Organobismuth(v) Compounds. Part VII.[1] Preparation, Characterization, and Vibrational Spectra of Four- and Five-co-ordinate Tetraphenylbismuth(v) Derivatives

By **Ronald E. Beaumont** and **Ram G. Goel**,* Department of Chemistry, University of Guelph, Guelph, Ontario, Canada

New tetraphenylbismuth(v) compounds Ph_4BiX (X = BF_4, PF_6, NCO, NCS, and CCl_3CO_2) have been prepared. These compounds, together with the previously known Ph_4BiClO_4 and Ph_4BiNO_3, have been studied by i.r. and laser Raman spectroscopy and by molecular-weight and conductance measurements. The vibrational spectra and conductance data for the derivatives, where X = ClO_4, BF_4, or PF_6, are consistent with an ionic constitution. The nitrate, trichloroacetate, thiocyanate, and cyanate compounds are indicated to be non-ionic, containing five-co-ordinate bismuth. Molecular-weight data for the nitrate and trichloroacetate compounds, in benzene, are also in accord with a five-co-ordinate structure; the thiocyanate and the cyanate compounds decompose in benzene. Assignments for vibrational frequencies associated with the Bi–Ph bonds for the ionic and five-co-ordinate derivatives are discussed.

ALTHOUGH quaternary organobismuth compounds [2] were first prepared in 1952, their chemistry has remained unexplored. From the reaction of pentaphenylbismuth(v) with hydrogen chloride or with bromine, Wittig and Claus [2] obtained tetraphenylbismuth(v) chloride, bromide, and the perbromide, all of which were found to decompose at room temperature. These workers also isolated relatively stable tetraphenylbismuth(v) tetraphenylborate, perchlorate, and nitrate. The formation of a water-soluble tetraphenylbismuth(v) sulphate [2] was also reported but the compound was not isolated. In another study,[3] Doak and his co-workers prepared tetraphenylbismuth(v) perchlorate from an unusual reaction of triphenylbismuth(v) dichloride with silver(i) perchlorate; the i.r. spectrum was also reported.

By analogy with quaternary organic derivatives of other main group V elements, the tetraphenylbismuth(v) derivatives have been described [4] as onium salts containing the tetraphenylbismuthonium cation, $BiPh_4^+$. Although the i.r. spectrum [3] of tetraphenylbismuth(v) perchlorate is in accord with an ionic structure, no structural information is available for other tetraphenylbismuth(v) derivatives. Recent studies on a number of

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tetraphenylantimony(V) compounds[5-12] have, however, shown that only a few derivatives, such as the perchlorate,[6] can be considered as salt-like stibonium compounds. Numerous other tetraphenylantimony(V) derivatives,[5-12] which have been studied in this laboratory or elsewhere, have been shown to be molecular compounds. The structures of tetraphenylantimony(V) methoxide[7] and hydroxide[8] have been determined by *X*-ray crystallography and both compounds have been found to possess a trigonal-bipyramidal structure.

The object of the present study was to isolate a variety of relatively stable tetraphenylbismuth(V) compounds and to elucidate their constitution and structural features. In a preliminary communication[13] evidence was presented for a five-co-ordinate structure for tetraphenylbismuth(V) nitrate and trichloroacetate. In this paper we report the preparation, characterization, and i.r. and laser Raman spectra of several four- and five-co-ordinate tetraphenylbismuth(V) compounds.

EXPERIMENTAL

Triphenylbismuth(V) dichloride was prepared as described previously.[14] Tetraphenylbismuth(V) chloride was prepared by the method of Wittig and Claus.[2] Except for spectroscopic grade benzene and nitromethane, all other chemicals and solvents were of reagent grade purity. Acetonitrile was dried by treatment with calcium hydride and subsequent distillation. Microanalyses were performed in this department or by the Schwarzkopf Microanalytical Laboratory, Woodside, New York. Analytical data are recorded in Table 1.

TABLE 1

Analytical (%) and conductance data for Ph_4BiX compounds

	C		H		Molar conductance, Λ_m [a]	
Compound	Calc.	Found	Calc.	Found	In $MeNO_2$	In MeCN
Ph_4BiClO_4	46·7	46·25	3·25	3·25		163·54
Ph_4BiBF_4	47·7	47·45	3·10	3·35	74·70	130·00
Ph_4BiPF_6	43·5	43·75	3·00	3·20		116·10
Ph_4BiNO_3 [b]	49·7	49·95	3·45	3·45	96·40	136·20
$Ph_4BiCCl_3CO_2$	45·9	45·4	2·95	2·95	1·50	29·28
Ph_4BiNCS [c]	52·15	51·7	3·50	3·50	61·10	150·28
Ph_4BiNCO [d]	53·65	52·0	3·60	3·65	22·00	53·90

[a] In Ω^{-1} cm^2 mol^{-1}; concn. *ca.* 10^{-3}M. [b] For N: calc., 2·45; found, 2·25%. [c] For N: calc., 2·25; found, 2·20%. [d] For N: calc., 2·50; found, 2·10%.

Preparation and Properties of Ph_4BiX *Derivatives.*—Contrary to the results of Doak and his co-workers,[3] the reaction between triphenylbismuth(V) dichloride and silver(I) perchlorate, afforded three products: acetonyltriphenylbismuth(V) perchlorate, $[Ph_3Bi(CH_2COMe)](ClO_4)$ (I); oxobis-(aquotriphenylbismuth) diperchlorate, $O[Ph_3Bi(H_2O)]_2(ClO_4)_2$ (II); and tetraphenylbismuth(V) perchlorate in very small yield. Further examination of this reaction has shown[15,16] that either (I) or (II) can be prepared in good yield from this reaction by selecting suitable solvents. However, tetraphenylbismuth(V) perchlorate was obtained as the only bismuth-containing species when the above reaction was carried out in acetylacetone or methyl ethyl ketone. Tetraphenylbismuth(V) tetrafluoroborate was also obtained in a similar manner, but reaction with other silver(I) salts did not result in the formation of a tetraphenylbismuth(V) compound. Metathetical reaction of tetraphenylbismuth(V) perchlorate with potassium thiocyanate afforded tetraphenylbismuth(V) thiocyanate but other derivatives could not be obtained by this method. The compounds Ph_4BiX ($X = PF_6$, CCl_3CO_2, NCO, and NO_3) were isolated by the metathetical reaction of tetraphenylbismuth(V) chloride. The reaction of the chloride with sodium azide or potassium selenocyanate afforded tetraphenylbismuth(V) azide * or selenocyanate * which decomposed rapidly at room temperature to give triphenylbismuth. Attempts to isolate a number of other derivatives such as the fluoride, hydroxide, acetate, trifluoroacetate, acetylacetonate, carbonate, oxalate, sulphate, selenate, and chromate, were unsuccessful.

Reaction of triphenylbismuth(V) *dichloride with silver*(I) *salts.* An ethanol solution of $AgClO_4$ and an acetone solution of Ph_3BiCl_2 were allowed to react as described by Doak and his co-workers.[3] After filtration of the precipitated silver(I) chloride and subsequent concentration and cooling (in a refrigerator) of the filtrate, a crystalline product was obtained which was filtered and dried. It was found to contain the compound $[Ph_3Bi(CH_2COMe)](ClO_4)$ and a

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* The i.r. spectra of these compounds showed azide and selenocyanate bands at 2020 and 2060 cm^{-1}, respectively. The phenyl bands for both compounds were also similar to those observed for the relatively stable derivatives.

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very small amount of Ph_4BiClO_4. Addition of an excess of water to the filtrate, dropwise with stirring, yielded a precipitate of $O[Ph_3Bi(H_2O)]_2(ClO_4)_2$. Reaction between two equivalents of $AgClO_4$ or $AgBF_4$ and a solution of Ph_3BiCl_2 in acetylacetone or methyl ethyl ketone caused immediate precipitation of AgCl. After stirring (0·5 h), the precipitated silver(I) chloride was filtered off and the filtrate was concentrated and cooled (in a refrigerator) to yield crystals of Ph_3BiClO_4 or Ph_3BiBF_4 which were recrystallized from acetone and diethyl ether. A similar reaction in ethanol, acetonitrile, or chloroform resulted in the isolation of $O[Ph_3Bi(H_2O)]_2(ClO_4)_2$ as the only bismuth-containing species.

Tetraphenylbismuth(V) *cyanate and thiocyanate.* (*a*) The compound Ph_4BiCl was converted into Ph_4BiNCS or Ph_4BiNCO by stirring it with an excess of KOCN or KSCN in cold water (0 °C) for 15 min. The mixture was then filtered and the solid was washed several times with cold water and finally with diethyl ether. Attempts to recrystallize either compound from benzene or acetone resulted in decomposition.

(*b*) The compound Ph_4BiClO_4 was dissolved in absolute alcohol at 0 °C. A large excess of KSCN was added and the solution was stirred on a cold plate (2 h). The excess of KSCN and insoluble $KClO_4$ were filtered off. Water was then added to the filtrate producing a white precipitate of Ph_4BiNCS which was filtered and washed with water and diethyl ether.

Tetraphenylbismuth(V) *trichloroacetate.* An aqueous solution of silver(I) trichloroacetate was prepared by dissolving a calculated amount of Ag_2O in an aqueous solution of trichloroacetic acid. One equivalent of Ph_4BiCl dissolved in cold acetone (0 °C) was added to this solution with constant stirring. After stirring for 15 min, the precipitated silver(I) chloride was filtered off and the filtrate concentrated *in vacuo* until it became cloudy. Upon cooling the solution in a refrigerator, fine needles of $Ph_4Bi(CCl_3CO_2)$ were obtained. No suitable solvent was found for recrystallization.

Tetraphenylbismuth(V) *nitrate.* An excess of potassium nitrate was added to a suspension of Ph_4BiCl in water at 0 °C. The mixture was stirred (15 min) and the white solid which formed was filtered off and washed with cold water and diethyl ether. Recrystallization from benzene and light petroleum gave fine needles of Ph_3BiNO_3. This compound was also obtained from the reaction of Ph_4BiCl with $AgNO_3$ in cold methanol (0 °C).

Tetraphenylbismuth(V) *perchlorate, tetrafluoroborate, and hexafluorophosphate.* One equivalent of $AgClO_4$ was added to a solution of Ph_4BiCl in anhydrous acetone at 0 °C. The mixture was stirred (15 min, 0 °C) and the precipitated AgCl was filtered off. Upon concentrating the filtrate, a white solid was deposited which was recrystallized from anhydrous acetone and diethyl ether to yield crystals of Ph_4BiClO_4. The tetrafluoroborate and the hexafluorophosphate compounds were obtained by a similar procedure.

Although all the tetraphenylbismuth(V) compounds prepared in this study eventually decompose at room temperature, the compounds listed in Table 1 are relatively stable and could be kept at room temperature for at least a few hours. The first three compounds did not show any noticeable decomposition over a period of 1 week. The last four compounds are less stable and their decomposition was noticeable within 24 h; among these the trichloroacetate appears to be the least stable. All the compounds in Table 1, except the nitrate, are insoluble in water. The perchlorate, tetrafluoroborate, and the hexafluorophosphate compounds are soluble in polar organic solvents such as acetone and alcohol, but are insoluble in benzene. The cyanate, thiocyanate, nitrate, and the trichloroacetate compounds are soluble in benzene.

Physical Measurements.—Molecular weights were determined with a Hitachi–Perkin-Elmer model 115 vapour osmometer. Electrical conductivities were measured with a Beckman model RE-18A conductivity bridge using a glass cell with platinized-platinum electrodes. Raman spectra were obtained on either a Spex model 1400 spectrometer equipped with a helium–neon laser or a Cary model 82 spectrophotometer equipped with an argon-ion laser. Spectra were measured on powdered samples in glass melting-point tubes. I.r. spectra were recorded on a Beckman IR-12 double-beam spectrophotometer. Solid samples were prepared as mulls in Nujol, Halocarbon oil, or hexachlorobuta-1,3-diene and spectra were obtained using KRS-5, caesium iodide, or polyethylene windows. Demountable silver(I) bromide cells were used for measuring spectra in solution.

RESULTS AND DISCUSSION

As shown in Table 1, the Ph_4BiX compounds ($X = ClO_4$, BF_4, PF_6, NO_3, and NCS) behave as 1 : 1 electrolytes,[17] in acetonitrile or nitromethane. The cyanate and the trichloroacetate compounds are only weakly conducting in these solvents. Thus, the behaviour of tetraphenylbismuth(V) compounds in nitromethane or acetonitrile is very similar to that of analogous tetraphenylantimony(V) compounds.[5,6] Tetraphenylbismuth(V) nitrate and trichloroacetate behave as molecular species in benzene as shown by the observed molecular-weight values of 574 and 686, respectively. The cyanate and the thiocyanate compounds decomposed in benzene, alcohol, or acetone to give triphenylbismuth as the sole bismuth-containing species.

I.r. spectra (4000—200 cm^{-1} region, in the solid state) of all the Ph_4BiX compounds included in this work showed very similar bands due to those of the phenyl group and their assignments will be discussed later. I.r. absorption frequencies for tetraphenylbismuth(V) perchlorate have been reported [3] previously and our results are in agreement. For each compound, i.r. wavenumbers due to the anion group and their suggested assignments are listed in Table 2. The observed wavenumbers for the perchlorate, tetrafluoroborate, and hexafluorophosphate compounds clearly show the presence of the free anion.[18,19] The spectrum for the nitrate compound showed a strong band at 1305 cm^{-1} and two bands of medium intensity at 1032 and 825 cm^{-1}, which can be assigned, respectively, to the NO_2 symmetric stretch, the NO stretch, and the out-of-plane rocking modes of a

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monodentate ONO_2 group.[20,21] The NO_2 antisymmetric stretching frequency,[19,20] expected for the monodentate nitrato-group at *ca.* 1450 cm^{-1}, could not be identified due to the complexity of the spectrum in the 1500—1305 cm^{-1} region. However, the solution spectrum in benzene, in the 1600—1200 cm^{-1} region, showed two strong nitrato-group bands at 1445 and 1295 cm^{-1}.

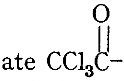
TABLE 2

Anion wavenumbers [a] of Ph_4BiX compounds

Compound	Wavenumber	Assignment
Ph_4BiClO_4	628s	δ(OClO), ν_4
	1080vs	ν_{asym}(Cl–O), ν_3
Ph_4BiBF_4	520s	δ(FBF), ν_4
	1075vs	ν_{asym}(B–F), ν_3
Ph_4BiPF_6	558s	δ(FPF). ν_4
	825—850vs	ν_{asym}(P–F), ν_3
Ph_4BiNO_3	825m	Out-of-plane rock
	1032m	ν(NO)
	1295s [b]	$\nu_{sym}(NO_2)$
	1442s [b]	$\nu_{asym}(NO_2)$
$Ph_4BiCCl_3CO_2$	1300s	ν(CO)
	1680s	ν(C=O)
Ph_4BiNCS	470w	δ(NCS)
	762w	ν(CS)
	2040s	ν(CN)
Ph_4BiNCO	626 636 } w	δ(NCO)
	1250m	ν(CO)
	2160s	ν(CN)

s = Strong, vs = very strong, b = broad, m = medium and w = weak.

[a] In cm^{-1} in the solid state, except stated otherwise. [b] In benzene.

The difference between the antisymmetric and symmetric NO_2 stretching frequencies is 150 cm^{-1} which is comparable to that observed for tetraphenylantimony(V) nitrate.[5] The spectrum of the trichloroacetate compound showed two strong bands at 1680 and 1300 cm^{-1} which can be assigned to the C=O and C–O stretching frequencies of the monodentate  $CCl_3\overset{O}{\overset{\|}{C}}–O$ group.[14,22] The separation between ν(C=O) and ν(C–O) is also comparable to that for the analogous antimony derivative.[5]

The NCS frequencies for tetraphenylbismuth(V) thiocyanate were observed at 2040, 762, and 470 cm^{-1}. These bands are also very similar to those for tetraphenylantimony(V) thiocyanate [5] and can be assigned, respectively, to ν(CN), ν(CS), and δ(NCS) modes of an *N*-bonded NCS group.[23] For tetraphenylbismuth(V) cyanate, ν(CN) and δ(NCO) frequencies, observed at 2160 and 646,626 cm^{-1}, respectively, are similar to those reported for the free cyanate ion.[24,25] However, a single band at 1210 cm^{-1} was observed for this compound due to the ν(CO) frequency, whereas for the free cyanate ion two bands at *ca.* 1300 and 1200 cm^{-1} are observed due to Fermi resonance between ν(CO) and the overtone of δ(NCO). Although i.r. spectral data [23] available for a number of metal cyanato-complexes indicate that Fermi resonance observed in the free cyanate ion is eliminated on co-ordination, the data do not provide reliable criteria [23] for determining the mode of bonding of the cyanate ion. Therefore, no conclusion regarding the constitution of tetraphenylbismuth(V) cyanate can be drawn from its i.r. spectrum. However, in view of the conductance results, there can be little doubt that this compound is also five-co-ordinate.

I.r. and Raman bands due to the Bi–Ph bonds for the Ph_4BiX compounds (X = ClO_4, NO_3, CCl_3CO_2, and NCS) in the low-frequency region, together with their assignments, are listed in Table 3. Due to limited solubility of these compounds or their decomposition in solution, Raman polarization measurements could not be carried

TABLE 3

Laser-Raman and i.r. spectroscopic data (cm^{-1}) for Ph_4BiX compounds in the solid state

Ph_4BiClO_4		Ph_4BiNCS		Ph_4BiNO_3		$Ph_4BiCCl_3CO_2$		
Raman	I.r.	Raman	I.r.	Raman	I.r.	Raman	I.r.	Assignments
	685s		685s		685s		685s	*v* mode
655 646 } ms	652mw	648 642 } s	650w	650ms	650mw	650ms	650w	*r* mode
610w	610w	610w	610w	610vw	610w		610w	*s* mode
	445 435 } s	448w	448 438 } s		445s		445 440 } s	*y* mode
		400vw	400vw		405vw			*w* mode
245mw	242s	240m	245s	245sh	245s	243sh	248s	ν_{asym}(Bi–Ph)
230sh	230sh	225mw	225w		230sh		235mw	*u* mode
214s		209s		215s		216s		ν_{sym}(Bi–Ph)
		199s		205s		206s		ν_{sym}(Bi–Ph)
163m		165m		166m		174m		*x* mode
104vs		100vs		105vs		105vs		Lattice mode

m = Medium, s = strong, v = very, w = weak.

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out. The assignments for the frequencies above 250 cm^{-1} are straightforward and follow from those suggested [26-31] for other phenyl derivatives of Group IV and V elements. Assignments for frequencies below the 250 cm^{-1} region have been made by comparison with those for triphenylbismuth(V) dihalide compounds [14,32] and phenyl derivatives of lead(IV).[27,28] A strong polarized Raman band at *ca.* 200 cm^{-1} is also observed for triphenylbismuth and it has been assigned to the *x* mode in one study [31] and to the *y* mode in another.[29] However, in view of the Raman data [32] for triphenylbismuth(V) dihalide compounds, there can be little doubt that this band is due to the symmetric Bi–Ph stretching mode.

Although it is difficult to establish the structures of Ph_4BiX compounds from the vibrational spectra, the observed Raman bands for Ph_4BiClO_4, in the Bi–Ph stretching region, are consistent with a tetrahedral BiC_4 skeleton. Raman spectra of five-co-ordinate Ph_4BiX compounds show an additional band in the region of the Bi–Ph symmetric stretching frequency. For a trigonal-bipyramidal skeleton, with four phenyl groups occupying one axial and three equatorial positions and the X group at the remaining axial position, the local symmetry is C_{3v} and three Raman-active bismuth–phenyl stretching frequencies are expected. Thus, Raman spectra of the five-co-ordinate compounds can be interpreted in terms of a C_{3v} local symmetry, and the two strong Raman bands in the 200 cm^{-1} region can be assigned to the two totally symmetric bismuth–phenyl stretching modes. Recently Orenberg and his co-workers [33] reported the low-frequency Raman spectra of some four- and five-co-ordinate tetraphenylantimony(V) derivatives. Although we do not agree with the assignments for the skeletal modes proposed by these workers, their spectral data also show that the Raman spectra of the five-co-ordinate tetraphenylantimony(V) derivatives are characterized by additional bands which are absent in the spectra of the four-co-ordinate species.

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