Carbon–Phosphorus Coupling in Representative Organophosphorus Compounds†

By G. MAVEL
(*IRCHA, 12 Quai Henri IV, Paris 4^e*)

and M. J. GREEN*
(*Perkin–Elmer Limited, Beaconsfield, Buckinghamshire*)

FOR experimental support for the molecular-orbital treatment of spin–spin couplings developed by Pople and Santry[1] and others,[2] the measurement of couplings involving nuclei other than protons is especially important. ^{13}C-Couplings to itself[3] and to ^{15}N, ^{77}Se, ^{119}Sn, ^{125}Te, ^{207}Pb,[4] ^{29}Si, and ^{119}Hg,[5] and ^{31}P-couplings to ^{11}B [6] and ^{29}Si [7] have been reported. In addition, some values of ^{13}C–^{31}P coupling constants have recently been presented. McFarlane has reported[8] "heteronuclear tickling" experiments on Me_2PPh and Me_2P^+HPh, giving for the methyl ^{13}C–^{31}P couplings -14 and $+56$ (± 1) Hz respectively, and Manatt and Elleman have obtained a value of 13·97 Hz for Me_3P,[10] by using Overhauser-effect enhancement on ^{31}P spectra. Finer and Harris[11] have estimated $J(^{13}C\text{–}P\text{–}^{31}P)$ for tetramethyldiphosphine.

To enlarge the basis for future discussion, we present here more data on ^{13}C–^{31}P couplings obtained by the direct observation of ^{13}C spectra. The spectra of neat samples of representative (non-enriched) compounds were recorded in the absorption mode on a Perkin–Elmer R10 spectrometer operating at 15·1 MHz, using spectrum accumulation for sensitivity enhancement. From our tabulated results, one can appreciate qualitatively the influence on the n.m.r. parameters of the following effects:

Phosphorus hybridization: nearly p^3 in $(CH_3)_3P$; probably with a significant *s*-content in CH_3PCl_2 and nearly sp^3 in thiophosphorylated and especially phosphorylated compounds.

Carbon hybridization: sp^3 in compounds 1 to 5, *sp* in compound 6‡.

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† "Etude par RMN de composés organo-phosphorés". Part XVII—Part XVI: ref. 14.

‡ Owing to the superimposition of vinylic and aromatic patterns in $(PhO)_2P(O)\,CH{=}CH_2$, we have failed to obtain similar data for a molecule with an sp^2 carbon.

Table[a]

	Compound	$J(^{13}C-^{31}P)$	$J(^{13}C-^{1}H)$	$\delta(^{13}C)$
1.	$MePCl_2$	45	133[b]	113·5
2.	$MeP(S)Cl_2$	81	135[b]	87·5
3.	$MeP(O)Cl_2$	104	135[b]	97·0
4.	$MeP(O)F_2$[c]	147	133[b]	107·0
5.	$(EtO)_2P(O)C^*H_2COMe$[d]	127	ca. 130	85·5
6.	$(EtO)_2P(O)C^*{\equiv}CMe$[d]	304	—	57·0
	$(EtO)_2P(O)C{\equiv}C^*Me$[e]	54	—	28·0

[a] For the starred carbon, when indicated. Couplings in Hz (±2); chemical shifts in p.p.m. (±0·5), measured upfield from benzene.

[b] From ^{13}C proton satellite spectra (G. Mavel and G. Martin, *Compt. Rend.*, 1963, **257**, 1730), one obtains respectively 131, 135, 134 and 132 Hz.

[c] $^{13}C-^{19}F$ coupling *ca.* 22 Hz.

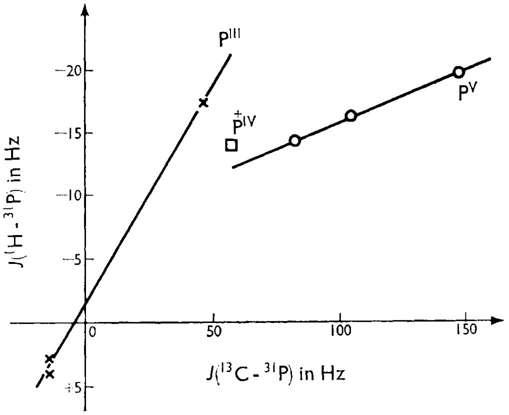
[d] No $^{13}C-^{31}P$ coupling noticeable for POEt groups.

[e] $^{13}C-C-^{1}H$ coupling *ca.* 10 Hz.

The nature of substituents on carbon or phosphorus.

$J(^{13}C-^{31}P)$ values may be rationalized in terms of the *s*-character of P–C bonds by using the Walsh rule,[12] that the *s*-character of a phosphorus atom tends to concentrate in bonds with the more electropositive groups, and on the basis of a qualitative extension of the Pople and Santry theory:[13] the coupling constant depends on the energies of the *s*-electrons of the coupled nuclei (taken as approximately constant for all P–C groups) and on the resonance integral between their outer-shell *s*-electrons.

We have assumed, on the basis of McFarlane's results,[8] that all our measured couplings are positive, the general trend for $^{13}C-^{31}P$ couplings then paralleling that predicted for $^{31}P-^{31}P$ ones[13] as *s*-character varies. Another interesting feature is the relationship of $^{13}C-^{31}P$ couplings for all the available methyl derivatives to the relevant $^{1}H-^{31}P$ couplings, the sign and value of which have been discussed recently.[14] Clear trends appear for P^{III}, $\overset{+}{P}{}^{IV}$, and P^{V} (see Figure) indicating that the same main factors contribute to both of these couplings, especially when anomalous signs appear[12] (positive for two-bonds $^{1}H-^{31}P$, negative for one-bond $^{13}C-^{31}P$), which may be due to the influence of the phosphorus lone-pair.[14]



FIGURE

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