Long-range Phosphorus–Hydrogen Spin–Spin Coupling in Aromatic Systems

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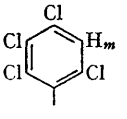
SPIN–SPIN interactions between aromatic protons and phosphorus not directly bonded to the aromatic ring have received limited attention[1] although their potential importance in theoretical and structural work is evident. The 60 Mc./sec. proton magnetic resonance spectra of a series of thionophosphates have been recorded and the results are summarized in the Table.

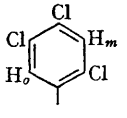
Phosphorus coupling through four bonds to the *ortho*-proton (1·41—1·66 c./sec.) and through

TABLE

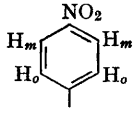
	Compound[a]	Solvent	δ_o(p.p.m.)	δ_m(p.p.m.)	J(P–H_o)[b]	J(P–H_m)[b]
(I)	$R^1O-P(=S)(NHEt)-OMe$	CCl_4	—	7·45	—	0·89
(II)	$R^2O-P(=S)(NHMe)-OMe$	CCl_4	7·60	7·48	1·55	1·02
(III)	$R^2O-P(=S)(NH\cdot CHMe_2)-OMe$	CCl_4	7·65	7·47	1·55	1·04
(IV)	$R^2O-P(=S)(NH\cdot CMe_3)-OMe$	$CDCl_3$	7·69	7·49	1·41	1·16
(V)	$R^2O-P(=S)(NHMe)-NHMe$	CCl_4 Me_2CO	7·58 7·68	7·46 7·64	1·66 1·6[c]	0·88 0·9[c]
(VI)	$R^2O-P(=S)(Cl)-Cl$	CCl_4 Me_2CO	7·54 7·74	7·58 8·14	2·8[c] 2·72	1·6[c] 1·43
(VII)	$R^3CH_2-P(=O)(OEt)-OEt$	CCl_4	7·48	8·08	2·5	<0·4



(R^1)



(R^2)



(R^3)

[a] We are indebted to Dr. E. Blair of the Dow Chemical Company, Midland, Michigan, for samples of compounds (I)—(VI).

[b] Coupling constants were measured to ±0·05 c./sec.

[c] Close overlap of lines limits the accuracy of this value.

five bonds to the *meta*-proton (0·88—1·16 c./sec.) is exhibited in compounds (II)—(V). Assignment of the smaller of the two coupling constants to the interaction between the phosphorus and the *meta*-proton is justified by the results obtained for compound (I) which contains only a *meta*-proton. Substitution of nitrogen for oxygen on the thionophosphate group has little effect on the magnitude of coupling constants; however, introduction of two chlorine substituents [compound (VI)] significantly increases both the *ortho*- and *meta*-hydrogen–phosphorus interactions. Similar effects have been observed[2,3] on increasing the electropositive nature of the phosphorus atom.

When phosphorus is attached to the aromatic ring by means of a methylene group rather than an oxygen [compound (VIII) and others reported in the literature[1]], there is no significant coupling between the phosphorus and the *meta*-proton. This indicates that the coupling, which is dependent on π-electron interactions between the phosphorus and the aromatic ring, is facilitated by the presence of the oxygen.

Finally it should be noted that a change of solvent from carbon tetrachloride to acetone causes a greater downfield shift of the *meta*-proton as compared with the *ortho*-proton, suggesting that the solvent has a rather intimate effect on the distribution of electrons of the π-system.

This work was supported by a Fellowship (to C.O.S.) from the U.S. Public Health Service.

(*Received, March 2nd*, 1967; *Com.* 202.)

[1] C. E. Griffin and M. Gordon, *J. Organometallic Chem.*, **1965**, **3**, 414.
[2] C. E. Griffin, *Tetrahedron*, **1964**, **20**, 2399.
[3] J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **1964**, **20**, 449.