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A CORRELATION OF $J_{Pb^{207}-C-H^{1}}$ WITH INDUCTIVE EFFECT PARAMETERS (σ^{*}-VALUES) OF ALKYL GROUPS

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Although sufficient effort has been made in recent years to relate chemical shifts with electronic properties of substituents (1-3), little is known about similar correlations between spin-spin coupling constants of protons with homo or hetero nuclei and the electronic parameters of the substituents. The purpose of this communication is to report such a correlation.

In the course of our continued interest in the proton magnetic resonance (p.m.r.) studies of organolead compounds (4), we have now prepared some alkyltrineopentyllead derivatives, and have measured their p.m.r. spectra. One of the interesting features of the p.m.r. data of these compounds is that a linear relationship exists between $J_{Pb^{207}-C-H^{1}}$ and the polar substituent constants (σ^{*}-values) (5) of the alkyl groups. The pertinent data are presented in Table I and the relationship is shown in Figure 1.

TABLE I

Proton Magnetic Resonance Data[a]

Compound	CH_2[b]	
	CH_2[c]	J_{Pb^{207}, H_α}[d]
$[(CH_3)_3CCH_2]_3PbCH_3$	1.65	40.5
$[(CH_3)_3CCH_2]_3PbC_2H_5$	1.67	36.4
$[(CH_3)_3CCH_2]_4Pb$	1.78	33.8
$[(CH_3)_3CCH_2]_3PbCH(CH_3)_2$	1.68	32.5
$[(CH_3)_3CCH_2]_3PbC(CH_3)_3$	1.73	27.5

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[a] The p.m.r. spectra were recorded on 0.5M solutions in deuteriochloroform, using a Varian A-60 spectrometer.

[b] Chemical shifts are in p.p.m. downfield from an internal standard of tetramethylsilane and are accurate to 0.01 p.p.m.

[c] Methylene belonging to the neopentyl groups.

[d] Coupling constants are in c.p.s. and are accurate to 0.2 c.p.s.

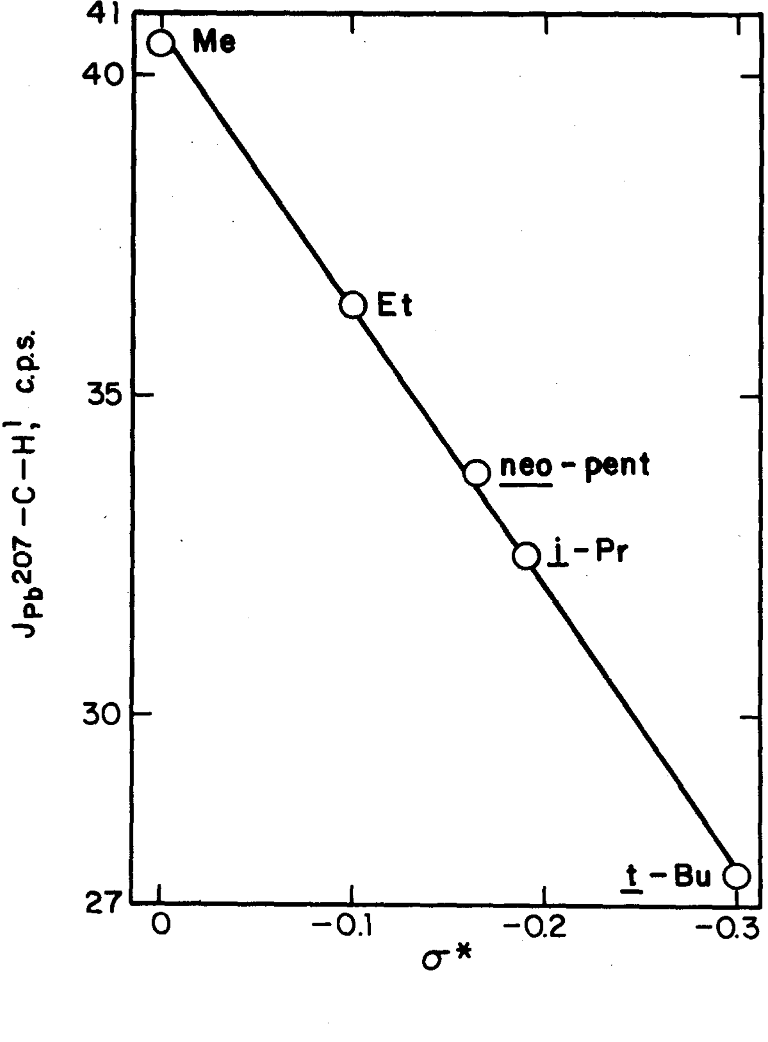
The alkyltrineopentyllead compounds were prepared by the reaction of trineopentylead bromide with appropriate Grignard reagents (eq. 1), and were characterized by C,H analysis,

$$[(CH_3)_3CCH_2]_3PbBr + RMgX \xrightarrow[THF]{Ether\ or} [(CH_3)_3CCH_2]_3PbR + MgBrX \qquad (1)$$

FIGURE 1

CORRELATION BETWEEN $Pb^{207}-C-H^1$ COUPLING CONSTANTS & σ^*-VALUES OF R

$[(H_3C)_3CCH_2]_3PbR$



R = CH_3, C_2H_5, $\underline{i}$-C_3H_7, $\underline{t}$-C_4H_9, and $\underline{neo}$-C_5H_{11}

molecular weight determination, and their p.m.r. spectra.

The linear relationship between $J_{Pb}{}^{207}$, H_α and the σ^*-values of the alkyl groups can be rationalized on the basis of electronic requirements of the alkyl groups. In tetraalkyllead compounds the configuration around the lead atom is tetrahedral, $\underline{sp}^3$ (6,7). The four $\underline{sp}^3$-hybridized atomic orbitals of lead, which form bonds with carbon, will have equal amount of $\underline{s}$-character in the case of symmetrical tetraneopentyllead. However, a redistribution of $\underline{s}$-character in the Pb-C bonds should be expected in the case of alkyltrineopentyllead derivatives depending upon the electronic requirements of the alkyl groups. Applying the principle that <u>s-character of an atom tends to concentrate in orbitals that are directed toward more electropositive groups</u> (8), the order of $\underline{s}$-character in the lead orbitals which are involved in bonding with the neopentyl groups should be: Alkyl = Me>Et>$\underline{neo}$-Pent>$\underline{i}$-Pr>$\underline{t}$-Bu. This is substantiated by the same order of increase in the $J_{Pb}{}^{207}$, H_α values for alkylneopentyllead derivatives (Table I). It is assumed, however, that Fermi contact is the sole contributor to the spin-spin coupling between lead and α protons.

Detailed discussion of the preparation and p.m.r. spectra of the compounds, used in this preliminary communication, will be presented at a later date.

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