BISMUTH

ANNUAL SURVEY COVERING THE YEAR 1973

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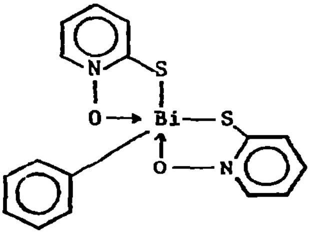
The chemistry of organobismuth compounds was not extensively reviewed in 1973. These substances were briefly discussed, however, in the second volume of The Chemical Society's Specialist Periodical Reports on organometallic compounds [1] and in reviews on the mass spectrometry of compounds containing the representative Group V elements [2] and NQR in organic and organometallic chemistry [3]. The use of tertiary bismuthines as ligands has been mentioned in a book devoted to transition metal complexes of phosphines, arsines, and stibines [4], and a list of the few organobismuth compounds that were subjected to X-ray analysis in 1971 and 1972 was published in Volume 4 of *Molecular Structures and Dimensions* [5].

It has been claimed in the patent literature [6] that bis(1-oxopyridine-2-thiolato)phenylbismuthine (I) was a highly effective antibacterial and antifungal agent and that it was, therefore, a desirable component of toothpaste, soap, cosmetics, wood preservatives, *etc.* The compound was prepared by the reaction of sodium 1-oxopyridine-2-thiolate with either acetatodiphenylbismuthine or a phenyldihalobismuthine.



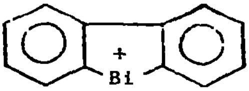
I

The conformation of tris(*p*-chlorophenyl)bismuthine in benzene solution has been investigated by means of molar Kerr constant, dipole moment, and dielectric relaxation measurements [7]. The results obtained were compared with an earlier study of the conformation of triphenylbismuthine in benzene. The experimental moment of 2.6D found for the chloro compound suggested that the zero moment previously reported for triphenylbismuthine was due to each Ph-Bi group being effectively non-polar. It was concluded that in terms of electron pair moments the resultant of the three C-Bi bonding electron pairs was equal in magnitude but opposite in direction to that of the bismuth lone pair. The assumption that the Ph-Bi group was non-polar led to a calculated value of 93° for the C-Bi-C bond angle in both tertiary bismuthines. The data also yielded the conclusion that the aryl groups were rotated (in the same sense) through an angle of 45° from a model in which these groups intersected along the symmetry axis.

Hellwinkel and coworkers [8] have included triphenylbismuthine, 5-phenyldibenzobismole, and pentaphenylbismuth in an investigation of the mass spectra of a variety of trivalent and pentavalent organic derivatives of phosphorus, arsenic, antimony, and bismuth. In agreement with earlier workers, it was found that the Bi^+ ion was the dominant peak in the spectrum of triphenylbismuthine. The second most intense peak corresponded to $PhBi^+$. Only two other bismuth-containing species were noted: a very weak molecular ion and a slightly stronger Ph_2Bi^+ ion. The presence of the appropriate metastable peaks showed that the Bi^+ ion was formed by fragmentation of both the $PhBi^+$ and the Ph_2Bi^+ ions:

$$\begin{tikzcd}
Ph_3Bi^+ \arrow[r, "*"] \arrow[d] & PhBi^+ \arrow[d, "*"] \\
Ph_2Bi^+ \arrow[r, "*"] & Bi^+
\end{tikzcd}$$

Three bismuth-containing fragments were noted in the spectrum of 5-phenyldibenzobismole, the most intense being the Bi^+ ion. Relatively weak peaks were found for the molecular ion and for an ion in which the heterocyclic ring was still intact:



The mass spectrum of pentaphenylbismuth exhibited five bismuth-containing fragments but no molecular ion. The most intense peak was for the Bi^+ ion, and there was a somewhat weaker peak for $PhBi^+$. There were also weak peaks for Ph_3Bi^+, Ph_2Bi^+, and $(Ph_2Bi-2H)^+$, the last of which was attributed to the dibenzoheterocyclic ion shown above. It was presumably formed by an "*ortho* coupling" reaction, but the exact pathway was not elucidated.

Several investigations in which tertiary bismuthines were involved have been reviewed under Antimony. Described in these publications were a study of the ^{19}F NMR spectra of a number of triarylbismuthines containing one or more fluorophenyl groups [9], the formation of *trans*-stilbene, biphenyl, and *trans, trans*-1,4-diphenylbutadiene by the interaction of triphenylbismuthine and styrene in the presence of palladium(II) acetate [10], and the attempted preparation of tris(3,3,3-trifluoro-1-propynyl)bismuthine from the corresponding organolithium reagent [11].

Calculation of the electron configuration of triphenylphosphine, -arsine, -stibine, and -bismuthine has been described in the Russian literature [12]. Another Russian paper has reported the behavior (including R_f values) of a series of organobismuth compounds during thin-layer chromatography on alumina [13].

Goel and Prasad [14] have prepared triphenylbismuth diazide and dicyanide by the metathetical reaction of triphenylbismuth dichloride with an aqueous solution of sodium azide or potassium cyanide, respectively. The diazide decomposed slowly in the solid state:

$$Ph_3Bi(N_3)_2 \longrightarrow Ph_2BiN_3 + PhN_3$$

The solid dicyanide was stable at room temperature but decomposed on heating. At 140°, complete cleavage of the Ph-Bi and Bi-CN bonds occurred, and evolution of cyanogen was observed. Both the diazide and dicyanide were insoluble in petroleum ether but soluble in other common organic solvents. In solution, however, the dicyanide decomposed in several hours to yield cyanodiphenylbismuthine and benzonitrile. Treatment of the dicyanide with mercuric oxide gave triphenylbismuthine oxide:

$$Ph_3Bi(CN)_2 + HgO \longrightarrow Ph_3BiO + Hg(CN)_2$$

Attempts to obtain triphenylbismuth dicyanate by oxidation of the dicyanide with manganese dioxide or treatment of the diazide with carbon monoxide were unsuccessful. Molecular weight and conductance measurements showed that the diazide and the dicyanide existed in solution as non-ionic, monomeric species. Infrared and laser Raman spectra indicated that both compounds had trigonal-bipyramidal structures analogous to that previously established for triphenylbismuth dichloride by X-ray diffraction studies.

Beaumont, Goel, and Prasad [15] have reported that treatment of μ-oxo-bis(triphenylbismuth) diperchlorate with O-donor bases resulted in the formation of pentacoordinate cationic complexes of the type $[(Ph_3BiL)_2O](ClO_4)_2$, where L was dimethyl sulfoxide (DMSO), pyridine N-oxide (PyO), triphenylphosphine oxide, or triphenylarsine oxide. Pentacoordinate complexes of the type $(Ph_3BiL_2)X_2$, where X was ClO_4, BF_4, or PF_6, were prepared by the following reaction:

$$Ph_3BiCl_2 + 2L + 2AgX \longrightarrow (Ph_3BiL_2)X_2 + 2AgCl$$

An unstable dinitrate, $[Ph_3Bi(OAsPh_3)_2](NO_3)_2$, was obtained in a similar manner. Except for this compound, all the complexes were stable in the solid state at room temperature for at least several months. In dichloromethane solution the complex $[Ph_3Bi(OAsPh_3)_2](BF_4)_2$ decomposed to yield triphenylbismuth difluoride:

$$[Ph_3Bi(OAsPh_3)_2](BF_4)_2 \longrightarrow Ph_3BiF_2 + 2Ph_3AsOBF_3$$

The IR spectra of the complexes clearly showed the presence of ionic perchlorate, tetrafluoroborate, hexafluorophosphate, or nitrate groups as well as cations of the type $Ph_3BiL_2^{2+}$ or $[(Ph_3BiL)_2O]^{2+}$ in which the ligands L were bonded to bismuth through their oxygen atoms. It was concluded that the bismuth atoms in these compounds possessed a trigonal-bipyramidal configuration with the phenyl groups occupying equatorial positions. Conductance measurements showed that the complexes behaved as 1:2 electrolytes in nitromethane. In dichloromethane, however, the molar conductance values for the oxybis complexes in which L was DMSO or PyO were lower than anticipated for 1:2 electrolytes. It was suggested that the decrease in conductivity resulted from the following type of equilibrium reaction:

$$[(Ph_3BiL)_2O]^{2+} + 2ClO_4^- \rightleftharpoons [Ph_3Bi(ClO_4)]_2O + 2L$$

In accordance with this hypothesis, the conductance of dichloromethane solutions of these DMSO or PyO complexes increased markedly upon addition of free ligand. The complexes $[Ph_3Bi(OAsPh_3)_2]X_2$, where X was BF_4 or PF_6, were found to form solvates with acetone, diethyl ketone, or acetylacetone. The IR and NMR spectra of the solvates showed, however, that the ketone was not coordinated to the bismuth.

Faraglia and coworkers [16] have investigated the structure of the organobismuth(V) derivatives $Ph_3BiCl(Ox)$ and $Ph_3BiBr(Ox)$, where Ox was the oxinate (8-quinolinolate) group. The compounds were obtained by the interaction of equimolar amounts of triphenylbismuth dihalide and sodium oxinate. It was concluded that the solid complexes contained bismuth atoms that were coordinated to the oxygen and nitrogen atoms of the oxinate ligands and to the halogen atom; *i.e.*, the bismuth was hexacoordinate and presumably octahedral. In methanol solution, however, the Bi-N bond was cleaved, and the complexes existed as monomeric, undissociated species in which the bismuth atom was bonded to the ligand only through the oxygen atom.

The first unambiguous determination of the structure of a quaternary organobismuth compound has been effected by an X-ray diffraction study of a single crystal of tetraphenylbismuth perchlorate [17]. The compound was found to consist of tetrahedral Ph_4Bi^+ and ClO_4^- ions. The C-Bi bond distance was 2.18(2)Å, a value not significantly different from the corresponding distance in other organobismuth(V) compounds. The C-C and Cl-O bond lengths were also in accord with accepted values. Tetraphenylbismuth perchlorate has been included in a study of the preparation and vibrational spectra of a number of tetraphenylbismuth derivatives [18]. The perchlorate was prepared by the interaction of triphenylbismuth dichloride and silver perchlorate in acetylacetone or methyl ethyl ketone. Tetraphenylbismuth tetrafluoroborate was obtained in a similar manner, but reaction of the dichloride with other silver salts did not result in the formation of tetraphenylbismuth compounds. Metathetical reaction of tetraphenylbismuth perchlorate with potassium thiocyanate yielded tetraphenylbismuth thiocyanate, but other derivatives could not be prepared by this method. The compounds Ph_4BiX, where X was PF_6, CCl_3CO_2, NCO, or NO_3, were obtained by the metathetical reaction of tetraphenylbismuth chloride with the appropriate silver salt. The reaction of the chloride with sodium azide or potassium selenocyanate yielded tetraphenylbismuth azide or selenocyanate, but these compounds decomposed rapidly at room temperature to give triphenylbismuthine. Attempts to prepare tetraphenylbismuth fluoride, hydroxide, acetate, trifluoroacetate, acetylacetonate, carbonate, oxalate, sulfate, selenate, and chromate were unsuccessful. The vibrational spectra of tetraphenylbismuth perchlorate, tetrafluoroborate, and hexafluorophosphate clearly showed the presence of the free anion and were consistent with a tetrahedral BiC_4 skeleton for the cation. In acetonitrile or nitromethane, these three bismuth compounds behaved as 1:1 electrolytes. Tetraphenylbismuth nitrate and thiocyanate were also 1:1 electrolytes in these solvents, but their IR spectra indicated that the anionic groups were present as monodentate ligands, and the Raman spectra suggested a trigonal-bipyramidal skeleton, with the four phenyl groups occupying one axial and three equatorial positions and the anionic group at the remaining axial position. Tetraphenylbismuth trichloroacetate and cyanate were weak electrolytes in both acetonitrile and nitromethane. Their vibrational spectra left little doubt that these compounds were non-ionic derivatives of five-coordinate bismuth. Molecular weight determinations in benzene gave normal values for the nitrate and trichloroacetate and hence confirmed the molecular constitution of these compounds. The cyanate and thiocyanate decomposed in benzene, alcohol, or acetone to give triphenylbismuthine as the sole bismuth-containing product.

A study has been made of the interaction of tetraphenylbismuth tetrafluoroborate with the electron donors tetramethyl-*p*-phenylenediamine (TMPD) and triphenylphosphine [19]. In both cases reactions occurred readily at room temperature in acetone under the influence of diffuse light. The reaction with TMPD gave triphenylbismuthine, benzene, and the radical cation $TMPD^{\dot{+}}$ (detected by ESR). It was concluded that the tetraphenylbismuth cation had accepted an electron and had been reduced to the corresponding radical. An analogous process was suggested for the photochemical reaction of tetraphenylbismuth tetrafluoroborate with triphenylphosphine, which led to the formation of tetraphenylphosphorus tetrafluoroborate (90% yield), benzene (10%), and triphenylbismuthine. A thermal reaction between tetraphenylbismuth tetrafluoroborate and triphenylphosphine in refluxing acetone was also observed. This reaction required several days to give a 50% yield of tetraphenylphosphorus tetrafluoroborate; triphenylbismuthine was also isolated from the reaction mixture.

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