

TETRAPHENYLBISMUTH DERIVATIVES CONTAINING PENTA-COORDINATE BISMUTH

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Quarternary organic derivatives of the main group V elements have been considered to be ionic compounds containing the tetrahedrally coordinated onium cation. Recently, however, a number of tetraphenyl- and tetramethyl-antimony derivatives<sup>1-8</sup> have been shown to be molecular compounds containing five - or six-coordinate antimony. Quarternary organobismuth compounds<sup>9</sup> were first prepared twenty years ago and by analogy with the corresponding phosphonium and arsonium derivatives, these derivatives have also been described as bismuthonium salts. In this communication we report for the first time examples of quarternary organobismuth derivatives possessing a molecular constitution.

Tetraphenylbismuth nitrate (I) and the trichloroacetate (II) were obtained by the metathetical reactions of tetraphenylbismuth chloride<sup>9</sup> (III). Unlike (III) which decomposes in a few minutes at room temperature, (I) and (II) are stable at room temperature for at least a few hours. Evidence for the molecular constitution of (I) and (II) is provided by the molecular weight and the i.r. spectroscopic data which are summarised in the Table. The nitrate frequencies as well as the CO<sub>2</sub> stretching frequencies are in accord with the presence of a monodentate ONO<sub>2</sub><sup>10</sup> or OCOCCl<sub>3</sub><sup>11</sup> group. Also, these frequencies are comparable to those observed for the analogous tetraphenylantimony derivatives<sup>3</sup>. The molar conductances for (II) in nitromethane or in acetonitrile are also in accord with a non-ionic constitution. (I) is, however, ionized in these solvents.

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TABLE  
I.r. frequencies ( $\text{cm}^{-1}$ ) and molecular weight  
data for  $\text{Ph}_4\text{BiONO}_2$  and  $\text{Ph}_4\text{BiOCOCCl}_3$

	Molecular Weight		I.r. frequencies	Assignments
	Found	Required		
$\text{Ph}_4\text{BiONO}_2$	574	579	1442s <sup>†</sup>	$\nu_{\text{asym.}}(\text{NO}_2)$
			1295s <sup>†</sup>	$\nu_{\text{sym.}}(\text{NO}_2)$
			1032m <sup>‡</sup>	$\nu(\text{NO})$
			825m <sup>‡</sup>	$\text{ONO}_2$ out of plane rock
$\text{Ph}_4\text{BiOCOCCl}_3$	686	680	1680s <sup>‡</sup>	$\nu_{\text{asym.}}(\text{OCO})$
			1300s <sup>‡</sup>	$\nu_{\text{sym.}}(\text{OCO})$

<sup>†</sup> In benzene; <sup>‡</sup> in solid state as mull in Nujol

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