Phosphorus–Phosphorus Nuclear Spin Coupling in Tetraorganobiphosphines and Some of Their Derivatives

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The signs and magnitudes of $^{31}P-^{31}P$ and $^{31}P-H$ spin-coupling constants in tetraorganobiphosphines RR'PPRR' with Me, Ph, and/or Bu^t as substituents, and in their sulphides and selenides RR'P(X)P(X)RR' (X = S or Se), have been determined by $^1H-\{^{31}P\}$ heteronuclear double resonance. Large variations in $^1J(^{31}P-^{31}P)$ arise as a result of changes in the phosphorus hybridization and/or effective nuclear charge, and smaller variations as a result of changes in the position of rotameric equilibrium in the *gauche* conformers of the biphosphines.

NUCLEAR spin–spin coupling between pairs of directly bound phosphorus atoms has been extensively studied for both its intrinsic theoretical interest and its possible diagnostic use.[1] It has been established that the magnitudes and signs of $^1J(^{31}P-^{31}P)$ are affected by the oxidation state and hybridization of the phosphorus atoms,[1] by the nature of the substituents on phosphorus,[1] and by the position of rotameric equilibrium about the P–P bond.[2] However, the relative importance of some of these effects remains unclear, although it is known that normally $^1J(^{31}P-^{31}P)$ is considerably less negative in P^V-P^V than in either P^V-P^{III} or $P^{III}-P^{III}$ species.[1] In the present paper we report determinations of the sign and magnitude of $^1J(^{31}P-^{31}P)$ for a range of biphosphines and some of their sulphides, selenides, disulphides, and diselenides. These had a variety of organo-groups attached to phosphorus so as to vary the interbond angles at phosphorus and also to stabilize preferentially particular rotamers.

A major problem encountered in this type of work is that the biphosphorus molecules which can be synthesized most readily are symmetrical, and often have long-chain alkyl and/or aryl substituents on phosphorus which give rise to very complex second-order spin systems having spectra from which it is difficult to extract even the magnitude of $^1J(^{31}P-^{31}P)$. Spin decoupling generally cannot be used as an aid to interpretation since this will destroy the magnetic asymmetry which otherwise makes available the desired information. In the present work we have therefore studied *chemically* symmetrical species in which phosphorus has methyl or t-butyl substituents so as to give $A_nA_n'XX'$ spin systems in which there is *magnetic* inequivalence, together with a number of chemically unsymmetrical molecules. The $^1H-\{^{31}P\}$ double-resonance method previously described[3] was used to measure $^1J(^{31}P-^{31}P)$ in many of the symmetrical compounds since it gives the sign as well as the magnitude of the coupling constant.

EXPERIMENTAL

$^1H-\{^{31}P\}$ double-resonance experiments were performed as described elsewhere using a modified JEOL C-60H spectrometer and a Schlumberger FS-30 frequency synthesizer.[3] The potential precision of the system was certainly better than ±0.1 Hz, and thus the quoted errors arise primarily from other factors such as rather large recorded line widths and undue complexity of splitting patterns. Samples were examined as *ca.* 30% solutions in CH_2Cl_2 or C_6H_6, at 23 ± 1 °C unless otherwise stated, in 5 mm tubes. Spectra were generally recorded in frequency-sweep mode with internal field-frequency locking and were calibrated by conventional methods.

Materials.—All air-sensitive substances were manipulated under an atmosphere of dry dinitrogen. The compound $[Me_2P(S)]_2$ was made by the ' anomalous Grignard ' reaction from PCl_3S and MgMeI, and was converted into $(Me_2P)_2$ by reduction with copper dust. The compounds $[PhMeP(S)]_2$ and $(PhMeP)_2$ were prepared similarly from $PPhCl_2S$. The compound $Me_2PP(S)Me_2$ was made by heating together equimolar amounts of $[Me_2P(S)]_2$ and $(Me_2P)_2$, and was then heated under reflux in benzene for 1 h with 1 equivalent of selenium to give an 80% yield of *tetramethylselenothiodiphosphane* † as air-stable white crystals, m.p. 199 °C (Found: C, 20.3; H, 5.1; P, 26.4; Se, 34.0. $C_4H_{12}P_2SSe$ requires C, 20.5; H, 5.1; P, 27.3; Se, 33.7%). *Tetramethyldiselenodiphosphane* was prepared in 75% yield by treating $(Me_2P)_2$ with 2 equivalents of selenium in benzene under reflux for 0.5 h, and gave air-stable white crystals, m.p. 278 °C (Found: C, 16.8; H, 4.1; P, 22.7; Se, 56.1. $C_4H_{12}P_2Se_2$ requires C, 17.0; H, 4.2; P, 22.6; Se, 56.0%).

The compound $(Bu^t_2P)_2$ was made by heating under reflux PBu^t_2Cl with 1 equivalent of sodium in dioxan for 20 h. The method of Scherer and Gick[4] was used to make $(Bu^tMeP)_2$ from PBu^tCl_2 and MgMeI, and this was obtained as a single diastereoisomer. However, its reaction with 2 equivalents of sulphur in boiling benzene gave a 70% yield of both diastereoisomers of $[Bu^tMeP(S)]_2$ in approximately equal amounts. After heating in benzene, a mixture of $(Me_2P)_2$ and $(Ph_2P)_2$ was found by ^1H n.m.r. spectroscopy to contain mainly Me_2PPPh_2 and this solution was examined directly. It was also treated with 2 equivalents of sulphur to give $Me_2P(S)P(S)Ph_2$, which was recrystallized from ethanol as white crystals, m.p. 141—144 (lit.,[5] 145 °C). When only 1 equivalent of sulphur was used the ^1H n.m.r. spectrum of the reaction mixture showed that the monosulphide $Me_2PP(S)Ph_2$ was formed preferentially, and this was examined in CH_2Cl_2 after pumping off the benzene, but without further purification.

RESULTS

The Table gives the n.m.r. parameters of the various species examined. Compounds (1) and (6) give proton spectra consisting of deceptively simple triplets arising from

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† A more systematic name for this compound, $Me_2P(S)P(Se)Me_2$, is tetramethyl-1-selenoxo-2-thioxodi-λ^5-phosphane.

the $A_pA_p'XX'$ spin systems with $p = 6$ and 18 respectively. The separation of the sharp outer lines of these triplets[6] is N [$= {}^nJ(^{31}P–H) + {}^{(n+1)}J(^{31}P–H)$, $n = 2$ and 3 respectively], and detailed analysis[6] of the broadened central line can in principle give L [$= {}^nJ(^{31}P–H) - {}^{(n+1)}J(^{31}P–H)$]. To determine $^1J(^{31}P–^{31}P)$ it is necessary to detect very weak ' outer ' lines in either the proton or the ^{31}P spectrum, and in the present work it was found convenient to locate those in the ^{31}P spectrum by $^1H–\{^{31}P\}$ double resonance experiments which involved observation of the sharp lines of the proton triplets.[3] In the case of (1) it was possible to detect and identify in this way the individual weak ^{31}P lines, and thus achieve high precision in the determination of $^1J(^{31}P–^{31}P)$; the result obtained agreed well with that in the literature.[6] In the case of (6) this degree of resolution was not possible and the precision was lower. This double-resonance experiment also gave the sign of $^1J(^{31}P–^{31}P)$ relative to that of N which is positive in both (1) and (6). In order to determine, L, spectra were recorded at low sweep rates (<0.1 Hz s^{-1}) and sufficiently low levels of B_1 to avoid saturation. The lineshape of the central band was then compared with that calculated for different values of L and the previously determined value of $^1J(^{31}P–^{31}P)$ using the program SHAPE[7] which is based upon an extended version of Harris's equations.[6] The errors in the individual couplings quoted as footnotes to the Table then indicate the range of values over which the fit was acceptable both as regards line width and peak height. It should be noted that notwithstanding this, systematic errors may not have been eliminated owing to the possibility that the transitions making up the central band and the N lines are associated with different values of T_2(H).

Hydrogen-1 and ^{31}P n.m.r. parameters of acyclic biphosphines and their sulphides and selenides[a]

Compound	$^1J(^{31}P–^{31}P)$	$^2J(^{31}P–C–H)$	$^3J(^{31}P–P–C–H)$	$^3J(P–C–C–H)$	$\delta(^1H)$	$\delta(^{31}P)$	Footnotes
(1) Me_2PPMe_2	-179.7 ± 0.3	2.9 ± 0.1	11.3 ± 0.1		1.04 ± 0.01	-58.5 ± 0.2	b, c
(2) $Me_2PP'Ph_2$	-197 ± 2	4.8 ± 0.1	10.9 ± 0.1		1.03 ± 0.01	-64.2, -11.5 ± 0.1	d d
(3) $MePhPPMePh$ (A)	-215 ± 2	$N =$ 15.0 ± 0.1			1.23 ± 0.01	-36.9 ± 0.1	d, e
(B)	-234 ± 2	$N =$ 15.9 ± 0.1			1.32 ± 0.01	-40.5 ± 0.1	d, e
(4) $Me_2PP'Bu^t{}_2$	-318 ± 5	5.3 ± 0.1	8.3 ± 0.1	11.2 ± 0.1	1.55, 1.46 ± 0.01	-64.6, 36.5 ± 0.1	f, g
(5) $MeBu^tPPMeBu^t$	-290 ± 3	$N =$ 8.1 ± 0.1		$N =$ 12.7 ± 0.1	1.02, 1.22 ± 0.01	-32.3 ± 0.2	d, h
(6) $Bu^t{}_2PPBu^t{}_2$	-451 ± 3			$N =$ 12.2 ± 0.1	1.62 ± 0.01	38.3 ± 0.2	d, i
(7) $Me_2P(S)P'Me_2$	-224 ± 5	-11.8 4.2 ± 0.1	20.4, 5.7 ± 0.1		0.95, 1.76 ± 0.01	-58.7, 35.6 ± 0.2	f, j
(8) $Me_2P(Se)P'Me_2$	-230 ± 5	-12.0, 4.2 ± 0.1	18.3, 5.8 ± 0.1		1.78, 2.03 ± 0.01	-57.5, 21.9 ± 0.2	f
(9) $Me_2P(S)P(S)Me_2$	-18.8 ± 0.2	-12.0 ± 0.1	7.2 ± 0.1		1.95 ± 0.01	35.0 ± 0.1	f, k
(10) $Me_2P(S)P'(Se)Me_2$	-40 ± 5	-12.7, -12.8 ± 0.1	7.7, 7.8 ± 0.1		2.02, 2.14 ± 0.01	33.9, 14.6 ± 0.4	f f
(11) $Me_2P(Se)P(Se)Me_2$	-67 ± 3	-12.5 ± 0.1	7.9 ± 0.1		2.15 ± 0.01	13.5 ± 0.2	f, l
(12) $PhMeP(S)P'MePh$ (A)	-230 ± 5	-12.4, 5.7 ± 0.1	17.2, 4.8 ± 0.1		1.72, 1.31 ± 0.01	23.7, -30.8 ± 0.2	f
(B)	-235 ± 5	-12.0, 5.5 ± 0.1	16.8, 6.4 ± 0.1		2.06, 1.58 ± 0.01	23.6, -28.5 ± 0.2	f
(13) $PhMeP(S)P(S)MePh$ (A)	-21.9 ± 0.2	-11.5 ± 0.5	6.0 ± 0.5		2.14 ± 0.01	35.1 ± 0.1	f
(14) $Ph_2P(S)P'Me_2$	-215 ± 1	3.9 ± 0.1	15.2 ± 0.1		1.14 ± 0.01	36.5, -67.9 ± 0.1	d
(15) $Me_2P(S)P'(S)Ph_2$	-24 ± 2	-12.5 ± 0.1	7.5 ± 0.1		1.98 ± 0.01	39.0, 30.9 ± 0.1	d
(16) $Bu^tMeP(S)P(S)MeBu^t$ (A)	-109 ± 5	$N =$ -4.5 ± 0.1		$N =$ 18.0 ± 0.1	1.77, 1.42 ± 0.01	58.9 ± 0.1	d, m
(B)	-103 ± 5	$N=$ -5.3 ± 0.1		$N=$ 17.5 ± 0.1	1.86, 1.38 ± 0.01	53.6 ± 0.1	d, m

[a] Coupling constants in Hz, chemical shifts in p.p.m. to low field of $SiMe_4$ or 85% H_3PO_4 as appropriate. Data refer to methyl and t-butyl groups only. Second entry refers to P'. [b] Neat liquid containing *ca.* 10% C_6H_6. [c] See ref. 6. [d] Solution in C_6H_6. [e] Diastereoisomers (A) and (B) present in *ca.* 55 : 45 ratio. Full spectral analysis not possible, see text. [f] Solution in CH_2Cl_2. [g] $J(^{31}P–P–C–C–H) = 0.3$ Hz. [h] Only one diastereoisomer present, approximate bandshape analysis gave L(Me) = 5.1 Hz, $L(Bu^t) = 9.4$ Hz; whence $^2J(^{31}P–C–H) = 1.5$, $^3J(^{31}P–C–C–H) = 11.1$, $^3J(^{31}P–P–C–H) = 6.6$, $^4J(^{31}P–P–C–C–H) = 1.6$ Hz. [i] Approximate bandshape analysis gave $L = 12.8$ Hz, whence $^3J(^{31}P–C–C–H) = 12.5$, $^4J(^{31}P–P–C–C–H) = -0.3$ Hz. [j] See R. K. Harris and R. G. Hayter, *Canad. J. Chem.*, 1964, **42**, 2282. [k] Sign obtained from $^{13}C–\{^1H,^{31}P\}$ triple-resonance experiments. See ref. 8. [l] Sign obtained from $^{31}P–\{^1H,^{77}Se\}$ triple-resonance experiments. [m] Full spectral analysis was not possible.

The deceptively simple triplets given by the methyl resonances of the two diastereoisomers of (3) partially overlapped, and had line widths of *ca.* 0.7 Hz. It was not therefore practicable to use bandshape analysis to extract a value of L, but the double-resonance experiment gave the sign and magnitude of $^1J(^{31}P–^{31}P)$ in each diastereoisomer without difficulty. In the case of (5) the proton spectrum showed that only one diastereoisomer was present, there being only one methyl and one t-butyl deceptively simple triplet, with less than 5% of any other component. $^1H–\{^{31}P\}$ experiments with observation of either the methyl or the t-butyl resonances readily gave a value for $^1J(^{31}P–^{31}P)$, and bandshape analysis treating the spin system as an $A_pA_p'XX'$ with $p = 3$ (for the methyl group) or $p = 9$ (for the t-butyl group) gave values of L. However, it should be stressed that this approach is of dubious validity in this case, since the effective ^{31}P chemical shift differences introduced by the coupling to protons of the unobserved proton group have not been taken into account. It was not possible to apply this method of analysis to the mixture of the two diastereoisomers of (16) owing to overlap of the broad central components of the deceptively simple triplets. However, the usual $^1H-\{^{31}P\}$ experiments gave $^1J(^{31}P-^{31}P)$ in each case, and also permitted unequivocal assignment of the phosphorus and proton resonances.

In the disulphide, (9), analysis of the proton spectrum gave values of all the coupling constants in close agreement with those already reported, but $^1J(^{31}P-^{31}P)$ was too small for an attempted determination of its sign by the $^1H-\{^{31}P\}$ method to yield unequivocal results. It subsequently proved possible [8] to use a $^{13}C-\{^1H, ^{31}P\}$ triple-resonance experiment to show this coupling to be negative, in agreement with other suggestions.[9] The proton spectrum of (11) was analysed similarly to yield the magnitude of $^1J(^{31}P-^{31}P)$ but again the results of the $^1H-\{^{31}P\}$ double-resonance experiment intended to give its sign were not satisfactory. In this case it was possible to use the isotope ^{77}Se ($I = \frac{1}{2}$, natural abundance $= 7\%$) to get the sign, since the ^{77}Se satellites in the proton-decoupled ^{31}P spectrum arise from an AA′X spin system, and a $^{31}P-\{^1H, ^{77}Se\}$ experiment gave the sign of $^1J(^{31}P-^{31}P)$ relative to that of $^1J(^{77}Se-^{31}P)$ which is known [10] to be negative.

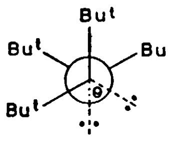
Only one diastereoisomer of (13) was sufficiently soluble to be examined, and analysis of the proton spectrum was used to give the coupling constants quoted in the Table. The sign of $^1J(^{31}P-^{31}P)$ is assumed to be negative by analogy with that in (9).

The other compounds examined have anisochronous phosphorus nuclei with large enough chemical-shift differences for their spectra to be treated on a first-order basis. The $^1H-\{^{31}P\}$ experiments were therefore used in a standard manner [11] to compare the signs of the various coupling constants [$^3J(^{31}P-H)$ in all cases being assumed to be positive [12]], and also to give $\delta(^{31}P)$ and to aid assignments of the various resonances.

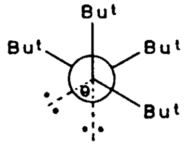
DISCUSSION

The well known tendency [1] for $^1J(^{31}P-^{31}P)$ to be less negative in P^V-P^V than in $P^{III}-P^{III}$ species is confirmed by the present work, and it also appears from a comparison of (9)—(11) that the greater polarizability of selenium as compared with sulphur makes it more closely resemble an electron lone pair. It is to be noted that the trend in the magnitudes of these coupling constants confirms the negative sign obtained in (9). In terms of the molecular orbital (m.o.) theory of Pople and Santry [13] the more negative values of $^1J(^{31}P-^{31}P)$ occur in the biphosphines because most of the 3*s* character of phosphorus is concentrated in the lone pairs, this leading to a small *s*-overlap integral for the P–P bond. As the C–P–C interbond angles increase (*e.g.* as more t-butyl groups are attached to phosphorus) *s* character will be directed to the P–C bonds and the P–P *s*-overlap integral should decrease even further, this leading to more negative values of $^1J(^{31}P-^{31}P)$, as is indeed observed for the sequence (1), (3), (4), (6), and also for the pair of compounds (9) and (16). Thus, it seems reasonable to attribute the main trends in the values of $^1J(^{31}P-^{31}P)$ to changes in the hybridization of phosphorus, at least in series of compounds in which the substituents on phosphorus are of comparable electronegativity. The results for species with phenyl groups on phosphorus are also in accord with this, since the phenyl group has somewhat greater bulk than methyl, *e.g.* the angle CPC is *ca.* 99° in PMe_3 [14] and *ca.* 103° in PPh_3,[15] but in this case the greater electron-withdrawing ability of the phenyl group may also play a part. It is noteworthy that $|^1J(^{31}P-^{31}P)|$ is larger in (3) than in (2), but is smaller in (5) than in (4); it is clear from this that one cannot assign a unique ' group contribution ' to the coupling constant from each fragment RR′P. This is confirmed by the observation of different values of $^1J(^{31}P-^{31}P)$ in the two diastereoisomers of (3), a result which we originally attributed to different rotamer populations in the two diastereoisomers.[2]

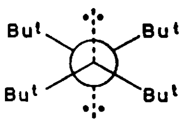
The dependence of $^1J(^{31}P-^{31}P)$ upon internal rotation about the P–P bond has been predicted theoretically,[16] and the different values of this coupling found [17] in $(MeP)_5$ almost certainly stem from this cause. This behaviour can be expected to affect the present results in two ways, since at ordinary temperatures rotation about the P–P bond is rapid on an n.m.r. time scale (although inversion at phosphorus is slow), and so the observed coupling constant is an average from the weighted contributions from the different rotamers. (*i*) Changes in the relative proportions of rotamers with lone pairs *gauche* or *trans* will affect the coupling constant; and (*ii*) variations in the actual lone-pair–lone-pair dihedral angle brought about by changes of substituent bulk in a *particular* rotamer will also affect $^1J(^{31}P-^{31}P)$. We now believe that the second of these is more important than the first in most of the systems we have examined. At temperatures below −50 °C the ^{13}C spectrum of (6) showed that rotation about the P–P bond is slow on an n.m.r. time scale and that no significant amount of *trans* rotamer (Ic) is present.[18] We ourselves obtained two deceptively simple triplets of equal intensity in the proton spectrum of (6) at low temperatures, associated with identical values of $^1J(^{31}P-^{31}P)$ and of $\delta(^{31}P)$, thus confirming this conclusion; it is most reasonable to interpret the results on the basis that the two equivalent *gauche* rotamers (Ia) and (Ib) are present in equal proportions. Strictly, by '*gauche*' we should mean ' non-*trans* ', but repulsion of the t-butyl groups on different phosphorus atoms should exclude eclipsed rotamers, although the dihedral angle θ is probably not equal to 60°. The factors which determine the stabilities of the rotamers of biophosphines are not understood, but when highly electronegative groups such as CF_3 are present the Coulombic repulsion apparently favours the *trans* rotamer. In the absence of this predominating electrostatic interaction there is evidently a factor favouring an approximately *gauche* relationship of the



(Ia)

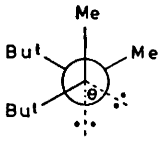


(Ib)

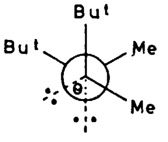


(Ic)

lone pairs which exceeds three *gauche* Bu^t–Bu^t steric repulsive interactions. The existence of only one diastereoisomer of (5) can then be understood in terms of the tendency of lone pairs to be *gauche* outweighing the repulsion of *gauche* t-butyl groups as follows. The idealised possible staggered rotamers of (5) are (IIa)—(IIf) and their mirror images, and we assume that the steric repulsions of *gauche* substituents decrease in the order Bu^t–Bu^t(x) $>$ Bu^t–Me(y) $>$ Me–Me(z), and further that the contributions of these to the instability of a particular rotamer are additive. In practice any deviation of θ from 60° would affect this and would prevent for example the stabilities of (IIa) and (IIb) from being the same, but at this stage this is neglected. If the factor favouring the *gauche* lone-pair–lone-pair relationship is f, we know from (6) that the quantity $f - x$ is large enough to exclude the *trans* rotamer. Both (IIa) and (IIb) will be stabilized with respect to (IIc) by $f - x + y - z$ and hence the *trans* rotamer will be absent in the *meso* diastereoisomer. (IId) is stabilized with respect to (IIf) by $f + x - 2y$ and hence again the *trans* rotamer of this diastereoisomer will be absent, although at this stage no judgement can be made on the likely proportion of (IIe) which is *destabilized* with respect to (IId) by $x - z$. However, the stabilities of the various *gauche* rotamers will be in the decreasing order (IId) $>$ (IIa) $\approx$ (IIb) $>$ (IIe), and since it is known that only *one* diastereoisomer is thermodynamically stable this must be (IId), there being no significant amount of (IIa) or (IIb), or of the other racemic rotamer (IIe). Isomer (IId) is actually stabilized with respect to (IIa) or (IIb) by $x - y$, whence it appears that the steric interaction Bu^t–Bu^t is *substantially* greater than Bu^t–Me, as is of course reasonable. This being so, the factor f must also be large, and an extension of these arguments to biphosphines such as (1)—(3) without bulky (or highly electronegative) substituents then implies that in these too the *trans* rotamer will be essentially absent. This conclusion is in conflict with suggestions of other workers,[19] but it should be emphasized there is currently no direct experimental evidence on this point.



(IIa)



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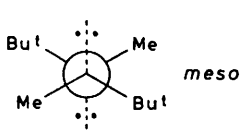
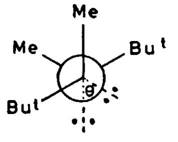
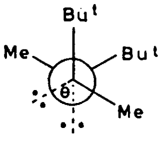


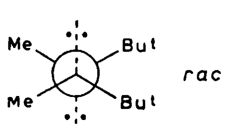
(IIc)



(IId)



(IIe)



(IIf)

We also found[20] that $^1J(^{31}P-^{31}P)$ in (6) changes monotonically from −427 Hz at −60 °C to −475 Hz at +140 °C, and the sense of this variation has been confirmed by Aime *et al.*[9] The origin of this behaviour is not clear; at the lower temperatures the measured figure certainly refers to the *gauche* rotamer since below *ca.* −40 °C the rotation about the P–P bond is frozen on the n.m.r. time scale. At the higher temperatures, where the rotation is rapid, there may be some contribution from the *trans* rotamer (although we believe that this will be small), and thus the observed change in $^1J(^{31}P-^{31}P)$ could be due to this. This would imply that in the *trans* rotamer the coupling constant is more negative than in the *gauche*, which conflicts with theoretical predictions.[16] A more probable explanation is that the dihedral angle θ in the *gauche* rotamer is an average over a wider spread of values at higher temperatures, and the observed change in $^1J(^{31}P-^{31}P)$ arises from a high sensitivity to relatively small changes in this angle.

We originally attributed[2] the difference in the values of $^1J(^{31}P-^{31}P)$ in the two diastereoisomers of (3) to differences in rotamer populations and hence to different contributions from rotamers with *gauche* or with *trans* lone pairs on phosphorus. We now consider it to be more likely that the effect arises from small differences in the dihedral angle θ in the *gauche* rotamers only (the *trans* rotamers being absent). Thus in (IIa) and (IIb) (with Bu^t replaced by Ph) θ will tend to be larger than 60° so as to minimize the dominant Ph–Ph steric interaction, whereas in (IId) a change in θ will have less effect and in (IIe) a value of θ of $>$60° will be needed to minimize the Ph–Ph interaction. Hence, it seems likely that in the *meso* diastereoisomer θ will be $>$60° and in the racemate θ will be $<$60°, which can easily account for the observed difference in $^1J(^{31}P-^{31}P)$. It is important to realise that even if the detailed assumptions made about the relative sizes of the various steric interactions are incorrect, the general principle of the foregoing argument remains valid, and it is possible to account for variations in $^1J(^{31}P-^{31}P)$ without postulating the presence of substantial proportions of the *trans* rotamer.

Aime *et al.*[9] found a correlation between $^1J(^{31}P-^{31}P)$ and $\delta(^{31}P)$ in P_2R_4 and RR′PPRR′, which they attributed to parallel influences upon both these parameters of the bulk of the groups R and R′. However, it is known that in tertiary, secondary, and primary phosphines the group contributions to the phosphorus shielding depend significantly upon factors other than the bulk of the substituents on phosphorus, and thus the apparent correlation may be misleading. In this connection it is of interest that the data for both diastereoisomers of (3) lie on the plot of Aime *et al.*,[9] as do those for (2) and (4) when the mean chemical shift of the two kinds of phosphorus atom is used. The concept of a 'group contribution' is of value[21,22] in the discussion of the effects of different organic substituents upon phosphorus shielding in tertiary phosphines and their derivatives. Our attempts to use the same group contributions to calculate the phosphorus chemical shifts of biphosphines were only partially successful in that while satisfactory predictions could be made for R = Me, Et, and Ph, the presence of Bu^t groups necessitated the inclusion of additional 'long-range' contributions. Since a major value of the group-contribution method lies in its use of only a single parameter for each alkyl group this approach was not pursued further.

It is well known [23] that phosphorus-proton coupling constants are sensitive to stereochemical relationships, and it is therefore reasonable to expect that pairs of diastereoisomers will have different values of $^2J(^{31}P-H)$ and of $^3J(^{31}P-H)$. In the case of (12) this effect is manifested directly, and in (3) and (16) the variations in N can be ascribed to this cause. The effect upon the phosphorus-proton couplings of replacing sulphur by selenium [*e.g.* in the species (7)—(11)] is minimal, and implies that the effective nuclear charge and hybridization of phosphorus are essentially unchanged, thus lending support to the idea that it is the variations in the *s*-overlap integral between the two phosphorus atoms which dominate the marked changes in $^1J(^{31}P-^{31}P)$.

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REFERENCES

[1] E. G. Finer and R. K. Harris, *Progr. N.M.R. Spectroscopy*, 1971, **6**, 61.

[2] H. C. E. McFarlane and W. McFarlane, *Chem. Comm.*, 1971, 1589.

[3] W. McFarlane and D. S. Rycroft, *J.C.S. Faraday II*, 1974, 377.

[4] O. J. Scherer and W. Gick, *Chem. Ber.*, 1970, **103**, 71.

[5] J. Koketsu, M. Okamura, Y. Ishii, G. Goto, and S. Shimuzu, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 15.

[6] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275; E. G. Finer and R. K. Harris, *Mol. Phys.*, 1967, **13**, 65.

[7] I. J. Colquhoun, Thesis, University of London, 1977.

[8] I. J. Colquhoun and W. McFarlane, *J. Magn. Resonance*, 1978, **31**, 63.

[9] S. Aime, R. K. Harris, E. M. McVicker, and M. Fild, *J.C.S. Dalton*, 1976, 2144.

[10] W. McFarlane and D. S. Rycroft, *J.C.S. Dalton*, 1973, 2162.

[11] W. McFarlane, *Ann. Rev. N.M.R. Spectroscopy*, 1968, **1**, 131.

[12] W. McFarlane, *Proc. Roy. Soc.*, 1968, **A306**, 185.

[13] J. A. Pople and D. P. Santry, *Mol. Phys.*, 1964, **8**, 1.

[14] L. S. Bartell, *J. Chem. Phys.*, 1960, **32**, 832; L. S. Bartell and L. O. Brockway, *ibid.*, p. 512; D. R. Lide, jun. and D. E. Mann, *ibid.*, 1958, **29**, 914.

[15] J. J. Daly, *J. Chem. Soc.*, 1964, 3799.

[16] J. P. Albrand, H. Faucher, D. Gagnaire, and J. B. Robert, *Chem. Phys. Letters*, 1976, **38**, 521.

[17] J. P. Albrand, D. Gagnaire, and J. B. Robert, *J. Amer. Chem. Soc.*, 1973, **95**, 64.

[18] S. Aime, R. K. Harris, E. M. McVicker, and M. Fild, *J.C.S. Chem. Comm.*, 1974, 426.

[19] J. R. Durig and J. S. DiYorio, *Inorg. Chem.*, 1969, **8**, 2796.

[20] H. C. E. McFarlane and W. McFarlane, *J.C.S. Chem. Comm.*, 1975, 582.

[21] S. O. Grim, W. McFarlane, and E. F. Davidoff, *J. Org. Chem.*, 1967, **32**, 781.

[22] S. O. Grim and W. McFarlane, *Nature*, 1965, **208**, 995.

[23] G. Mavel, *Ann. Rev. N.M.R. Spectroscopy*, 1973, **B5**, 1.