The Dependence of $^1J_{PP}$ Upon Internal Rotation in Biphosphines

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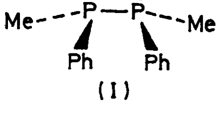
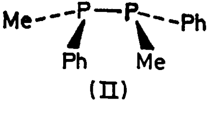
Summary A difference of 19 Hz in $^1J_{PP}$ in the two diastereomers of 1,2-dimethyl-1,2-diphenylbiphosphine indicates that this coupling constant depends markedly upon the molecular conformation.

CURRENT interest in nuclear spin–spin coupling between directly bound phosphorus atoms stems from the wide range of variation that $^1J_{PP}$ can display according to the substituents and oxidation states of the phosphorus atoms.[1,2] Theoretical attempts to predict $^1J_{PP}$ have been only moderately successful,[3] but it does appear that the coupling constant is very sensitive to the degree of 3*s*-overlap between the two phosphorus atoms.[4] It has also been predicted[3] that the coupling between the nuclei of a pair of directly bound tervalent phosphorus atoms may vary substantially according to the molecular conformation adopted, but hitherto the only experimental indication of this has been the observation of a slight temperature dependence ($-230{\cdot}3$ Hz at $-101°$ to $-228{\cdot}5$ Hz at $-1°$) for $^1J_{PP}$ in tetrafluorobiphosphine.[5]

We have now observed a substantial difference in $^1J_{PP}$ in the two diastereomers of 1,2-dimethyl-1,2-diphenylbiphosphine, (I) and (II). A mixture of these was prepared by reducing the biphosphine disulphide with copper,[6] and was examined as a *ca.* 40% solution in benzene on a JEOL C-60-H n.m.r. spectrometer at 24°. The magnitude and sign (relative to $[^2J_{PH} + {}^3J_{PH}] = N$) of $^1J_{PP}$ in each case were determined by a heteronuclear $^1H-\{^{31}P\}$ tickling technique[7] which involved observing the *strong* lines in the proton spectrum and irradiating *weak* ^{31}P transitions. The sign of N is taken as positive by analogy with tetramethylbiphosphine in which $N = +\,14{\cdot}2$ Hz. In principle, individual values (but not assignments) for the two P–H coupling constants could be obtained from line-shape considerations, but this proved to be impossible in the present system.[8] The data are presented in the Table, and the ^{31}P chemical shifts and relative abundances of the two isomers agree with those found by other workers.[6]


(I)


(II)

Inversion at tervalent phosphorus in biphosphines at ordinary temperatures is slow,[6] but rotation about the P–P bond is rapid, and owing to differences in steric interaction

TABLE

N.m.r. parameters of the two isomers of $(MePhP)_2$

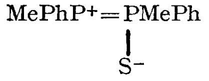
Isomer	$^1J_{PP}$ Hz	$^2J_{PH} + {}^3J_{PH}|$ Hz	δ (CH_3) p.p.m.[a]	Ξ (^{31}P) Hz[b]	δ (^{31}P) p.p.m.[c]	Amount present
A	-215 ± 2	$+15{\cdot}0 \pm 0{\cdot}1$	$1{\cdot}23 \pm 0{\cdot}01$	$40{,}479{,}245 \pm 1$	36·9	55%
B	-234 ± 2	$+15{\cdot}9 \pm 0{\cdot}1$	$1{\cdot}32 \pm 0{\cdot}01$	$40{,}479{,}102 \pm 1$	40·5	45%

[a] To low-field of $(CH_3)_4Si$. [b] This is the resonant frequency at a polarizing magnetic field strength which gives a $(CH_3)_4Si$ proton resonance at exactly 100 MHz. [c] To high-field of 85% H_3PO_4.

the rotamer populations in the two diastereomers will be different. In these circumstances any difference in $^1J_{PP}$ between different rotamers will show up as a difference between the two diastereomers, and our result thus provides experimental evidence that $^1J_{PP}$ is affected by internal rotation about the P–P bond. This appears to be the first authenticated example of such a dependence for any pair of coupled directly bound nuclei, although the steric dependence of geminal and vicinal coupling constants is now well established.

It is not possible to say which diastereomer corresponds to isomer A because the same mixture is obtained when either of the isomeric biphosphine disulphides, and a variety of reducing agents, are used. The conditions under which the reduction is performed are such as to permit ready isomerization and the composition of the product is governed by the relative thermodynamic stabilities of the two diastereomeric biphosphines. The greater stability of isomer A may be due to an ability to adopt conformations which are less strained sterically than those adopted by B. This may be associated with a slightly shorter mean P–P bond length in A, and this in turn would be reflected in rather greater overlap of the phosphorus 3*s* orbitals which should make $^1J_{PP}$ more positive in this isomer as is in fact observed. However since other factors including the relative orientation of the phosphorus lone pairs also affect the coupling this agreement is probably fortuitous.

$^1J_{PP}$ is more negative in each of the diastereomers of $(MePhP)_2$ than in $(Me_2P)_2$ in which it is $-179{\cdot}9$ Hz.[8] This may be due to the greater electronegativity of the substituents of phosphorus as has been suggested previously,[4] but it is now clear that a different distribution of rotamers could also give this effect. We have examined the diastereomeric biphosphine monosulphides $Me_2Ph_2P_2S$ similarly, and find values of -230 and -235 ± 5 Hz for $^1J_{PP}$. These are more negative than in Me_4P_2S (-220 Hz)[10] as would be predicted,[4] but the difference between them cannot be regarded as significant. This may be due to a contribution from the structure (III) which would stabilize a particular rotamer.



$$\underset{\displaystyle S^-}{MePh\overset{}{P}{}^+}{=}PMePh \qquad \text{(III)}$$

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