Synthesis and Crystal and Molecular Structure of Tetraphenyldibismuthine, Bi_2Ph_4, the First Crystallographically Characterized Tetraorganyl Derivative of Bismuth(II)

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Tetraphenyldibismuthine, Bi_2Ph_4, was prepared by reducing $BiPh_2Cl$ with sodium in liquid ammonia and characterized by conventional methods, including *X*-ray diffractometry.

Dimeric alkyl and aryl derivatives containing bismuth–bismuth bonds are rare and only recently have the thermally unstable Bi_2Et_4[1] and Bi_2Me_4[2] been reported. Earlier attempts[3] to synthesize Bi_2Ph_4 failed and no structural data about this type of compounds are available as yet.

We now report that Bi_2Ph_4 was obtained in about 50% yield by treating $BiPh_2Cl$[4] with the stoicheiometric amount of sodium in liquid ammonia at −40 to −80 °C, followed by filtration of the resulting suspension; the compound was separated from NaCl by dissolution in toluene, followed by evaporation to dryness. It was purified by crystallization from hot absolute ethanol, and obtained in about 45% yield.† Tetraphenyldibismuthine is an orange solid at room temperature, yellow at liquid nitrogen temperature, and with no intermediate darker colours, as in the case of Bi_2R_4[1,2] (R = Me,Et); when pure, it is stable up to 100 °C under argon, sensitive to air (oxygen was absorbed rapidly in toluene solution), and rapidly reacts with di-iodine to give iodinated products. Its i.r. spectrum in the 4000—250 cm^{-1} region is analogous to spectra of the other E_2Ph_4 (E = P, As, Sb) compounds, and its mass spectrum (20 eV; 120 °C) shows ions at *m/z* 726 (<1 %, M^+), 649 (1, M^+ − Ph), 572 (<1, M^+ −

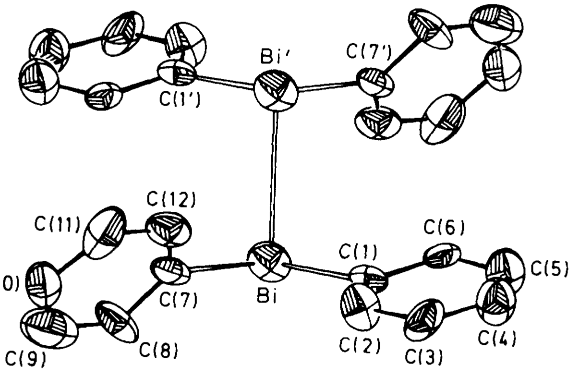

Figure 1. An ORTEP view of Bi_2Ph_4. Selected bond distances and angles are: Bi–Bi', 2.990(2); Bi–C(1), 2.28(2); Bi–C(7), 2.26(2) Å; C(1)–Bi–Bi', 91.6(5); C(7)–Bi–Bi', 90.9(5); C(1)–Bi–C(7), 98.3(8)°.

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† Satisfactory elemental analyses were obtained.

2 Ph), 495 (<0.1, M^+ − 3 Ph), 440 (2.5, M^+ − BiPh), 363 (4.3, M^+ − $\mathrm{BiPh_2}$), 286 (100, M^+ − $\mathrm{BiPh_3}$), and 209 (84, $\mathrm{Bi^+}$). Its structure was determined by *X*-ray crystallography.

Crystal Data: $\mathrm{C_{24}H_{20}Bi_2}$, M = 726.38, triclinic, space group $P\bar{1}$, a = 7.865(4), b = 11.444(5), c = 6.257(3) Å, α = 105.24(4), β = 94.20(7), γ = 96.52(6)°, U = 536.7 Å^3, D_c = 2.247 g cm^{-3}, Z = 1, μ(Mo-K_α) = 163.3 cm^{-1}, F(000) = 330. The intensities of 1788 unique reflections were measured on a Philips PW 1100 diffractometer using Mo-K_α radiation (λ = 0.71069 Å). The structure was solved by the heavy-atom method and refined by full-matrix least-squares with anisotropic thermal parameters. The hydrogen atoms were not located. The final conventional R factor was 0.0560 (R' = 0.0555) for 1097 absorption-corrected reflections having $I \geqslant 3\sigma(I)$.‡

As shown in Figure 1, the molecule of $\mathrm{Bi_2Ph_4}$ has a staggered *trans*-conformation, as in the case of $\mathrm{Sb_2Ph_4}$.[5] Bismuth, which is approximately pyramidal, is displaced 1.31 Å from the plane defined by C(1)–C(7)–Bi′ (′=2−x, 1−y, −z). The Bi–Bi′ distance is 2.990(2) Å, slightly longer than those [2.936(2) and 2.941(2) Å] reported[6] for the $\mathrm{Bi_4^{2-}}$ anion, and close to the nearest-neighbour distance of 3.071(1) Å in elemental bismuth.[7] The bond angles about bismuth (see Figure 1) are significantly smaller than the tetrahedral value, suggesting that the lone pair has essentially s character. The Bi–C bond distances (see Figure 1) agree well with those found[8–11] in the four structurally characterized phenyl–bismuth(III) derivatives. The molecular packing is dominated by van der Waals' interactions, the shortest contacts being C(4)· · ·C(10) (1−x, 1−y, 1−z), 3.65(4), and C(10)· · ·C(10) (2−x, 2−y, 1−z), 3.58(4) Å. Steric hindrance by the phenyl rings probably minimizes intermolecular Bi–Bi interactions, which explains the failure to observe dramatic thermochromic phenomena with this compound.[12] The compound was found to be diamagnetic (X_M = −160 × 10^{-6} c.g.s.u.) and no e.s.r. signals were observed at room temperature both in the solid state and in toluene solution, thus suggesting no tendency for Bi–Bi bond cleavage under these conditions. The ligand properties of $\mathrm{Bi_2Ph_4}$ are presently being investigated.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.