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[2-{E(CH₂CH₂)₂NCH₂}C₆H₄]_nBiX_{3-n} (E = O, NMe; X = Cl, Br, I; n = 1-3) and [2-(Me₂NCH₂)C₆H₄]BiBr₂ – new hypervalent organobismuth(III) compoundsHans J. Breunig,^{*[a]} Mihai G. Nema,^[b] Cristian Silvestru,^{*[b]} Albert Soran,^[b] and Richard A. Varga^[b]*To the Memory of Professor Dr. rer. nat. Herbert Schumann***Keywords:** Bismuth; Hypervalent; NMR studies; X-ray diffraction; Supramolecular

The homoleptic [2-{E(CH₂CH₂)₂NCH₂}C₆H₄]₃Bi [E = O (**1**), MeN (**2**)], the chlorides [2-{E(CH₂CH₂)₂NCH₂}C₆H₄]₂BiCl [E = O (**3**), MeN (**4**)] and the dichloride [2-{E(CH₂CH₂)₂NCH₂}C₆H₄]BiCl₂ [E = O (**5**), MeN (**6**)] have been synthesized by reacting the corresponding *ortho*-lithium derivative with BiCl₃ in corresponding molar ratios. The dihalides [2-{E(CH₂CH₂)₂NCH₂}C₆H₄]BiX₂ [X = Br, E = O (**7**), MeN (**9**); X = I, E = O (**8**), MeN (**10**)] as well as [2-(Me₂NCH₂)C₆H₄]BiBr₂ (**11**) were obtained by halide exchange reactions between RBiCl₂ and excess aqueous solution of KX. The compounds were characterized by multinuclear (¹H, ¹³C) 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 (C₆H₄CH₂)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 R₃Bi 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)₃Bi 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)₂BiCl 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)BiX₃ (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-(CF₃)₃C₆H₂]₂BiCl [11], [(Me₃Si)₂CH]₂BiCl [12], or [2,6-Mes₂C₆H₃]₂BiCl [13]. Even with such bulky ligands the dihalides usually form at least dimers, e.g. [2,4,6-Ph₃C₆H₂]₂BiCl₂ [14] or [2,6-Mes₂C₆H₃]₂BiX₂ (X = Cl [15], Br [16]). Another strategy is to use one pendant arm ligand such as 2-(Me₂NCH₂)C₆H₄ [9] and 2-(Et₂NCH₂)C₆H₄ [17], or “pincer” ligands like 2,6-(Me₂NCH₂)₂C₆H₃ [9,18] and 2,6-[MeN(CH₂CH₂)₂NCH₂]₂C₆H₃ [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-(Me₂NCH₂)C₆H₄]₂BiX (X = Cl [19], Br, I [9]), [2-(Et₂NCH₂)C₆H₄]₂BiX [17] and [2,6-(Me₂NCH₂)₂C₆H₃]₂BiCl [20] are monomeric. The corresponding dihalides usually exhibit low solubility in nonpolar solvents and for [2-(Me₂NCH₂)C₆H₄]BiCl₂ 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

use of the “pincer” ligands 2,6-(Me₂NCH₂)₂C₆H₃ and 2,6-[MeN(CH₂CH₂)₂NCH₂]₂C₆H₃ afforded monomeric organobismuth(III) dihalides with a T-shaped CBiX₂ core (X = Cl, Br, I) [18,20].

With the aim to increase the sterical protection and to study the influence of the nature of the organic groups on the nitrogen of the pendant arm we have used now the bulkier one pendant arm groups 2-[E(CH₂CH₂)₂NCH₂]₂C₆H₄ (E = O, MeN), capable to act as (C,N) ligands. In addition, these groups contain additional donor atoms from the morpholinyl or piperazinyl rings, respectively, available for coordination to other metal centers, which might result in interesting homo- and heterometallic species. We report here the syntheses, structures and spectroscopic properties of compounds [2-{E(CH₂CH₂)₂NCH₂]₂C₆H₄Bi [E = O (1), MeN (2)], [2-{E(CH₂CH₂)₂NCH₂]₂C₆H₄BiCl [E = O (3), MeN (4)] and [2-{E(CH₂CH₂)₂NCH₂]₂C₆H₄BiX₂ [E = O, X = Cl (5), Br (7), I (8); E = MeN, X = Cl (6), Br (9), I (10)], as well as [2-(Me₂NCH₂)C₆H₄]₂BiBr₂ (11).

Results and Discussion

The homoleptic triorganobismuthanes 1 and 2, the diorganobismuth(III) chlorides 3 and 4 and organobismuth(III) dichlorides 5 and 6 were obtained by reacting the corresponding organolithium derivative with bismuth trichloride in appropriate molar ratios, in diethyl ether, at low temperature (-78 °C). The dibromides 7, 9 and 11, and the diiodides 8 and 10 were obtained by halide exchange reactions starting from the corresponding organobismuth dichloride in dichloromethane and excess aqueous solution of the appropriate potassium halide. The synthetic pathways are depicted in Scheme 1. All compounds were obtained as crystalline solids in fairly good yields and are stable in solid state for more than two months. The triorganobismuthanes 1 and 2 and the monochlorides 3 and 4 are soluble in common organic solvents, while the dihalides 5–11 are well soluble only in DMSO.

Scheme 1. The preparation of compounds 1–10

The solution behavior of the new compounds 1 - 11 was investigated by multinuclear (¹H, ¹³C) NMR spectroscopy, at room temperature. The ¹H and ¹³C resonances were assigned using 2D NMR experiments, according to the numbering diagram depicted in Scheme 2.

Scheme 2. Numbering scheme for NMR resonance assignments.

The ¹H and ¹³C NMR spectra of 1–4, in CDCl₃, exhibit only one set of resonances for the three, respectively two organic groups attached to a metal atom, thus suggesting their equivalence at the NMR time scale. In absence of an intramolecular N→Bi interaction in solution a fast conformational change of the six-membered morpholinyl and piperazinyl ring, respectively, would result in a pattern of the alkyl region of the ¹H spectrum similar with that observed for the free organic ligands 2-[O(CH₂CH₂)₂NCH₂]₂C₆H₄Br [21] and 2-[MeN(CH₂CH₂)₂NCH₂]₂C₆H₄Br or the 1,3-[MeN(CH₂CH₂)₂NCH₂]₂C₆H₄ [18]. Indeed, the aliphatic regions of the ¹H NMR spectra exhibit only two broad resonance signals for protons H-8,11 and H-9,10 for 1 and 3, and one broad resonance for all protons H-8-11 for 2 and 4, respectively. This suggests that, at room temperature, the intramolecular N→Bi interaction in solution is weak enough to allow a fluxional behaviour. The resonance for the H-7 methylene protons in all compounds 1–4 appears as a singlet.

The dihalides 5, 7 and 8, containing the morpholinyl-based ligand, as well as the dibromide 9, exhibit a different pattern in the ¹H NMR spectra at room temperature, i.e. four well separated, multiplet resonances for the methylene protons of the morpholinyl / piperazinyl ring. This behaviour is not so evident for the dichloride 6 and the diiodide 10, containing the pyperazinyl-based ligand, the resonances being in these cases considerably overlapped. The non-equivalence of these protons is consistent with the presence of a strong intramolecular N→Bi interaction in solution, at room temperature, as found in solid state (see subsequent discussion). Such an interaction will prevent a fluxional process and the conformational change of the six-membered morpholinyl and piperazinyl ring. A similar behaviour was reported for organoselenium derivatives containing the same pendant arm ligands [22] and the related dihalides [2,6-{MeN(CH₂CH₂)₂NCH₂]₂C₆H₃BiX₂ [18]. As a result of the intramolecular N→Bi interaction the H-8,11 (N-CH₂-CH₂-E) and H-9,10 (N-CH₂-CH₂-E) protons became non-equivalent, i.e. pro-*cis* and pro-*trans* with respect to the position of the bismuth atom in relation to the morpholinyl / piperazinyl ring (see also ref. 18). Thus, the room-temperature ¹H NMR data for these dihalides provided evidences for the presence of the intramolecular N→Bi interactions in solution, the inversion at the nitrogen atom being frozen at this temperature.

Single crystals suitable for X-ray diffraction were obtained by slow diffusion of *n*-hexane into a CH₂Cl₂ solution for 1–4, while crystals of the dihalides 5 and 11 were obtained from a concentrated solution in DMSO.

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(CH₂CH₂)₂NCH₂}C₆H₄]₃Bi (**1**) [*all-R_N* 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.

	1 ^[a]	2 ^[a]
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-(R₂NCH₂)C₆H₄]₃Bi (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-(Me₂NCH₂)C₆H₄]₃Bi [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-(Et₂NCH₂)C₆H₄]₃Bi [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)₃Bi 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 BiC₃N rings induces planar chirality (with the aromatic ring and the nitrogen atom as chiral plane and pilot atom, respectively; isomers given as *S_N* and *R_N*) [27] and the crystals of the triorganobismuthanes **1** and **2** contain a 1:1 mixture of *all-R_N* and *all-S_N* 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(CH₂CH₂)₂NCH₂}C₆H₄]₂BiCl (**4**) [*(R_{NL}, S_{N2}, A_{Bi})* 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 atom 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.^[a]

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

Bi(1)–Cl(1)	2.623(4)	2.733(3)
Bi(1)–N(1)	2.660(11)	2.744(14)
Bi(1)–X(2)	3.095(11)	3.061(14)
C(1)–Bi(1)–X(1)	91.3(5)	94.7(6)
C(1)–Bi(1)–Cl(1)	90.6(4)	92.5(4)
X(1)–Bi(1)–Cl(1)	93.5(3)	90.6(4)
N(1)–Bi(1)–C(1)	70.4(4)	69.3(5)
N(1)–Bi(1)–X(1)	88.2(4)	98.1(5)
N(1)–Bi(1)–Cl(1)	161.0(2)	160.3(3)
N(1)–Bi(1)–X(2)	110.2(3)	115.7(4)
X(2)–Bi(1)–C(1)	155.0(4)	162.7(5)
X(2)–Bi(1)–X(1)	63.9(4)	68.5(5)
X(2)–Bi(1)–Cl(1)	87.4(2)	83.9(3)
Bi(1)–N(1)–C(7)	100.0(7)	92.9(10)
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 $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{BiCl}$ [2.570(5) Å] [19], but close to that observed for the ethyl analogue $[2-(\text{Et}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{BiCl}$ [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 $[2-(\text{R}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{BiCl}$ [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 $[2-(\text{R}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{BiCl}$ and, taking into account both intramolecular N→Bi interactions *per* metal atom, the coordination geometry features distorted square-pyramidal [(C,N)₂BiCl 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.* $[2-(\text{R}_2\text{NCH}_2)\text{C}_6\text{H}_4]_2\text{BiCl}$ [2.667(2) Å for R = Me [19]; 2.602(2) Å for R = Et [17]] or $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4](4\text{-MeC}_6\text{H}_4)\text{BiCl}$ [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.* $[2,4,6-(\text{CF}_3)\text{C}_6\text{H}_2]_2\text{BiCl}$ [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 BiC₃N rings folded along the Bi⋯C_{methylene} axis, with the nitrogen atom lying out of the best plane defined by the residual BiC₃ 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)₂BiCl 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_{Bi} and A_{Bi} isomers [30]. Indeed, the crystals of **3** and **4** contain a 1:1 mixture of (*R*_{N1},*S*_{N2},C_{Bi}) / (*S*_{N1},*R*_{N2},A_{Bi})-**3** isomers and (*S*_{N1},*R*_{N2},C_{Bi}) / (*R*_{N1},*S*_{N2},A_{Bi})-**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*_{N1},A_{Bi}) and (*R*_{N1},C_{Bi}) isomers in the crystal of $[2-\{\text{O}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\}\text{C}_6\text{H}_4]\text{BiCl}_2$ (**5**) (thermal ellipsoids are represented at 30% probability level; hydrogen atoms are omitted for clarity).

Figure 4. Dimer association between (*R*_{N1},A_{Bi}) and (*S*_{N1},C_{Bi}) isomers in the crystal of $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{BiBr}_2$ (**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.^[a]

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

Bi(1)–X(2)	2.527(4)	2.720(2)
Bi(1)–N(1)	2.548(9)	2.485(13)
Bi(1)–X(1')	3.021(4)	3.0695(19)
C(1)–Bi(1)–X(1)	91.4(3)	89.2(4)
C(1)–Bi(1)–X(2)	92.4(3)	89.2(4)
X(1)–Bi(1)–X(2)	90.91(12)	92.97(6)
N(1)–Bi(1)–C(1)	73.5(4)	74.2(5)
N(1)–Bi(1)–X(1)	164.0(2)	160.7(3)
N(1)–Bi(1)–X(2)	84.6(2)	96.5(3)
N(1)–Bi(1)–X(1')	101.1(2)	85.6(3)
X(1')–Bi(1)–C(1)	84.7(3)	87.3(4)
X(1')–Bi(1)–X(1)	82.29(10)	83.78(5)
X(1')–Bi(1)–X(2)	172.55(12)	175.26(6)
Bi(1)–N(1)–C(7)	103.7(7)	104.4(9)
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 $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{BiX}_2$ ($\text{X} = \text{Cl}$ [9], 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 Bi_2X_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_{aryl} [Cl(1)⋯H(15b) 2.93 Å] and Cl⋯H_{morpholinyl} [Cl(1)⋯H(10Aa) 2.95 Å] contacts. Additional weak Cl⋯H_{morpholinyl} [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 $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{BiX}_2$ ($\text{X} = \text{Cl}$ [9], 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_{aryl} [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 $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{BiBr}_2$ (**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 $[2-\{\text{O}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\}\text{C}_6\text{H}_4]\text{BiCl}_2$ (**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 $[2-\{\text{E}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\}\text{C}_6\text{H}_4]_3\text{Bi}$, $[2-\{\text{E}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\}\text{C}_6\text{H}_4]_2\text{BiCl}$ and $[2-\{\text{E}(\text{CH}_2\text{CH}_2)_2\text{NCH}_2\}\text{C}_6\text{H}_4]\text{BiX}_2$ ($\text{E} = \text{O}, \text{MeN}; \text{X} = \text{Cl}, \text{Br}, \text{I}$), as well as $[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4]\text{BiBr}_2$ were prepared and their structures were investigated both in solution and in

	1	2	3	4	5	11
Empirical formula	C ₃₃ H ₄₂ BiN ₃ O ₃	C ₃₆ H ₅₁ BiN ₆	C ₂₂ H ₂₈ BiClN ₂ O ₂	C ₂₄ H ₃₄ BiClN ₄	C ₂₂ H ₂₈ Bi ₂ Cl ₄ N ₂ O ₂	C ₁₈ H ₂₄ Bi ₂ Br ₄ N ₂
Crystal system	Rhombohedral	Rhombohedral	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Space group	<i>R</i> -3	<i>R</i> -3	<i>Pbca</i>	<i>P2₁/c</i>	<i>Pbca</i>	<i>P2₁/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)
α /°	90	90	90	90	90	90
β /°	90	90	90	102.016(2)	90	100.078(3)
γ /°	120	120	90	90	90	90
Volume /Å ³	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 ⁻³	1.607	1.419	1.788	1.649	2.278	2.666
Crystal size /mm ³	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> ₁ = 0.0348, <i>wR</i> ₂ = 0.0650	<i>R</i> ₁ = 0.0287, <i>wR</i> ₂ = 0.0617	<i>R</i> ₁ = 0.0577, <i>wR</i> ₂ = 0.1277	<i>R</i> ₁ = 0.0846, <i>wR</i> ₂ = 0.2063	<i>R</i> ₁ = 0.0614, <i>wR</i> ₂ = 0.0938	<i>R</i> ₁ = 0.0637, <i>wR</i> ₂ = 0.1147
Largest difference peak and hole (e Å ⁻³)	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)₃Bi core for triorganobismuthanes, (C,N)₂BiCl for diorganobismuth(III) chlorides, and (C,N)BiX₃ for dimeric organobismuth(III) dihalides. The room temperature ¹H 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(CH₂CH₂)₂NCH₂]C₆H₄Br [21], 2-[MeN(CH₂CH₂)₂NCH₂]C₆H₄Br [31], [2-(Me₂NCH₂)C₆H₄]Li [32], and [2-(Me₂NCH₂)C₆H₄]BiCl₂ [19].

Room temperature ¹H, ¹³C and 2D NMR spectra were recorded in dried CDCl₃ (1–4) or DMSO-*d*₆ (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. CHCl₃: ¹H 7.26, ¹³C 77.0 ppm; DMSO-*d*₆: ¹H 2.50, ¹³C 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-Kα 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].

Synthesis of [2-{O(CH₂CH₂)₂NCH₂}C₆H₄]₃Bi (1)

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(CH₂CH₂)₂NCH₂]C₆H₄Br (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(CH₂CH₂)₂NCH₂}C₆H₄]Li as a white compound. To the solid product suspended in 100 mL anhydrous diethyl ether was added, at –78 °C, a solution of BiCl₃ (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 $C_{33}H_{42}BiN_3O_3$: C 53.73 (53.94) %; H 5.74 (5.65) %; N 5.70 (5.59) %. 1H NMR ($CDCl_3$, 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, $^3J_{HH} = 7.1$ Hz), 7.21 (t, 3H, *H*-4, $^3J_{HH} = 7.2$ Hz), 7.26 (d, 3H, *H*-3, $^3J_{HH} = 7.7$ Hz), 7.64 (d, 3H, *H*-6, $^3J_{HH} = 7.1$ Hz). ^{13}C NMR ($CDCl_3$, 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*]⁺, 561 (100) [*R*₂Bi]⁺, 209 (5) [Bi]⁺, 176 (20) [*R*]⁺ [*R* = 2- $\{O(CH_2CH_2)_2NCH_2\}C_6H_4$].

Synthesis of [2-{MeN(CH₂CH₂)₂NCH₂}C₆H₄]₃Bi (**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(CH₂CH₂)₂NCH₂]C₆H₄Br (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(CH₂CH₂)₂NCH₂}C₆H₄]₃Li 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 BiCl₃ (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 $C_{36}H_{51}BiN_6$: C 55.66 (55.96) %; H 6.62 (6.44) %; N 10.82 (10.94) %. 1H NMR ($CDCl_3$, 200 MHz): δ 1.95 (s, 9H, NCH₃), 2.30 (s, br, 24H, *H*-8-11), 3.58 (s, br, 6H, *H*-7), 7.06 (t, 3H, *H*-5, $^3J_{HH} = 7.2$ Hz), 7.19 (t, 3H, *H*-4, $^3J_{HH} = 7.2$ Hz), 7.24 (m, 3H, *H*-3), 7.71 (d, 3H, *H*-6, $^3J_{HH} = 6.8$ Hz). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 45.93 (s, NCH₃), 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*₂Bi]⁺, 398 (10) [RBi]⁺, 209 (11) [Bi]⁺, 189 (28) [*R*]⁺ [*R* = 2-{MeN(CH₂CH₂)₂NCH₂}C₆H₄].

Synthesis of [2-{O(CH₂CH₂)₂NCH₂}C₆H₄]₂BiCl (**3**)

A suspension of [2-{O(CH₂CH₂)₂NCH₂}C₆H₄]₂Li [obtained from *n*-BuLi in *n*-hexane (14.65 mL 1.6 M, 23.43 mmol) and 2-[O(CH₂CH₂)₂NCH₂]C₆H₄Br (6.0 g, 23.43 mmol)] in 100 mL anhydrous diethyl ether was added dropwise, at -78 °C, to a solution of BiCl₃ (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 $C_{22}H_{28}BiClN_2O_2$: C 44.27 (44.11) %; H 4.73 (4.75) %; N 4.69 (4.66) %. 1H NMR ($CDCl_3$, 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, $^3J_{HH} = 6.9$ Hz), 8.57 (d, 2H, *H*-6, $^3J_{HH} = 7.3$ Hz). ^{13}C NMR ($CDCl_3$, 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]⁺, 420 (20) [M-R]⁺, 385 (19) [RBi]⁺, 209 (28) [Bi]⁺, 176 (80) [*R*]⁺ [*R* = 2-{O(CH₂CH₂)₂NCH₂}C₆H₄].

Synthesis of [2-{MeN(CH₂CH₂)₂NCH₂}C₆H₄]₂BiCl (**4**)

A suspension of [2-{MeN(CH₂CH₂)₂NCH₂}C₆H₄]₂Li [obtained from *n*-BuLi in *n*-hexane (5.66 mL 1.6 M, 9.18 mmol) and 2-[MeN(CH₂CH₂)₂NCH₂]C₆H₄Br (2.47 g, 9.18 mmol)] in 100 mL anhydrous diethyl ether was added dropwise, at -78 °C, to a solution of BiCl₃ (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 $C_{24}H_{34}BiClN_4$: C 46.27 (46.72) %; H 5.50 (5.72) %; N 8.99 (9.26) %. 1H NMR ($CDCl_3$, 200 MHz): δ 2.32 (s, 6H, NCH₃), 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, $^3J_{HH} = 6.8$ Hz), 8.65 (d, br, 2H, *H*-6). ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 46.01 (s, NCH₃), 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]⁺, 432 (27) [M-R]⁺, 209 (11) [Bi]⁺, 189 (30) [*R*]⁺ [*R* = 2-{MeN(CH₂CH₂)₂NCH₂}C₆H₄].

Synthesis of [2-{O(CH₂CH₂)₂NCH₂}C₆H₄]₂BiCl₂ (**5**)

A suspension of [2-{O(CH₂CH₂)₂NCH₂}C₆H₄]₂Li [obtained from *n*-BuLi in *n*-hexane (7.32 mL 1.6 M, 11.71 mmol) and 2-[O(CH₂CH₂)₂NCH₂]C₆H₄Br (3.0 g, 11.71 mmol)] in 60 mL anhydrous diethyl ether was added dropwise, at -78 °C, to a solution of BiCl₃ (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 $C_{11}H_{14}BiCl_2NO$: C 28.97 (28.67) %; H 3.09 (3.48) %; N 3.07 (3.03) %. 1H NMR ($DMSO-d_6$, 360 MHz): δ 2.58 [t, 2H, $H_{pro-trans}$ -8,11, $^2J_{HH} \approx ^3J_{HH} = 11.7$ Hz], 3.26 [d, 2H, $H_{pro-cis}$ -8,11, $^2J_{HH} = 12.1$ Hz], 3.67 [t, 2H, $H_{pro-trans}$ -9,10, $^2J_{HH} \approx ^3J_{HH} = 11$ Hz], 3.79 [d, 2H, $H_{pro-cis}$ -9,10, $^2J_{HH} = 12.2$ Hz], 4.27 (s, 2H, *H*-7), 7.41 (t, 1H, *H*-4, $^3J_{HH} = 7.4$ Hz), 7.67 (t, 1H, *H*-5, $^3J_{HH} = 7.4$ Hz), 7.81 (d, 1H, *H*-3, $^3J_{HH} = 7.5$ Hz), 9.16 (d, 1H, *H*-6, $^3J_{HH} = 7.5$ Hz). ^{13}C NMR ($DMSO-d_6$, 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*]⁺, 420 (60) [M-Cl]⁺, 209 (24) [Bi]⁺, 176 (38) [*R*]⁺ [*R* = 2-{O(CH₂CH₂)₂NCH₂}C₆H₄].

Synthesis of [2-{MeN(CH₂CH₂)₂NCH₂}C₆H₄]₂BiCl₂ (**6**)

A suspension of [2-{MeN(CH₂CH₂)₂NCH₂}C₆H₄]₂Li [obtained from *n*-BuLi in *n*-hexane (12.50 mL 1.6 M, 20 mmol) and 2-[MeN(CH₂CH₂)₂NCH₂]C₆H₄Br (5.38 g, 20 mmol)] in 50 mL anhydrous diethyl ether was added dropwise with stirring, at -78 °C, to a solution of BiCl₃ (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 $C_{12}H_{17}BiCl_2N_2$: C 30.72 (30.36) %; H 3.65 (3.72) %; N 5.97 (5.56) %. 1H NMR ($DMSO-d_6$, 360 MHz): δ 2.68 (s, br, 3H, NCH₃), 3.41 (br, 8H, *H*-8-11), 4.27 (s, 2H, *H*-7), 7.42 (t, 1H, *H*-4, $^3J_{HH} = 6.9$ Hz), 7.69 (t, 1H, *H*-5, $^3J_{HH} = 7.2$ Hz), 7.83 (d, 1H, *H*-3, $^3J_{HH} = 7.4$ Hz), 9.18 (d, 1H, *H*-6, $^3J_{HH} = 7.5$ Hz). ^{13}C NMR ($DMSO-d_6$, 50.3 MHz): δ 42.14 (s, NCH₃), 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]⁺, 398

(10) [RB⁺], 209 (26) [Bi⁺], 189 (18) [R⁺] [R = 2-{MeN(CH₂CH₂)₂NCH₂}C₆H₄].

Synthesis of [2-{O(CH₂CH₂)₂NCH₂}C₆H₄]BiBr₂ (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 Na₂SO₄. 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 C₁₁H₁₄BiBr₂NO: C 24.24 (24.41) %; H 2.59 (2.13) %; N 2.57 (2.22) %. ¹H NMR (DMSO-*d*₆, 200 MHz): δ 2.73 [t, 2H, *H*_{pro-trans}-8,11, ²*J*_{HH} ≈ ³*J*_{HH} = 11.6 Hz], 3.19 [d, 2H, *H*_{pro-cis}-8,11, ²*J*_{HH} = 12.0 Hz], 3.67 [t, 2H, *H*_{pro-trans}-9,10, ²*J*_{HH} ≈ ³*J*_{HH} = 11.0 Hz], 3.82 [d, 2H, *H*_{pro-cis}-9,10, ²*J*_{HH} = 11.6 Hz], 4.34 (s, 2H, *H*-7), 7.51 (t, 1H, *H*-4, ³*J*_{HH} = 7.3 Hz), 7.73 (t, 1H, *H*-5, ³*J*_{HH} = 7.2 Hz), 7.94 (d, 1H, *H*-3, ³*J*_{HH} = 7.4 Hz), 9.42 (d, 1H, *H*-6, ³*J*_{HH} = 7.0 Hz). ¹³C NMR (DMSO-*d*₆, 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]⁺, 385 (19) [RBi]⁺, 209 (40) [Bi]⁺, 176 (22) [R]⁺ [R = 2-{O(CH₂CH₂)₂NCH₂}C₆H₄].

Synthesis of [2-{O(CH₂CH₂)₂NCH₂}C₆H₄]BiI₂ (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 C₁₁H₁₄BiI₂NO: C 20.67 (20.51) %; H 2.21 (2.24) %; N 2.19 (1.86) %. ¹H NMR (DMSO-*d*₆, 200 MHz): δ 2.76 [t, 2H, *H*_{pro-trans}-8,11, ²*J*_{HH} ≈ ³*J*_{HH} = 10.2 Hz], 3.25 [d, 2H, *H*_{pro-cis}-8,11, ²*J*_{HH} = 12.8 Hz], 3.65 [t, 2H, *H*_{pro-trans}-9,10, ²*J*_{HH} ≈ ³*J*_{HH} = 11.2 Hz], 3.83 [d, 2H, *H*_{pro-cis}-9,10, ²*J*_{HH} = 11.5 Hz], 4.38 (s, 2H, *H*-7), 7.57 (t, 1H, *H*-4, ³*J*_{HH} = 7.3 Hz), 7.68 (t, 1H, *H*-5, ³*J*_{HH} = 7.2 Hz), 7.93 (d, 1H, *H*-3, ³*J*_{HH} = 7.2 Hz), 9.73 (d, 1H, *H*-6, ³*J*_{HH} = 6.5 Hz). ¹³C NMR (DMSO-*d*₆, 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]⁺, 385 (22) [RBi]⁺, 209 (24) [Bi]⁺, 176 (22) [R]⁺ [R = 2-{O(CH₂CH₂)₂NCH₂}C₆H₄].

Synthesis of [2-{MeN(CH₂CH₂)₂NCH₂}C₆H₄]BiBr₂ (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 C₁₂H₁₇BiCl₂N₂: C 25.83 (25.36) %; H 3.07 (3.12) %; N 5.02 (5.26) %. ¹H NMR (DMSO-*d*₆, 200 MHz): δ 2.60 (s,br, 3H, NCH₃), 2.75 [t, 2H, *H*_{pro-trans}-8,11, ²*J*_{HH} ≈ ³*J*_{HH} = 12.4 Hz], 2.97 [t, 2H, *H*_{pro-trans}-9,10, ²*J*_{HH} ≈ ³*J*_{HH} = 11.8 Hz], 3.23 [d, 2H, *H*_{pro-cis}-9,10, ²*J*_{HH} = 11.6 Hz], 3.43 [d, 2H, *H*_{pro-cis}-8,11, ²*J*_{HH} = 12.3 Hz], 4.34 (s, 2H, *H*-7), 7.48 (t, 1H, *H*-4, ³*J*_{HH} = 7.1 Hz), 7.71 (t, 1H, *H*-5, ³*J*_{HH} = 6.9 Hz), 7.91 (d, 1H, *H*-3, ³*J*_{HH} = 7.2 Hz), 9.47 (d, 1H, *H*-6, ³*J*_{HH} = 7.3 Hz). ¹³C NMR (DMSO-*d*₆, 50.3 MHz): δ 42.56 (s, NCH₃), 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]⁺, 477 (100) [M-Br]⁺, 268 (22) [RBr]⁺, 209 (44) [Bi]⁺, 189 (21) [R]⁺ [R = 2-{MeN(CH₂CH₂)₂NCH₂}C₆H₄].

Synthesis of [2-{MeN(CH₂CH₂)₂NCH₂}C₆H₄]BiI₂ (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 C₁₂H₁₇BiI₂N₂: C 22.10 (21.87) %; H 2.63 (2.42) %; N 4.30 (4.06) %. ¹H NMR (DMSO-*d*₆, 200 MHz): δ 2.80 (s,br, 3H, NCH₃), 3.32 (br, 8H, *H*-8-11), 4.34 (s, 2H, *H*-7), 7.55 (t, 1H, *H*-4, ³*J*_{HH} = 7.3 Hz), 7.70 (t, 1H, *H*-5, ³*J*_{HH} = 7.4 Hz), 7.93 (d, 1H, *H*-3, ³*J*_{HH} = 7.4 Hz), 9.68 (s,br, 1H, *H*-6). ¹³C NMR (DMSO-*d*₆, 50.3 MHz): δ 41.99 (s, NCH₃), 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]⁺, 398 (10) [RBi]⁺, 209 (37) [Bi]⁺, 189 (38) [R]⁺ [R = 2-{MeN(CH₂CH₂)₂NCH₂}C₆H₄].

Synthesis of [2-(Me₂NCH₂)C₆H₄]BiBr₂ (11)

Compound **11** was prepared similar to **9**, from a suspension of [2-(Me₂NCH₂)C₆H₄]BiCl₂ (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 C₉H₁₂BiBr₂N: C 21.49 (21.18) %; H 2.40 (2.46) %; N 2.78 (2.42) %. ¹H NMR (DMSO-*d*₆, 200 MHz): δ 2.70 (s, 6H, NCH₃), 4.39 (s, 2H, *H*-7), 7.49 (t, 1H, *H*-4, ³*J*_{HH} = 7.1 Hz), 7.71 (t, 1H, *H*-5, ³*J*_{HH} = 7.8 Hz), 7.84 (d, 1H, *H*-3, ³*J*_{HH} = 7.3 Hz), 9.29 (d, 1H, *H*-6, ³*J*_{HH} = 7.4 Hz). ¹³C NMR (DMSO-*d*₆, 50.3 MHz): δ 46.02 (s, NCH₃), 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]⁺, 422 (100) [M-Br]⁺, 288 (7) [RBi]⁺, 209 (22) [Bi]⁺, 134 (42) [R]⁺ [R = 2-(Me₂NCH₂)C₆H₄].

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**.

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Entry for the Table of Contents

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[2-{E(CH₂CH₂)₂NCH₂}C₆H₄]_nBiX_{3-n} (E = O, NMe; X = Cl, Br, I; n =
1-3) and [2-(Me₂NCH₂)C₆H₄]BiBr₂ – new hypervalent
organobismuth(III) compounds

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