

Dedicated to Professor Cristian Silvestru
on the occasion of his 65th anniversary

DISPERSION INTERACTION OF THE TYPE BISMUTH $\cdots\pi$ ARENE IN SUBSTITUTED BENZYL BISMUTHINES

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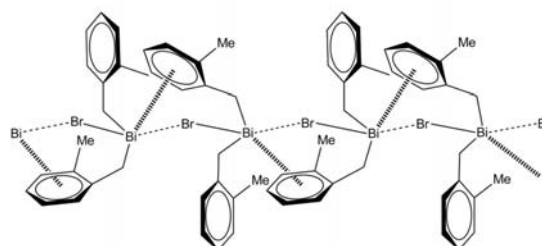
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The reaction of the benzyl *Grignard* reagent 2-X-C₆H₄CH₂MgBr (X = Me, Br) in Et₂O with BiBr₃ gave the bismuth compounds Bi(CH₂C₆H₄-X-2)₂Br [X = Me (**1**), Br (**2**)] and Bi(CH₂C₆H₄-Br-2)Br₂ (**3**). The molecular structures in the solid state of **1** and **3** were determined by single-crystal X-ray diffraction. They show the formation of intermolecular Bi–Br \cdots Bi donor-acceptor interactions to give one-dimensional coordination polymers. These bonds are accompanied by additional London dispersion interactions of the type bismuth $\cdots\pi$ arene with distances between bismuth and the centroids of the benzyl ring of 3.73 Å to 3.96 Å. These weak interactions are not structure-directing but complement the coordination sphere at bismuth.

London dispersion interaction accompany
strong donor acceptor bonds in supramolecular systems



INTRODUCTION

Although organobismuth compounds have been known for more than a century, the chemistry of organometallic bismuth compounds containing benzyl ligands has not been explored extensively, as it is the case for transition metals.¹⁻⁵ Within the family of main group metals of group 15 the benzyl ligand was introduced to bismuth chemistry first in 1957 by Bähr and Zoche.⁶ The authors described the synthesis of benzyl bismuth derivatives, *i.e.* Bi(CH₂C₆H₄-X-2)₃ (X = H, Cl, Br), starting from the corresponding organomagnesium reagent and BiCl₃, but only the melting points and

elemental analyses were reported.⁶ Later on Remington et al. published the spectroscopic characterization of Bi(CH₂C₆H₅)₃ (¹H and ¹³C NMR, IR),⁷ while its crystallographic characterisation was reported only recently by Evans and coworkers.⁸ In an experimental and theoretical study in 2009 the first crystal structure of a trisbenzyl bismuth derivative, [Bi(CH₂C₆H₄-Cl-2)₃]₂, was reported. The latter shows the presence of intermolecular dispersion interactions of the type Bi $\cdots\pi$ arene between two neighboring molecules, which provides dimers, and as a result of these Bi $\cdots\pi$ interactions and $\pi\cdots\pi$ stacking a 2D network is formed.⁹ For the lighter homologues the

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crystal structures of $E(\text{CH}_2\text{Ph})_3$, ($E = \text{N},^{10,11} \text{P},^{12} \text{Sb}^{13}$) were determined, but neither for these compounds nor for $\text{Bi}(\text{CH}_2\text{Ph})_3$ dispersion interactions of the type element $\cdots\pi$ arene are mentioned. Currently, we are interested in heavy main group elements as dispersion energy donors (DED) and in the last few years our focus was towards a better understanding of the bonding situation in metal $\cdots\pi$ arene complexes and how to make use of this weak interaction in terms of supramolecular chemistry. The metal $\cdots\pi$ arene interaction of main group metals has been known for more than a century and its importance has increased significantly in the last two decades.^{9,14-17} In a recent review Liptrot and Power discussed the high relevance of London dispersion interactions in molecular organometallic chemistry. They reported that the London dispersion forces play an important role in structure formation and that they have a stabilizing intramolecular influence in sterically crowded inorganic and organometallic molecules that are otherwise less or even un-stable.¹⁸ In addition, it has been demonstrated by Caracelli *et al.* and Tiekink *et al.* that intermolecular dispersion interactions of the type metal $\cdots\pi$ arene play an important role in the formation of supramolecular assemblies.¹⁹⁻²¹ Intermolecular London dispersion interaction of the type bismuth $\cdots\pi$ arene were investigated recently experimentally and theoretically, *i.e.* in various arylbismuth compounds including investigations on their supramolecular assemblies.^{9, 22-27} In a study on several Ar_3Bi compounds ($\text{Ar} = \text{C}_4\text{H}_3\text{NMe}, \text{C}_4\text{H}_3\text{O}, \text{C}_4\text{H}_3\text{S}, \text{C}_4\text{H}_3\text{Se}$) enantiotropic phase transitions, which are driven by dispersion interaction of the type $\text{Bi}\cdots\pi$ arene, are discussed.^{23, 26} In addition a series of reports regarding the significance of intramolecular $\text{Bi}\cdots\pi$ arene interactions in organobismuth compounds has been published recently, where mainly bulky ligands were used to stabilise unusual compounds.²⁸⁻³⁷

Motivated by our earlier results on $[\text{Bi}(\text{CH}_2\text{C}_6\text{H}_4\text{-Cl-2})_3]_2$,⁹ it was envisaged to prepare similar compounds with different electronic properties by using flexible ligands such as benzyl derivatives. While attempts to synthesize $[\text{Bi}(\text{CH}_2\text{C}_6\text{H}_4\text{-X-2})_3]_2$ ($\text{X} = \text{Me}, \text{Br}$) failed so far, we were able to isolate and characterize three new compounds, $\text{Bi}(\text{CH}_2\text{C}_6\text{H}_4\text{-X-2})_2\text{Br}$ [$\text{X} = \text{Me}$ (**1**), Br (**2**)] and $\text{Bi}(\text{CH}_2\text{C}_6\text{H}_4\text{-Br-2})\text{Br}_2$ (**3**). The crystal structures of **1** and **3** are presented here. Both compounds show intermolecular bismuth-bromine donor-acceptor interactions to give one-dimensional coordination polymers, which are accompanied by additional bismuth $\cdots\pi$ arene interaction.

RESULTS AND DISCUSSION

Synthesis

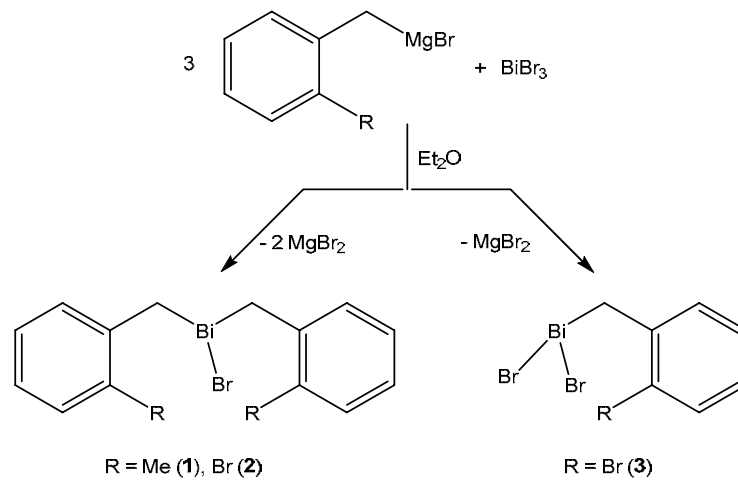
The reaction of BiBr_3 with the corresponding *Grignard* reagent $2\text{-X-C}_6\text{H}_4\text{CH}_2\text{MgBr}$ ($\text{X} = \text{Me}, \text{Br}$) in a 3:1 molar ratio in Et_2O at -20°C (for **1** and **3**) or -40°C (for **2**) provided the bismuthines $\text{Bi}(\text{CH}_2\text{C}_6\text{H}_4\text{-X-2})_2\text{Br}$ [$\text{X} = \text{Me}$ (**1**), Br (**2**)] and $\text{Bi}(\text{CH}_2\text{C}_6\text{H}_4\text{-Br-2})\text{Br}_2$ (**3**) (Scheme 1). The compounds **1-3** were isolated as orange (**1**), yellow (**2**) and red (**3**) crystals in low yields, which is related to the fact that the benzyl *Grignard* reagents generate significant amounts of the *Wurtz* coupling by-product, in particular from the more reactive bromine-substituted benzyl *Grignard* reagent.³⁸ Another issue concerning the benzyl bismuthine derivatives is their stability, which is limited especially in solution. They tend to dibismutate and easily decompose by exposure to light and air. The ^1H NMR spectra in C_6D_6 of freshly isolated compounds **1-3** are consistent with the expected resonances for the aliphatic and aromatic protons of the substituted benzyl ligands, but with time the compounds decompose. As might be expected the diorganobismuth compounds **1** and **2** show only one set of resonances, indicating the equivalence of the organic ligands in solution.

Solid state structures

Single crystals suitable for X-ray structure analysis were grown from *n*-hexane at 4°C and structure analysis of **1** and **3** revealed the monoclinic space groups $P2_1/c$ and $P2_1/n$, respectively (Figures 1 and 2). The selected bond lengths and angles are listed in the Figure captions and the crystallographic data are given in Table 1. The bismuth atom in **1** and **3** (Figures 1a and 2a) adopts a trigonal pyramidal arrangement with $\text{Bi-C}_{(\text{benzyl})}$ bond lengths of Bi1-C1 2.278(12) Å, Bi1-C9 2.312(11) Å for **1** and Bi1-C1 2.310(3) Å for **3**, which are in the range of distances observed for other bismuth compounds, *i.e.* 2.289(4) Å to 2.295(4) Å for $\text{Bi}(\text{CH}_2\text{C}_6\text{H}_5)_3$,⁸ 2.295(7) Å to 2.318(8) Å for $[\text{Bi}(\text{CH}_2\text{C}_6\text{H}_4\text{-Cl-2})_3]_2$ ⁹ and 2.299(4) Å, 2.340(4) Å for $[\text{2,6-Me}_2\text{NCH}_2\text{C}_6\text{H}_3]\text{Bi}(\text{CH}_2\text{C}_6\text{H}_5)_2$.⁸ The bond angles Bi1-C1-C2 $115.0(8)^\circ$ and Bi1-C9-C10 $118.3(8)^\circ$ in **1** and Bi1-C1-C2 $114.3(4)^\circ$ in **3** are larger than those found in other benzyl bismuthines: $105.0(3)^\circ$, $107.9(3)^\circ$ for $\text{ArBi}(\text{CH}_2\text{Ph})_2$ ($\text{Ar} = \text{2,6-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3$),⁸ $109.6(2)^\circ$, $110.8(2)^\circ$, $110.9(2)^\circ$ for $\text{Bi}(\text{CH}_2\text{Ph})_3$,⁸ but they are comparable to those observed for $[\text{Bi}(\text{CH}_2\text{C}_6\text{H}_4\text{-Cl-2})_3]_2$

(111.5(10)°, 114.9(8)°, 115.9(8)°).⁹ The primary Bi1–Br1 bond length of 2.887(16) Å in **1** is significantly longer than the corresponding

distances described in the literature for monomeric Mes₂BiBr (Bi1–Br1 2.696(2) Å).³⁹



Scheme 1 – Synthesis of the di- and monoorganobismuth compounds 1–3.

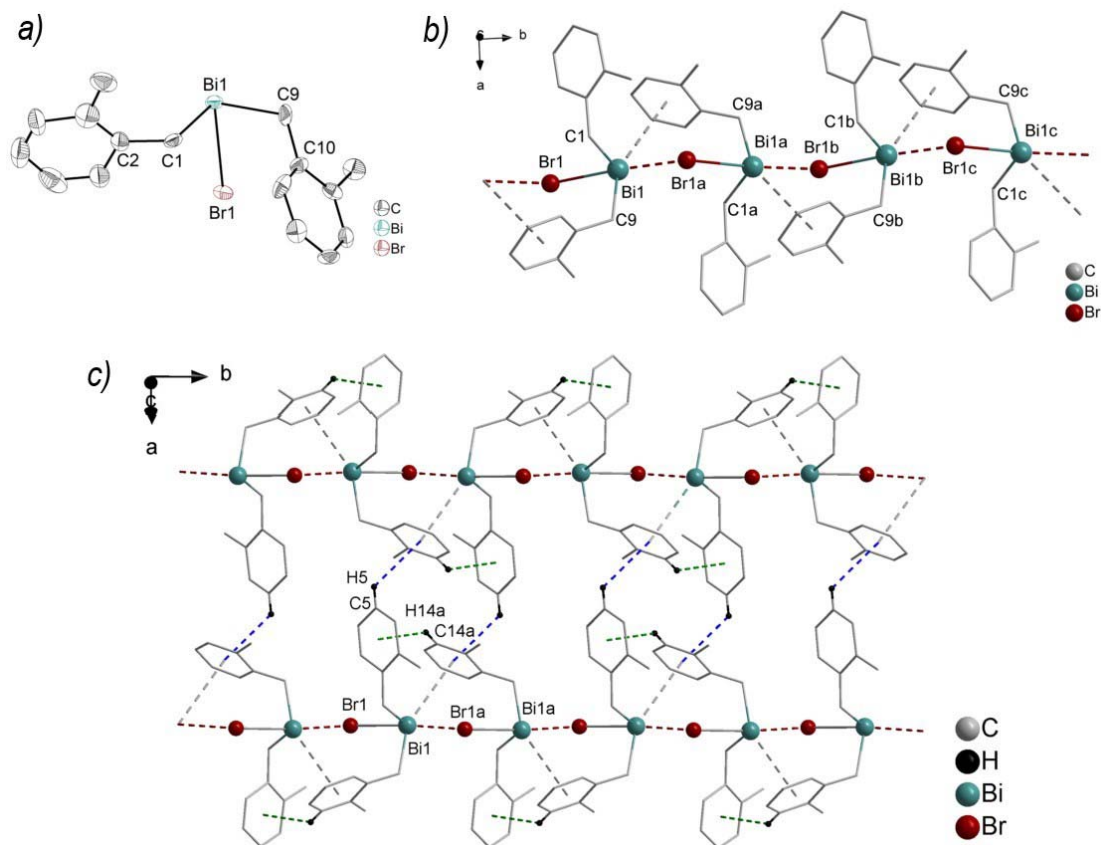


Fig. 1 – *a*) Thermal ellipsoid model of Bi(CH₂C₆H₄-Me-2)₂Br (**1**) at 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å]: Bi1–C1 2.278(12), Bi1–C9 2.312(11), Bi1–Br1 2.887(16). Selected bond angles [°]: C1–Bi1–C9 89.3(5), C1–Bi1–Br1 90.2(3), C9–Bi1–Br1 92.6(3), C1–Bi1–Br1a 90.1(3), C9–Bi1–Br1a 83.6(3), Br1–Bi1–Br1a 176.2(2), Bi1–Br1–Bi1a 118.4(4), Bi1–C1–C2 115.0(8), Bi1–C9–C10 118.3(8)°. *b*) Wire and stick model of a 1D ribbon (view along the *c*-axis) formed via Bi–Br and Bi⋯π (arene_{centroid}) intermolecular interactions with Bi1–Br1a 2.967(16) Å and Bi1–Arene_{centroid(1)} 3.727 Å, C14a–H14a⋯π arene_{centroid} 2.687 Å (green dashed line, γ = 6.3°). *c*) Wire and stick model of the 2D network (view along the *c*-axis) formed via intermolecular C–H⋯π arene_{centroid} 2.919 Å (blue dashed line, γ = 21.9°). Symmetry transformations: $a = 2 - x, \frac{1}{2} + y, \frac{1}{2} - z$.

In the molecular structure of **1** both intermolecular Bi $\cdots\pi$ arene contacts and Bi–Br \cdots Bi donor-acceptor interactions are present, resulting in a 1D coordination polymer (Figure 1b). In the supramolecular structure of **1** the bromine atom bridges two neighbouring bismuth atoms with the bridging Bi1 \cdots Br1a distance of 2.967 Å. The latter is longer than the terminal Bi–Br1 bond [2.887(16) Å] and lies within the sum of the van der Waals radii of both atoms [$\Sigma r_{\text{vdW}}(\text{Bi}, \text{Br}) = 3.90\text{--}4.40$ Å].^{40–42}

In **1** only one benzyl ligand is involved in intermolecular Bi $\cdots\pi$ arene interactions with a Bi1–arene_{centroid} distance of 3.727 Å, while the other benzyl ligand is flipped away from the Bi atom of the neighbouring molecule, but facing the other benzyl ligand. Moreover, the latter is involved in short C–H_{benzyl} $\cdots\pi$ (arene_{centroid}) contacts for C14a–H14a_{benzyl} $\cdots\pi$ (arene_{centroid}) 2.687 Å (green dashed line, $\gamma = 6.3^\circ$) which are competing with the dispersion type interaction, both contributing to the formation of a 1D supramolecular structure (Figure 1b). The geometry at the Bi atom becomes distorted square pyramidal, in which the C1 atom occupies the axial sites, while C9, the two bromine atoms (Br1, Br1a) and the arene_{centroid} are placed on equatorial sites. This is supported by the bond angles C1–Bi1–C9 89.3(5)°, C1–Bi1–Br1 90.2(3)°, C1–Bi1 \cdots Br1a 90.1(3)°, C1–Bi1 \cdots arene_{centroid} 104.5°, Br1–Bi1 \cdots Br1a 176.2° and C9–Bi1 \cdots arene_{centroid} 155.9°. In addition to the contacts described above, C–H_{benzyl} $\cdots\pi$ (arene_{centroid}) contacts between the 1D layers are observed with C5–H5 $\cdots\pi$ arene_{centroid} 2.919 Å (blue dashed line, $\gamma = 21.9^\circ$) leading to the formation of a 2D network (Figure 1c).

The crystal structure of compound **3** shows the presence of two intermolecular donor-acceptor Bi–Br \cdots Bi interactions with two different Bi–Br distances (Bi1–Br2a of 2.775(2) Å and Bi1–Br3a of 3.130(2) Å) leading to the formation of a polymeric chain (1D ribbons in Figure 2b). The latter are accompanied by dispersion interactions between the bismuth atom and the aryl ring of the adjacent molecule of 3.957 Å, which is larger than in **1** (Bi $\cdots\pi$ arene_{centroid} 3.727 Å). This might be due to the influence of the substituent X on the benzyl ligand as recently reported in a theoretical study with focus on BiCl₃ adducts with various substituted benzenes.⁴³ This assumption is supported by the Bi $\cdots\pi$ arene interaction found in [Bi(CH₂C₆H₄-Cl-2)₃]₂ forming dimers via Bi $\cdots\pi$ arene interaction with an even shorter distance of 3.659 Å.⁹ If the bonding of the aryl ring via dispersion is taken into account the

overall geometry at the Bi atom in **3** becomes distorted octahedral, with C1 of the benzyl ligand in the axial positions *trans* to the arene_{centroid} (C1–Bi1–arene_{centroid} 146.9°). The four bromine atoms are placed on the equatorial sites describing the basal plane with the corresponding bond angles Br2–Bi1–Br2a 162.2(6)° and Br3–Bi1–Br3a 161.4(6)°. In **3** both of the bromine atoms form a bridge to the bismuth atom of the neighbouring molecule with bond distances of Bi1–Br2a of 2.967 Å and Bi1–Br3a of 3.130 Å, which slightly differ from the Bi–X bond distance Bi1–Br2 3.101(2) Å and Bi1–Br3 2.730(2) Å. Even the shortest Bi–X bond distances are longer than the sum of the covalent radii ($\Sigma r_{\text{cov}}(\text{Bi}, \text{Br}) = 2.68$ Å),⁴⁴ while the other distances are within the sum of the van der Waals radii [$\Sigma r_{\text{vdW}}(\text{Bi}, \text{Br}) = 3.90\text{--}4.40$ Å].^{40–42} The 1D layers in **3** are connected via $\pi_{\text{arene}}\cdots\pi_{\text{arene}}$ contacts to give a 2D network (Figure 2c). The ring sections are parallel displaced with respect to each other with the arene_{centroid}–arene_{centroid} distance of 4.174 Å, a plane–plane distance of 3.676 Å (green dashed line in Figure 2c) and a displacement angle of $\gamma = 19.1^\circ$. Similar to the benzyl-substituted compounds, one-dimensional coordination polymers as a result of donor-acceptor bonds that are supplemented by bismuth $\cdots\pi$ arene interactions were reported previously in the case of, *i.e.* [PhBiX₂(thf)] (X = Cl, Br, I).^{45, 46} The Bi $\cdots\pi$ arene distances in **3** are significantly longer when comparing to those observed in [PhBiBr₂(thf)] (3.471 Å).⁴⁶

In **1** and **3** the intermolecular distances between heavy atoms (Bi \cdots Bi distances of 5.029 Å for **1** and 4.490 Å for **3**) are considerably longer than the ones observed in solid Me₃Bi (Bi \cdots Bi distances 3.899 Å and 4.318 Å),⁴⁷ but they are in the range of the sum of the van der Waals radii of bismuth atoms; [$\Sigma r_{\text{vdW}}(\text{Bi}, \text{Bi}) = 4.08\text{--}5.14$ Å].^{40–42}

None of the presented structures exhibited intramolecular Bi $\cdots\pi$ arene interactions and this might be due to the flexibility of the benzyl ligand, which is flipped away from the bismuth atom, but they show intermolecular dispersion interactions of the type Bi $\cdots\pi$ arene. These interactions are in the upper distance range of so far reported London dispersion interactions in organobismuth compounds, *i.e.* benzyl-, aryl- and heteroaryl bismuthines with the Bi–arene_{centroid} distances in the range of 3.44–3.91 Å,^{9, 23–27, 29} and various modifications of Ph₃Bi with Bi–arene_{centroid} distances in the range from 3.47 to 3.96 Å.^{25, 48–52} The Bi $\cdots\pi$ interactions in **1** and **3** accompany the much stronger Bi–Br \cdots Bi donor-acceptor bonds and build up an organic shell surrounding the polymeric inorganic entity.

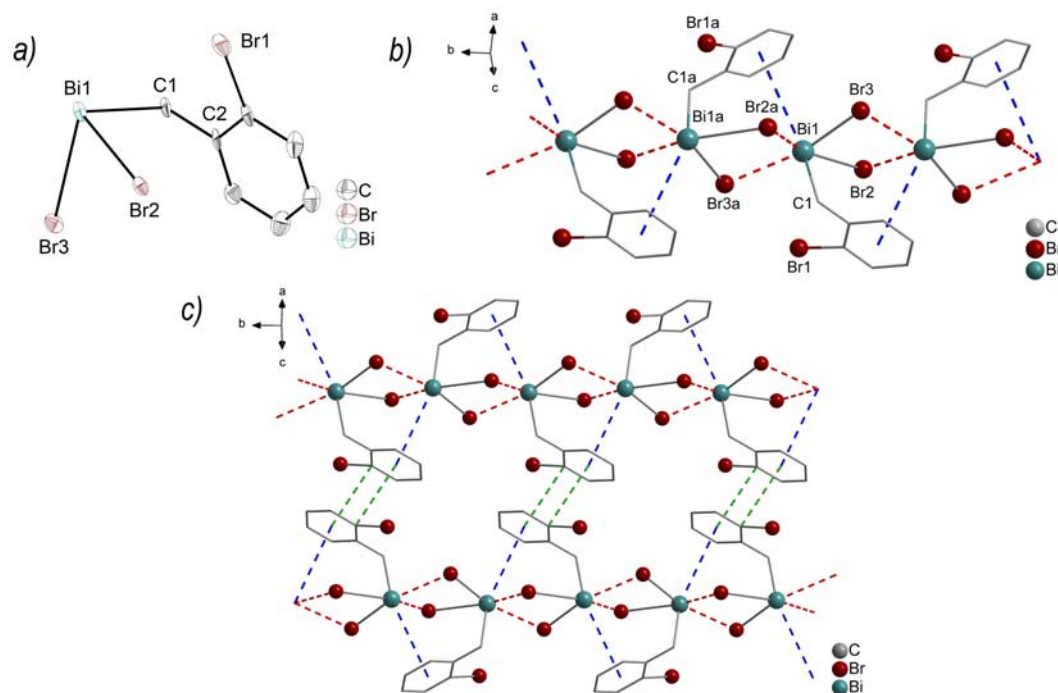


Fig. 2 – *a*) Thermal ellipsoid model of $\text{Bi}(\text{CH}_2\text{C}_6\text{H}_4\text{-Br-2})\text{Br}_2$ (**3**) at 50% probability level. Hydrogen atoms were omitted for clarity. Selected bond lengths [Å]: Bi1–C1 2.310(17), Bi1–Br2 3.101(2), Bi1–Br3 2.730(2). Selected bond angles [°]: C1–Bi1–Br2 91.6(5), C1–Bi1–Br3 94.1(5), Br2–Bi1–Br3 77.7(6), Bi1–C1–C2 114.3(12). *b*) Wire and stick model of 1D ribbon formed via Bi–Br and Bi $\cdots\pi$ arene_{centroid} intermolecular interactions with Bi1–Br2a 2.775(2) Å, Bi1–Br3a 3.130(2) Å and Bi1–Arene_{centroid(1)} 3.957 Å. *c*) Wire and stick model of 2D network formed via intermolecular $\pi_{\text{arene}}\cdots\pi_{\text{arene}}$ contacts of arene_{centroid} \cdots arene_{centroid(1)} 4.174 Å, plane–plane distance of 3.676 Å (green dashed line, $\gamma = 21.9^\circ$). Symmetry transformations: $a = \frac{3}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

EXPERIMENTAL

General procedure

All procedures were carried out under nitrogen or argon atmosphere using standard Schlenk techniques. All solvents were freshly distilled over appropriate drying reagents immediately prior to use. 2-Methylbenzyl bromide and 2-bromobenzyl bromide were purchased from commercial suppliers and were used as received. BiBr_3 was used without further purification. ATR-FTIR spectra were recorded with a Bio Rad FTS-165 spectrometer (Bio-Rad) with a Golden Gate (SpectroMat) sample adapter. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at ambient temperature in C_6D_6 (dried over sodium mirror) with an *Avance III 500* spectrometer (Bruker) at 500.30 and 125.81 MHz, respectively, and are referenced internally to the deuterated solvent relative to $\text{Si}(\text{CH}_3)_4$ ($\delta = 0.00$ ppm). The NMR spectra were processed using the software *MestReNova* (version 11.0.4-18998⁵³). The CHN analyses were performed with a *FlashEA 1112* analyzer (Thermo Fisher Scientific). The melting points of compounds were determined with a Melting Point B-540 apparatus (Büchi). Figures and schemes were created with *ChemDraw Prime*[®] (version 17.1)⁵⁴ and *Origin*[®] Pro 2017.⁵⁵

Crystallographic studies

Crystal data, data collection and refinement parameters for compounds **1** and **3** are given in Table 1. The data were collected with a Rigaku-Oxford Gemini S diffractometer (CrysAlisPro Version 1.171.37.35, Agilent Technologies) using $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å) at 120 K (**1**) and $\text{CuK}\alpha$ radiation ($\lambda = 1.54184$ Å) at 110 K (**3**). Crystals of the

compounds were embedded in an inert oil (Krytox[®], GPL107) and a suitable crystal was selected under an optical microscope and mounted on a CryoLoop (Hampton Research, type: 20 micron and 0.2–0.3 mm diameter), with the CryoLoop fixed on a glass needle. The structures were solved by direct methods using *SHELXS-2013*^{56,57} and refined by full matrix least-squares procedures on F^2 using *SHELXL-2013*.^{58,59} All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were geometrically placed and refined isotropically in riding modes using default parameters. Visualization of the crystal structures was performed with *Diamond* (version 4.5⁶⁰).

The crystals of **1** were all twinned. The finally chosen crystal was composed of two nearly equally populated domains (60:40 ratio of all reflections), of which both were integrated and combined into one hklf 5 file. Twinning was noticed for crystals of **3** as well, although all trials to integrate the data sets with different domains did not give reliable results. Alerts reported by CheckCif have been commented in the final cif file and are attributed to be originated by non-resolvable twinning/disorder, cf. CCDC 1948636.

Synthesis of $\text{Bi}(\text{CH}_2\text{C}_6\text{H}_4\text{-Me-2})_2\text{Br}$ (**1**)

A solution of 2-methylbenzyl bromide (1.000 g, 5.40 mmol) in Et_2O (50 mL) was added dropwise under stirring to magnesium filings (0.144 g, 5.92 mmol, 10% excess) activated with 1,2-dibromoethane (0.25 mL). Afterwards the reaction mixture was stirred for 2 h under reflux. Then it was cooled to ambient temperature and the unreacted Mg was separated by filtration. The Grignard solution was added dropwise to a solution of BiBr_3 (0.808 g, 1.80 mmol) in Et_2O (25 mL) at -20 °C and the reaction mixture was stirred at this

temperature for 1 h, then overnight at ambient temperature. The solvent was removed under vacuum and the green residue was extracted with *n*-hexane (5 x 7 mL). The volume of the solution was reduced in vacuum to its half and the solution was stored at 4 °C for crystallization to give **1** as orange single crystals suitable for X-ray analysis. Yield = 0.138 g (10%); M.p. = 140–142 °C, dec. Elemental analysis calcd. (%) for C₁₆H₁₈BiBr (499.20 g·mol⁻¹): C, 38.50; H, 3.63. Found: C, 36.13; H, 3.52. ATR FTIR (cm⁻¹): ν = 3056 (w), 3020 (w), 2936 (w, br), 2858 (w), 1598 (m), 1486 (s), 1459 (m), 1413 (w), 1375 (m), 1293 (w), 1261 (m), 1220 (w), 1190 (w), 1156 (w), 1136 (w), 1066 (m), 1028 (s, br), 941 (m), 863 (w), 836 (w), 802 (m, br), 766 (s), 745 (vs), 722 (s), 715 (s), 698 (s), 607 (w), 587 (w), 550 (w), 516 (w), 459 (m), 418 (w). ¹H NMR (C₆D₆): δ 2.16 [s, 6H, CH₃], 3.32 [s, 4H, CH₂], 6.64 [d, 2H, *H*-3, ³J_{H-H} = 7.6 Hz, C₆H₄], 6.70 [dd, 2H, *H*-5, ³J_{H-H} = 7.5 Hz, ⁴J_{H-H} = 1.1 Hz, C₆H₄], 7.01–7.09 [m, 4H, *H*-4, *H*-6, C₆H₄]. ¹³C{¹H} NMR (C₆D₆): δ 20.12, 57.91, 125.57, 127.38, 129.37, 130.33, 136.40, 136.57. The CHN analyses differs from the calculated values due to the high moisture and light sensitivity of the compounds.

Synthesis of Bi(CH₂C₆H₄-Br-2)₂Br (2)

A solution of 2-bromobenzyl bromide (1.401 g, 5.60 mmol) in Et₂O (80 mL) was added dropwise under stirring to magnesium filings (0.149 g, 6.15 mmol, 10% excess) activated with 1,2-dibromoethane (0.25 mL). Afterwards the reaction mixture was stirred for 2 h under reflux. Then it was cooled to ambient temperature and the unreacted Mg was separated by filtration. The *Grignard* solution was added dropwise to a solution of BiBr₃ (0.838 g, 1.86 mmol) in Et₂O (25 mL) at -40 °C and the reaction mixture was stirred at this temperature for 2 h, then stirred overnight at ambient temperature. The solvent was removed under vacuum and the yellow residue was extracted with toluene (4 x 5 mL), filtered off and the toluene was removed under vacuum to give a yellow solid. The solid was recrystallized from a *n*-hexane solution at 4 °C to give a crop of yellow crystals of **2**, which were not suitable for X-ray crystallography. Elemental analysis calcd. (%) for C₁₄H₁₂BiBr₃ (628.94): C, 26.74; H, 1.92. Found: C, 26.65; H, 1.72. ATR FTIR (cm⁻¹): ν = 3053 (w), 3016 (w), 2325 (w), 2136 (w), 1907 (w), 1874 (w), 1792 (w), 1689 (w), 1591 (m), 1561 (m), 1466 (s), 1435 (s), 1398 (m), 1291 (w), 1277 (m), 1210 (m), 1159 (w), 1133 (w), 1062 (w), 1041 (m), 1011 (s), 934 (s), 860 (w), 816 (m), 735 (vs), 715 (vs), 654 (s), 604 (w), 560 (m), 546 (m), 451 (m), 421 (w), 401 (w). ¹H NMR (C₆D₆): δ 3.24 [s, 4H, CH₂], 6.31 [ddd, 2H, *H*-5, ³J_{H-H} = 7.8 Hz, ⁴J_{H-H} = 1.7 Hz; C₆H₄], 6.76 [dd, 2H, *H*-3, ³J_{H-H} = 7.7 Hz, ⁴J_{H-H} = 1.6 Hz; C₆H₄], 6.92 [ddd, 2H, *H*-4, ³J_{H-H} = 7.5 Hz, ⁴J_{H-H} = 1.3 Hz; C₆H₄], 7.31 [dd, 2H, *H*-6, ³J_{H-H} = 8.0 Hz, ⁴J_{H-H} = 1.1 Hz; C₆H₄]. ¹³C{¹H} NMR (C₆D₆): δ 61.77, 125.84, 126.80, 128.43, 131.20, 132.30, 138.58.

Synthesis of Bi(CH₂C₆H₄-Br-2)Br₂ (3)

A solution of 2-bromobenzyl bromide (1.500 g, 6.00 mmol) in Et₂O (75 mL) was added dropwise under stirring to magnesium filings (0.158 g, 6.50 mmol, 10% excess) activated with 1,2-dibromoethane (0.25 mL). Afterwards the reaction mixture was stirred for 2 h under reflux. Then it was cooled to ambient temperature and the unreacted Mg was separated by filtration. The *Grignard* solution was added dropwise to a solution of BiBr₃ (0.897 g, 1.99 mmol) in Et₂O (30 mL) at -20 °C and the reaction mixture was stirred at this temperature for 2 h, then overnight at ambient temperature.

The solvent was removed under vacuum and the yellow residue was extracted with toluene (5 x 5 mL), filtered off and the toluene was reduced under vacuum to give an orange solid. Single crystals suitable for X-ray crystallography were grown from a *n*-hexane solution at 4 °C to give a crop of red crystals of **3**. M.p. = 165–167 °C. Elemental analysis calcd. (%) for C₇H₆BiBr₃ (538.82 g·mol⁻¹): C, 15.60; H, 1.12. Found: C, 16.95; H, 2.60. ATR FTIR (cm⁻¹): ν = 3054 (w), 2997 (w), 2962 (w), 2931 (w), 2122 (w), 1949 (w), 1912 (w), 1877 (w), 1798 (w), 1605 (vs, br), 1561 (m), 1466 (s), 1434 (s), 1274 (m), 1258 (m), 1220 (w), 1128 (w), 1091 (w), 1059 (w), 1040 (w), 1015 (s), 939 (m), 860 (w), 800 (m, br), 752 (vs), 740 (m), 712 (w), 652 (m), 551 (m), 497 (w), 456 (w), 424 (w), 414 (w), 402 (w). ¹H NMR (C₆D₆): δ 3.01 [s, 2H, CH₂], 6.43 [ddd, 1H, *H*-5, ³J_{H-H} = 7.6 Hz, ⁴J_{H-H} = 1.7 Hz, C₆H₄], 6.66 [dd, 1H, *H*-3, ³J_{H-H} = 7.7 Hz, ⁴J_{H-H} = 1.8 Hz, C₆H₄], 6.90 [ddd, 1H, *H*-4, ³J_{H-H} = 7.5 Hz, ⁴J_{H-H} = 1.3 Hz, C₆H₄], 7.37 [dd, 2H, *H*-6, ³J_{H-H} = 8.0 Hz, ⁴J_{H-H} = 1.4 Hz, C₆H₄]. The CHN analyses differs from the calculated values due to the high moisture and light sensitivity of the compounds.

CONCLUSIONS

Herein, the synthesis, structure and bonding of three new bismuthines of the type Bi(CH₂C₆H₄-X-2)₂Br [X = Me (**1**), Br (**2**)] and Bi(CH₂C₆H₄-Br-2)Br₂ (**3**) are reported. The crystal structure analyses revealed that the typically strong Bi–Br···Bi donor-acceptor interactions are accompanied by additional bismuth··· π arene dispersion interaction between two neighbouring bismuth atoms, which together gives rise to the formation of 1D coordination polymers. The dispersion interactions are supplemented by other, competing, weak interactions such as π ··· π or C–H_{benzyl}··· π and thus 2D networks are formed in the solid state. The flexibility of the benzyl ligand allows the formation of intermolecular Bi··· π arene interaction in the organobismuth compounds, whereas intramolecular bismuth··· π arene interactions are not observed.

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SUPPLEMENTARY DATA

The crystallographic data for **1** and **3** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publications CCDC 1948635 (**1**) and 1948636 (**3**) and can be obtained free of charge from the CCDC via www.ccdc.cam.ac.uk/data_request/cif.

Table 1

Crystallographic data and structure refinement details for Bi(CH₂C₆H₄-Me-2)₂Br (**1**) and Bi(CH₂C₆H₄-Br-2) Br₂ (**3**)

	1	3
Empirical formula	C ₁₆ H ₂₈ BiBr	C ₇ H ₆ BiBr ₃
<i>M</i> (g mol ⁻¹)	499.19	538.82
Temperature (K)	120	110
λ (Å)	0.71073 Å	1.54184
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> (Å)	12.0433(10)	11.2788(13)
<i>b</i> (Å)	10.0507(8)	8.9270(7)
<i>c</i> (Å)	13.6439(9)	11.6130(14)
β (deg)	114.456(7)	118.712(15)
<i>V</i> (Å ³)	1503.3(2)	1025.5(2)
<i>Z</i>	4	4
<i>D</i> _{calc} (g cm ⁻³)	2.206	3.490
μ (mm ⁻¹)	14.367	46.937
<i>F</i> (000)	928	944
Crystal size (mm)	0.16 x 0.1 x 0.1	0.2 x 0.06 x 0.06
Reflections collected	10787	4475
Independent reflections	5146	1716
<i>R</i> _{int}	0.0588	0.0871
Number of data / restraints / parameters	5146 / 0 / 164	1716 / 75 / 88
Goodness-of-fit on <i>F</i> ²	0.856	1.033
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]		
<i>R</i> ₁	0.0473	0.0836
<i>wR</i> ₂	0.1119	0.2060
<i>R</i> indices (all data)		
<i>R</i> ₁	0.0879	0.0946
<i>wR</i> ₂	0.1178	0.2156
$\Delta\rho_{\min}$ and $\Delta\rho_{\max}$ (e Å ⁻³)	-1.507 and 1.758	-6.638 and 7.494

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