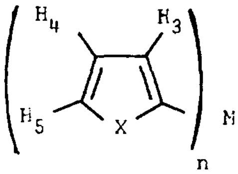
Tetrahedron Letters No. 31, pp. 2921-2924, 1971. Pergamon Press. Printed in Great Britain.

A PROTON NMR STUDY OF TETRA(2-FURYL)- AND TETRA(2-THIENYL)LEAD: A COMPARISON WITH THE RELATED DIMERCURIALS

(Mrs.) A.P. Ebdon, T.N. Huckerby[1], and F.G. Thorpe
Department of Chemistry, The University, Bailrigg, Lancaster

In this note we report proton NMR data for tetra(2-furyl)- and tetra(2-thienyl)lead (Ia,b), and compare their spectral parameters with those from the analogous difuryl- and dithienylmercury derivatives (IIa,b). The chemical shifts and coupling constants (derived by ABC and ABCX iterative analyses using



I M = Pb, n = 4
II M = Hg, n = 2

a X=O; b X=S

the computer program LAME[2]) for the lead derivatives are summarised in the Table, together with those obtained in this Laboratory[3] for the related dimercurials.

It can be seen that the proton-proton and proton-heteroatom couplings for the lead and for the mercury derivatives are not only identical in their relative signs, but are also fairly similar in their magnitudes with the notable exception of J(H(3), Pb) in Ia. It seems reasonable to assume that the mechanisms of heteronuclear coupling are identical for Pb and Hg organometal derivatives of this general type.

TABLE

X=	O		S	
M=	Pb[a,b]	Hg[a,c]	Pb[a,b]	Hg[a,c]
δ(3)	408.1	399.5	445.5	430.1
δ(4)	391.2	405.2	437.8	443.0
δ(5)	466.2	480.5	460.8	403.0
J(3,4)[d]	3.285 ± 0.008	3.124 ± 0.015	3.411 ± 0.021	3.347 ± 0.016
J(3,5)	0.633 ± 0.008	0.525 ± 0.016	0.886 ± 0.021	0.779 ± 0.017
J(4,5)	1.777 ± 0.008	1.731 ± 0.016	4.882 ± 0.022	4.829 ± 0.016
J(3,M)	10.526 ± 0.064	22.981 ± 0.065	59.248 ± 0.062	71.716 ± 0.166
J(4,M)	15.726 ± 0.064	12.603 ± 0.158	17.491 ± 0.062	14.223 ± 0.224
J(5,M)	18.191 ± 0.064	19.789 ± 0.048	31.748 ± 0.084	36.647 ± 0.220

[a] All shifts are given in Hz downfield from TMS at 60 MHz

[b] in $CDCl_3$ solution

[c] in dioxan solution

[d] All couplings are of similar sign, and are given in Hz

The presence of 21.11% of the spin-½ isotope ^{207}Pb in organolead derivatives is of great value to the NMR spectroscopist. The higher natural abundance of ^{207}Pb compared with ^{199}Hg (16.86%) means, moreover, that with the former higher accuracy should be possible in the determination of satellite line positions. A further advantage to be gained from the study of R_4Pb derivatives in comparison with R_2Hg compounds is that due to their higher valence state solutions of the same molarity give proton NMR signals of twice the intensity obtained from a dimercurial.

Providing that suitable corrections could be made for differences in metal electronegativities, data derived from lead compounds could well be useable to complement parameters from mercurials in the rationalisation of these coupling processes, with the advantage of enhanced relative sensitivity outlined above.

One important difference is observed between the pairs of spectral parameters; there is a consistent reversal in the relative chemical shifts of H(3) and H(4) between the lead and mercury compounds. We suggest that this is a consequence of the tetrahedral central atom in Pb(IV) derivatives, and arises from a ring-current deshielding of H(3) via the partial structure shown in III. The transient coplanarity of two heteroaromatic rings would be facilitated by a weak interaction as illustrated, with the other pair of substituents similarly participating in a perpendicular plane.

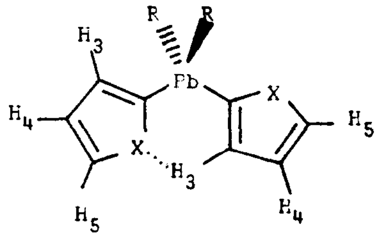


Fig. III

A useful consequence of the tetrahedral nature of Pb(IV) derivatives is that they appear to be more readily soluble in the normal spectroscopic solvents; this should allow the acquisition of data which can be more directly correlated with existing parameters for other systems.

This work comprises part of a series of studies on the chemical and spectroscopic properties of organometallic and heterocyclic compounds currently being pursued in this Department.

1. Author to whom all correspondence should be addressed.
2. A revised and improved version of LAOCN3 with magnetic equivalence factorisation; C.W. Haigh, University of Swansea, personal communication.
3. T.N. Huckerby and F.G. Thorpe, unpublished work. These parameters are very similar to those recently published by L. Lunazzi, M. Tiecco, C.A. Boicelli and F. Taddei, J.Mol.Spectroscopy, 35, 190 (1970).