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Preparation and Structure of Tri-*p*-tolylbismuth Dibromide

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Abstract—Interaction of tri-*p*-tolylbismuth with bromine in carbon tetrachloride has yielded tri-*p*-tolylbismuth dibromide. According to X-ray diffraction studies, bismuth atoms in both symmetrically independent dibromide molecules were in distorted trigonal bipyramid surrounding with equatorial aryl substituents.

Keywords: tri-*p*-tolylbismuth, synthesis, X-ray diffraction analysis, trigonal bipyramid coordination

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Interest towards structural studies of the Ar_3BiX_2 compounds is due to their significant synthetic potential. In particular, phenylation and oxidation of organic compounds with derivatives of quinquivalent bismuth have been described in [1–5]. By now structures of many phenyl-containing compounds of general formula Ph_3BiX_2 (X being mono- or bidentate ligand) have been elucidated, but similar derivatives of tritolylbismuth have been scarcely reported so far [6, 7]. Tri-*p*-tolylbismuth dibromide prepared from tri-*p*-tolylbismuth and bromine in diethyl or petroleum ether crystallizes from mixture of chloroform and ethyl alcohol in the form of yellow shiny needles with mp of 111–112°C [8].

Here we report on further studies of tri-*p*-tolylbismuth dibromide **I** prepared via oxidation of tri-*p*-tolylbismuth in carbon tetrachloride followed by the product recrystallization from diethyl ether–acetone mixture. Compound **I** crystallized in the form of colorless lamellar crystals with mp of 122°C; we elucidated its crystal structure.

According to the X-ray diffraction data, bismuth atoms in the two symmetrically independent molecules of compound **I** were characterized by distorted trigonal-bipyramidal coordination with axially located bromine atoms (Fig. 1).

Two symmetrically non-equivalent molecules A and B were located in the independent part of the crystal unit cell. The angles between equatorial tolyl substituents were unequal [118.5(2)°, 118.2(2)°, and 123.2(2)° in molecule A; 116.0(2), 117.4(2), and 126.4(2)° in molecule B] and deviated from the ideal value of 120°. Trigonal-bipyramidal geometry of tri-*p*-tolylbismuth dichloride was less distorted [9]. In the latter compound, equatorial angles CBiC [119.1(4), 119.2(4), 121.6(5)] were less different as compared with the values observed in the case of compound **I**. The bond lengths Bi–Br in compound **I** were 2.7285(6), 2.7619(6) Å (molecule A) and 2.7136(7), 2.8065(8) Å (molecule B). The Bi–C distances, ranging from 2.201(6) to 2.246(7) Å, were close to those in the corresponding dichloride [2.19(1)–2.23(2) Å], but they were somewhat shorter than in the *p*-$Tol_5Bi\cdot(LiCl\cdot THF)_2$ adduct. Bismuth atom in the latter compound existed in the square-pyramidal coordination [Bi–C_{eq} 2.28(3)–2.36(3) Å] [10]. The axial angles BrBiBr in compound **I** were 179.31(2)º (molecule A) and 173.74(2)° (molecule B), whereas the sum of equatorial angles was 359.96º (molecule A) and 359.88° (molecule B). Deviation of bismuth atom from the equatorial plane of aryl ligands was higher in molecule B (0.057 Å) than in molecule A (0.008 Å).

Aromatic rings of tolyl ligands were arranged in pseudo propeller shape with respect to the pyramid base plane (BiC_3), and the corresponding dihedral angles were 36.97°, 52.78°, and 45.56° (molecule A) and 31.85°, 54.29°, and 88.79° (molecule B). The plane of one of tolyl ligands of molecule B was almost perpendicular to the equatorial plane of the molecule, and therefore *ortho* hydrogen atoms of that tolyl fragment approached the bromine atoms. The $H^{30}Br^3$ and $H^{34}Br^4$ distances were 2.702 and 2.695 Å, respectively, less that the sum of van der Waals radii

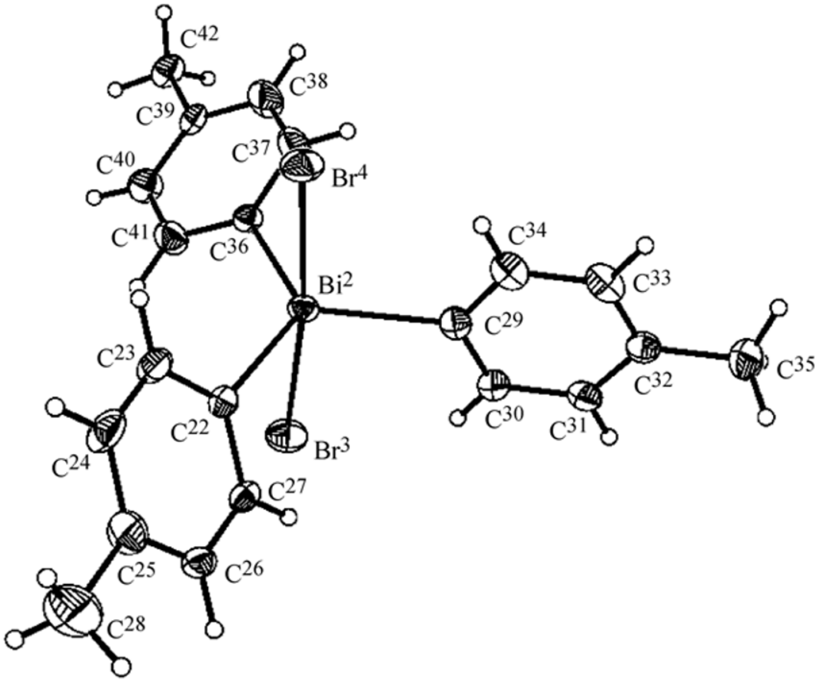

Fig. 1. General view of molecule B and compound **I** (thermal ellipsoids at 50% probability).

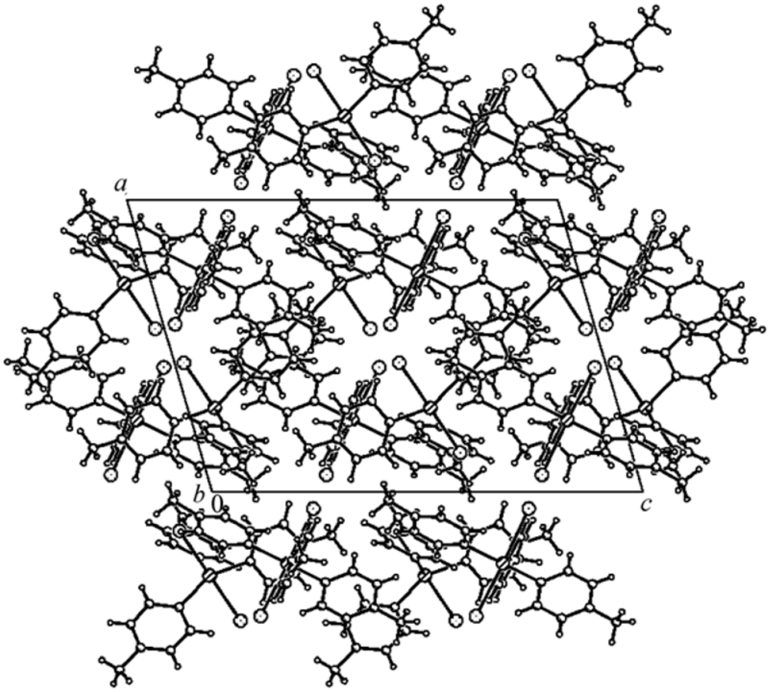

Fig. 2. Packing of molecules A and B of compound **I** in the crystal unit cell.

of H and Br atoms (3.1 Å) [11]. Similar contacts were observed in the case of the corresponding dichloride, where the H–Cl distances were 2.566 and 2.653 Å, the sum of van der Waals radii being 3.0 Å [11].

In crystals of compound **I** molecules A were packed longitudinally along axis *a* (due to intermolecular interactions between the H^9Br^1 and $H^{13}Br^2$ atoms, the respective distances being 3.021 and

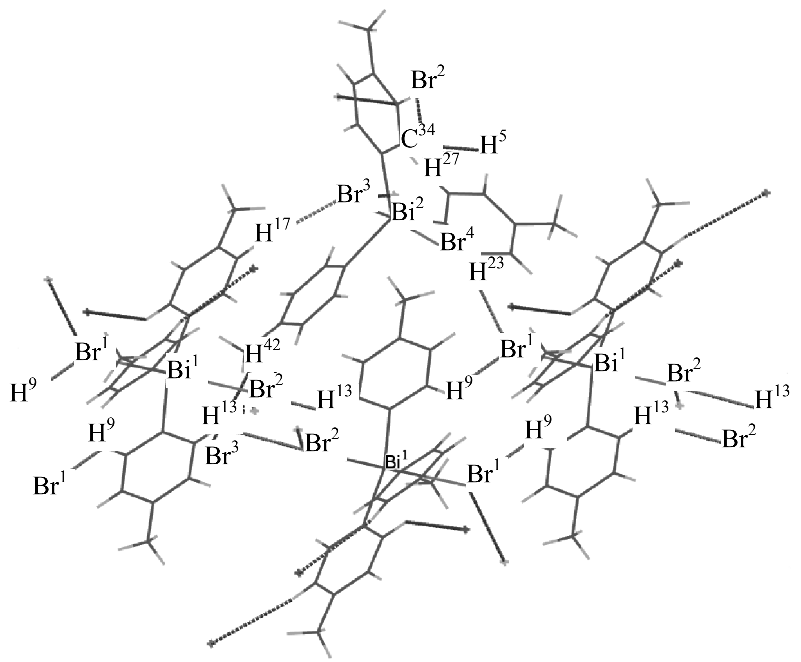

Fig. 3. Intermolecular interactions in the crystal of compound **I**.

3.024 Å (Fig. 2). Molecules B of compound **I** formed chains along axis *c* due to the intermolecular contacts $H^{42}Br^3$ (3.035 Å). The interchain interactions were characterized by the following distances: 2.966 (Br^3H^{17}), 2.959 ($H^{23}Br^1$), 2.910 ($H^{27}Br^2$), and 2.864 ($C^{34}H^5$) Å (sum of van der Waals radii of carbon and hydrogen atoms is 2.9 Å [11]) (Fig. 3).

Comparison of the structural parameters of compound **I** with those of the corresponding dichloride demonstrated that the increase in the halogen ligand volume did not change the crystal system; however, the space group was changed, and the crystal lattice parameters increased.

EXPERIMENTAL

X-ray diffraction analysis of compound I. Crystal lattice parameters of a single crystal of compound **I** (0.33×0.21×0.15 mm^3) were elucidated from 38933 reflections (11025 independent) recorded by the Bruker APEX II CCD diffractometer [120(2) K, MoK_α radiation, graphite monochromator]. The data were collected over the hemisphere (θ = 2.00°–29.00°). Experimental data were processed and the equivalent reflections were averaged using the software complex [12]. The structure was solved by the direct method and refined by the full-matrix least-squares method with respect to F^2 in the anisotropic approximation for non-hydrogen atoms. Hydrogen atoms coordinates were calculated geometrically and refined under the isotropic approximation in the *rider* model. $R_1 = 0.0385$ and $wR_2 = 0.0883$, $F^2 > 2\sigma(F^2)$, GOF = 1.007. Minimal and maximal values of residual electron density of $\Delta\rho_{\min}/\rho_{\max} = -2.682/2.713$ e/Å^3. All computations were performed using the SHELXTL software package [13].

Crystals of $C_{21}H_{21}BiBr_2$ (M = 642.18): monoclinic, a = 13.9616(7), b = 15.7426(8), c = 19.7421(11) Å, β = 106.2830(10)°, V = 4165.1(4) Å^3, Z = 8, d_{calc} = 2.048 g/cm^3, space group $P21/c$.

The X-ray diffraction data were deposited at the Cambridge Crystallographic Data Centre (CCDC 966123).

Tri-*p*-tolylbismuth dibromide. 1.10 mL of bromine (0.021 mol) in 40 mL of CCl_4 was added to a solution of 10.00 g (0.021 mol) of tri-*p*-tolylbismuth in 150 mL of CCl_4. The formed precipitate was filtered off and recrystallized from diethyl ether–acetone 1 : 1 v/v mixture. Yield 86%, mp 122°C. Found, %: C 39.51; H 3.06. $C_{21}H_{21}BiBr_2$. Calculated, %: C 39.28; H 3.27.

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