Signs and Magnitudes of $^1J_{P-C}$, $^2J_{P-C}$, and $^3J_{P-H}$ in some Acetylenic P^{III} and P^{IV} Organophosphorus Compounds

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Summary Coupling constants display a reversal of sign in acetylenic phosphines, $^1J_{P-C} < 0$, $^2J_{P-C} > 0$, $^3J_{P-H} < 0$; they are positive in acetylenic phosphine oxides and their values suggest dominance by the Fermi contact interaction.

INTEREST in phosphorus–carbon coupling constants has been concentrated on saturated and aromatic or hetero-aromatic phosphorus derivatives.[1] Results concerning acetylenic phosphorus compounds are scarce[2] and the signs of $^1J_{P-C}$, $^2J_{P-C}$, and $^3J_{P-H}$ involving *sp* hybridized carbons are still unknown.

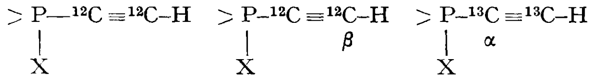
We now report a study of the signs and magnitudes of coupling constants in the $>P(X)-C\equiv C-H$ fragment (X = lone pair, oxygen) which indicates that the signs of $^1J_{P-C}$ and $^3J_{P-H}$ are dependent on phosphorus co-ordination.

TABLE. N.m.r. parameters[a] of acetylenic organophosphorus compounds.

Compound	δ_H	$^3J_{P-H}$	$^1J_{C_\beta-H}$	$^2J_{C_\alpha-H}$	δ_{C_α}	δ_{C_β}	$^1J_{P-C_\alpha}$	$^2J_{P-C_\beta}$
$(H\text{-}C\equiv C\text{-})_2P\text{-}N(C_6H_5)_2$[b]	2·81	$-$ 1·3$_3$	+248	+45	80·1	96·2	$-$9·8	+ 9·2
$H\text{-}\overset{\beta}{C}\equiv\overset{\alpha}{C}\text{-}P(OEt)_2$[b]	2·93	$-$ 2·4	+245	+43·5	85·0	91·8	$-$ 50	+ 0·4
$H\text{-}C\equiv C\text{-}P(O)(C_6H_5)_2$[c]	3·48	+10	+252·7	+45·7	77·9	95·3	+164·6	+29
$H\text{-}C\equiv C\text{-}P(O)(NMe_2)_2$[b]	3·93	+11·3	+249	+246	76·4	91·3	+224	+37
$H\text{-}C\equiv C\text{-}P(O)(OEt)_2$[b]	4·42	+13·7	+253	—	73·9	92·2	+294	+51

[a] Varian XL-100-12-W.G. Chemical shifts are in p.p.m. downfield from internal Me_4Si. Coupling constants are in Hz. [b] C_6D_6 solvent. [c] $CDCl_3$ solvent.

The signs of $^1J_{P-C}$ and $^2J_{P-C}$ were compared to those of $^2J_{C-H}$ and $^1J_{C-H}$, which are known to be positive,[3] using heteronuclear double resonance experiments performed by irradiating ^{31}P at 40 MHz, and observing at 100 MHz absorption lines due to the isotopic species:



$$\underset{X}{\underset{|}{>P}}{-}{}^{12}C\equiv{}^{12}C{-}H \qquad \underset{X}{\underset{|}{>P}}{-}{}^{12}C\overset{\beta}{\equiv}{}^{13}C{-}H \qquad \underset{X}{\underset{|}{>P}}{-}\overset{\alpha}{{}^{13}C}\equiv{}^{12}C{-}H$$

The signs of $^1J_{P-C}$ and $^2J_{P-C}$ were related to that of $^3J_{P-H}$ by $^{13}C-\{^1H\}$ double resonance experiments using off-resonance technique; the magnitude of residual splittings on both components of a given carbon has been shown to be dependent on the relative spin state of phosphorus in carbon and proton spectra.[4] ^{13}C n.m.r. spectra were observed at 25·2 MHz (c.w. mode, ^2H lock, 10 mm tubes). Resonances of C_α and C_β were assigned from non-decoupled spectra or by off-resonance; C_α resonates at higher field than C_β in every case. Full experimental details will be published elsewhere, but the results are shown in the Table.

$^1J_{P-C}$ is negative in the two acetylenic phosphines examined, as earlier found in saturated, aromatic and hetero-aromatic phosphines,[1a,d] The sign of this direct coupling constant seems to be independent of carbon hybridization and this suggests that Pople and Santry's M.O. treatment[5] may be qualitatively extended to $^1J_{P-C}$ coupling constants. A change from three- to four-co-ordinate phosphorus leads to a positive $^1J_{P-C}$ as previously observed in saturated organophosphorus compounds.[1a]

$^3J_{P-H}$ which is generally positive in fragments P–C–C–H, P–O–C–H, P–N–C–H and P–C=C–H[1a,b] involving a three-co-ordinate phosphorus, is negative in fragment P–C≡C–H. This is the first example of negative $^3J_{P-H}$ in an acyclic fragment. Furthermore, this coupling constant is small and only slightly dependent on the groups attached to phosphorus.

In acetylenic phosphine oxides, $^1J_{P-C}$ and $^2J_{P-C}$ are positive and higher than those reported in saturated and aromatic phosphine oxides. These coupling constants depend on the groups attached to phosphorus in the same way that $^3J_{P-H}$ does and increase in the order: $Ph < NMe_2 < OEt$. In agreement with Bent's theory,[7] higher values are observed for electron-attracting groups. These results suggest that $^1J_{P-C}$, $^2J_{P-C}$, and $^3J_{P-H}$ in acetylenic phosphine oxides are principally dependent on the Fermi contact term. Moreover, a roughly linear relationship is observed between either $^1J_{P-C}$ or $^2J_{P-C}$ and $^3J_{P-H}$, but as pointed out by McFarlane for tin derivatives,[8] the lines obtained do not pass through the origin, so that contributions other than the Fermi contact interaction, are probably involved in J_{P-C} and/or J_{P-H}.

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