The N.m.r. Spectra of Substituted Diphosphines and Their Derivatives. Deceptively Simple Spectra

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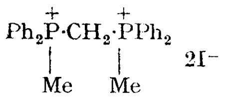
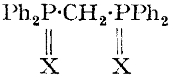
ALTHOUGH (H, ^{31}P) coupling constants have been reported for quite a large number of phosphines and phosphonium salts,[1] there are few data in the literature concerning diphosphines and their derivatives except for compounds with a direct P–P bond.[2] We report here the n.m.r. spectra of bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, and related compounds. Chemical shifts and (H, ^{31}P) coupling constants for the compounds are summarised in the Table. In all cases, the phenyl proton resonances occurred as a broad complex band between τ 2 and 3 and were not analysed further. The methylene proton spectra of $Ph_2P\cdot CH_2\cdot PPh_2$(I) and of (II), (III), (IV), and (V) were straightforward. The magnitude of ${}^2J_{PH}$ for (I) and (II) may be compared with values of 2·7 c./sec. and 14·4 c./sec. found for Me_3P and $Me_4\overset{+}{P}I^-$. On the basis of relative signs suggested earlier[2–4] we assign opposite signs to the coupling constants, with the larger value negative. The methyl resonance of (II) consists of a simple doublet indicating that ${}^2J_{PP}$ is probably small and ${}^4J_{PMe} \sim 0$, $|{}^2J_{PMe}| = 13·1$ c./sec.



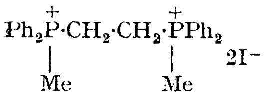
$\mathrm{Ph_2}\underset{\underset{\mathrm{Me}}{|}}{\overset{+}{\mathrm{P}}}\cdot\mathrm{CH_2}\cdot\underset{\underset{\mathrm{Me}}{|}}{\overset{+}{\mathrm{P}}}\mathrm{Ph_2}\quad 2\mathrm{I}^-$

(II)



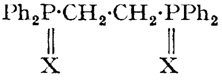
$\mathrm{Ph_2}\underset{\underset{\mathrm{X}}{\|}}{\mathrm{P}}\cdot\mathrm{CH_2}\cdot\underset{\underset{\mathrm{X}}{\|}}{\mathrm{P}}\mathrm{Ph_2}$

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



$\mathrm{Ph_2}\underset{\underset{\mathrm{Me}}{|}}{\overset{+}{\mathrm{P}}}\cdot\mathrm{CH_2}\cdot\mathrm{CH_2}\cdot\underset{\underset{\mathrm{Me}}{|}}{\overset{+}{\mathrm{P}}}\mathrm{Ph_2}\quad 2\mathrm{I}^-$

(VII)



$\mathrm{Ph_2}\underset{\underset{\mathrm{X}}{\|}}{\mathrm{P}}\cdot\mathrm{CH_2}\cdot\mathrm{CH_2}\cdot\underset{\underset{\mathrm{X}}{\|}}{\mathrm{P}}\mathrm{Ph_2}$

(VIII) X = O
(IX) X = S
(X) X = Se

For compounds containing the group $P\cdot CH_2\cdot CH_2\cdot P$, the proton resonances may be treated approximately as due to the X part of an AXX′X″X‴A′ spin system (neglecting the phenyl protons). However, there are some similarities between predicted spectra of the X nuclei for these systems and spectra of the $X_2AA'X'_2$ type analysed by Harris.[5] Thus half the total intensity of the X resonance will still be concentrated in a doublet of spacing $|{}^2J_{PH} + {}^3J_{PH}|$ and limiting conditions for the occurence of deceptively simple spectra are still relevant. The diphosphine $Ph_2P\cdot CH_2\cdot CH_2\cdot PPh_2$ (VI) has a deceptively simple methylene proton spectrum which resembles a 1 : 2 : 1 triplet [Figure (a)]. The central line is slightly less than twice the height of the doublet lines, but it is probable that $({}^2J_{PH}-{}^3J_{PH})^2/|J_{PP}|$ is small.[5] Now $|{}^2J_{PH} + {}^3J_{PH}| = 8·5$ c./sec., and both ${}^3J_{PH}$ and ${}^2J_{P}III_{H}$ are normally positive,[2,3] although the latter is often small and can be negative. Moreover, for (I) ${}^2J_{PH}$ is 1·5 c./sec., probably positive. Thus for (VI) we assign ${}^2J_{PH} \sim {}^3J_{PH} \sim +4·2$ c./sec., though values through to ${}^2J_{PH} \sim +1·5$ c./sec., ${}^3J_{PH} \sim +7·0$ c./sec. may apply if ${}^3J_{PP}$ is large. For (VII) the CH_2 resonance is a broadened doublet and a deceptively simple methyl resonance is observed [Figure (b)]. The separation of the outer lines of the methyl resonance gives $|{}^2J_{PMe} + {}^5J_{PMe}| = 13·0$ c./sec. Since no (H, ³¹P) coupling has been observed over five bonds in saturated systems,[1] it is reasonable to assume ${}^5J_{PMe} = 0$ and ${}^2J_{PMe} = -13·0$ c./sec. The CH_2 doublet then gives $|{}^2J_{PH} - {}^3J_{PH}| \neq 0$ and $|{}^2J_{PH} + {}^3J_{PH}| = 5·6$ c./sec. Using a value for ${}^2J_{PH} = -16·6$ c./sec. found from the spectrum of (II) we obtain ${}^3J_{PH} \sim +11·0$ or $+22·2$ c./sec. Although it is not possible to decide which value is more correct on the present evidence, comparison with other (H, ³¹P) coupling constants and with (H, ²⁰⁵Tl),[6] (H, ¹¹⁹Sn), (H, ²⁰⁷Pb)[7] systems, suggests that ${}^3J_{PH}$ is likely to be larger than $|{}^2J_{PH}|$. The latter value therefore seems somewhat the more probable. It can be seen that $|{}^2J_{PH}|$ and $|{}^3J_{PH}|$ do increase markedly on salt formation although this is not at first apparent from the spectra. Similar arguments can be applied to the

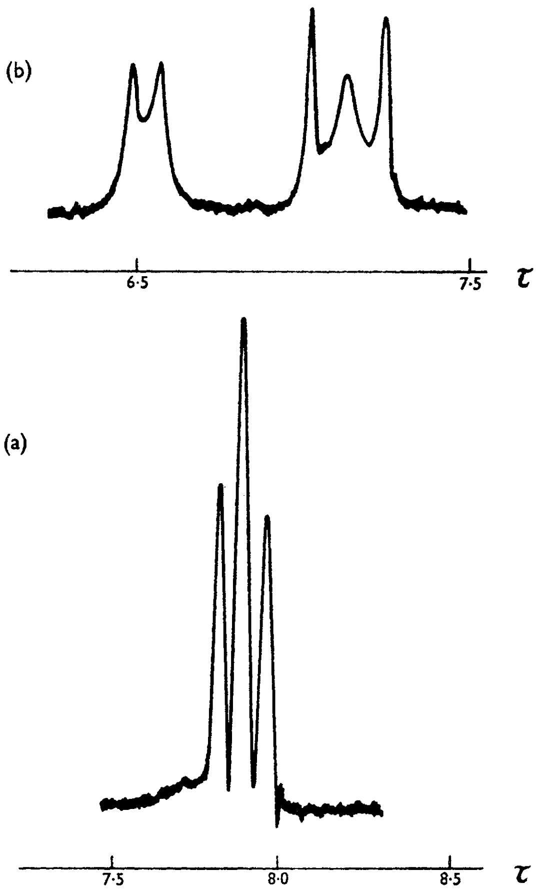


FIGURE. *Varian A60 n.m.r. spectra of* (a) CH_2 *protons of* (VI) *in* $CDCl_3$. (b) CH_2 *and* CH_3 *protons of* (VII) *in* $CF_3\cdot CO_2H$. *Tetramethylsilane was used as an internal standard.*

TABLE[a,b]

Compound	$^2J_{\mathrm{PH}}$	$^3J_{\mathrm{PH}}$	$^2J_{\mathrm{PH}} + {}^3J_{\mathrm{PH}}$	$^2J_{\mathrm{PMe}}$	$\tau\mathrm{CH}_2$	$\tau\mathrm{CH}_3$	Solvent
(I)	+1·5				7·23		$CDCl_3$
(II)	−16·6			−13·1	4·37	7·39	$CF_3{\cdot}CO_2H$
(III)	−14·0				5·92		$CF_3{\cdot}CO_2H$
(IV)	−13·2				5·48		$(CD_3)_2SO$
(V)	−13·4				5·17		$(CD_3)_2SO$
(VI)	c	c	+8·5		7·90		$CDCl_3$
(VII)	~−16·6[d]	~+11·0 or ~+22·2	±5·6	−13·0	6·53	7·13	$CF_3{\cdot}CO_2H$
(VIII)	~−14·0[d]	~+11·2 or ~+16·8	±2·8		7·46		$CF_3{\cdot}CO_2H$
(IX)	~−13·2[d]	~+11·3 or ~+15·1	±1·9		7·29		$(CD_3)_2SO$
(X)	~−13·4[d]	~+11·4 or ~+15·4	±2·0		7·13		$(CD_3)_2SO$

[a] Coupling constants in c./sec. The notation $^2J_{\mathrm{PH}}$ and $^3J_{\mathrm{PH}}$ refers to coupling to CH_2 protons.

[b] The relative signs of coupling constants have not been determined; the signs given are consistent both internally and with literature values.

[c] See text.

[d] Values assumed to be close to those for the corresponding $PCH_2{\cdot}P$ compounds.

dioxide, disulphide, and diselenide. The height ratio of the central to outer bands of the methyl triplet of (VII) increases from 0·77 to ~1·0 when the phenyl resonances are irradiated with a second radiofrequency magnetic field. This is probably due to an indirect effect of phosphorus–phenyl proton coupling. The height ratio obtained from the decoupled spectra indicates that $^3J_{\mathrm{PP}}$ is probably large ($\geqslant$ 80 c./sec.), in contrast to the inference that $^2J_{\mathrm{PP}}$ is small for (II).

Diphosphines were prepared by literature methods,[8] as were the diselenides[9] and diphosphonium salts.[1] The disulphides were prepared by shaking a warm benzene solution of the diphosphine with solid P_4S_{10} for two days.

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