Variations in Sign for the Coupling Constants between Directly-bonded Phosphorus Nuclei

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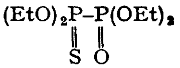
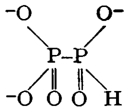
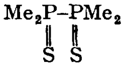
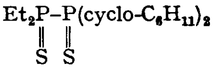
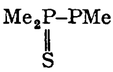
THE range of magnitudes for coupling constants between directly-bonded phosphorus nuclei is extremely large (*cf.* Table). Among these values are a number which are of relatively small magnitude, in particular 18·7 c./sec. for tetramethyldiphosphine disulphide.[1] In this situation it is reasonable to suggest that not all the values are of the same sign (thus making the range of values even larger than is indicated by the magnitudes alone). Such a suggestion receives support from the apparent lack of any rational order in the magnitudes. For instance, the magnitudes for $F_2P{\cdot}PF_2$ and $Ph_2P{\cdot}P(cyclo\text{-}C_6H_{11})_2$ are very similar in spite of the great difference in the nature of the substituents. Moreover it is curious that the largest magnitude for P^{III}–P^{III} coupling is for a compound with highly electropositive substituents (including lithium), whereas for P^{V}–P^{V} coupling the largest magnitude is for tetraethyl monothiohypophosphate which has four highly electronegative ethoxy-substituents. For certain reasons we were led to suppose that $^1J_{PP}$ may be positive for those values marked with a dagger in the Table, and negative for the remaining values. Such a hypothesis would remove most of the anomalies mentioned above; directly-bonded (P,P) coupling constants would range from large negative values to large positive values. We have since shown that the sign of $^1J_{PP}$ is indeed negative for tetramethyldiphosphine[2] (negative signs have also been strongly suggested for diphosphine[3] and tetramethyldiphosphine sulphide[1]).

TABLE

*Some reported *values of* $^1J_{PP}$ *(in c./sec.)*

Compound	$^1J_{PP}$	ref.
(I) F_2P-PF_2	227·4†	9
(II) H_2P-PH_2	−108	3
(III) Me_2P-PMe_2	−179·7	2
(IV) $Ph_2P-P(cyclo\text{-}C_6H_{11})_2$	**224**	10
(V) $Et_2P-P(cyclo\text{-}C_6H_{11})_2$	**282**	10
(VI) LiEtP–PPhEt	396	11
(VII)  $(EtO)_2\underset{\overset{\|}{S}}{P}-\underset{\overset{\|}{O}}{P}(OEt)_2$	583†	12
(VIII) 	+465·5†	this work
(IX)  $Me_2\underset{\overset{\|}{S}}{P}-\underset{\overset{\|}{S}}{P}Me_2$	18·7	1
(X)  $Et_2\underset{\overset{\|}{S}}{P}-\underset{\overset{\|}{S}}{P}(cyclo\text{-}C_6H_{11})_2$	69	10
(XI)  $Me_2\underset{\overset{\|}{S}}{P}-PMe_2$	−220	1

* Signs are only included where known. It is suggested that the values marked with a dagger are positive and the rest negative (except possibly the disulphides).

These considerations led us to measure the sign of $^1J_{PP}$ for the diphosphite anion, $[HP_2O_5]^{3-}$; our reasoning suggested this should be positive. The ^{31}P spectrum (the AB region of an ABX spin system) was reported by Callis *et al.*[4] at 9440 gauss, and it was later inferred that the signs of $^1J_{PH}$ and $^2J_{PH}$ for this molecule are the same.[3] Recently, McFarlane[5] has shown that $^1J_{PH}$ is positive for $(MeO)_2PHO$. Since relatively low magnitudes of $^1J_{PH}$ are not known, it may be concluded that this coupling constant is positive for the diphosphite anion also. We have carried out heteronuclear double resonance measurements† on an aqueous (D_2O) solution of sodium diphosphite prepared by the method of Blaser,[6] by observing the 100 Mc./sec. proton spectrum while "tickling" in the ^{31}P region. These experiments show that $^1J_{PP}$ is indeed positive in this case. The magnitude is found to be 465·5 ± 1·0 c./sec., which differs somewhat from that reported by Callis *et al.*[4] (480 ± 10 c./sec.). We have also confirmed by ^1H n.m.r. measurements at both 60 and 100 Mc./sec. that $^1J_{PH}$ and $^2J_{PH}$ have the same sign for the diphosphite anion. Our measurements, including those derived from the tickling experiment, give $^1J_{PH} = +451{\cdot}2 \pm 0{\cdot}5$ c./sec. and $^2J_{PH} = +88{\cdot}9 \pm 0{\cdot}5$ c./sec. (Callis *et al.* report[4] 444 and 94 c./sec. respectively).

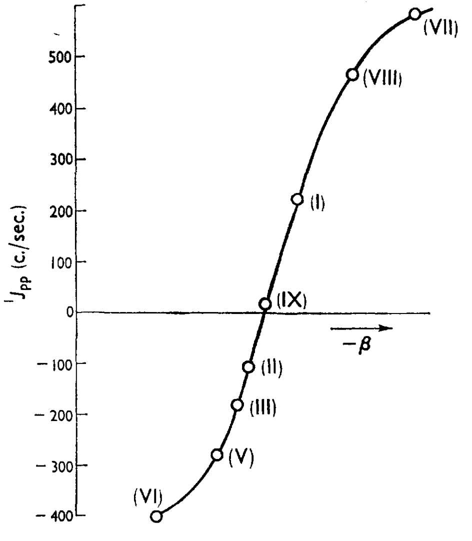


FIGURE. *Re-plotted Pople–Santry graph* (diagrammatic) *for coupling between directly-bonded phosphorus nuclei.* [The experimental values of $^1J_{PP}$ for some of the compounds listed in the Table are plotted with suggested signs (where these are unknown) to give a rational order for β, the resonance integral between the two phosphorus 3*s* orbitals, this order being dependent on substituent electronegativity and bulk.]

The signs of coupling constants are clearly of importance in the development of the appropriate theory. While this work was in progress it was reported[7] that values of $^1J_{CP}$ can also take either

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† Spectra were obtained at the National Physical Laboratory, Teddington, using a Varian Associates HA 100 spectrometer and a Rohde and Schwartz frequency synthesizer.

sign; no other cases of changes in sign for coupling constants between directly-bonded nuclei are known at present. The variations in $^1J_{PP}$ can, we believe, be explained satisfactorily by an extension of the theory given by Pople and Santry.[8] This theory, originally developed in detail only for first row elements, shows that the coupling constant depends on the energies of the *s* electrons of the coupled nuclei relative to the energies of *p,d*··· electrons, and also on the resonance integral between the outer-shell *s*-electrons of the two nuclei. If it is considered that the first factor remains approximately constant for all P–P groups, the variation of $^1J_{PP}$ can be qualitatively explained by the dependence of the second factor on the electronegativity and bulk of the substituents. Highly electronegative (or small) substituents will use less of the phosphorus 3*s* electrons in bonding, leaving a higher *s*-character in the P–P bond. Such a change could shift the value of $^1J_{PP}$ from a negative region of the Pople–Santry plot to a positive region (see Figure). In general it might be expected that P^V–P^V coupling constants will be more positive than corresponding P^{III}–P^{III} values. We are at present attempting to put these concepts on a quantitative basis. Further details of both experiment and theory will be reported later.

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