

## Research Article

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# Bismuth $\cdots\pi$ arene interaction in $[\text{Bi}\{\text{OC}_6\text{H}_4(\text{CH}_2\text{C}_6\text{H}_5)_2\}_3]_2$

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**Abstract:** We report on the synthesis of a new bismuth aryloxy molecule  $\text{Bi}[\text{OC}_6\text{H}_4(\text{CH}_2\text{C}_6\text{H}_5)_2]_3$  (**1**), which was characterized by NMR and IR spectroscopy as well as single-crystal X-ray diffraction analysis. A characteristic structural feature is the dimeric unit with a central  $\text{Bi}_2\text{O}_2$  core resulting from  $\mu$ -binding phenolates. In addition, both bismuth atoms show a  $\text{Bi}\cdots\pi$  arene interaction with a quite short  $\text{Bi}\cdots\pi_{\text{centroid}}$  distance of 3.11 Å in the solid state.

**Keywords:** bismuth; aryloxy;  $\text{Bi}\cdots\pi$  arene interaction

Bismuth alkoxides hold potential as precursors in the synthesis of bismuth oxide containing materials by either deposition methods (ALD, CVD, MOCVD) or by the sol-gel process (Cosham et al., 2014; Hanna, 2004; Hatanpaa et al., 2010; Marchand and Carmalt, 2013; Massiani et al., 1991; Mehring, 2007; Vuorinen et al., 2013; Williams et al., 2001). Until today, several bismuth alkoxides i.e., alkyloxides, aryloxides as well as siloxides were reported, which show a diversity of different oligomeric structures, dominated by intermolecular bismuth-oxygen coordination (Hanna et al., 2001; Jones et al., 1992; Jones et al., 1993; Kaur

and Singh, 2012; Kou et al., 2009; Mansfeld et al., 2004; Mansfeld et al., 2005; Massiani et al., 1991; Matchett et al., 1990; Mehring, 2007; Paalasmaa et al., 2005; Preda et al., 2017a; Schmidbaur and Bergfeld, 1968). We are interested in bismuth alkoxides as precursors in synthetic chemistry, but more recently the evaluation of bismuth compounds with the bismuth atom acting as a dispersion energy donor (DED) came into the focus of our research and we currently study the role of bismuth as DED in structure formation (Auer et al., 2009, Krasowska et al., 2018; Preda et al., 2017a; Preda et al., 2017b; Preda et al., 2018). The general impact of the rather weak but nevertheless important dispersion energy contribution on stability and reactivity of sterically crowded molecules was recently also discussed in a topical review on inorganic and organometallic compounds (Liptrot and Power, 2017). With regard to dispersion energy contributions on structure formation, bismuth aryloxides are of great interest due to their intrinsic ability to form either inter- or intramolecular  $\text{Bi}\cdots\pi$  arene interactions, which results from the high polarizability of bismuth. In a computational approach, Auer and coworkers have demonstrated that  $\text{Bi}(\text{OMe})_3$  forms a strong interaction with benzene, which is mainly based on dispersion interaction, exhibiting a  $\text{Bi}\cdots\pi_{\text{centroid}}$  distance of 3.33 Å in the equilibrium state (Krasowska et al., 2018). Noteworthy, a similar model compound, i.e.  $\text{BiCl}_3\cdots\text{C}_6\text{H}_6$  revealed an increased donor-acceptor contribution  $\pi$  to  $\sigma^*$ , but still the dispersive interaction dominates. Similarly, a strong contribution of dispersion was reported for a  $\text{SbCl}_3\cdots$ toluene complex in a combined experimental and theoretical study (Lo et al., 2015). A key point mentioned by Lo et al., is the interplay between dispersion and electrostatic interaction, which is complemented by a low exchange-repulsion. For bismuth the first report on a metal  $\cdots\pi$  arene interaction dates back to the end of the 19<sup>th</sup> century, but the first single-crystal X-ray diffraction analyses of the complexes  $[\{\text{C}_6\text{H}_3(\text{CH}_3)_{3-1,3,5}\}\text{BiCl}_3]$  and  $[\{\text{C}_6(\text{CH}_3)_6\}\text{BiCl}_3]$  were reported more recently in 1986 (Schmidbaur and Schier, 2008; Schier et al., 1986). However, these compounds show an intermolecular  $\text{Bi}-\text{Cl}-\text{Bi}$  coordination and a strong electron transfer contributes to the  $\text{Bi}\cdots\pi$  arene

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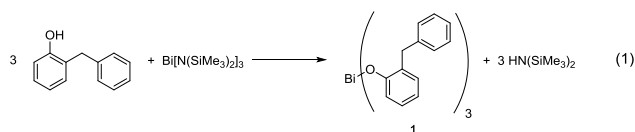
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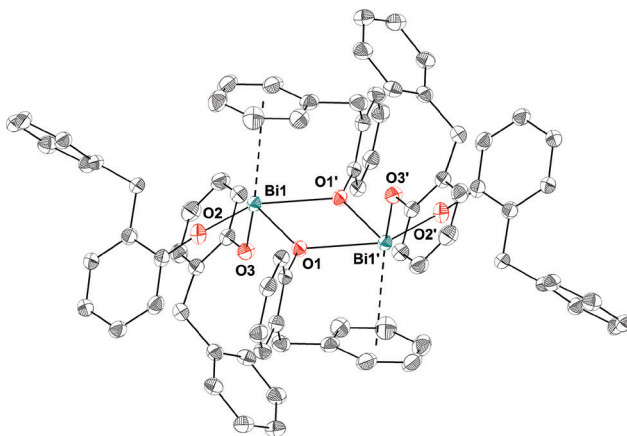
interaction as demonstrated for the above mentioned model compound  $\text{BiCl}_3 \cdots \text{C}_6\text{H}_6$ . In contrast to bismuth halides showing  $\text{Bi} \cdots \pi$  arene interaction, so far only a limited number of bismuth aryloxides are reported, e.g.,  $[\text{Bi}(\text{OC}_6\text{F}_5)_3] \cdot \text{toluene}$ ,  $[\text{Bi}(\text{OC}_6\text{H}_3\text{R}-2,6)_3]$  ( $\text{R} = i\text{Pr}$ ,  $\text{C}_6\text{H}_5$ ,  $\text{CH}_2\text{C}_6\text{H}_5$ ) and a bismuth aminetrisphenolate complex (Brym et al., 2006; Hanna et al., 2002; Jones et al., 1993; Jones et al., 1992; Kou et al., 2009; Turner et al., 2006). Other aryloxides such as  $[\text{Bi}(\text{OC}_6\text{H}_3\text{R}-2-\text{R}'-4)_3]$  [i]  $\text{R} = t\text{Bu}$ ,  $\text{CH}_2\text{-CH=CH}_2$ ,  $\text{CH=CH-CH}_3$ ,  $\text{NO}_2$ ,  $\text{OH}$ ;  $\text{R}' = \text{H}$ ; ii)  $\text{R} = \text{H}$ ;  $\text{R}' = \text{CH}_3$ ,  $\text{NH}_2$ ,  $\text{NO}_2$ ],  $[\text{Bi}(\text{OC}_6\text{H}_2\text{R}_2-2,6-\text{R}'-4)_3]$  [i]  $\text{R} = \text{R}' = t\text{Bu}$ ; ii)  $\text{R} = i\text{Pr}$ ;  $\text{R}' = \text{Cl}$ ,  $\text{Br}$ ,  $\text{OMe}$ ] and some bismuth calixarene complexes were reported as well, but  $\text{Bi} \cdots \pi$  arene interactions are not discussed for these compounds (Brym et al., 2006; Hanna et al., 2002; Kaur and Singh, 2012; Kou et al., 2009; Mendoza-Espinosa and Hanna, 2009a; Mendoza-Espinosa and Hanna, 2009b; Mendoza-Espinosa and Hanna, 2009c; Mendoza-Espinosa et al., 2009; Sauer et al., 1990; Whitmire et al., 2000).

Here, we add the bismuth aryloxide  $[\text{Bi}(\text{OC}_6\text{H}_4(\text{CH}_2\text{C}_6\text{H}_5)_2)_3]$  (**1**) to the list of molecules that show  $\text{Bi} \cdots \pi$  arene interactions in the solid state. Compound **1** was synthesized by an alcohol-amide exchange reaction starting from  $\text{Bi}[\text{N}(\text{SiMe}_3)_2]_3$  and 2-benzylphenol in THF (equation 1) and was isolated as a yellow, moisture sensitive solid with an overall yield of 79%.



Spectroscopic analysis ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  NMR and IR) and elemental analysis are in agreement with the molecular composition of **1**. One signal for the benzylic protons at 3.91 ppm and six signals in the range of 6.52 ppm to 7.19 ppm in case of its aromatic protons are assigned in the  $^1\text{H}$  NMR spectrum at ambient temperature ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ), which is in agreement with a monomeric structure in solution. Even at low temperature ( $\text{CD}_2\text{Cl}_2$ ,  $-60^\circ\text{C}$ ), splitting of the  $^1\text{H}$  NMR signals is not observed, which rules out that a dimer as found in the solid state is formed. In toluene- $d_8$  the  $^1\text{H}$  NMR spectrum does not change significantly with the characteristic benzylic protons being located as singlet at 3.95 ppm. In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1**, the expected number of signals is found with chemical shifts of 36.9 ppm in case of the benzylic carbon atom and ten signals with chemical shifts of 121.8 ppm to 155.8 ppm for the aromatic carbon atoms. The signal at the highest frequency is attributed to the phenolic carbon atom. IR spectroscopy revealed

absorption bands that are assigned to C–H ( $2750\text{ cm}^{-1}$  to  $3100\text{ cm}^{-1}$ ), C=C ( $1450\text{ cm}^{-1}$  to  $1600\text{ cm}^{-1}$ ) as well as C–O ( $1100\text{ cm}^{-1}$  to  $1270\text{ cm}^{-1}$ ) stretching vibrations (Lin-Vien et al., 1991; Socrates, 2001). In contrast, single-crystal X-ray diffraction analysis shows a dimeric molecular structure. Single-crystals of compound **1** were grown from THF solution by diffusion of *n*-pentane into the solution. Compound **1** crystallizes in the triclinic space group *P*-1. As a result of the dimerization via intermolecular Bi–O coordination, a planar rhombohedral  $\text{Bi}_2\text{O}_2$  unit is obtained (Figure 1) with bond angles of  $114.88(8)^\circ$  ( $\text{Bi1-O1-Bi1}'$ ) and  $65.12(9)^\circ$  ( $\text{O1-Bi1-O1}'$ ). Each bismuth atom is coordinated by four oxygen atoms with equal bond lengths for the two covalently bonded oxygen atoms O2 and O3 [ $2.116(2)\text{ \AA}$  and  $2.115(2)\text{ \AA}$ ]. The bond length in case of Bi1–O1 is slightly longer [ $2.1309(19)\text{ \AA}$ ], most probably due to the additional coordination to the second bismuth atom Bi1', while the coordinative bond Bi1–O1' is significantly longer [ $2.554(2)\text{ \AA}$ ]. Molecules in which  $\text{Bi} \cdots \pi$  interactions are obtained show Bi–O bond lengths in the range  $2.082(3)\text{ \AA}$  to  $2.210(8)\text{ \AA}$  (Evans et al., 1989; Jones et al., 1992; Jones et al., 1993; Kou et al., 2009). In addition, the dimeric unit is stabilized by an intermolecular  $\text{Bi} \cdots \pi$  arene interaction, which allows the interpretation that the phenolate moiety acts as a  $\text{O}, \pi$ -pincer ligand. As a result, a fivefold coordinated bismuth atom is observed, which might be described as a distorted *pseudo*-octahedron with one corner being not occupied. Four oxygen atoms and the  $\pi$ -arene ligand fill five positions at the corners of this *pseudo*-octahedron, and one might speculate that a stereochemically



**Figure 1:** Molecular structure of (**1**)<sub>2</sub> in the solid state (50% probability level of displacement ellipsoids, hydrogen atoms are omitted for clarity). Selected bond lengths [ $\text{\AA}$ ] and bond angles [ $^\circ$ ]: Bi1–O1 2.1309(19), Bi1–O2 2.116(2), Bi1–O3 2.115(2), Bi1–O1' 2.554(2), Bi– $\pi_{\text{centroid}}$  3.11, Bi–C 3.28 – 3.53. Symmetry transformations used to generate equivalent atoms: i denotes  $-x, -y, 1-z$ .

active lone pair of electrons is present. However, this geometrical situation does not necessarily imply that a lone pair of electrons is placed at the vacant coordination site as was discussed for example by Whitmire et al. (Whitmire et al., 2000). The  $\text{Bi}\cdots\pi$  arene interaction of  $\text{Bi}\cdots\pi_{\text{centroid}}$  3.11 Å is quite short, hence indicative of quite strong interaction, as compared to  $\text{Bi}\cdots\pi$  arene interactions in other bismuth aryloxide molecules (2.96–4.07 Å) (Jones et al., 1992; Jones et al., 1993; Kou et al., 2009; Turner et al., 2006). It is significantly shorter than the calculated distance of 3.33 Å in the model compound  $\text{Bi}(\text{OMe})_3\cdots\text{C}_6\text{H}_6$ , for which an interaction energy of  $-24 \text{ kJ}\cdot\text{mol}^{-1}$  was calculated (Krasowska et al., 2018). The  $\text{Bi}\cdots\text{C}$  arene distances in **1** [ $\text{Bi}\cdots\text{C}$  3.28 – 3.56 Å] are much shorter than the sum of the van der Waals radii of bismuth and carbon [ $\text{Bi}$  2.54 Å;  $\text{C}$  1.77 Å;  $\sum r_{\text{vdW}}(\text{Bi},\text{C})$  4.31 Å] (Alvarez, 2013).

In conclusion, the new bismuth aryloxide **1** forms a dimer and exhibits an additional intermolecular  $\text{Bi}\cdots\pi$  arene interaction in the solid state ( $\text{Bi}\cdots\pi_{\text{centroid}}$  3.11 Å), while a central  $\text{Bi}_2\text{O}_2$  unit is present. The formation of dimers, oligomers and coordination polymers in the solid state via intermolecular  $\text{Bi}\cdots\text{O}\cdots\text{Bi}$  coordination is typical for bismuth alkoxides. However, on the basis of  $^1\text{H}$  NMR studies we assume, that in solution the dimeric structure of **1** is not preserved. This is in line with results on  $\text{Sb}(\text{O}^i\text{Pr})_3$ , which dimerizes in the solid and liquid state, but does not dimerize in solution (Fleischer, 2001). The calculated standard enthalpy of dimer formation of  $\text{Sb}(\text{OMe})_3$  as calculated from density functional theory amounts to  $-23.8 \text{ kJ}\cdot\text{mol}^{-1}$ , a value which is similar to values as calculated for the dispersion interaction of  $\text{M}(\text{OMe})_3$  ( $\text{M} = \text{Sb}, \text{Bi}$ ) with benzene (Krasowska et al., 2018), but it is too small to favor intermolecular association in solution. Noteworthy, in comparison with the model system  $\text{Bi}(\text{OMe})_3\cdots\text{C}_6\text{H}_6$  ( $\text{Bi}\cdots\pi_{\text{centroid}}$  calculated: 3.33 Å) significantly shorter  $\text{Bi}\cdots\pi$  arene distances are observed for **1**. This might be a result of the  $\text{O},\pi$ -pincer type coordination, that is composed of cooperative donor-acceptor and dispersion type interactions.

## Experimental

### General remarks

The syntheses were carried out in an argon atmosphere using Schlenk techniques. Solvents were dried over sodium-potassium alloy (*n*-pentane, *n*-hexane, THF) and freshly distilled prior to use.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker spectrometer (Avance

III 500, 500 MHz) at ambient temperature and on a Bruker spectrometer (Avance Neo 600, 600 MHz) at low temperature (Bruker Corporation, Karlsruhe, Germany). The  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are reported in  $\delta$  units (ppm) relative to the residual peak of the deuterated solvent (ref.  $\text{CDCl}_3$ :  $^1\text{H}$ : 7.26 ppm;  $^{13}\text{C}$ : 77.16 ppm) (Fulmer et al., 2010). ATR FTIR spectra were recorded with a BioRad FTS-165 spectrometer (Bio-Rad Laboratories GmbH, München, Germany). Melting points were measured with a melting point B-540 apparatus (Büchi Labortechnik GmbH, Essen, Germany). Elemental analyses were carried out using a vario MICRO (Elementar Analysensysteme GmbH, Langenselbold, Germany).

The chemicals 1,1,1-trimethyl-*N*-(trimethylsilyl)silanamine and bismuth trichloride were purchased from Alfa Aesar GmbH & Co KG (Karlsruhe, Germany), 2.5 M *n*-butyllithium in *n*-hexane from Acros Organics (Geel, Belgium) and 2-benzylphenol from Aldrich (München, Germany). Bismuth trichloride and 2-benzylphenol were freshly purified either by sublimation or flash column chromatography (95/5 *n*-hexane/ethyl acetate) before usage. The bismuth compound  $\text{Bi}[\text{N}(\text{SiMe}_3)_2]_3$  was synthesized according to literature procedures (Vehkamaki et al., 2004).

### Single-crystal X-ray diffraction analyses

Single yellow block-shaped crystals of compound **1** were obtained by diffusion of *n*-pentane into a THF solution. A suitable crystal ( $0.15 \times 0.12 \times 0.08 \text{ mm}^3$ ) was selected and mounted in Paratone® on a STOE IPDSII diffractometer with  $\text{Mo-K}_\alpha$  radiation and a graphite monochromator ( $\lambda = 0.71073 \text{ Å}$ ). The crystal was kept at  $T = 100 \text{ K}$  during data collection. Using Olex2 (Dolomanov et al., 2009), the structure was solved with the ShelXS (Sheldrick, 2008) structure solution program, using the Direct Methods solution method. The model was refined with version 2014/7 of ShelXL (Sheldrick, 2015) using Least Squares minimization. The figures were created with the Diamond program (Putz and Branderburg, 2001).

Crystal Data for (**1**)<sub>2</sub>:  $\text{C}_{78}\text{H}_{66}\text{Bi}_2\text{O}_6$ ;  $M = 1517.26 \text{ g mol}^{-1}$ ; crystal size  $0.15 \times 0.12 \times 0.08 \text{ mm}^3$ ; triclinic; space group *P*-1;  $a = 10.9527(5) \text{ Å}$ ;  $b = 11.7624(3) \text{ Å}$ ;  $c = 12.9221(5) \text{ Å}$ ;  $\alpha = 100.543(3)^\circ$ ;  $\beta = 110.828(3)^\circ$ ;  $\gamma = 91.347(3)^\circ$ ;  $V = 1522.58(10) \text{ Å}^3$ ;  $Z = 1$ ;  $D_c = 1.655 \text{ g}\cdot\text{cm}^{-3}$ ;  $\mu = 5.828 \text{ mm}^{-1}$ ;  $F(000) = 748$ ;  $1.723 \leq \theta \leq 29.171$ ; completeness to  $2\theta$ : 99.4%; max./min. residual electron density:  $3.271/-1.826 \text{ e}\cdot\text{Å}^{-3}$ . Of a total of 32865 reflections collected, 8156 reflections were independent ( $R_{\text{int}} = 0.0707$ ). Final  $R_1 = 0.0281$  [for 8038 reflections  $I > 2\sigma(I)$ ] and  $wR_2 = 0.0706$  (all data). CCDC 1847419.

## Syntheses

### $\text{Bi}[\text{OC}_6\text{H}_4(\text{CH}_2\text{C}_6\text{H}_5)_2]_3$ (1)

The bismuth amide  $\text{Bi}[\text{N}(\text{SiMe}_3)_2]_3$  (749 mg, 1.1 mmol) was dissolved in 10 ml *n*-hexane and 2-benzylphenol (600 mg, 3.3 mmol) was added in one portion. Subsequently, the solution was heated for three hours at reflux and then filtered after cooling to room temperature, while a yellow solid was isolated. The as-obtained solid was washed with a small amount of *n*-hexane and dried in vacuum.

Yield: 649 mg (79%), yellow crystals suitable for single-crystal X-ray diffraction were grown from THF/*n*-pentane solution at room temperature;  $\text{C}_{39}\text{H}_{33}\text{BiO}_3$  ( $M = 758.66 \text{ g}\cdot\text{mol}^{-1}$ ) requires C 61.74; H 4.38%; found: C 61.32; H 4.50%; m.p. 167-168°C;  $^1\text{H}$  NMR (500.3 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  3.91 (s, 2H), 6.52 (d, 1H), 6.78 (td, 1H), 6.92 (dd, 2H), 6.98 (m, 3H), 7.04 (td, 1H), 7.19 ppm (dd, 1H);  $^{13}\text{C}\{^1\text{H}\}$ -NMR (125.8 MHz,  $\text{CDCl}_3$ , 298 K):  $\delta$  36.8, 121.8, 122.8, 126.4, 127.1, 129.0, 129.2, 130.5, 133.5, 142.6, 155.8 ppm.

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