Sign and Magnitude of ^1J(PP) in Some Biphosphines with Bulky Substituents

By H. Christina E. McFarlane and William McFarlane*

(*Chemistry Department, City of London Polytechnic, Jewry Street, London* E.C.3)

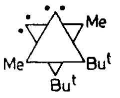
Summary Replacement of methyl by t-butyl in tetraorganobiphosphines leads to very large negative increments in ^1J(PP); these arise mainly from changes in phosphorus hybridization rather than from alterations in rotamer populations.

Nuclear spin–spin coupling constants between directly bound phosphorus atoms vary over a range of at least 1000 Hz according to the nature of the substituents on the two phosphorus atoms, but the relative importance of the various factors which might affect this coupling is not well understood.[1–3] We now report measurements of ^1J(PP) in some biphosphines with methyl or t-butyl substituents which permit us to distinguish the effects of internal rotation about the P–P bond from those of changes in the interbond angles at phosphorus.

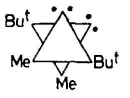
The results (Table) were obtained by ^{1}H-{^{31}P} double resonance techniques described elsewhere,[4] and gave the sign of ^1J(PP) relative to that of ^3J(^{31}P–CCH$_3$) which is known to be positive. In conformity with other results[5] a single deceptively simple triplet was obtained for the proton spectrum of (**4**) at room temperature, but at $-60°$ two equally intense triplets were obtained which were associated with identical values of ^1J(PP) of -427 ± 5 Hz which strongly confirms the original suggestion[5] that only the *gauche* conformer is present. Only one of the two diastereoisomers of (**3**) was observed to be present and there were no changes in the spectra of (**1**), (**2**), or (**3**) at temperatures down to −60°. The value of ^1J(PP) in (**4**) appears to be the most negative value yet reported for this coupling constant.

The differences in effective electronegativity between methyl and t-butyl would be expected to lead to differences in ^1J(PP) of at most a few Hz, and therefore the observed very large differences between the four biphosphines must arise from differences in the orientation of the lone pairs on the two phosphorus atoms[3] and/or differences in phosphorus hybridization arising from the bulk of the t-butyl groups.[1] We believe that the second of these is the major factor for the following reasons.

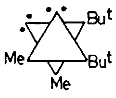
Our own and the published[5] spectra show that the amount of *trans* conformer in (**4**) is less than 5% at −60°, and this implies that at room temperature the proportion will not exceed 10%. The measured parameters of (**4**) at room temperature therefore apply essentially to the *gauche* rotamer. Since the rotamers with lone pairs *gauche* are not those which minimise steric repulsion between the t-butyl groups in the two halves of the molecule, it follows that the tendency of the lone pairs to adopt a *gauche* configuration is the factor whhich dominates rotamer stability. This will apply to an even greater extent in (**1**), (**2**), and (**3**), and hence these also must exist predominantly in conformations with lone pairs *gauche*. In the case of (**3**), if it is assumed that the vicinal steric repulsions decrease in the order Bu^t–Bu^t > Bu^t–Me > Me–Me then the four rotamers with *gauche* lone pairs will have stabilities which decrease in the order (Ib) > (IIa) ~ (IIb) > (Ia). Since only one of the two diastereoisomers (I) and (II) is present, [the possibility that the two diastereoisomers have identical values for δ(^{1}H)(Me), δ(^{1}H)(Bu^t), δ(^{31}P), ^1J(PP), ^2J(PH), ^3J(PH) and ^4J(PH) in several different solvents may reasonably be discounted] it follows that *only* the rotamer (Ib) is actually present to any significant extent at ordinary temperatures. A temperature dependence of *ca.* −0·25 Hz/°C was observed for ^1J(PP) in (**4**) in the range −60 to +140°; if this is due to an increasing proportion of *trans* isomer at higher temperatures this implies that the coupling is substantially more negative when the lone pairs are *trans*. However, the main observed differences in ^1J(PP) clearly arise from changes in the phosphorus hybridization as a result of differences in the bulk of methyl and t-butyl groups in the present compounds.



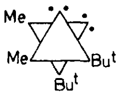
(Ia)



(Ib)



(IIa)



(IIb)

It is to be expected that the CPC interbond angle will be increased by t-butyl groups and hence the *s*-character of hybrid orbitals used to form the P–P bond will be reduced. This in turn should reduce β, the *s*-overlap integral for this bond, and make π_{pp}, the mutual polarizability of the valence *s*-orbitals on phosphorus, more negative; thus ^1J(PP) will become more negative as is observed.[6] The extent of these effects will probably be greater in (**2**) than in (**3**) and thus the coupling is more negative in (**2**).

TABLE. N.mr. parameters at room temperature

	Molecule	^1J(PP)/Hz	N(Me)/Hz[a]	N(Bu^t)/Hz[a]
(**1**)	Me$_2$PPMe$_2$[b]	−179·7	+14·2±0·1	—
(**2**)	Me$_2$PPBu$_2^t$	−318±5	+13·6±0·1[d]	+11·1±0·3[c]
(**3**)	MeBu^{t}PPBu^{t}Me	−290±3	+ 8·1±0·1[e]	+12·7±0·1
(**4**)	Bu$_2^t$PPBu$_2^t$	−451±3	—	+12·3±0·1
(**5**)	MeBu^{t}P(S)Bu^{t}Me[a]	−109±5	− 4·5±0·1	+18·0±0·1
(**6**)	MeBu^{t}P(S)P(S)Bu^{t}Me[b]	−103±5	− 5·6±0·1	+17·5±0·1

[a] N is the algebraic sum of the couplings to the nearer and more distant phosphorus nuclei. [b] *Cf.* E. G. Finer and R. K. Harris, *Mol. Phys.*, 1967, **12**, 465. [c] Error depends upon sign of ^4J(P–H). [d] ^2J = + 5·3$_5$, ^3J = + 8·3 Hz. [e] The marked difference between N(Me) in (**3**) and in (**1**) and (**2**) supports our contention that only one rotamer is present in (**3**).

Hitherto only one of the diastereoisomers of the disulphide of (**3**) has been reported;[7] however, direct reaction of (**3**) with sulphur gave a mixture of very nearly equal proportions of the two diastereoisomers, thus showing that (**5**) and (**6**) are of comparable stability. The values of ^1J(PP) are the first authenticated examples of large negative couplings between two directly bound P^V atoms and may again be attributed to abnormally low *s*-character for the orbitals used to form the P–P bond.[6] Unfortunately the disulphide of (**4**) has not been prepared,[8] but would be expected to exhibit an even larger negative value of ^1J(PP). The small difference in ^1J(PP) between (**5**) and (**6**) is to be expected in the absence of any lone pairs on phosphorus since the amount of steric distortion should be comparable in the two diastereoisomers.

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