

## Long-range Spin-Spin Coupling in Toly-lead Compounds

By W. KITCHING, V. G. KUMAR DAS, and P. R. WELLS

(Chemistry Department, University of Queensland, Brisbane, Australia)

WITH the notable exception of some organothallium derivatives,<sup>1</sup> spin-spin coupling between aromatic protons and metal-containing substituents has not been reported. There have in fact been few <sup>1</sup>H nuclear magnetic resonance studies on arylmetal compounds.<sup>2</sup>

Solubility problems notwithstanding, the *p*-tolyl-lead compounds are ideal subjects for a preliminary examination of the magnitude and sign of some of the spin-spin coupling constants. Since the *meta* and *para* proton-proton coupling constants are small, the AA'BB' aromatic proton spectrum approximates fairly closely to an AB spectrum and some of the satellites arising from <sup>207</sup>Pb of natural abundance 21.1% are clearly visible.

The results tabulated were obtained employing an AB analysis for the main aromatic proton spectrum and an ABX analysis, where X = <sup>207</sup>Pb, for the satellites. Not all of the AB lines of the ABX spectra are visible, but from the 60 Mc./sec.

and 100 Mc./sec. spectra together with the values of  $\nu_{AB}$ ,  $J_{AB}$ ,  $\nu_A - \nu_B$  from the main spectrum, unique values for  $J_{AX}$  and  $J_{BX}$  can be obtained.

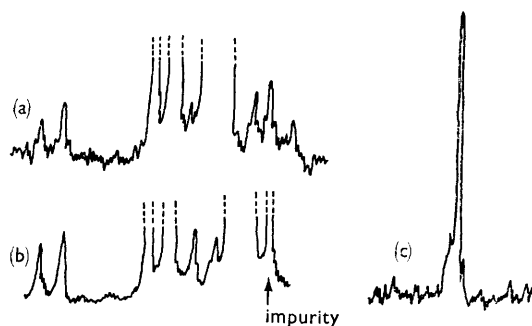


FIGURE. <sup>1</sup>H n.m.r. spectra of tetra-*p*-tolyl-lead in CDCl<sub>3</sub> solution: (a) aromatic region at 60 Mc./sec., (b) at 100 Mc./sec., (c) methyl region at 60 Mc./sec.

TABLE

	CDCl <sub>3</sub>		(p-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> ) <sub>4</sub> Pb CH <sub>2</sub> Cl <sub>2</sub> *		THF	(p-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> ) <sub>6</sub> Pb <sub>2</sub>	
	60 Mc./sec.	100 Mc./sec.	60 Mc./sec.	100 Mc./sec.	60 Mc./sec.	CDCl <sub>3</sub> 60 Mc./sec.	CH <sub>2</sub> Cl <sub>2</sub> 60 Mc./sec.
<i>p</i> -CH <sub>3</sub> (τ) .. ..	7.65	7.69 ± 0.01	7.67	7.64 ± 0.01	—	7.65	7.69
<i>J</i> (Pb-CH <sub>3</sub> ) (c./sec.)	~6	5.40 ± 0.3	~6	~6	—	~6	~6
$\nu_A$ (τ) .. ..	2.48	2.52 ± 0.02	2.52	2.51 ± 0.02	2.57	2.51	2.55
$\nu_B$ (τ) .. ..	2.77	2.80 ± 0.02	2.79	2.75 ± 0.02	2.83	2.78	2.85
<i>J</i> <sub>AB</sub>   (c./sec.) ..	7.9	7.7 ± 0.5	~7	7.8 ± 0.4	~7.5	8	8
<i>J</i> <sub>AX</sub> (c./sec.) ..	±80		±79		±80	±80	—
<i>J</i> <sub>BX</sub> (c./sec.) ..	±24		±25		±24	±24	—

\* CH<sub>2</sub>Cl<sub>2</sub> at τ 4.68 ± 0.03 with *J*(<sup>13</sup>C-<sup>1</sup>H) = 176.5 ± 5 c./sec.

Since the high-field half-spectrum, *i.e.*, proton B, is broadened relative to the low-field half-spectrum, we identify this as the proton *ortho* to the methyl group. Its  $\tau$ -value is essentially that corresponding to the aromatic protons of toluene. Proton A shows the result of a small low-field shift due to the lead substituent.† The  $^{207}\text{Pb}$ - $^1\text{H}$  coupling constant is largest for proton A which is *ortho* to the metal and both coupling constants have the same sign. Most noteworthy is  $J(^{207}\text{Pb}-\text{CH}_3)$  arising from an interaction which formally traverses *six* covalent bonds.

† Bearing in mind the electropositive character of the metal a small *high*-field shift might have been expected. Presumably the low-field shift is to be ascribed to the paramagnetic shielding observed by Drago and Matwiyoff in tetramethyl-lead (ref. 3).

<sup>1</sup> J. P. Maher and D. F. Evans, *J. Chem. Soc.*, 1963, 5534.

<sup>2</sup> *cf.*, M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organometallic Chem.*, 1965, 3, 1.

<sup>3</sup> R. S. Drago and N. A. Matwiyoff, *J. Organometallic Chem.*, 1965, 3, 62.

It is of some interest that both the aromatic proton chemical shifts and the coupling constants are almost unaffected by the change from the  $\text{Ar}_4\text{Pb}$  to the  $\text{Ar}_6\text{Pb}_2$  species. There also appears to be essentially no solvent effect, although this needs to be probed for a wider range of solvent types. We are currently examining a series of substituted phenyl derivatives of lead, mercury, and tin to gather further information in this area.

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