^{13}C–^{31}P Spin–Spin Coupling in Organophosphorus Compounds

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THERE have been comparatively few determinations of the signs or magnitudes of coupling constants between directly bound nuclei,[1,2,3] when neither nucleus is ^{1}H or ^{19}F. Such measurements are of considerable importance to theories of chemical bonding,[4] particularly when one of the nuclei involved is in the first row of the periodic table, and this Communication describes the first determination of the signs and magnitudes of ^{13}C–^{31}P coupling constants.

Dimethylphenylphosphine (kindly supplied by Mr. E. J. Finer, University of East Anglia) and its protonated cation, Me_2PhP^+H' were selected because the ^{31}P spectra are relatively uncomplicated by coupling with the protons of the phenyl group, and the compounds are more easily manipulated than trimethylphosphine. Heteronuclear tickling experiments were performed as described elsewhere,[1,5] by observing the ^{1}H magnetic resonance spectrum of the neat phosphine (to which a small amount of methylene dichloride had been added to actuate the field-frequency locking circuits of the Varian spectrometer) at 100 Mc./sec. and simultaneously irradiating at either the ^{13}C (*ca.* 25·14 Mc./sec.) or the ^{31}P (*ca.* 40·48 Mc./sec.) resonant frequency. A 25% solution of the phosphine in methylene dichloride was saturated with hydrogen bromide to give $Me_2PhP^+H\ Br^-$, in which the resonance of H′ displays coupling to the protons of the methyl groups provided that the hydrogen ion concentration of the solution is kept high enough to minimize exchange.[6] The results of seven sets of tickling experiments are given in the Table, in which $J(^{13}C–^{1}H)$ is taken to be positive.[7]

The change in sign of $J(^{31}P \cdots {}^{1}H)$ on quaternization of the phosphorus atom confirms the results of Cullingworth, Pidcock, and Smith's study of Group III complexes of trimethyl phosphine[8] and it is evident from the present work that the absolute value of the coupling constant decreases on complex formation. The large difference between the values of $J(^{13}C–^{31}P)$ in the phosphine and its hydrobromide suggests that this parameter is sensitive to the groups attached to the phosphorus atom, and it may assume considerable importance in studies of organophosphorus compounds.

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TABLE

Compound	Coupled nuclei	J in c./sec.	Tickled nucleus
Me_2PhP	^{13}C–^{1}H	+130·3 ± 0·2	^{31}P
	^{13}C–^{31}P	−14 ± 1	^{13}C
	^{31}P–C–^{1}H	+3·0 ± 0·1	
$Me_2PhP^+H'Br^-$	^{13}C–^{1}H	+134·0 ± 0·2	^{31}P
	^{13}C–^{31}P	+56 ± 1	^{13}C
	^{31}P–C–^{1}H	−15·5 ± 0·1	^{1}H
	^{31}P–$^{1}H'$	+525 ± 1	^{31}P
	^{1}H–C–P–$^{1}H'$	+5·5 ± 0·1	^{13}C
	^{13}C–P–$^{1}H'$	+4 ± 2	

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