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The ^{1}H nuclear magnetic resonance spectra of some organobismuth compounds

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Complex ^{1}H NMR spectra of organic compounds are sometimes transformed so that they become amenable to first-order analysis, by the addition of derivatives of transition metals or inner-transition metals. These so-called paramagnetic shifts occur particularly in the presence of metals with high nuclear magnetic moments, such as cobalt[1], europium[2,3], and praeseodymium[4]. It is shown here that certain organobismuth compounds show spectra which are analysed easily without the addition of a shift reagent, and provide simpler models than other metal aryls[5] for the study of the anisotropy associated with carbon—metal bonds[6].

Compounds of the type $ArBiX_2$, where X is an electronegative group, give apparent first order spectra at 60 MHz. The resolution is much greater than in Ar_2BiX, Ar_3Bi, or Ar_3BiX_2. Some disproportionation occurs in solution, and the products are identified by their chemical shifts. Typical data are recorded in Table 1. The ^{1}H NMR spectra of phenylbismuth dichloride in dimethyl sulphoxide is reproduced in Fig.1. The *o*-, *m*-, and *p*-protons appear as well-defined doublet, triplet, and triplet respectively, $^3J(H—H) \sim 8.0$ Hz, $^4J(H—H) \sim 1.5$ Hz. Solutions in acetonitrile and other donor solvents give similar spectra, in which the seperation between *m*- and *p*-protons is even greater than that reported for benzyl alcohol in the presence of tris(dipivalomethanato)europium[3].

TABLE 1

^{1}H NMR DATA FOR ARYLBISMUTH COMPOUNDS IN DIMETHYL SULPHOXIDE

	τ (ortho)	τ(meta)	τ (para)
$PhBiCl_2$	1.00	2.08	2.62
$PhBi(O_2SPh)_2$	1.21	2.08	^{d}
o-$TolBiBr_2$	0.66	2.17 ^{b}, 2.23 ^{c}	2.68
m-$TolBiBr_2$	0.95 ^{a}, 1.01 ^{b}	2.14	2.77
p-$TolBiBr_2$	0.97	2.30	—
$(p\text{-}Tol)_2BiBr$	1.76	2.60	—
$(p\text{-}Tol)_3Bi$	2.40	2.82	—

^{a} Singlet. ^{b} Doublet. ^{c} Triplet. ^{d} Obscured by benzenesulphinato signal.

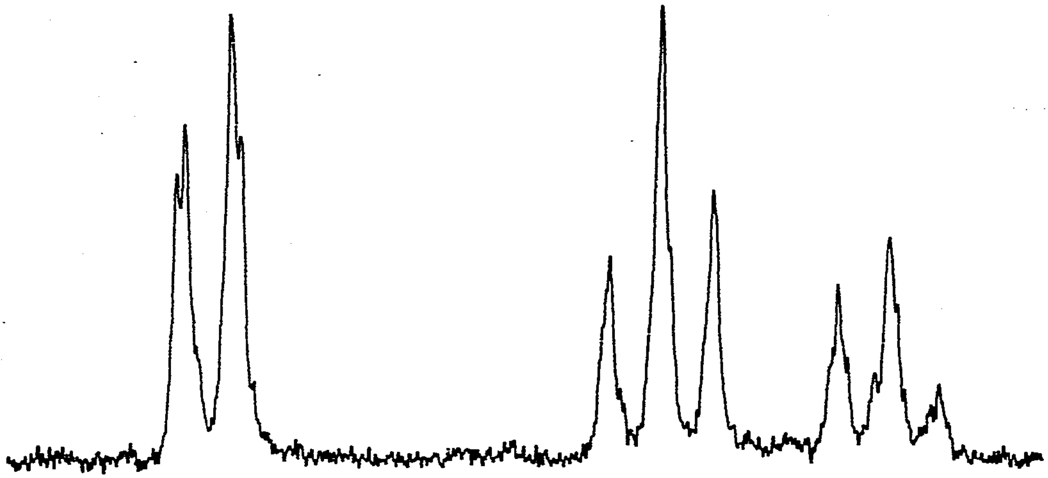

Fig.1. 60 MHz ^{1}H NMR spectrum of $PhBiCl_2$ in dimethyl sulphoxide.

Mono-, bis-, and tris-sulphinato derivatives have been prepared from reactions of various organobismuth compounds with liquid sulphur dioxide. The ^{1}H NMR spectrum of $PhBi(O_2SPh)_2$, which is prepared also from phenylbismuth dichloride with salts of benzene sulphinic acid, and triphenylbismuth with the free acid[7], confirms that sulphur dioxide undergoes insertion, and that a dithionite structure[8] can be rejected.

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