BISMUTH–OXYGEN BONDING AND COORDINATION GEOMETRY IN TETRAPHENYLBISMUTH ARYLOXIDES

Eshonqulov Uchqun Xudaynazar o'g'li
Karshi State Technical University
Uzbekistan, Karshi
E-mail: *uchqun.eshonqulov91@mail.ru*
Aminov Umidjon Gaybulla ugli
Karshi International University
Uzbekistan, Karshi
E-mail: *umid9070707@gmail.com*

Abstract: *Organobismuth chemistry offers unique opportunities for developing selective reagents and catalysts due to the element's accessible Bi(III)/Bi(V) redox states, pronounced Lewis acidity, and comparatively low toxicity among heavy elements. In this study, more than 150 previously unreported bismuth derivatives were synthesized, with 74 structures determined by single-crystal X-ray diffraction. Particular attention was given to tetraphenylbismuth aryloxides, which are obtained in high yields under mild conditions through the phenyl–proton exchange reaction between pentaphenylbismuth and phenols. to seven, producing systematic perturbations in equatorial bond angles.*

Keywords: *Organobismuth compounds; Tetraphenylbismuth aryloxides; Single-crystal X-ray diffraction; Coordination geometry; Phenyl–proton exchange; Structure–property relationships*

In recent years, organometallic compounds have become integral to organic synthesis, functioning as reagents and catalysts that deliver high chemoselectivity, accelerated kinetics, and compatibility with comparatively mild conditions. Continued advances in the field hinge on expanding this toolkit. Within main-group (non-transition) chemistry, a particularly promising direction is the development of robust organobismuth species. Bismuth's accessible Bi(III)/Bi(V) redox states, pronounced

Lewis acidity, and comparatively low toxicity among heavy elements make organobismuth frameworks attractive for selective bond-forming processes. However, the reliable synthesis and stabilization of well-defined C–Bi motifs remains a fundamental challenge, constraining systematic evaluation of their reactivity and catalytic potential. This study addresses that gap by preparing thermally and hydrolytically stable organobismuth compounds and assessing their behavior as reagents and catalysts in representative transformations, with the broader goal of enlarging the organometallic repertoire available for efficient, selective, and operationally simple organic synthesis.

It is well established that phenyl-substituted bismuth reagents in both the +3 and +5 oxidation states effect chemoselective oxidations and efficient O-, C-, and N-phenylations across diverse substrates, enabling the synthesis of numerous biologically active architectures—including analogues of natural alkaloids and derivatives of indole, 4-hydroxycoumarin, chroman-4-one, methylhydrogenate, quinones, ginkgolides, and macrolides—yet the set of bismuth compounds routinely used in organic synthesis remains narrow, being largely confined to triphenylbismuth, pentaphenylbismuth, tetraphenylbismuth tosylate and trifluoroacetate, selected carbonates, triphenylbismuth dichloride, the corresponding diacetate, and μ-oxobis(chlorotriphenylbismuth), a limitation that stems from the genuinely small number of well-defined, bench-stable organobismuth species reported to date; at the outset of our work no systematic strategy for preparing such compounds had been articulated, and expanding the family of accessible organobismuth derivatives therefore promises to materially widen their utility across multiple areas of chemistry.

Recent studies have revealed that ionic bismuth-containing complexes can display technologically significant functions, including ferroelectricity, superconductivity, and semiconducting behavior. Progress in this area will depend on synthetic approaches that deliver precise, predictive control over both the cationic and anionic sublattices, enabling deliberate tuning of structure–property relationships. By developing methods that predefine the composition, geometry, and packing of ions, researchers can systematically access targeted electronic and ferroic responses, thereby broadening the scope of materials accessible for investigation across solid-state chemistry, condensed-matter physics, and device-oriented applications.

Beyond their practical utility, organobismuth compounds are intellectually compelling: the large covalent radius of bismuth and the distinctive, relativistically influenced valence shell—often featuring a stereochemically active $6s^2$ lone pair—create an unusually capacious and tunable coordination sphere. Systematic structural studies of highly coordinated bismuth complexes, including the delineation of hemidirected versus holodirected geometries and the quantification of secondary bonding and other weak contacts, will sharpen our understanding of noncovalent interactions and inform modern theories of chemical bonding.

Scientific novelty and practical significance. Building on ligand-redistribution reactions between pentaphenylbismuth and bismuth compounds of general formula Ph_3BiX_2 (X = OAr, OSO_2R, OC(O)CR, $OSi(CH_3)_3$, F, ReO_4, NO_3), we propose a new, direct route to bismuth derivatives of the type Ph_3BiX. The same redistribution manifold applies to phenyl derivatives of phosphorus and arsenic (PhE and PhE_2X; E = P, As). An analogous exchange is observed in antimony chemistry—specifically between pentaphenylantimony and bis(arylsulfonates) or the dialkoxides of triphenylantimony—thereby outlining a preparative platform for aryl compounds of group-15 elements. For the first time, we show that reacting pentaphenylbismuth with non-activated Bi(III) species $ArBiX_2$ and Ar_2BiX (X = Hal, OSO_2Ar; and in selected cases X = Br, NO_3, OC(O)CR) on a triphenylbismuthyl substrate effects concurrent oxidation and phenyl transfer to the partner, furnishing mixed bismuth products with either symmetric (Ph_3BiX_2) or unsymmetric (Ph_4BiX) connectivity; the outcome is governed by the nature of the substituent X.

More than 150 previously unreported bismuth derivatives in the +3 and +5 oxidation states were prepared, and 74 of these were authenticated by single-crystal X-ray diffraction. Within the Ph_4BiX series, the immediate environment of bismuth is dictated by the substituent X: as the electronegativity of X increases, the geometry acquires a stronger tetrahedral component. Triarylbismuth dicarboxylates, $Ph_3Bi(O_2CR)_2$, display intramolecular Bi···O(carbonyl) contacts that raise the effective coordination number to seven and systematically perturb the equatorial angles of the framework; notably, the maximum equatorial C–Bi–C angle shows a linear correlation with the Bi–O(C) distance. In the anion $[BiI_5]^{2-}$ the metal center adopts an essentially ideal trigonal-bipyramidal coordination, illustrating the stereochemical inertness of the lone pair, whereas other complex anions most often approach a distorted octahedral arrangement formed without participation of that lone pair.

It was found that pentaphenylbismuth reacts rapidly with phenols in toluene at ambient temperature (≈20 °C, 0.5–5 min) to furnish tetraphenylbismuth aryloxides according to the formal phenyl–proton exchange

$Ph_5Bi + HOAr \rightarrow Ph_4BiOAr + PhH.$ (1)

The products are air-stable, crystalline solids, typically yellow to yellow-brown, and are readily soluble in both aliphatic and aromatic hydrocarbons. Representative isolated yields and melting points for the aryloxide series are summarized in Table 1, underscoring the efficiency and operational simplicity of this room-temperature transformation.

Table 1

Yields and melting points of tetraphenylbismuth aroxides obtained from pentaphenylbismuth and phenols

No.	Compound	m.p. (°C)	Yield (%)
1	$Ph_4BiOC_6H_2(Br_2\text{-}2,6)(t\text{-}Bu\text{-}4)$	112	74
2	$Ph_4BiOC_6H_3Cl_2\text{-}2,6$	115 (decomp.)	80
3	$Ph_4BiOC_6H_2(NO_2)_3\text{-}2,4,6$	175	81
4	$Ph_4BiOC_6H_3(Br_2\text{-}2,6)(NO_2\text{-}4)$ PhH	155	86
5	$Ph_4BiOC_6H_3(NO_2)$2-2,4	152 (decomp.)	83
6	$Ph_4BiOC_6H_2Br_3\text{-}2,4,6$	133	80
7	$Ph_4BiOC_6H_2Cl_3\text{-}2,4,6$	132	83
8	$Ph_4BiOC_6H_4Br_2\text{-}2,4$	112	80

9	$Ph_4BiOC_6H_2(Br_2\text{-}2,6)(Cl\text{-}4)$	134 (decomp.)	82
10	$Ph_4BiOC_6H_2(Br_2\text{-}2,6)(Me\text{-}4)$	112 (decomp.)	79

Molecules of tetraphenylbismuth aroxides have a trigonal-bipyramidal configuration characteristic of most pentacoordinated bismuth derivatives, with the aroxyl ligand in the axial position, for example (Figure 1)

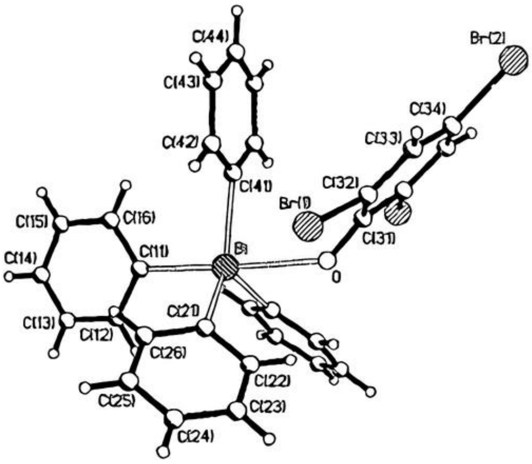

Figure 1. Structure of the *2,4,6-tribromophenoxide tetraphenylbismuth* **molecule.**

The bismuth atom in tetraphenylbismuth aroxide molecules is displaced from the equatorial plane toward the carbon atom of the axially positioned phenyl ligand. Notably, the **Bi–O bond length** exceeds the sum of the covalent radii of the corresponding atoms, indicating a deviation from ideal coordination geometry.

CONCLUSION

This study has significantly broadened the scope of organobismuth chemistry by synthesizing and characterizing more than 150 new derivatives, including a series of tetraphenylbismuth aryloxides obtained under mild conditions with high yields and stability. Single-crystal X-ray diffraction data revealed clear correlations between substituent electronegativity, bond angles, and coordination numbers, thereby deepening the understanding of stereoelectronic effects in bismuth frameworks. The discovery of intramolecular Bi···O interactions that elevate coordination numbers, alongside the observation of both ideal and distorted geometries in bismuth anions, highlights the versatile bonding behavior of this main-group element. Importantly, the displacement of the bismuth atom from the equatorial plane in tetraphenylbismuth aryloxides and the elongated Bi–O bond distances emphasize deviations from classical covalent models, offering new perspectives for modern bonding theory. Taken together, these results establish a robust platform for the rational design of bench-stable organobismuth compounds with tailored reactivity, paving the way for their wider application as reagents, catalysts, and functional materials in both organic and materials chemistry.

REFERENCES

1. Silvestru, C., *Structural Chemistry of Bismuth Compounds. I. Organobismuth Derivatives*, Chemical Reviews, 1999, 99 (11), 3277–3328.

2. Poddel’sky, A. I., *Heteroelement Organobismuth Compounds in 2010–2020*, Journal of Organometallic Chemistry, 2022.

3. Xiaodi Kou, Xiaoyu Wang, Daniel Mendoza-Espinosa, Lev N. Zakharov, Arnold L. Rheingold, *Bismuth Aryloxides*, Inorganic Chemistry, 2009.

4. Islam, A., *Novel Triphenylantimony(V) and Triphenylbismuth(V) Complexes with Carboxylate Ligands*, Molecules, 2014.

5. Kumar, I., *Facile One-Pot Synthesis of Triphenylbismuth(V) Bis-…* (synthesis and crystallography), Organometallics, 2014.

6. Абдисамиевич С.А., Мамарасулович Р.У. и Азаматугли К.О. (2025). РАЗРАБОТКА ТЕХНОЛОГИИ ПОЛУЧЕНИЯ ГЛИНОЗЕМИЯ ИЗ МЕСТНОГО СЫРЬЯ. *Sanoatda raqamli technologiyalar/Цифровые технологии в промышленности* , *3* (2), 105-111.

7. O‘G‘Li, T. S. S., Mamarasulovich, R. Z. U. B., & O‘G‘Li, E. U. X. (2024). KALSIY TARKIBLI QO ‘SHIMCHALAR TARKIBIDAGI ALYUMOGETIT VA BOKSITDAN GLINOZEMNI AJRATIB OLISH. *Строительство и образование*, *3*, 203-210.

8. Abdisamiyevich, S. A., Xudaynazar o‘g‘li, E. U., Mamarasulovich, R. U., & Ilyosjon o‘g‘li, X. I. (2025). ROASTING OF ALUMINA-CONTAINING MATERIAL IN A ROTARY KILN. *GREAT BRITAIN-SCIENTIFIC REVIEW OF THE PROBLEMS AND PROSPECTS OF MODERN SCIENCE AND EDUCATION*, *1*(1), 22-28.

9. Mamarasulovich, R. U. (2025). INFLUENCE OF ULTRASOUND ON NITRIC ACID LEACHING OF ALUMINA FROM KAOLIN CLAYS. *Лучшие интеллектуальные исследования*, *46*(5), 338-348.