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New Synthesis of Triphenylbismuth Diaroxides

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Abstract—The reaction of triphenylbismuth, hydrogen peroxide, and phenol (molar ratio 1 : 1 : 2) in ether was used to synthesize triphenylbismuth diaroxides $Ph_3Bi(OAr)_2$ [Ar = $C_6H_3(NO_2)_2$-2,4, $C_6H_2(NO_2)_3$-2,4,6, $C_6H_3Cl_2$-2,6, $C_6H_2Cl_3$-2,4,6, $C_6H_3Br_2$-2,4, $C_6H_2Br_3$-2,4,6, $C_6H_2Br_2$-2,4,Me-6, $C_6H_2Br_2$-2,6, NO_2-4]. At an equimolar reagent ratio, bridged bismuth compounds $(Ph_3BiOAr)_2O$ are formed. The crystal structure of bis(2,4-dinitrophenoxy)triphenylbismuth $Ph_3Bi[OC_6H_3(NO_2)_2$-2,4$]_2$ was studied by X-ray diffraction to show that the bismuth atom has a distorted trigonal bipyramidal coordination and the 2,4-dinitrophenoxyl ligands are axial. The CBiC and OBiO angles are 109.6(5)°, 122.3(5)°, 128.1(5)°, and 175.6(3)°. The Bi–$O^{1,6}$ and Bi–C bond lengths are 2.256(10), 2.242(9) and 2.18(1), 2.18(1), 2.19(1) Å, respectively.

Triphenylbismuth diaroxides are prepared from triphenylbismuth dibromide and sodium aroxide [1]. In the present communication we propose a new synthetic approach to such triphenylbismuth derivatives via oxidative addition involving treatment of triphenylbismuth with hydrogen peroxide in the presence of phenol in ether. The reactions occurred at room temperature (reagent molar ratio 1 : 1 : 2, respectively) and were compete within 1–2 h; therewith, the solutions changed from colorless to yellow, and triphenylbismuth diaroxides formed as yellow crystals in yields of up to 72%.

$$Ph_3Bi + H_2O_2 + 2HOAr \longrightarrow \underset{\textbf{I–VII}}{Ph_3Bi(OAr)_2} + 2H_2O,$$

Ar = $C_6H_3(NO_2)_2$-2,4 (**I**), $C_6H_2(NO_2)_3$-2,4,6 (**II**), $C_6H_3Cl_2$-2,6 (**III**), $C_6H_2Cl_3$-2,4,6 (**IV**), $C_6H_3Br_2$-2,4 (**V**), $C_6H_2Br_3$-2,4,6 (**VI**), $C_6H_2Br_2$-2,4,Me-6 (**VII**).

At an equimolar reagent ratio, bridged bismuth compounds are formed as yellow crystals that are poorer soluble in organic solvents that triphenylbismuth diaroxides.

$$2Ph_3Bi + 2H_2O_2 + 2HOAr \longrightarrow \underset{\textbf{VIII–X}}{(Ph_3BiOAr)_2O} + 3H2O,$$

Ar = $C_6H_2(NO_2)_3$-2,4,6 (**VIII**), $C_6H_3Br_2$-2,4 (**IX**), $C_6H_2Br_3$-2,4,6 (**X**).

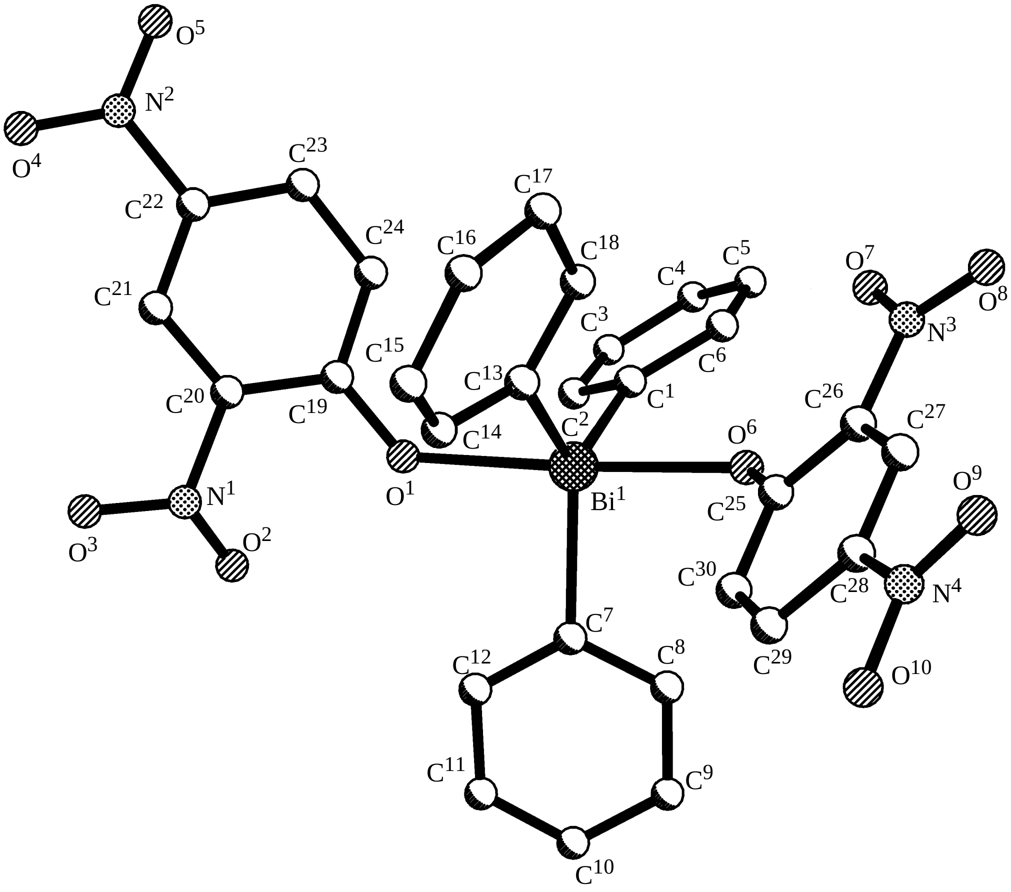
The yields and melting points of the synthesized compounds are listed in Table 1.

According to X-ray diffraction data, the bismuth atoms in compound **I** have a trigonal bipyramidal coordination. The axial positions are occupied by the oxygen atoms of the aroxyl ligands whose *o*-nitro groups are turned outwards the central atom (see figure). The torsion angles of the C^{25}–C^{29} and C^{19}–C^{24} rings of the aroxyl ligands with respect to the equatorial plane are 39.8° and 53.8°, respectively.

The axial angle OBiO is 175.6(3)°, and the equatorial angles C(Ph)BiC(Ph) slightly differ from each other [109.6(5), 122.3(5), and 128.1(5)°] (Table 2) at their sum of 360°; therewith, the $C^7Bi^1C^{13}$ angle is increased [128.1(5)°] compared with ideal (120°) from the side where the *o*-nitro groups of the aroxyl ligand approach the central atom. Note that the O^2 atom in the $O^2N^1O^3$ group is disordered over two positions. The $Bi^1\cdots O^2$ and $Bi^1\cdots O^{2'}$ distances are 4.538 and

Table 1. Yields and melting points of bismuth compounds **I**–**X** obtained from triphenylbismuth, phenol, and hydrogen peroxide

Comp. no.	Yield, %	mp, °C
I	55	148 (decomp.)
II	72	170 (decomp.)
III	20	117 (decomp.)
IV	62	113
V	55	148 (decomp.)
VI	56	124 (decomp.)
VII	25	28
VIII	96	149
IX	56	142
X	78	215



General view of a molecule of (2,4-dinitrophenoxy)triphenylbismuth (**I**).

4.293 Å, respectively, which is much larger than the sums of the van der Waals radii of Bi and O (3.9 Å [3]). Note that the difference in the equatorial angles in bis(pentafluorophenoxy)triphenylbismuth is appreciably smaller {119.0(3)°, 119.3(3)°, and 121.8(3)° [1]} because of the lack of nonbonded interactions between the bismuth atom and the aroxyl *o*-fluorine atoms. At the same time, in bis(2,4,6-tribromophenoxy)triphenylbismuth, where there are intramolecular contacts between bismuth and two aroxyl *o*-bromine atoms (3.629 Å), the equatorial angle on the side of these contacts is much larger than 120° and is 143.8° [2]. The shortest of the respective contacts in bis(pentachlorophenoxy)triphenylbismuth are 3.401 and 3.908 Å, which is smaller than the sum of the van der Waals radii of bismuth and chlorine (4.2 Å [3]); therewith, the angles on the side of intramolecular contacts are 142.6° and 113.4°, respectively.

The Bi atom in compound **I** deviates from the equatorial plane by 0.011 Å. The Bi–C^1, Bi–C^{13}, and Bi–C^7 bond lengths are 2.18(1), 2.18(1), and 2.19(1) Å, respectively. The equatorial benzene ring planes are tilted to the equatorial plane $C^1C^7C^{13}$ by 69.6° (C^7–C^{12}), 31.0° (C^1–C^6), and 25.2° (C^{13}–C^{18}), thereby weakening intramolecular interactions.

EXPERIMENTAL

Single-crystal X-ray diffraction analysis of compound I was performed on a Bruker-AXS SmartApex diffractometer ($\lambda \mathrm{Mo}K_\alpha$ 0.71073 Å, graphite monochromator, φ–ω scanning, $\theta \le 25.00°$). The crystals of $Ph_3Bi[OC_6H_3(NO_2\text{-}2,4)]_2$ (**I**) are triclinic; at 20°C, *a* 9.5983(7), *b* 12.1987(9), *c* 12.7375(9); α 83.9970(10), β 84.8060(10), γ 83.1730(10)°; *V* 1468.09(18) Å^3, *Z* 2, d_{calc} 1.824 g cm^{-3}, space group *P*-1. The unit cell parameters and the intensities of 11450 reflections were measured, 5154 of which had $I \ge 3\sigma$). The structure was solved by the direct method and refined by anisotropic least squares for all non-hydrogen atoms. Hydrogen atoms were located geometrically and refined using the rider model. Final divergence factors: *R* 0.0429 and R_W 0.1133. The principal bond lengths and angles are given in Table 2 (other X-ray characteristic of the molecule can be requested from the authors). Data collection and treatment, refinement of unit cell parameters, and

Table 2. Principal bond lengths and bond angles in the molecule of bis(2,4-dinitrophenoxy)triphenylbismuth (**I**)

Bond	*d*, Å	Angle	ω, deg
$\mathrm{Bi^{1}{-}C^{1}}$	2.178(12)	$\mathrm{C^{1}Bi^{1}C^{13}}$	122.3(5)
$\mathrm{Bi^{1}{-}C^{13}}$	2.178(13)	$\mathrm{C^{1}Bi^{1}C^{7}}$	109.6(5)
$\mathrm{Bi^{1}{-}C^{7}}$	2.192(12)	$\mathrm{C^{13}Bi^{1}C^{7}}$	128.1(5)
$\mathrm{Bi^{1}{-}O^{6}}$	2.242(9)	$\mathrm{C^{1}Bi^{1}O^{6}}$	88.5(4)
$\mathrm{Bi^{1}{-}O^{1}}$	2.256(10)	$\mathrm{C^{13}Bi^{1}O^{6}}$	87.6(4)
$\mathrm{O^{1}{-}C^{19}}$	1.317(17)	$\mathrm{C^{7}Bi^{1}O^{6}}$	95.0(4)
$\mathrm{O^{2}{-}N^{1}}$	1.209(11)	$\mathrm{C^{1}Bi^{1}O^{1}}$	92.8(4)
$\mathrm{O^{2'}{-}N^{1}}$	1.210(10)	$\mathrm{C^{13}Bi^{1}O^{1}}$	88.2(4)
$\mathrm{O^{3}{-}N^{1}}$	1.235(18)	$\mathrm{C^{7}Bi^{1}O^{1}}$	88.6(4)
$\mathrm{O^{4}{-}N^{2}}$	1.22(2)	$\mathrm{O^{6}Bi^{1}O^{1}}$	175.6(3)
$\mathrm{O^{5}{-}N^{2}}$	1.20(2)	$\mathrm{C^{19}O^{1}Bi^{1}}$	124.2(8)
$\mathrm{O^{6}{-}C^{25}}$	1.308(17)	$\mathrm{C^{25}O^{6}Bi^{1}}$	122.9(8)
$\mathrm{O^{7}{-}N^{3}}$	1.188(19)	$\mathrm{O^{2}N^{1}O^{2'}}$	66(2)
$\mathrm{O^{8}{-}N^{3}}$	1.207(17)	$\mathrm{O^{2}N^{1}O^{3}}$	115(2)
$\mathrm{O^{9}{-}N^{4}}$	1.19(2)	$\mathrm{O^{2'}N^{1}O^{3}}$	120.4(19)
$\mathrm{O^{10}{-}N^{4}}$	1.23(2)	$\mathrm{O^{2}N^{1}C^{20}}$	116(2)
$\mathrm{N^{1}{-}C^{20}}$	1.47(2)	$\mathrm{O^{2'}N^{1}C^{20}}$	114.0(16)
$\mathrm{N^{2}{-}C^{22}}$	1.47(3)	$\mathrm{O^{3}N^{1}C^{20}}$	116.3(15)
$\mathrm{N^{3}{-}C^{26}}$	1.463(19)	$\mathrm{O^{5}N^{2}O^{4}}$	124(2)
$\mathrm{N^{4}{-}C^{28}}$	1.48(2)	$\mathrm{O^{5}N^{2}C^{22}}$	119.0(17)

correction for absorption were performed using SMART [4], SAINT-Plus [5], and SADABS programs [6]. The structure was solved and refined using Bruker SHELXTL programs [7].

Bis(2,4-dinitrophenoxy)triphenoxybismuth (I). To a solution of 0.30 g of triphenylbismuth in 15 ml of ether, 0.25 g of 2,4-dinitrophenol and 0.08 ml of 30% aqueous hydrogen peroxide were added (reagent molar ratio 1 : 2 : 1), and the mixture was left to stand for 12 h at 20°C. Yellow crystals formed. The solvent was removed, and the residue was treated with hexane to isolate 0.30 g (55%) of compound **I**, mp 148°C (decomp.).

Compounds **II**–**X** were prepared in a similar way. Compounds **VIII**–**X** were synthesized at a 1 : 1 : 1 molar ratio.

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