# $^{207}$Pb Satellite Spectra and $^{207}$Pb–H Long-range Coupling Constants of the Symmetrical Isomers of Tetrafuryl- and Tetrathienyl-lead

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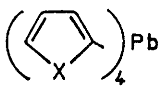
The $^1$H n.m.r. spectra and the $^{207}$Pb satellite bands of the two symmetrical isomers of tetrafuryl- and tetrathienyl-lead have been analysed and all the coupling constants and proton chemical shifts derived. The relative signs of long-range $J(^{207}\text{Pb–H})$ coupling constants appear to be alike, as may be seen by comparing experimental and simulated spectra.

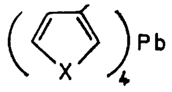
Proton chemical shifts can be interpreted in terms of some degree of $(d-p)\pi$ interactions, while proton–proton coupling constants seem to be only slightly affected by such perturbation.

Long-range $J(^{207}\text{Pb–H})$ coupling constants were found to be mainly determined by the Fermi contact mechanism.

THE n.m.r. properties of the symmetrical isomers of furyl and thienyl compounds of mercury [1] and tin [2] have been the subject of previous reports. Long-range coupling constants between hydrogen and tin or mercury nuclei are proportional to the corresponding proton–proton coupling constants in these systems.[1,2] This indicates that changes in these constants are mainly determined by the Fermi contact mechanism. Proton chemical shifts show behaviour which is in agreement with $(p-d)\pi$ interactions between empty $d$ orbitals of tin and the $\pi$-electron cloud of the heterocyclic ring,[2] this being less important in the case of mercury derivatives. The effectiveness of this kind of interaction seems to be connected with the character of the $d$ orbitals in tin, these being less diffuse than in the mercury atom. The effectiveness of $(d-p)\pi$ interactions for lead derivatives should be lower than for the corresponding compounds of tin, as pointed out previously in studies on the behaviour of Group IVB elements.[3]

Little has so far been published on organometallic compounds of lead containing unsaturated organic systems,[4-9] and the present paper seems to be the first report on heterocyclic derivatives of lead which gives a complete set of long-range lead–proton coupling constants.[†]


(I) X=O
(II) X=S


(III) X=O
(IV) X=S

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[†] A note has recently appeared (A. P. Ebdon, T. N. Huckerby, and F. G. Thorpe, *Tetrahedron Letters*, 1971, 2921) dealing with the n.m.r. spectra of tetra-(2-furyl)lead and tetra-(2-thienyl)lead. The results are in close agreement with ours.

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## RESULTS AND DISCUSSION

The $^{1}$H n.m.r. spectra of compounds (I)—(IV) were recorded with particular attention to the satellite bands generated by the $^{207}$Pb isotope with spin of one half, natural abundance 21·11%.

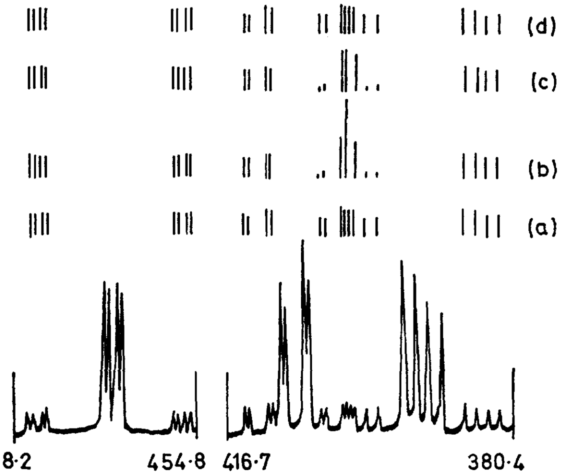
Neither satellite bands nor the main proton spectrum were of the first order, and the parameters were obtained from a complete analysis carried out by means of the LAOCN 3 program.[10] One sample spectrum is shown in the Figure and the results of the spectral analysis in Table 1. The errors in the parameters reported in the Tables refer to the probable error given by the LAOCN program. The reproducibility of the parameters derived both from satellites and main proton spectrum, represented by the Δ values, is within 0·01 p.p.m. for chemical shifts and 0·18 Hz for coupling constants. All the spectra were recorded for solutions in [$^{2}$H]chloroform at room temperature except for compound (IV) where a sample temperature of 50 °C was employed, in order to be able to use a higher concentration and to obtain more intense satellite bands.

TABLE 1

Chemical shifts (p.p.m.) and coupling constants (Hz) of compounds (I)—(IV) resulting from the analysis of both the proton and satellite spectra (in CDCl$_3$); Δ is the difference between parameters obtained from the proton and $^{207}$Pb satellite spectrum

| | Proton spectrum | Satellite spectrum | Δ |
|---|---|---|---|
| | Tetra-(2-furyl)lead | | |
| δ-3 | 6·8009 ± 0·0006 | 6·8009 ± 0·0005 | 0·0000 |
| δ-4 | 6·5431 ± 0·0006 | 6·5402 ± 0·0005 | −0·0029 |
| δ-5 | 7·7721 ± 0·0006 | 7·7799 ± 0·0005 | −0·0078 |
| *J*(3–4) | 3·16 ± 0·05 | 3·05 ± 0·04 | 0·11 |
| *J*(3–5) | 0·61 ± 0·05 | 0·62 ± 0·04 | −0·01 |
| *J*(4–5) | 1·63 ± 0·05 | 1·63 ± 0·04 | 0·00 |
| *J*(Pb–3) | | 9·82 ± 0·06 | |
| *J*(Pb–4) | | 15·78 ± 0·06 | |
| *J*(Pb–5) | | 18·29 ± 0·06 | |
| | Tetra-(2-thienyl)lead | | |
| δ-3 | 7·4316 ± 0·0006 | 7·4282 ± 0·0003 | 0·0034 |
| δ-4 | 7·3178 ± 0·0006 | 7·3272 ± 0·0004 | −0·0094 |
| δ-5 | 7·7091 ± 0·0006 | 7·7159 ± 0·0005 | −0·0068 |
| *J*(3–4) | 3·23 ± 0·04 | 3·37 ± 0·03 | −0·14 |
| *J*(3–5) | 0·87 ± 0·04 | 0·80 ± 0·03 | 0·07 |
| *J*(4–5) | 4·79 ± 0·04 | 4·82 ± 0·03 | 0·03 |
| *J*(Pb–3) | | 58·71 ± 0·03 | |
| *J*(Pb–4) | | 18·11 ± 0·05 | |
| *J*(Pb–5) | | 30·28 ± 0·05 | |
| | Tetra-(3-furyl)lead | | |
| δ-2 | 7·4064 ± 0·0002 | 7·4068 ± 0·0003 | −0·0004 |
| δ-4 | 6·5294 ± 0·0002 | 6·5311 ± 0·0003 | −0·0017 |
| δ-5 | 7·6551 ± 0·0002 | 7·6552 ± 0·0003 | −0·0001 |
| *J*(2–4) | 0·72 ± 0·02 | 0·71 ± 0·02 | 0·01 |
| *J*(2–5) | 1·35 ± 0·02 | 1·36 ± 0·03 | −0·01 |
| *J*(4–5) | 1·72 ± 0·02 | 1·70 ± 0·03 | 0·02 |
| *J*(Pb–2) | | 16·13 ± 0·04 | |
| *J*(Pb–4) | | 24·92 ± 0·04 | |
| *J*(Pb–5) | | 14·90 ± 0·04 | |
| | Tetra-(3-thienyl)lead | | |
| δ-2 | 7·5024 ± 0·0019 | 7·5017 ± 0·0009 | 0·0007 |
| δ-4 | 7·2871 ± 0·0005 | 7·2881 ± 0·0009 | −0·0010 |
| δ-5 | 7·5354 ± 0·0020 | 7·5370 ± 0·0009 | −0·0016 |
| *J*(2–4) | 0·94 ± 0·18 | 1·03 ± 0·06 | −0·09 |
| *J*(2–5) | 2·61 ± 0·07 | 2·51 ± 0·08 | 0·10 |
| *J*(4–5) | 4·87 ± 0·15 | 4·82 ± 0·08 | 0·05 |
| *J*(Pb–2) | | 54·24 ± 0·11 | |
| *J*(Pb–4) | | 25·27 ± 0·12 | |
| *J*(Pb–5) | | 15·71 ± 0·10 | |

Attempts have been made to obtain information on the relative signs of the three long-range *J*(Pb–H) coupling constants by comparing experimental and simulated satellite bands. The traces of simulated satellite bands for a sample compound are reported in the Figure above the experimental peaks for the different combinations of signs of long-range *J*(Pb–H) coupling constants. For compounds (II)—(IV) the best agreement between experimental and simulated patterns is given when all *J*(Pb–H) values have like signs. For compound (I), as can be seen in the Figure, two combinations of signs give the best agreement with the experimental pattern, namely (a) and (d). On the other hand, in the corresponding mercury derivatives[1] the long-range *J*(Hg–H) values have like signs in the four compounds examined and the same is very likely true for the lead derivatives.



Experimental spectrum of tetra-(2-furyl)lead with the enhancement of lead satellites, and their calculated patterns as a function of the relative sign of the *J*(Pb–H) values: (a) all *J*(Pb–H) of like sign; (b, c, d) *J*(Pb–3), *J*(Pb–4), and *J*(Pb–5), respectively, opposite in sign to the other coupling constants

The proton chemical shifts of compounds (I)—(IV) are at lower field relative to those of the corresponding unsubstituted compounds, furan and thiophen, and seem to indicate that (*d*–*p*)π interactions between the π-electron cloud of the heteroaromatic ring and the empty *d* orbitals of lead are taking place. On the other hand, these shifts towards lower field do not show the same regular behaviour as those of the corresponding tin derivatives,[2] and cannot be employed for quantitative comparison of (*d*–*p*)π interactions in tin and lead derivatives.[11]

It has been reported previously that proton–proton coupling constants in 2-substituted thiophens[6] are linearly correlated to substituent electronegativity. By

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[10] Program supplied by Dr. S. Castellano, Carnegie Mellon Institute.

[11] For a review of the argument, see C. J. Attridge, *Organometallic Chem. Rev.*, 1970, *A*, **5**, 323.

employing the data reported in this paper and recently published results,[1,2] in addition to those for substituted furans and thiophens,[6,12,13] it is possible to check analogous correlations for 3-substituted thiophens and for 2- and 3-substituted furans. The linear equations representing these correlations, (1), have been evaluated

$$J = aE_X + b \qquad (1)$$

and the slopes, *a*, and intercepts, *b*, together with the relative deviations, estimated by a least-squares treatment (9—15 experimental values were included for each correlation) are reported in Table 2. The sensitivity of proton–proton coupling constants to substituent effects is higher in thiophen than in furan and, when comparison is possible, in 2- than in 3-substituted compounds. The slopes, *a*, are positive for all the coupling constants and show that the metal substituents decrease these values with respect to unsubstituted derivatives. Even if the changes in these constants are small they seem to indicate that the metal atoms influence proton–proton coupling constants by an essentially inductive effect.

TABLE 2

Slopes (*a*) and intercept (*b*) and relative deviations of equations (1) representing the correlations between proton–proton coupling constants and substituent electronegativity in 2- and 3-substituted furans and thiophens

| | | $J$(2–4) | $J$(2–5) | $J$(3–4) | $J$(3–5) | $J$(4–5) | $\Sigma J$ |
|---|---|---|---|---|---|---|---|
| 2-Furyl | *a* | | | 0·10 ± 0·07 | 0·27 ± 0·05 | 0·24 ± 0·04 | 0·62 ± 0·07 |
| | *b* | | | 3·03 ± 0·18 | 0·14 ± 0·13 | 1·26 ± 0·11 | 4·43 ± 0·19 |
| 2-Thienyl | *a* | | | 0·34 ± 0·04 | 0·42 ± 0·02 | 0·59 ± 0·05 | 1·36 ± 0·06 |
| | *b* | | | 2·66 ± 0·11 | 0·08 ± 0·06 | 3·67 ± 0·13 | 6·41 ± 0·16 |
| 3-Furyl | *a* | 0·10 ± 0·06 | 0·21 ± 0·06 | | | 0·18 ± 0·05 | 0·49 ± 0·07 |
| | *b* | 0·58 ± 0·15 | 0·95 ± 0·14 | | | 1·33 ± 0·13 | 2·86 ± 0·18 |
| 3-Thienyl | *a* | 0·38 ± 0·10 | 0·41 ± 0·07 | | | 0·20 ± 0·08 | 0·99 ± 0·18 |
| | *b* | 0·24 ± 0·22 | 1·82 ± 0·17 | | | 4·42 ± 0·19 | 6·48 ± 0·44 |

*Long-range $J(^{207}\text{Pb–H})$ Coupling Constants.*—In the corresponding derivatives of mercury [1] and tin [2] $J$(M–H) values were found to be proportional to the corresponding $J$(H–H) values in thiophen and furan. This indicates that the Fermi contact mechanism should determine both long-range proton–proton and proton–metal coupling constants in these systems. The existence of an analogous correlation for lead derivatives was verified and it was found that the behaviour of mercury and tin also applies to lead derivatives. The corresponding equation is represented by expression (2). As in the case of tin [2] derivatives it can be shown, assuming that

$$J(^{207}\text{Pb–H}) = 9{\cdot}69\,(\pm\,1{\cdot}29) J(\text{H–H}) + 2.05(\pm\,3{\cdot}60) \quad (2)$$

the contribution of the Fermi contact mechanism to these coupling constants is dominant, that the ratio of long-range $J(^{207}\text{Pb–H})$ to $J(^{199}\text{Hg–H})$ values should be expressed by the approximate equation (3), derived from

$$\frac{|J(^{199}\text{Hg–H})|}{|J(^{207}\text{Pb–H})|} = \frac{\gamma(^{199}\text{Hg})}{\gamma(^{207}\text{Pb})} \cdot \frac{\alpha^2(^{199}\text{Hg})}{\alpha^2(^{207}\text{Pb})} \cdot \frac{|^{6s}\text{Hg}^{(0)}|^2}{|^{6s}\text{Pb}^{(0)}|^2} \quad (3)$$

the formalism given by Juan and Gutowsky.[14] By using hydrogen-like wave functions where $Z_{\text{eff}}$ was put equal to the atomic number and $\alpha^2(\text{Hg}) = 0{\cdot}5$, $\alpha^2(\text{Pb}) = 0{\cdot}25$, the right hand side of equation (3) becomes 1·58. The ratio of the slope (14·35) of the correlation [2] between long-range $J(^{199}\text{Hg–H})$ and the corresponding $J$(H–H) values and the slope of equation (2) is 1·5, which is close to the calculated value. This indicates that for lead derivatives also the long-range coupling mechanism is mainly dominated by the Fermi contact term.

We have checked whether the same conclusions hold for phosphorus derivatives. All the long-range $J(^{31}\text{P–H})$ values of the symmetrical isomers of trifuryl- and trithienyl-phosphine have been recently reported,[15–19] and the corresponding correlation is represented by equation (4). Applying a treatment similar to that represented

$$J(^{31}\text{P–H}) = 0{\cdot}90\,(\pm\,0{\cdot}19) J(\text{H–H}) + 0{\cdot}18\,(\pm\,0{\cdot}54) \quad (4)$$

by equation (3) and considering $sp^3$ hybridization for the phosphorus atom, the ratio $|J(^{199}\text{Hg–H})|/|J(^{31}\text{P–H})|$ is evaluated to be 16·70, while from the slope of the correlations of these long-range coupling constants with the corresponding $J$(H–H) in furan and thiophen an experimental ratio of 15·94 is obtained. Thus it seems that for phosphorus derivatives macroscopic changes of long-range $J(^{31}\text{P–H})$ are also dominated by the Fermi contact mechanism. This is likely to hold for other elements with non-zero nuclear spin, and is clearly related to previous suggestions, in which the $J$(X–H) values over two bonds in $(CH_3)_4X$ compounds, where X is an element of Group IVB, were correlated [20] with the square of atomic number of element X ($Z_X$) provided the orbital hybridization at X was exactly maintained. On the other hand the zero-point wave functions are roughly proportional to the $(Z_X)^2$ values, and for elements of other Groups the long-range $J$(X–H) values, estimated

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by means of simplified expressions of the Fermi contact term, the hybridization of the atom X should also be included.

## EXPERIMENTAL

$^1$H N.m.r. spectra were recorded at 60 MHz with a JEOL-C60-HL spectrometer in the internal lock mode. Tetramethylsilane was added to each sample to act both as reference and locking signal. Line positions are correct to within ±0·1 Hz.

*Tetra-(2-furyl)lead* (I).—Lead(II) chloride (7·8 g) was slowly added to a solution of 2-furyl-lithium[2] [from furan (3·9 g) and lithium (0·9 g)] in anhydrous ether (75 ml) cooled at −20 °C. The mixture was stirred for ½ h at −20 °C and then for ½ h at room temperature. After the ether had been evaporated off the solid residue was extracted with benzene: from this solution a white material was obtained which afforded a crystalline compound (2·0 g), m.p. 52—53 °C (lit.,[21] m.p. 52—53°) (from pentane).

*Tetra-(2-thienyl)lead* (II).—Lead(II) chloride (6·6 g) was slowly added to a solution of 2-thienyl-lithium[2] [from thiophen (4·1 g) and lithium (0·7 g)] in anhydrous ether (60 ml) maintained at room temperature. The mixture was stirred for ½ h. The same procedure as for compound (I) was then adopted and crystallization from ether gave material (3·9 g) of m.p. 152 °C (lit.,[22] 152 °C).

*Tetra-(3-furyl)lead* (III).—Lead(II) chloride (4·5 g) was slowly added to a solution of 3-furyl-lithium[2] [from 3-iodofuran (6·3 g)] in ether under dry nitrogen at −70 °C. The mixture was stirred for 3 h at −70 °C and then allowed to warm to room temperature. After evaporation to dryness and extraction with pentane a solid was obtained, which after crystallization from the same solvent gave white *needles* (0·8 g), m.p. 71—73 °C (Found: C, 41·6; H, 2·7. $C_{16}H_{12}O_4Pb$ requires C, 40·4; H, 2·55%).

*Tetra-(3-thienyl)lead* (IV).—Lead(II) chloride (1·7 g) was slowly added to a solution of 3-thienyl-lithium[2] [from 3-bromothiophen (2 g) and lithium (0·3 g)] in anhydrous ether (50 ml) maintained at −70 °C. The mixture was stirred at −70 °C for 3 h and then for ½ h at room temperature. The same procedure as for compound (I), followed by crystallization from benzene–ethanol gave the *product* (1·5 g), m.p. 223—224 °C (Found: C, 35·6; H, 2·45. $C_{16}H_{12}PbS_4$ requires C, 35·6; H, 2·25%).

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