Studies of Phosphorus–Phosphorus Nuclear-spin Coupling in Species with Phosphorus–Nitrogen Bonds

By **Ian J. Colquhoun** and **William McFarlane**,* Department of Chemistry, City of London Polytechnic, Jewry Street, London EC3N 2EY

^1H-{^{31}P} double-resonance experiments have been used to study 34 organophosphorus species with a P–N–P skeleton. The geminal ^{31}P–^{31}P coupling constant is large and positive in derivatives of three-co-ordinate phosphorus and is increased by bulky or electronegative substituents on phosphorus. The results for several pairs of diastereoisomers, and also the temperature dependence, indicate a strong conformational dependence of the coupling which is related to the relative orientation of the lone pairs on phosphorus. In species with at least one four-co-ordinate phosphorus atom this last feature is absent, and the coupling constant is much smaller.

ALTHOUGH it cannot be claimed that one-bond ^{31}P–^{31}P nuclear spin–spin coupling constants are 'understood' there is nonetheless a considerable body of systematic data on both the magnitude and the signs of $^1J(^{31}P–^{31}P)$ so that in the majority of cases reasonably accurate predictions can be made.[1] The situation with regard to $^2J(^{31}P \cdots {}^{31}P)$ and longer-range coupling constants is less satisfactory, for many of the measurements have been of the magnitudes only, and the nature of the intervening atom has to be taken into account also. There is evidence [1] that the following factors can significantly affect $^1J(^{31}P–^{31}P)$: (*i*) oxidation state of the phosphorus atoms; (*ii*) effective electronegativity of the substituents on phosphorus; (*iii*) the bulk of the substituents on phosphorus, which affects the interbond angles at phosphorus and hence the hybridisation; and (*iv*) degree of rotation about the P–P bond. These factors can be expected to affect $^2J(^{31}P–E–^{31}P)$ also [with (*iv*) replaced by degree of rotation about the two P–E bonds], and, in addition, (*v*) the extent of π bonding between P and E and (*vi*) the interbond angles at E, might be important. In studies of diphosphinoamines Cross *et al.*[2] showed that $^2J(^{31}P–N–^{31}P)$ is very dependent on the bulk of the remaining substituent on N and interpreted this in terms of the relative orientations of the electron lone pairs on P, an explanation which effectively corresponds to (*iv*) above; in complexes of transition metals with phosphorus-donor atoms $^2J(^{31}P–M–^{31}P)$ depends on the geometry at M and can often be used to distinguish *cis* and *trans* arrangements,[3] and in cyclic phosphonitrilics substituent effects on $^2J(^{31}P–N–^{31}P)$ point to the importance of substituent electronegativity.[4] Very little is known about longer-range phosphorus–phosphorus couplings.

It is clear that a proper appreciation of the various factors which determine geminal and longer-range phosphorus–phosphorus coupling constants would be valuable in structural and preparative work, and with this in view we have examined a series of molecules with a PN(Me)P skeleton and with different substituents on phosphorus. In species of low symmetry (specifically with chemically inequivalent phosphorus atoms) it is convenient to use direct observation of the phosphorus n.m.r. spectrum to obtain $J(^{31}P–^{31}P)$, and much of the work reported on $^2J(^{31}P \cdots {}^{31}P)$ was done in this way.[1] However, the signs of coupling constants are not normally obtained in such experiments, and there are synthetic and aesthetic advantages in studying symmetrical molecules. Provided that the phosphorus nuclei in an organophosphorus compound are magnetically inequivalent it is possible to obtain $J(^{31}P–^{31}P)$ from either the ^{31}P or the proton (provided there is proton–phosphorus spin coupling) spectrum,[1] and it is often advantageous to use ^1H-{^{31}P} double-resonance experiments to do this since these provide high sensitivity and usually give the sign as well as the magnitude of the coupling constant.[5] This is the approach adopted in the present work; previously it has been used in studies of diphosphanes [5,6] and organometallics.[7-9]

EXPERIMENTAL

All the compounds were prepared and handled under an atmosphere of dry oxygen-free nitrogen, and solvents were dried over sodium. Starting materials [10-12] and compounds $NMe(PPh_2)_2$ (3),[13] $NMe(PPhCl)_2$ (5),[11] $NMe(PPh_2)(PCl_2)$ (8),[14] $NMe(PCl_2)_2$ (10),[15] $NEt(PCl_2)_2$ (21),[15] and $NMe(PPh_2)(PPh_2S)$ (24) [14] were prepared according to published procedures and the remainder were made as follows.

Methylbis(methylphenylphosphino)amine (2).—The method of ref. 13 with PPh_2Cl replaced by the equivalent amount of PMePhBr was used and the *product* was distilled as an air-sensitive colourless oil, b.p. 160—170 °C (0.5 Torr), yield 20%.† It was characterised by treating it with sulphur to

---

† Throughout this paper: 1 Torr = (101 325/760) Pa.

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

[2] R. J. Cross, T. H. Green, and R. Keat, *J.C.S. Dalton*, 1976, 1424.

[3] J. G. Verkade, *Co-ordination Chem. Rev.*, 1973, **9**, 1.

[4] E. G. Finer, *J. Molecular Spectroscopy*, 1967, **23**, 104.

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

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

[7] J. D. Kennedy and W. McFarlane, *J. Organometallic Chem.*, 1974, **80**, C47.

[8] H. C. E. McFarlane, W. McFarlane, and D. S. Rycroft, *J.C.S. Dalton*, 1976, 1616.

[9] J. D. Kennedy, W. McFarlane, R. J. Puddephatt, and P. J. Thompson, *J.C.S. Dalton*, 1976, 874.

[10] L. Maier, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1073.

[11] R. Jefferson, J. F. Nixon, T. N. Painter, R. Keat, and L. Stobbs, *J.C.S. Dalton*, 1973, 1414.

[12] G. W. Parshall, *Inorg. Synth.*, 1974, **15**, 192; L. Birkofer and G. Schmidtberg, *Ber.*, 1971, **104**, 3831.

[13] G. Ewart, A. P. Lane, J. McKechnie, and D. S. Payne, *J. Chem. Soc.*, 1964, 1543.

[14] R. Keat, *J. Chem. Soc.* (*A*), 1970, 1795.

[15] J. F. Nixon, *J. Chem. Soc.* (*A*), 1968, 2689.

give the *disulphide* as white crystals, m.p. 102 °C (Found: C, 53.4; H, 5.50; P, 18.5. $C_{15}H_{19}NP_2S_2$ requires C, 53.1; H, 5.60; P, 18.3%).

Bis[bis(dimethylamino)phosphino]methylamine (16).—A stream of dry dimethylamine was passed into a solution of $NMe(PCl_2)_2$ (10) (2.33 g, 10 mmol) in light petroleum (30 cm^3, b.p. 40—60 °C) until no more was absorbed. The precipitated amine hydrochloride was then filtered off and solvent was removed from the filtrate under high vacuum to leave the *product* as colourless air-sensitive needles, with ^1H n.m.r. parameters identical to those given in the literature.[16]

[Chloro(dimethylamino)phosphino](dichlorophosphino)-methylamine (18).—A few drops of $P(NMe_2)_3$ were added to (10) in an n.m.r. sample tube. The product formed within a few minutes and was identified by its n.m.r. spectrum.

Bis[chloro(dimethylamino)phosphino]methylamine (17).—A few drops of PCl_3 were added to a *ca.* 50% solution of $NMe[P(NMe_2)_2]_2$ in benzene contained in an n.m.r. sample tube. The product formed rapidly and had n.m.r. parameters identical to those given in the literature,[17] although only one isomer was present.

Bis(dimethoxyphosphino)methylamine (19).—Compound (10) (2.33 g, 10 mmol) in light petroleum (10 cm^3) was syringed into a flask containing methanol (1.28 g, 40 mmol), pyridine (3.16 g, 40 mmol), and light petroleum (30 cm^3). The mixture was stirred for 0.5 h and filtered. The solvent was removed *in vacuo* and the product was distilled at 90 °C (10 Torr) [lit.,[18] 91—94 °C (12 Torr)].

[Chloro(phenyl)phosphino](dichlorophosphino)methylamine (9).—An equimolar mixture of $NMe(PPhCl)(SiMe_3)$ and PCl_3 on standing overnight gave the *product* (identified by its ^{31}P spectrum) as the only phosphorus-containing component.

[Chloro(phenyl)phosphino](diphenylphosphino)methylamine (7).—This compound was made in the same way as (9) using PPh_2Cl instead of PCl_3. Another method of preparation is reported in ref. 2.

Bis[bis(methylthio)phosphino]methylamine (20).—Methanethiol (3 cm^3, an excess) was condensed into a flask at −78 °C and cooled light petroleum (30 cm^3) was added. Pyridine (3.16 g, 40 mmol) and (10) (2.33 g, 10 mmol) in light petroleum (10 cm^3) were then added and the mixture was stirred at 20 °C for 0.5 h. The precipitated pyridine hydrochloride was filtered off, and after removal of the solvent *in vacuo* the *product* was distilled to give an air-sensitive colourless viscous oil, b.p. 140—144 °C (0.2 Torr), yield 70% (Found: C, 21.3; H, 5.40. $C_5H_{15}NP_2S_4$ requires C, 21.5; H, 5.35%).

Bis[chloro(methyl)phosphino]methylamine (4).—A mixture of $PMeCl_2$ (0.21 g, 1.8 mmol), $NMe(SiMe_3)_2$ (0.158 g, 0.9 mmol), and benzene (0.5 cm^3) was allowed to stand overnight at room temperature in an n.m.r. sample tube. The spectral parameters showed that conversion to a single diastereoisomer of the product was essentially complete.[19] *Bis(dimethylphosphino)methylamine* (1) was made similarly, the $PMeCl_2$ being replaced by PMe_2Cl. It had n.m.r. parameters identical to those reported in the literature.[16]

2,4-*Dimethoxy*-1,3-*di*-*t*-*butylcyclodiphosphazane* (23).—The compound $(Bu^tNPCl)_2$ (1.43 g, 5.2 mmol) in light petroleum (5 cm^3) was added to methanol (0.33 g, 10.4 mmol) and pyridine (0.82 g, 10.4 mmol) in light petroleum (30 cm^3). The mixture was stirred for 1 h, precipitated pyridine hydrochloride was filtered off, solvent was removed *in vacuo*, and the *product* was distilled to give a colourless liquid, b.p. 66—68 °C (0.5 Torr), yield 60% (Found: C, 45.2; H, 9.1. $C_{10}H_{24}N_2O_2P_2$ requires C, 45.1; H, 9.00%).

2,4-*Dimethoxy*-1,3-*di*-*t*-*butyl*-2,4-*dithioxocyclo*-2λ^5,4λ^5-*diphosphazane* (27).—Compound (23) (2.66 g, 1.0 mmol) was heated under reflux in benzene (15 cm^3) with sulphur (0.064 g) for 1 h. The *product* separated on cooling and was recrystallised from benzene as white crystals, m.p. 124 °C (Found: C, 36.5; H, 7.4. $C_{10}H_{24}N_2O_2P_2S_2$ requires C, 36.4; H, 7.25%). When the course of the foregoing reaction was followed by n.m.r. a large proportion of monosulphide was detected early in the reaction and was examined without purification.

[Bis(diphenylphosphino)methylamine]pentacarbonyltungsten(0) (25).—A molar equivalent of $NMe(PPh_2)_2$ was used to displace tetrahydrofuran (thf) from photolytically prepared [6] $[W(CO)_5(thf)]$ and the *product* was recrystallised from pentane as yellow crystals, m.p. 180 °C (decomp.).

Proton n.m.r. spectra were recorded at 24 °C unless otherwise stated on samples in tubes (outside diameter, 5 mm) containing *ca.* 10% benzene to actuate the field-frequency locking circuits of the Jeol C 60 H continuous-wave spectrometer. ^1H-$\{^{31}P\}$ double-resonance experiments were performed as described elsewhere,[5] power at 24.3 MHz being provided by a Schlumberger FS 30 frequency synthesizer and supplied *via* a tuned amplifier to an extra coil in the probe. All the frequencies used were referenced to a single-crystal oscillator and proton spectra were calibrated by conventional methods. Phosphorus chemical shifts are based on a value of 40.480 740 MHz for $\Xi(^{31}P)$ for 85% H_3PO_4.

RESULTS

Almost all the species studied here give spectra which are second-order and often deceptively simple, and a variety of methods were used to obtain the magnitude and sign of $^2J(^{31}P \cdots {}^{31}P)$. For example, in $NMe(PPh_2)_2$ (3) if only the phosphorus and methyl proton spins are considered the system is A_2X_3 in which it is impossible to determine $^2J(^{31}P \cdots {}^{31}P)$. However, the coupling constant $^3J(^{31}P \cdots H)$ to the *ortho*-protons of the phenyl groups is likely to be several Hz and the system is really at least $AA'X_3Y_2Y_2'$ which introduces weak 'outer' lines in the phosphorus spectrum in positions [20] which depend on $^2J(^{31}P \cdots {}^{31}P)$. These lines may be detected by observing connected lines in the proton spectrum and simultaneously irradiating at the appropriate ^{31}P frequency with a sufficiently strong radiofrequency (r.f.) field to compensate for their low transition moments.[5] Inspection of the energy-level diagram for this system shows that both the *o*-phenyl and the *N*-methyl proton resonance are suitably connected, and it will in general be more convenient to observe the latter since they are unsplit by further couplings to other nuclei in the molecule. The *N*-methyl proton resonance will be a truly simple triplet of which the outer components are associated with either the $\alpha\alpha$ or the $\beta\beta$ spin states of the two phosphorus nuclei.[21] The weak 'outer' lines in the ^{31}P spectrum [situated at approximately $\nu(^{31}P) \pm {}^2J(^{31}P\text{—}^{31}P)$] are also associated with one or other of these spin states and thus the ^1H-$\{^{31}P\}$ double-resonance experiments used to detect these

---

[16] H. G. Metzinger, *Org. Mag. Res.*, 1971, **3**, 485.

[17] R. Keat, *J.C.S. Dalton*, 1974, 876.

[18] H. Binder and F. Fischer, *Ber.*, 1974, **107**, 205.

[19] U. Wannagat and H. Autzen, *Z. anorg. Chem.*, 1976, **420**, 119.

[20] R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

[21] I. J. Colquhoun, J. D. Kennedy, W. McFarlane, and R. J. Puddephatt, *J.C.S. Chem. Comm.*, 1975, 638.

lines also give the sign of $^2J(^{31}P-^{31}P)$ relative to that of $^3J(^{31}P-NCH_3)$. Strictly the centre of a group of these weak lines is at $\nu(^{31}P) \pm \frac{1}{2}[J + (4L^2 + J^2)]^{\frac{1}{2}}$, where L is the algebraic difference of the long- and short-range coupling constants between phosphorus and the protons causing the magnetic asymmetry, and for large $^2J(^{31}P \cdots {}^{31}P)$ can be approximated to $\nu(^{31}P) \pm {}^2J(^{31}P \cdots {}^{31}P)$ without significant error. In cases where several different groups of protons contribute to the magnetic asymmetry [as for example with (3) where the *o*-, *m*-, and *p*-protons will be significantly coupled to phosphorus and must therefore be taken into account] and/or there is broadening of lines in the phosphorus spectrum due to the presence of quadrupolar ^{14}N, the accuracy with which the positions of these outer lines may be determined may well be only ±5 Hz. Figure 1 depicts the results of double-resonance experiments of this type on $NMe[P(OMe)_2]_2$ (19) using observations of the *N*-methyl proton resonance. In this case it was possible to confirm the validity of the method by also observing asymmetric perturbation of the resonance of the *O*-methyl protons actually responsible for the magnetic asymmetry. Typically, in such experiments, in order to compensate for the low transition moments of the ' outer ' lines it is necessary to use amplitudes of ν_2 several orders of magnitude larger than are needed to determine $\nu(^{31}P)$. The magnitude and sign of $^2J(^{31}P \cdots {}^{31}P)$ relative to that of $^3J(^{31}P-NCH_3)$ (which can be taken as positive) was determined in this way for compounds (1)—(6), (16), (17), (19), (20), and (28), although in a number of these it was also possible to use observation of magnetically inequivalent protons instead. After a preliminary account [19] of our work had appeared, other workers [2] reported that for (3) it was possible to obtain the sign and magnitude of $^2J(^{31}P \cdots {}^{31}P)$ by observing the *ortho*-proton resonances of the phenyl groups and irradiating near $\nu(^{31}P) \pm {}^2J(^{31}P \cdots {}^{31}P)$. Their result agrees with ours.

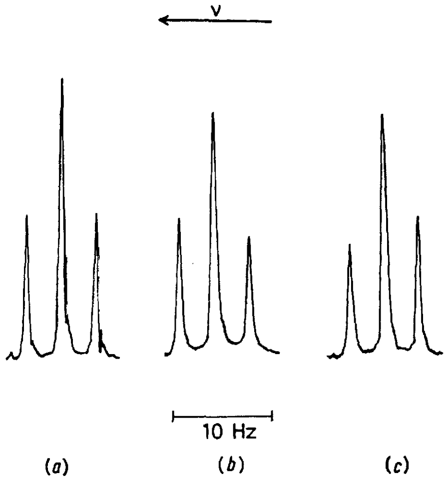


FIGURE 1 *N*-Methyl proton resonance of $NMe[P(OMe)_2]_2$ at 60 MHz: (*a*) normal spectrum; (*b*) with simultaneous irradiation at $[\nu(^{31}P) - {}^2J(^{31} \cdots {}^{31}P)]$ and $\gamma(^{31}P)B_2/2\pi \simeq 25$ Hz; and (*c*) with simultaneous irradiation at $[\nu(^{31}P) + {}^2J(^{31}P \cdots {}^{31}P)]$ and $\gamma(^{31}P)B_2/2\pi \simeq 25$ Hz

In $[Bu^tNP(OMe)]_2$ (23) and $[Bu^tNP(OMe)S]_2$ (29) the coupling from phosphorus to the protons of the symmetrically placed t-butyl groups was too small for the above method to succeed and the required data were obtained by observing the *P*-methoxy proton resonances. In fact the ratio $^2J(^{31}P-^{31}P) : L$ for these protons was small enough for weaker ' outer ' lines to be visible in the proton spectrum so that the magnitude of the geminal coupling was obtained by spectral analysis [20] and the double-resonance experiments were needed only to give the sign of this coupling constant. In (7)—(9), (18), (22), and (24)—(27) the two phosphorus nuclei are in chemically different environments and so standard $^1H-\{^{31}P\}$ double-resonance experiments sufficed. In $NMe(PCl_2)_2$ (10) the two phosphorus nuclei are chemically and magnetically equivalent if the spins of ^{35}Cl and ^{37}Cl are ignored, and thus $^2J(^{31}P \cdots {}^{31}P)$ is not accessible. However, if scalar coupling to these nuclei (each has $I = \frac{3}{2}$) were incompletely averaged by quadrupolar relaxation then the two phosphorus nuclei might acquire a sufficient degree of magnetic inequivalence for there to be transitions of finite intensity near $\nu(^{31}P) \pm {}^2J(^{31}P \cdots {}^{31}P)$. Attempts to detect these by double resonance have so far been unsuccessful. In view of the interest of the geminal phosphorus–phosphorus coupling constant in (10) a chemical solution to the problem was sought. It was found that halogen redistribution took place rapidly at room temperature in a mixture of (10) and $NMe(PBr_2)_2$ (15) to yield the intermediate species (11)—(14) in approximately statistical proportions. The *N*-methyl proton resonance of each species is a (possibly deceptively simple) triplet [see Figure 2(*a*)] and an assignment of the complex pattern of overlapping signals can be made with the aid of ^{31}P decoupling [see Figure 2(*b*)] and reasonable assumptions regarding the trends in the proton and ^{31}P chemical shifts, and the relative intensities of the six peaks in the decoupled spectrum. In species NMe-

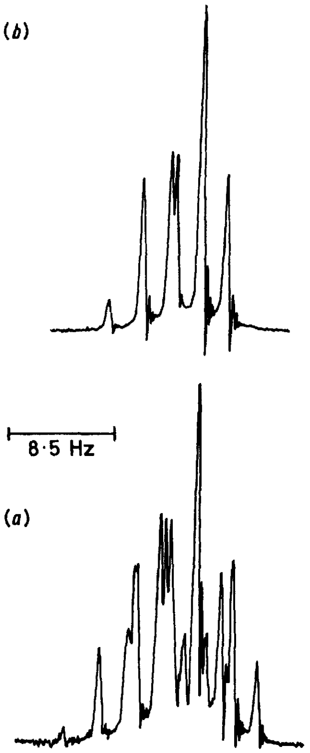


FIGURE 2 60-MHz Proton n.m.r. spectra of a mixture of $NMe(PCl_2)_2$ and $NMe(PBr_2)_2$ showing resonances due to intermediate species: (*a*) normal spectrum; (*b*) with ^{31}P decoupling [from left to right the peaks are assigned to species (15), (14), (13), (12), (11), and (10) respectively]

$(PBrCl)(PCl_2)$ (11), $NMe(PBr_2)(PCl_2)$ (13), and $NMe(PBr_2)(PBrCl)$ (14) the two phosphorus nuclei are chemically inequivalent and thus the ^{31}P spectrum should be of the AB type, further split by coupling to the *N*-methyl protons. In these systems the ratio $\delta_{AB}\nu : J_{AB}$ is of the order of 0.03 : 1 or less and so the outer lines of the AB pattern are only *ca.* 0.000 3 of the intensity of the inner; nonetheless, their positions can be determined by ^1H-{^{31}P} double resonance. In order to produce observable effects in the proton spectrum by irradiating a strong inner ^{31}P line it was necessary to have $\gamma(^{31}P)B_2/2\pi \simeq 1$ Hz, and it was then possible to obtain a precision of ±2 Hz. However, since the inner lines of this type of AB spectrum are only *ca.* 0.3 Hz apart (and furthermore there is a splitting of *ca.* 3 Hz by the *N*-methyl protons to be taken into account) it was not possible to obtain individual values of $\delta(^{31}P)$ and $\delta(^{31}P')$ and the quoted results are therefore the mean chemical shift for the two environments. The transition moment of an outer ^{31}P line is *ca.* 0.017 of that of an inner and thus $\gamma(^{31}P)B_2/2\pi$ needs to be 60—100 Hz to produce comparable perturbations of the connected proton resonances when an outer line is irradiated. In practice it was found that by using fields of this amplitude the positions of the outer lines in the ^{31}P spectra of (11) and (14) could be determined to ±2 Hz, but in (13) this was not possible owing to overlap of lines in the proton spectrum. These experiments thus gave the magnitude and sign of $^2J(^{31}P\cdots{}^{31}P)$ relative to that of $^3J(^{31}P\cdots H)$ in (11) and (14). It was also found that r.f. fields of this amplitude had negligible off-resonance effects on the strong inner lines in the ^{31}P spectra, a result which

Coupling constants (*J*/Hz) and chemical shifts (δ/p.p.m.)

Species	$^2J(^{31}P\cdots{}^{31}P)$ [a]	$^3J(^{31}P\cdots H)$ [b]	$\delta(^{31}P)$ [c,d]	$\delta(^1H)$ [e,f]	Notes
$NMe(PMe_2)_2$ (1)	+168 ± 3	+5.39	+38.9	2.40 ± 0.02	*g, h*
$NMe(PMePh)_2$ (2) (a)	+278 ± 5	+3.2	−58.1	2.22 ± 0.02	*i, j*
(b)	+225 ± 5	+4.2	+55.1	2.35 ± 0.02	*i, k*
$NMe(PPh_2)_2$ (3)	+280 ± 10	+3.0	+72.8	2.40 ± 0.02	*i*
$NMe(PMeCl)_2$ (4)	+350 ± 3	+4.2	+143.4	2.90 ± 0.02	*g, l, m*
$NMe(PPhCl)_2$ (5) (a)	+341 ± 3	+3.7	+134.8	2.37 ± 0.02	*n*
(b)	+421 ± 3	+3.2	+137.1	2.33 ± 0.02	*n*
$NMe(PBrPh)_2$ (6) (a)	+310 ± 10	+3.25	+138.2	2.44 ± 0.03	*n*
(b)	+390 ± 10	+3.25	+141.2	2.44 ± 0.03	*n*
$NMe(PPh_2)(P'PhCl)$ (7)	+330 ± 5	+3.40, +3.40	+70.1, +143.4	2.53 ± 0.02	*i, o*
$NMe(PPh_2)(P'Cl_2)$ (8)	+500 ± 2	+2.10, +4.10	+55.2, +167.1	2.75 ± 0.02	*n*
$NMe(PPhCl)(P'Cl_2)$ (9)	+530 ± 2	+3.19, +3.19	+121.1, +166.6	2.80 ± 0.02	*n, o*
$NMe(PCl_2)_2$ (10)	?	+2.93	+159.5	3.27 ± 0.01	*p, q*
$NMe(P'BrCl)(PCl_2)$ (11)	+662 ± 3	+2.93, 2.93	+159.6, 159.6	3.29 ± 0.01	*o, r, s*
$NMe(PBrCl)_2$ (12)	?	+2.85	+159.7	3.32 ± 0.01	*r*
$NMe(PBr_2)(P'Cl_2)$ (13)	?	+2.85, +2.85	+158.6, +158.6	3.33 ± 0.02	*o, r, s, t*
$NMe(PBr_2)(P'BrCl)$ (14)	+665 ± 3	+2.85, +2.85	+158.6, +158.6	3.37 ± 0.01	*o, r, s*
$NMe(PBr_2)_2$ (15)	?	+2.85	+157.7	3.41 ± 0.01	*p*
$NMe[P(NMe_2)_2]$ (16)	+315 ± 5	+3.3	+118.1	2.52 ± 0.02	*g, u*
$NMe[PCl(NMe_2)]_2$ (17)	+315 ± 5	+5.2	+143.3	3.01 ± 0.02	*p, l, v*
$NMe(P'Cl_2)[PCl(NMe_2)]$ (18)	+280 ± 3	+7.4, +4.0	+137.4, 167.2	2.98 ± 0.02	*p, w*
$NMe[P(OMe)_2]_2$ (19)	+355 ± 5	+3.4	+145.4	2.55 ± 0.02	*g, x*
$NMe[P(SMe)_2]_2$ (20)	+400 ± 5	+2.8	+128.9	2.99 ± 0.02	*g, y*
$NEt(PCl_2)_2$ (21)	?	+5.7	+164.6	1.50 ± 0.02	*p, z*
$NEt(P'BrCl)(PCl_2)$ (22)	+535 ± 5	+5.7	+164.7	1.50 ± 0.02	*
$[NBu^tP(OMe)]_2$ (23)	+15 ± 5		+133.8	1.34 ± 0.01	*g*, †
$NMe(PPh_2)(P'Ph_2S)$ (24)	+93 ± 2	+1.6, +11.7	+54.1, +75.5	2.60 ± 0.02	*g*
$[W(CO)_5\{NMe(PPh_2)(P'Ph_2)\}]$ (25)	+200 ± 5	+1.5, +7.2	+65.9, +88.9	2.20 ± 0.02	*g*
$NMe(PMePh)(P'MePhS)$ (26) (a)	+78 ± 5	+1.9, +12.3	+41.3, +70.4	2.37 ± 0.02	*i*, ‡
(b)	+82 ± 5	+1.9, +12.0	+43.8, +71.4	2.43 ± 0.02	*i*, §
$NBu^t\cdot P(OMe)\cdot NBu^t\cdot P'(OMe)S$ (27)	±15 ± 1		+92.5, +60.3	1.25 ± 0.02	*g*, ¶
$NMe(PMePhS)_2$ (28) (a)	0 ± 5	+11.1	+69.3	2.70 ± 0.01	*i*, ‖
(b)	0 ± 5	+11.7	+67.9	2.57 ± 0.01	*i*, **,‡‡
$[NBu^tP(OMe)S]_2$ (29)	+27.4 ± 0.5		+51.8	1.25 ± 0.01	*g*, ††,§§

[a] Relative to $^3J(^{31}P\cdots H)$ positive. [b] Assumed to be positive (see text); error ±0.2 Hz. [c] First number refers to P, second to P′. [d] To low field of 85% H_3PO_4. [e] Refers to methyl group on bridging N. [f] To low field of internal $SiMe_4$. [g] *ca.* 50% in C_6H_6. [h] $[^2J(^{31}PCH) + {}^4J(^{31}P\cdots H)]$ +6.0 Hz, $\delta(^1H)$(*P*–Me) 0.9 p.p.m. [i] *ca.* 50% in CH_2Cl_2. [j] $[^2J(^{31}PCH) + {}^4J(^{31}P\cdots H)]$ +6.3 Hz, $\delta(^1H)$(*P*–Me) 1.57 p.p.m. [k] $[^2J(^{31}PCH) + {}^4J(^{31}P\cdots H)]$ +6.3 Hz, $\delta(^1H)$(*P*–Me) 1.51 p.p.m. [l] Only one diastereoisomer was detected. [m] $[^2J(^{31}PCH) + {}^4J(^{31}P\cdots H)]$ 13.1 Hz. [n] *ca.* 50% in $CDCl_3$. [o] Owing to second-order features it is not certain that $^3J(^{31}P\cdots H) = {}^3J(^{31}P'\cdots H)$. [p] Neat liquid. [q] $\delta(^{15}N)$ +69.9 p.p.m. relative to $[NMe_4]I$ in water and $\delta(^{13}C)$ +29.4 p.p.m. relative to $SiMe_4$; $^2J(^{15}N\cdots H)$ 0.6 ± 0.04, $^1J(^{31}P{-}^{15}N)$ +86 ± 1, and $^2J(^{31}P\cdots{}^{13}C)$ −1.8 Hz. [r] Present in a mixture of (10) and (15). [s] $|\delta(^{31}P)-\delta(^{31}P')| < 0.2$ p.p.m. [t] Presence of overlapping lines prevented determination of $^2J(^{31}P\cdots{}^{31}P)$. [u] $\delta(^1H)$ (terminal Me) 2.45 ± 0.02 p.p.m.; $[^3J(^{31}P\cdots H) + {}^5J(^{31}P\cdots H)]$ +9.5 ± 0.1 Hz. [v] $\delta(^1H)$ (terminal Me) 2.51 ± 0.02 p.p.m.; $[^3J(^{31}P\cdots H) + {}^5J(^{31}P\cdots H)]$ +13.8 ± 0.1 Hz. [w] $\delta(^1H)$ (terminal Me) 2.67 ± 0.02 p.p.m.; $^3J(^{31}P\cdots H)$ +12.6 and $^5J(^{31}P\cdots H)$ +1.2 Hz. [x] $\delta(^1H)$(MeO) 3.35 p.p.m.; $[^3J(^{31}P\cdots H) + {}^5J(^{31}P\cdots H)]$ +13.1 Hz. [y] $\delta(^1H)$(MeS) 2.11 p.p.m.; $[^3J(^{31}P\cdots H) + {}^5J(^{31}P\cdots H)]$ +13.9 Hz. [z] $\delta(^1H)$ (CH_2) 4.00 p.p.m.; $^3J(H\cdots H)$ 7.4 Hz.

* Present in mixture of (21) and PBr_3; $\delta(^1H)(CH_2)$ 4.05 p.p.m.; $^3J(H\cdots H)$ 7.4 Hz. † Predominant isomer. $\delta(^1H)$(MeO) 3.56 p.p.m.; $[^3J(^{31}P\cdots H) + {}^5J(^{31}P\cdots H)]$ +9.9 Hz. ‡ $\delta(^1H)$(*P*–Me) 1.58 and $\delta(^1H)$(*P′*–Me) 2.25 p.p.m.; $^2J(^{31}P\cdots H)$ +6.9, $^4J(^{31}P\cdots H)$ 0.6, $^2J(^{31}P\cdots H')$ −13.2, and $^4J(^{31}P\cdots H')$ +3.0 Hz. § $\delta(^1H)$(*P*–Me) 1.58 and $\delta(^1H)$(*P′*–Me) 2.24 p.p.m.; $^2J(^{31}P\cdots H)$ +6.9, $^4J(^{31}P\cdots H)$ 0.6, $^2J(^{31}P\cdots H')$ −13.2, and $^4J(^{31}P'\cdots H)$ −13.2 Hz. ¶ Predominant isomer. $\delta(^1H)$ (MeOP) 3.40 and $\delta(^1H)$ (MeOP′) 3.60 p.p.m.; $^3J(^{31}P\cdots H)$ +8.6, $^3J(^{31}P\cdots H')$ +14.8, and $|^4J(^{31}P\cdots H)| = |^4J(^{31}P'\cdots H)| < 0.5$ Hz. ‖ $\delta(^1H)(^{31}$*P*–Me) 1.86 p.p.m.; $^2J(^{31}P\cdots H)$ −13.2 Hz. ** $\delta(^1H)(^{31}$*P*–Me) 2.18 p.p.m.; $^2J(^{31}P\cdots H)$ −13.0 Hz. †† Predominant isomer. $\delta(^1H)$ (*O*–Me) 3.3 p.p.m.; $|^4J(^{31}P\cdots H)| < 0.5$ Hz. ‡‡ Ref. 2 gives $^2J(^{31}P\cdots{}^{31}P)$ +273 ± 3 Hz. §§ Ref. 2 gives $^2J(^{31}P\cdots{}^{31}P)$ +333.5 ± 1 Hz.

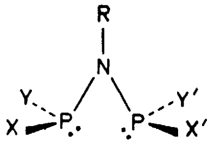
can be confirmed by reference to Freeman and Anderson's plots.[22]

The geometry at phosphorus in most of our compounds is expected to be non-inverting trigonal pyramidal and this is confirmed by the observation of diastereoisomers of (2), (5), (6), (26), and (28). In several other cases where diastereoisomers might be expected they were not observed, namely (4), (12), and (17). The reasons for this are not clear, but it should be noted that none of these compounds had been exposed in the course of preparation to temperatures high enough to permit inversion at phosphorus. Keat reported [17] that $NMe[PCl(NMe_2)]_2$ (17) exhibits diastereoisomerism and thus it seems likely that the exchange reactions used to make $NMe(PMeCl)_2$ (4) and (17) are stereospecific. In (11) it may be that the differences between chlorine and bromine are insufficient to produce appreciable variation in the n.m.r. parameters in different isomers. In the cases of (27) and (29) two forms were detected but only the predominant isomer was studied. The temperature dependence of $^{2}J(^{31}P\cdots{}^{31}P)$ was found to be -0.8 Hz K^{-1} over the range 25—150 °C for (11), and -1.2 Hz K^{-1} over the range 25—85 °C for $NEt(PBrCl)(PCl_2)$ (22).

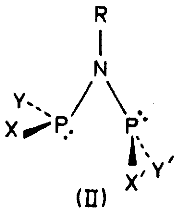
The n.m.r. parameters are in the Table, it being assumed in all cases that $^{3}J(^{31}P{-}NCH_3)$ is positive. This is in agreement with the observations of other workers,[23] and was also confirmed by us in the case [24] of (10) enriched to 90% in ^{13}C so that the sign could be compared with that of $^{1}J(^{13}C{-}H)$.

DISCUSSION

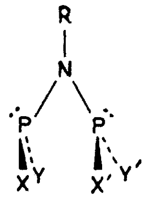
An electron-diffraction study [25] of $NMe(PF_2)_2$, and an *X*-ray diffraction study [26] of $NMe(PPh_2)(PPh_2S)$ have shown that compounds of this type contain planar-trigonal nitrogen, there presumably being d_π–p_π overlap between phosphorus and nitrogen. There is thought [25,27,28] to be a tendency for the electron lone pairs on nitrogen and phosphorus in species with P–N bonds to be orthogonal, and on this basis the idealised conformations (I)—(III) can be drawn. However, it should be recognised that significant departures from these conformations are possible, especially in solution.



(I)



(II)



(III)

Molecular models indicate that when R is bulky (*e.g.* Bu^t) steric interaction with the groups X and Y will destabilise (I) and it has been suggested [2] that (II) and (III) will then predominate. This is supported by the observation [2] that in $NR(PPh_2)(PPhCl)$ ($R = Pr^i$ or Bu^t) $^{2}J(^{31}P\cdots{}^{31}P)$ is small and negative, while with R = Et or Pr the coupling is about half that when R = Me and is very temperature dependent. However, conformation (III) requires very close approaches of the groups X and Y: for example with X = Y = Cl we calculate $r(XX') = 260$ pm, which is sufficiently less than the van der Waals diameter of chlorine to preclude this conformation. Similarly, with X = X' = Ph it is necessary in (III) for the phenyl rings to twist into a position in which they are approximately parallel with their planes only *ca.* 200 pm apart. This again is extremely improbable and we therefore reject the idealised conformation (III). Of course, an enlargement of the PNP interbond angle would reduce this type of steric interaction, but evidence on this point is lacking; however, a very substantial increase would be needed to make (III) a feasible conformation.

It is most reasonable to assume that the large differences in $^{2}J(^{31}P\cdots{}^{31}P)$ between pairs of diastereoisomers (a) and (b) of $NMe(PMePh)_2$ (2), $NMe(PPhCl)_2$ (5), and $NMe(PBrPh)_2$ (6) stem from differences in rotamer populations. This implies that the geminal coupling is sensitive to conformational changes, and also that the configuration at one phosphorus atom affects rotation of the other about the P–N bond. This in turn implies that there is significant through-space interaction [which is almost certainly steric in origin in (2), and also probably in (5) and (6)] between the groups on the different phosphorus atoms. In these circumstances conformers (I) and (II) might be differently populated in the diastereoisomers, and thus the observed $^{2}J(^{31}P\cdots{}^{31}P)$ which will be a rotationally averaged mean would be different in the two. It is difficult accurately to assess the extent of steric interaction in these species solely by studying molecular models, but it certainly appears that for most of the substituents on phosphorus studied here the effects would be slight in the idealised conformations (I) and (II). For example, in either diastereoisomer of (2) the closest approach of the centres of the phenyl rings in the appropriate conformer is *ca.* 600 pm. On this basis then, the relative populations of (I) and (II) might be expected to be very similar in the two diastereoisomers and thus the difference in $^{2}J(^{31}P\cdots{}^{31}P)$ is surprising.

Conformer (I) requires a close approach of the electron lone pairs on the two phosphorus atoms, and this is unlikely to be favourable. It is known [25] that this apparently occurs in $NMe(PF_2)_2$, but in species with P–F bonds the electron lone pair on phosphorus has high *s*, and therefore low directional, character, and so this molecule is probably a special case. In compounds with a direct P^{III}–P^{III} bond there is a strong tendency for the favoured conformation to have the lone pairs *gauche*,[29]

---

[22] R. Freeman and W. A. Anderson, *J. Chem. Phys.*, 1962, **37**, 2053.

[23] R. D. Bertrand, F. Ogilvie, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1970, **92**, 1908.

[24] I. J. Colquhoun and W. McFarlane, *J.C.S. Faraday II*, 1977, 722.

[25] E. Hedberg, L. Hedberg, and K. Hedberg, *J. Amer. Chem. Soc.*, 1974, **96**, 4417.

[26] K. M. Ghouse, R. Keat, H. H. Mills, J. M. Robertson, T. S. Cameron, K. D. Howlett, and C. K. Prout, *Phosphorus*, 1972, **2**, 47.

[27] A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, 1970, **92**, 5206.

[28] E. D. Morris and C. E. Norman, *Inorg. Chem.*, 1969, **8**, 1673; G. C. Holywell, D. W. H. Rankin, B. Beagley, and J. M. Freeman, *J. Chem. Soc.* (*A*), 1971, 785.

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

even when steric effects oppose this,[6] as in $P_2Bu^t_4$, and we believe that there may be a similar tendency in these species. The idea of a *gauche* or other relation of the lone pairs requires a notional P–P link about which rotation is supposed to occur, and it is therefore more exact to use the dihedral angles[2] θ and θ' between the P_2NR plane and the bisector of the XPY or the X′PY′ angle. In (I) $\theta = \theta' = 0°$, and in (II) $\theta = 0$ and $\theta' = 180°$. If the analogy with the diphosphanes is correct then neither (I) nor (II) should be favoured, and instead intermediate conformations would be preferentially adopted in which steric interaction between the groups on the different phosphorus atoms would be sufficient to produce the observed differences in ${}^2J({}^{31}P \cdots {}^{31}P)$. For example, with $\theta = -\theta' = 70°$ the phosphorus electron lone pairs are approximately *gauche* and there are differences in the estimated amounts of steric interaction in the two diastereoisomers, which would therefore probably adopt significantly different conformations.

Support for the idea that conformational changes are partially responsible for the observed variations in ${}^2J({}^{31}P \cdots {}^{31}P)$ is provided by the values of ${}^3J({}^{31}P\text{–}NCH_3)$. It is known[27] that this coupling depends on molecular conformation, and there is evidence[30] that it is larger when $\theta = 0$ than 180°, although nothing is known about its size for intermediate conformations. In (1)—(3), where there is little change in the effective nuclear charge on phosphorus the variations of ${}^3J({}^{31}P \cdots H)$ parallel those of ${}^2J({}^{31}P \cdots {}^{31}P)$ but are in the opposite sense, which might indicate that the latter coupling constant is smallest in conformer (I). It should be further noted that (1) has the smallest substituents on phosphorus and the smallest value of ${}^2J({}^{31}P \cdots {}^{31}P)$, and also that the temperature dependences in (11) and (22) are such that the coupling constant becomes smaller as more sterically hindered conformers become populated. These results are in marked contrast to those of Cross *et al.*[2] who find that a bulky group on nitrogen can substantially reduce ${}^2J({}^{31}P \cdots {}^{31}P)$, and it is clear that the question of the detailed relation between this coupling constant and molecular conformation is still open.

When some of the substituents on phosphorus become more electronegative the magnitudes of the coupling constants associated with the other bonds to phosphorus generally increase. This is observed for ${}^2J({}^{31}P \cdots {}^{31}P)$ in our species, for when *P*-methyl or -phenyl is replaced by chlorine the coupling increases substantially and the dependence on molecular conformation remains, as shown by the different values obtained for the diastereoisomers of $NMe(PPhCl)_2$ (5) and $NMe(PPhBr)_2$ (6). The series of compounds (10)—(15) is of interest in that it enables us to estimate the otherwise inaccessible coupling ${}^2J({}^{31}P \cdots {}^{31}P)$ in (10) as 660 Hz. This is substantially larger than in $NMe(PF_2)_2$ (433 Hz)[31] and may indicate that (I) is not the only conformation adopted. In compounds (16)—(20) both the bulk and electronegativity of the substituents of phosphorus vary, and in addition π bonding between phosphorus and its substituents may be important; it is therefore difficult to comment usefully at this stage.

The effect of changing the oxidation state of *one* phosphorus atom is brought out well by compounds (3), (25), and (24). It is often the case that when a phosphorus atom co-ordinates to a transition metal it behaves as though its oxidation number were between III and V; this is exemplified for example by the values of ${}^1J({}^{31}P\text{–}{}^{13}C)$ in PMe_2Ph (−14 Hz),[32] $[W(CO)_5(PMe_2Ph)]$ (30 Hz),[33] and $[PMe_2PhH]^+$ (56 Hz).[32] There is a clear parallel in the behaviour of ${}^2J({}^{31}P \cdots {}^{31}P)$, although in (25) the coupling is perhaps closer to that in (3) than might have been expected. Presumably the bulk of the $W(CO)_5$ moiety leads to conformations being favoured in which ${}^2J({}^{31}P \cdots {}^{31}P)$ is larger. Such an effect is less probable in (24) because only one phosphorus atom has an electron lone pair. The close similarity of the values of ${}^2J({}^{31}P \cdots {}^{31}P)$ in the two diastereoisomers of NMe(PMePh)(PMePhS) (26) confirms that it is the relation of the electron lone pairs on each phosphorus atom that determines the conformation dependence of the coupling constant; that is, both θ and θ' must be considered. Similarly in $NMe(PMePhS)_2$ (28) no conformational dependence of ${}^2J({}^{31}P \cdots {}^{31}P)$ is apparent. This behaviour is completely analogous to that of ${}^1J({}^{31}P\text{–}{}^{31}P)$ in diphosphanes.[1]

Our main conclusions are that the geminal phosphorus–phosphorus nuclear-spin coupling constant in species with essentially unstrained P–N–P linkages is large and positive when both phosphorus atoms are three-co-ordinate and decreases greatly on increase of co-ordination number of phosphorus. The coupling also increases with the effective nuclear charge on phosphorus, and in species with phosphorus(III) atoms only is sensitive to molecular conformation, being primarily determined by the relative orientation of the electron lone pairs on phosphorus. The presence of bulky groups on phosphorus increases the coupling constant, whilst a bulky group on nitrogen reduces it. This indicates that there are rather complicated conformational changes involved, and we tentatively suggest that in the latter case non-planar nitrogen may be involved.

We thank the S.R.C. for support, and Mr. B. Saunderson for microanalyses.

[7/269 *Received*, 15*th February*, 1977]

---

[30] A. H. Cowley, M. J. S. Dewar, W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, 1970, **92**, 1085.

[31] J. F. Nixon, *J. Chem. Soc.* (*A*), 1969, 1087; R. W. Rudolph and R. A. Newmark, *J. Amer. Chem. Soc.*, 1970, **92**, 1195.

[32] W. McFarlane, *Chem. Comm.*, 1967, 58.

[33] W. McFarlane and D. S. Rycroft, *J.C.S. Chem. Comm.*, 1973, 336.