sub>N: C 21.49 (21.18) %; H 2.40 (2.46) %; N 2.78 (2.42) %. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 200 MHz): δ 2.70 (s, 6H, NCH<sub>3</sub>), 4.39 (s, 2H, *H*-7), 7.49 (t, 1H, *H*-4, <sup>3</sup>*J*<sub>HH</sub> = 7.1 Hz), 7.71 (t, 1H, *H*-5, <sup>3</sup>*J*<sub>HH</sub> = 7.8 Hz), 7.84 (d, 1H, *H*-3, <sup>3</sup>*J*<sub>HH</sub> = 7.3 Hz), 9.29 (d, 1H, *H*-6, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz). <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 50.3 MHz): δ 46.02 (s, NCH<sub>3</sub>), 69.07 (s, C-7), 127.98 (s, C-4), 129.52 (s, C-3), 131.13 (s, C-5), 140.41 (s, C-6), 151.09 (s, C-2), 213.25 (s, C-1). MS-EI 70 eV (200 °C) m/z (rel. int. %), 503 (2) [M]<sup>+</sup>, 422 (100) [M-Br]<sup>+</sup>, 288 (7) [RBi]<sup>+</sup>, 209 (22) [Bi]<sup>+</sup>, 134 (42) [R]<sup>+</sup> [R = 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>].

**Supporting Information** (see footnote on the first page of this article): X-ray crystallographic data in CIF format for **1-5** and **11**, figures representing the molecular structure of compounds **2** and **3**, optical isomers of **1-5** and **11**, supramolecular architectures in the crystals of compounds **3**, **5** and **11**.

#### Acknowledgement

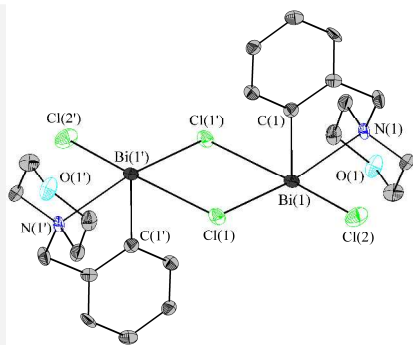
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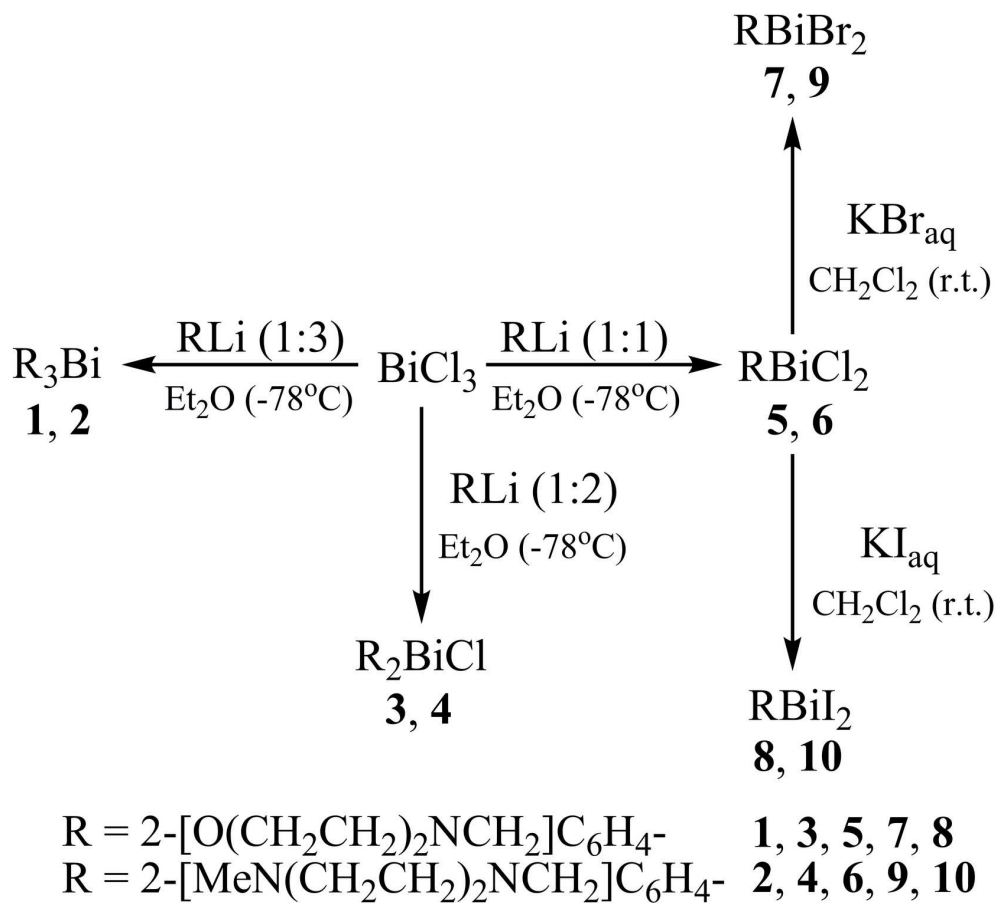
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## Entry for the Table of Contents

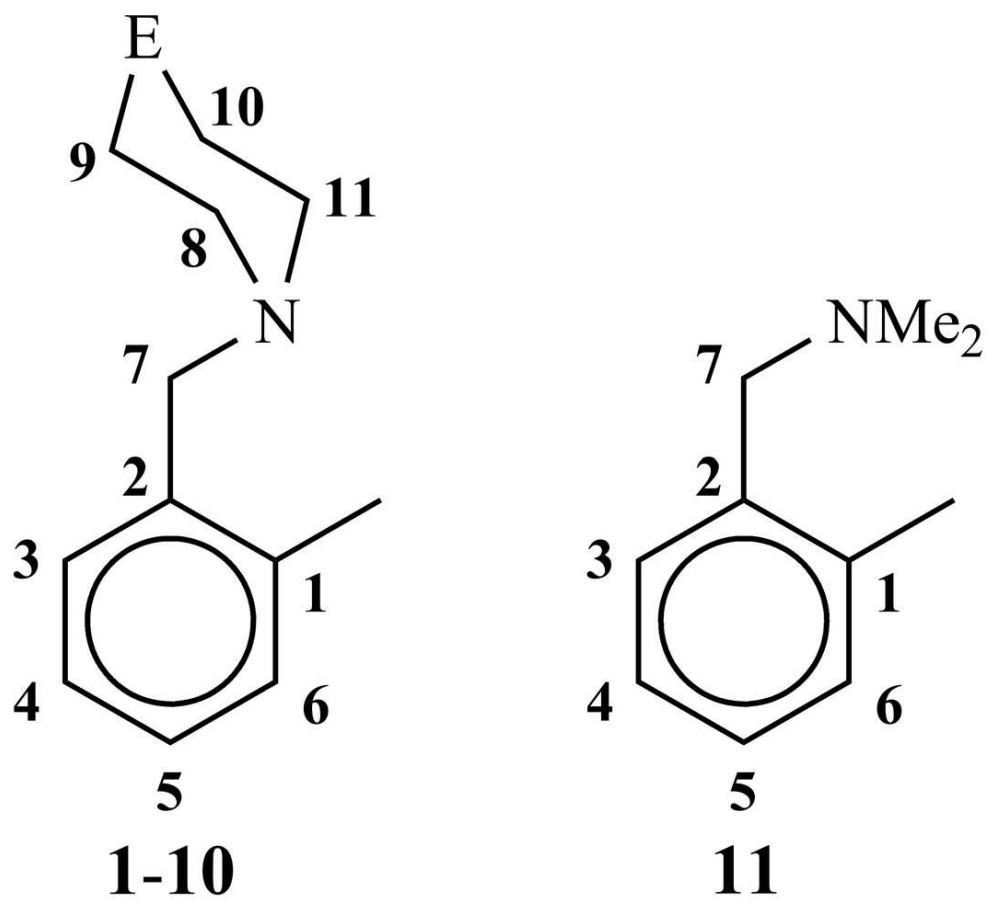


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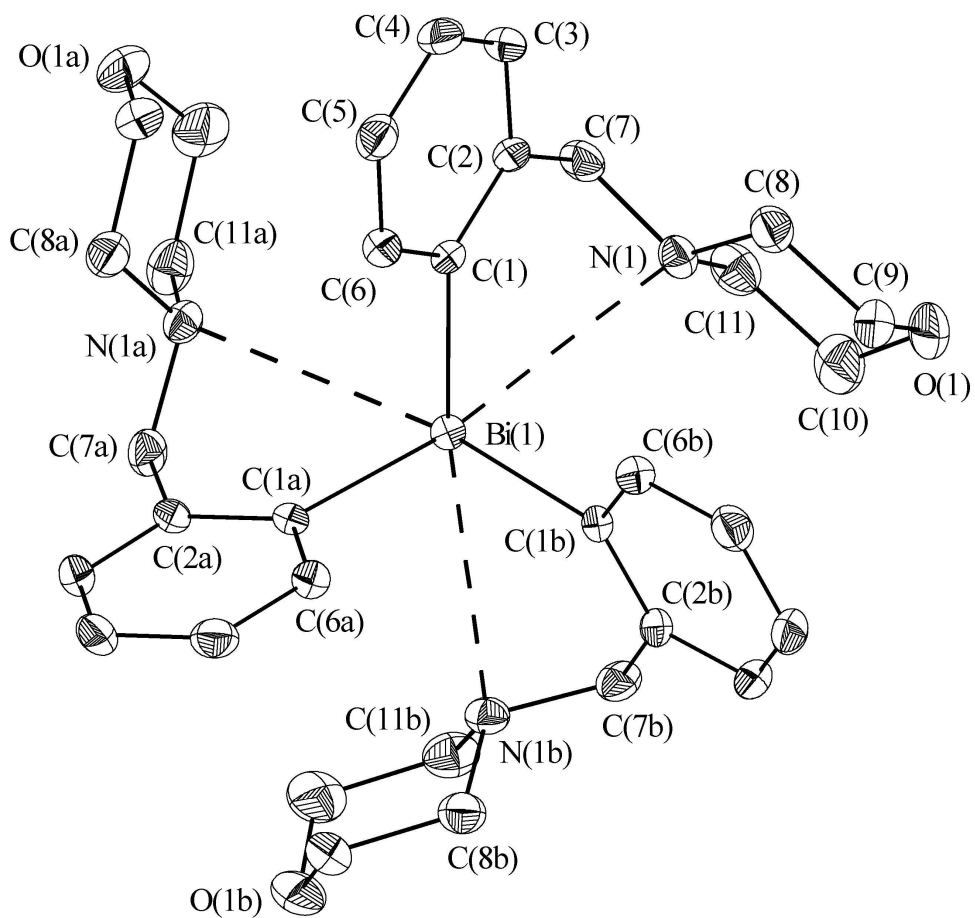
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1-3) and [2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>4</sub>]BiBr<sub>2</sub> – new hypervalent  
organobismuth(III) compounds



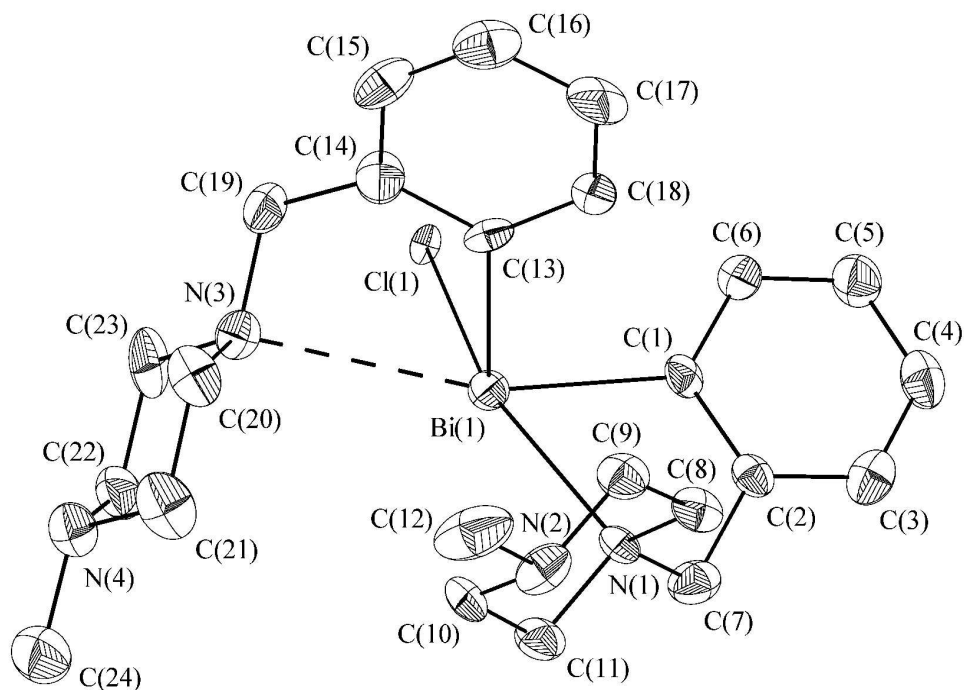
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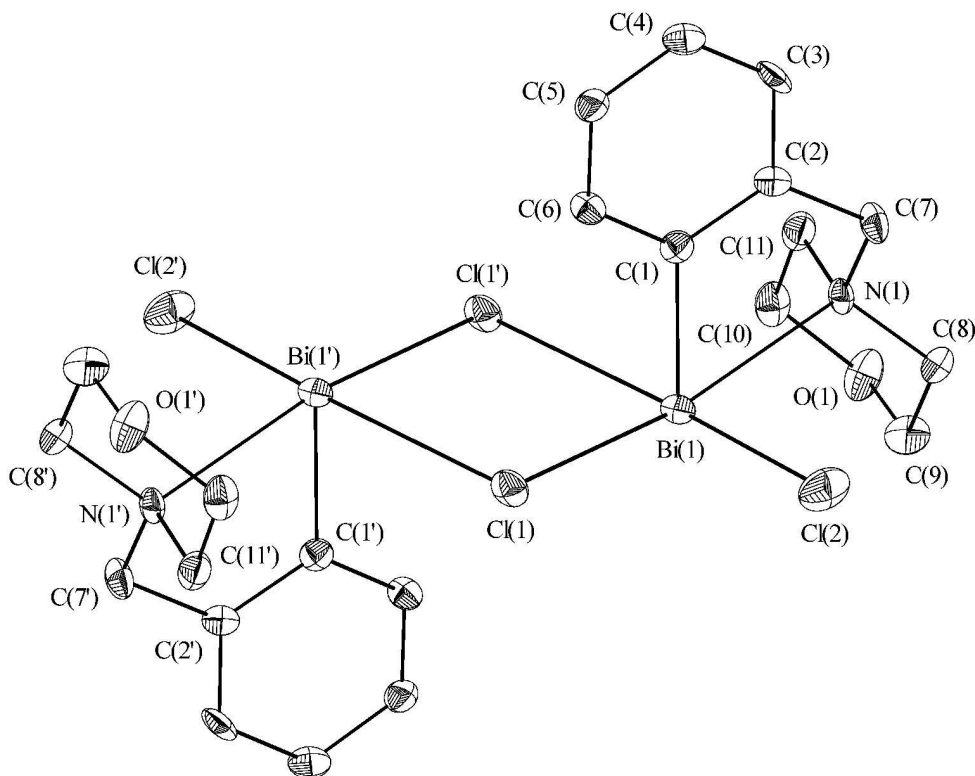


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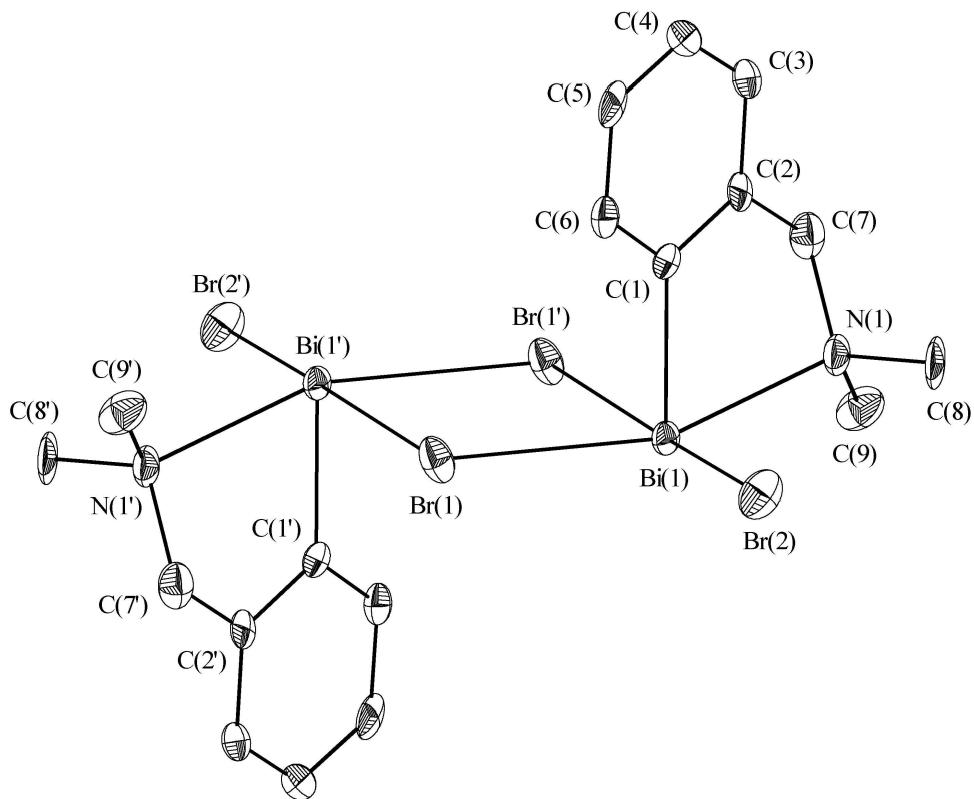


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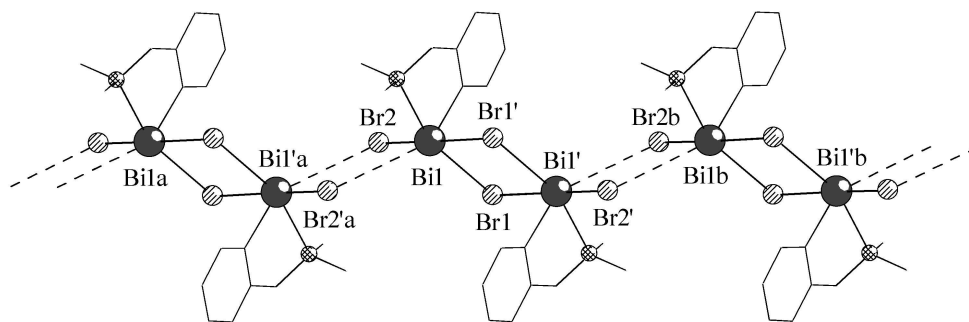




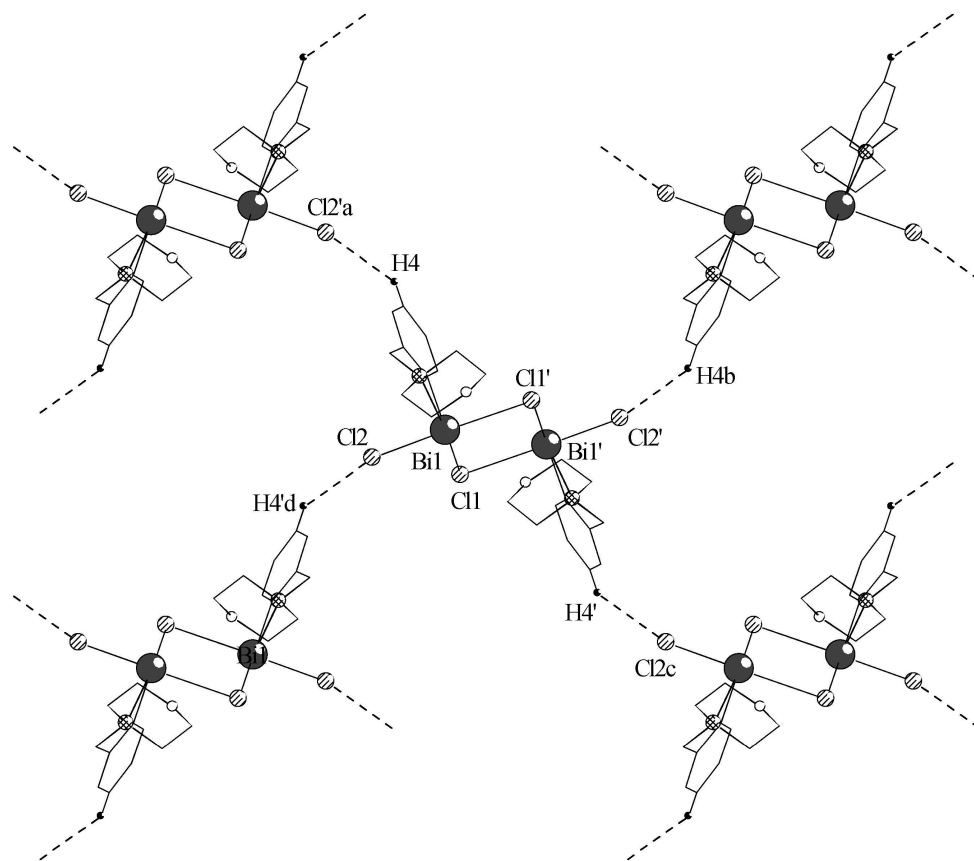
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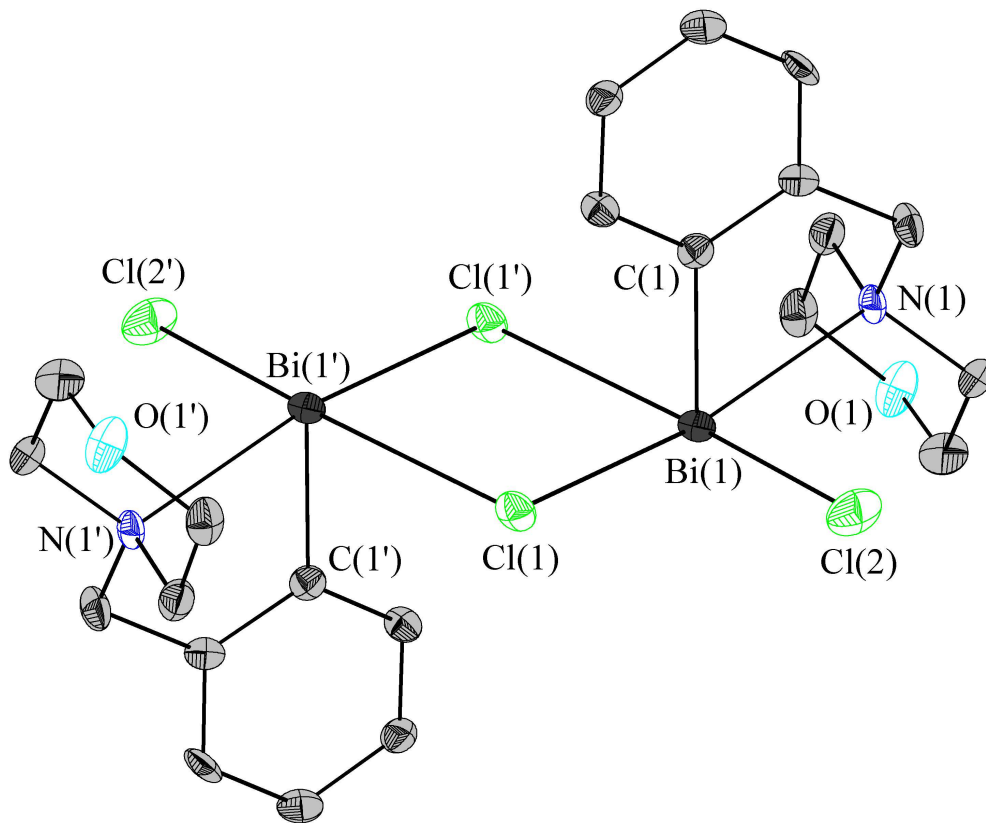
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