Studies of Nitrogen-15–Phosphorus-31 Nuclear Spin–Spin Coupling by Heteronuclear Magnetic Double Resonance

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The signs and magnitudes of $^1J(^{31}P-^{15}N)$, $^2J(^{31}PNH)$, $^3J(^{15}NPCH)$, and certain other coupling constants, and phosphorus-31 and nitrogen-15 chemical shifts, have been determined in 24 organophosphorus compounds with P–N bonds and enriched in nitrogen-15. The coupling $^1K(PN)$ has substantial negative values in phosphorus(III) compounds and becomes more positive with values near zero when phosphorus is four-co-ordinate. The behaviour of $^2J(^{31}PNH)$ is consistent with the hybridization of nitrogen being close to sp^2 in these species, and this is attributed to $p_\pi-d_\pi$ overlap with phosphorus and/or $p_\pi-p_\pi$ overlap with *N*-phenyl groups.

THE following factors have been suggested [1] as affecting reduced nuclear spin–spin coupling constants {defined [2] as $K(XY) = J(XY)[4\pi^2/h\gamma(X)\gamma(Y)]$} between directly bound elements X and Y: the *s* characters of the hybrid orbitals of X and Y used to form the X–Y bond; the quantities $\psi_X{}^2(0)$ and $\psi_Y{}^2(0)$ which increase as the substituent groups on X and/or Y become more electronegative; and the *s*-overlap integral β_{XY} which is specially important if either or both of X and Y has a lone pair and the mean excitation-energy approximation is invalid. Similar considerations also apply to couplings over more than one bond, although the nature of the intermediate atom(s) and interbond and dihedral angles have also to be taken into account.[2,3] As β_{XY} becomes small the effect of changes in substituents will become complex and $^1K(XY)$ will pass through zero and may assume large negative values.[2,4,5]

In Group 5 of the Periodic Table these features are well documented [6-8] for couplings involving phosphorus (^{31}P has $I = \frac{1}{2}$, natural abundance 100%) but relatively unstudied for nitrogen because ^{14}N ($I = 1$, abundance 99.6%) has a quadrupole moment and ^{15}N ($I = \frac{1}{2}$, abundance 0.35%, γ negative) is of low abundance and has only *ca.* 0.1% of the sensitivity of the proton to n.m.r. detection.[9] In particular, the effects on $^1J(^{31}P-^{31}P)$ of molecular conformation, substituent electronegativity, and phosphorus oxidation state and hybridization have been studied in some detail, and many observed trends have been rationalized.[6-8] Measurements of $^1J(^{31}P-^{15}N)$ have until very recently been confined to molecules in which the phophorus atom bears substituents (*e.g.* F or CF_3) of extremely high electronegativity,[10-12] but a preliminary account of our own work has shown that $^1J(^{31}P-^{15}N)$ depends in a characteristic way on the oxidation state of the phosphorus atom.[13]

In this paper we report measurements by $^1H-\{^{15}N\}$ and $^1H-\{^{31}P\}$ heteronuclear double resonance of the signs and magnitudes of the $^{31}P-^{15}N$, $^{31}P-^1H$, $^{15}N-^1H$, and certain other coupling constants in a representative range of simple organophosphorus compounds with P–N bonds. Samples enriched to *ca.* 96% in ^{15}N were used (although it transpired that a lower degree of enrichment would have been sufficient) and only 2 g of ^{15}N-enriched aniline was used to prepare and examine 24 different species.

EXPERIMENTAL

Preparations were performed and compounds were manipulated under an atmosphere of dry nitrogen. The aniline was enriched to 96.5% in ^{15}N and was used as supplied by Prochem Ltd. Typically, a scale of 5—10 mmol was used. Samples for analysis were obtained by repeating the preparations on a larger scale using unenriched aniline, and the analytical figures are based on the atomic mass for nitrogen of 14.01.

Dimethylphosphinophenylamine.—Freshly distilled dimethylphosphinous chloride (3.22 g, 33 mmol) in diethyl ether (10 cm³) was slowly added to a ice-cooled mixture of aniline (3.1 g, 33 mmol) and triethylamine (4.7 cm³, 33 mmol) in diethyl ether (20 cm³). The precipitate was filtered off, the ether was removed from the filtrate, and the residue was distilled to give the *compound* (4.5 g, 87%) as a colourless liquid, b.p. 48—49 °C (1 Torr) * (Found: C, 62.6; H, 8.0; N 9.0; P, 20.4. $C_8H_{12}NP$ requires C, 62.8; H, 7.9; N, 9.2; P, 20.2%).

PP-*Dimethyl*-N-*phenylphosphinoselenoic Amide*.—Equivalent amounts of the preceding compound and elemental selenium were heated under reflux in toluene from which the *compound* (m.p. 114—116 °C) crystallized as colourless needles (Found: C, 41.5; H, 5.1; N, 6.0; P, 13.6. $C_8H_{12}NPSe$ requires C, 41.4; H, 5.2; N, 6.0; P, 13.4%). The corresponding tellurium derivative was made similarly but was found to be contaminated with the oxide. Lack of starting materials precluded a second attempt. The compound $NPhH(PMe_2O)$ was made by passing oxygen

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* 1 Torr = (101 325/760) Pa.

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through $NPhH(PMe_2)$ in boiling toluene, and $NPhH(PMe_2S)$ (m.p. 128—131 °C) was made from PMe_2ClS, aniline, and triethylamine in diethyl ether, and was recrystallized from light petroleum (b.p. 40—60 °C)–diethyl ether. The salts $[NPhH(PMe_3)]I$, $[NPhH\{PMe_2(SMe)\}]I$, and $[NPhH\{PMe_2(SeMe)\}]I$ were made by the reaction between methyl iodide and $NPhH(PMe_2)$, $NPhH(PMe_2S)$, or $NPhH(PMe_2Se)$ respectively.

Di-t-butylphosphinophenylamine.—Lithium anilide was prepared from aniline (0.476 g, 5.16 mmol) and n-butyl lithium (15 mmol) in diethyl ether (30 cm^3). The dry salt was suspended in mesitylene (20 cm^3). Di-t-butylphosphinous chloride (0.932 g, 5.16 mmol) was added and the mixture was heated under reflux (190 °C) for 2 h. After cooling the solid material was removed by filtration, and distillation of the filtrate gave the *compound* (0.49 g, 40%) as a colourless liquid, b.p. 80—82 °C (1 Torr). It was characterized by preparing the sulphide, m.p. 144—145 °C (Found: C, 62.4; H, 8.85; N, 5.1. $C_{13}H_{24}NPS$ requires C, 62.4; H, 9.0; N, 5.2%) and the selenide, m.p. 150—151 °C (Found: C, 53.9; H, 7.65; N, 4.2. $C_{14}H_{24}NPSe$ requires C, 53.2; H, 7.65; N, 4.4%) by reaction with sulphur and selenium respectively.

The compound $NPhH(Bu^t{}_2O)$ was made by oxidizing $NPhH(PBu^t{}_2)$ in mesitylene with 30% aqueous hydrogen peroxide, and the $[NPhH(PMeBu^t{}_2)]I$ and $[NPhH\{PBu^t{}_2(SeMe)\}]I$ salts were made by the same method as the *PP*-dimethyl analogues. The reaction of equimolar amounts of $P(NMe_2)_3$ and aniline gave a mixture containing $P(NMe_2)(NPhH)_2$ and $P(NMe_2)_2(NPhH)$ which was examined without further purification.[14] The reaction between aniline and $PCl(MeNCH_2CH_2NMe)$ in the presence of triethylamine gave $P(NPhH)(MeNCH_2CH_2NMe)$ [b.p. 132—136 °C (1 Torr)] in 85% yield, and the derivatives of this were made as for the *PP*-dimethyl series. The *compound* $NPh(PMe_2)(SnMe_3)$ was made by heating $NPhH(PMe_2)$ with an equimolar amount of $NMe_2(SnMe_3)$ in benzene until evolution of dimethylamine ceased; it was converted into the *compound* $NPh(PMe_2S)(SnMe_3)$ by reaction with sulphur. The *compounds* $NPh(PBu^t{}_2)(SnMe_3)$ and $NPh(PBu^t{}_2S)(SnMe_3)$ were prepared similarly from $NPhH(PBu^t{}_2)$.

$^1H-\{X\}$ Heteronuclear double-resonance experiments were made on a Jeol C60 H spectrometer operating at a proton frequency of 60 MHz. A Schlumberger FS 30 frequency synthesizer provided power at the resonant frequencies (15.08, 6.07, 24.28, and 22.37 MHz respectively) of ^{13}C, ^{15}N, ^{31}P, and ^{119}Sn, and also controlled the radio frequency (r.f.) oscillator of the spectrometer. Samples were examined in the solvents listed in the Table at 24 °C in tubes of 5 mm outside diameter.

RESULTS

Nitrogen-15 and ^{31}P resonant frequencies and chemical shifts and the various coupling constants are in the Table. In general these were obtained by standard methods,[15] it being assumed the $^1J(^{15}N-H)$ is negative in deriving the various signs. For compound (1) this result was confirmed by comparing the signs of $^1J(^{13}C-H)$ (known to be positive) and $^2J(^{31}PCH)$ by $^1H-\{^{31}P\}$ and $^1H-\{^{13}C\}$ double-resonance experiments. There is no reason to doubt that this will be the case in all the other species examined as the range of variation of $^1J(^{15}N-H)$ is small compared with its magnitude.[1] Allowance was made for the negative magnetogyric ratios of ^{15}N and of ^{119}Sn in the interpretation of the experiments. For compounds (7), (8), and (15) the absence of any coupling between the added methyl group and ^{15}N confirmed their formulation as *X*-methyl (X = S or Se) rather than *N*-methyl derivative. There is some doubt about the identity of compound (5) which was made by adding tellurium to (1); some accidental exposure to the atmosphere led to the formulation of *ca.* 25% of (2) (identified by comparison of its n.m.r. parameters with those of an authentic specimen) in the presence of which (5) was examined. The trends in $^1J(^{31}P-^{15}N)$ and $^2J(^{31}PCH)$ in the series (2)—(5) are consistent with the proposed formulation, although the change in passing from (4) to (5) is perhaps larger than might have been expected.

The method of preparation of compound (20) led to its being doubly labelled in ^{15}N and it was therefore possible to obtain a value for $^2J(^{15}N-P-^{15}N)$ by studying the resonances of the protons attached to ^{15}N. The $H^{15}NP^{15}NH$ fragment constitutes two overlapping identical AA′XX′ spin systems (associated with opposite spin states of ^{31}P) in each of which $J(AX)$ [*i.e.* $^1J(^{15}N-H)$] is large compared with $J(A'X)$ and $J(XX')$ and $J(AA')$ [*i.e.* $^4J(H\cdots H)$] is effectively zero. The proton spectrum of either sub-system therefore consisted of two sharp lines separated by $^1J(^{15}N-H) + {}^3J(^{15}N\cdots H)$ and flanked by weaker lines whose positions enable one to obtain the magnitudes of the various couplings and also the relative signs of $^1J(^{15}N-H)$ and $^3J(^{15}N\cdots H)$. $^1H-\{^{15}N\}$ Double-resonance experiments similar to the $^1H-\{^{31}P\}$ experiments used in a study of the $[O(O_2PH)_2]^{2-}$ ion then gave the signs of the coupling constants.[16]

The selected data on compounds (25)—(31) are included for purposes of comparison; the sign of $^2J(^{31}P-^1H)$ for (27) is apparently anomalous [12] and indeed it has been suggested that this coupling constant should actually be positive.[10]

DISCUSSION

Our results show that the behaviour of $^1K(PN)$ is similar to that of $^1K(PC)$ in that there is a substantial positive increment in the coupling constant when the co-ordination number of phosphorus changes from three to four.[4] However, whereas opposite signs of $^1K(PC)$ are generally associated with three- and four-co-ordinate phosphorus respectively, this is the exception with $^1K(PN)$. This feature can be attributed to greater negative contributions in the case of the latter coupling which would imply a smaller value of β_{PN} than of β_{PC} so that the mutual polarizability π_{PN} never takes large positive values for the phosphorus–nitrogen bond. In contrast, in four-co-ordinate phosphorus compounds π_{PC} is often quite large positive, and indeed the mean excitation-energy approximation may provide a good description of $^1K(PC)$ in such species.

In percentage terms the P–N coupling appears to be more sensitive in the four-co-ordinate compounds to changes in the substituents than is the P–C coupling. Compare, for example, the values of $^1J(^{31}P-^{15}N)$ in (3) and (4) with values of 56.1 and 48.5 Hz in PMe_3S and PMe_3Se respectively.[4] This suggests that for the P–N couplings changes in β_{PN} are playing a large part, as

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Nitrogen-15 and ^{31}P n.m.r. parameters [a] of species with phosphorus–nitrogen bonds

Compound	$\Xi(^{31}P)$ [b]	$\delta(^{31}P)$ [c]	$\Xi(^{15}N)$ [b]	$\delta(^{15}N)$ [d]	$^1J(^{31}P-^{15}N)$	$^1K(PN)$	$^1J(^{15}N-H)$	$^2J(^{31}PCH)$	$^2J(^{31}P-NH)$	$^3J(^{15}NPCH)$	$^3J(^{31}PCCH)$	Solvent	Notes
	Hz	p.p.m.	Hz	p.p.m.	Hz	nm^{-3}	Hz						
(1) $NPhH(PMe_2)$	40 481 330 ± 8	13.4	10 133 637 ± 2	28.2	53.0	−10.8	−81.0	−6.0	4.9	−2.7		C_6H_6	*e*
(2) $NPhH(PMe_2O)$	40 482 055 ± 5	31.2	10 133 793 ± 1	43.7	−0.5	0.1	−83.0	11.1	−13.5	−1.2		$[^2H_6]Me_2SO$	
(3) $NPhH(PMe_2S)$	40 482 863 ± 2	51.2	10 133 718 ± 1	36.3	11.3	−2.29	−82.0	8.4	−12.8	−1.2		Dioxan	
(4) $NPhH(PMe_2Se)$	40 482 416 ± 3	40.2	10 133 683 ± 2	32.7	16.5	−3.35	−83.0	5.3	−12.8	−1.0		CH_2Cl_2	
(5) $NPhH(PMe_2Te)$	40 480 375 ± 15	−10.3	10 133 648 ± 3	29.3	36.0	−7.30	−79.5		−4.5	−1.7		$C_6H_6 + CH_2Cl_2$	
(6) $[NPhH(PMe_3)]\ I$	40 482 761 ± 5	48.7	10 133 503 ± 2	15.0	4.1	−0.83	−83.3	6.4	−13.8	−1.4		CH_2Cl_2	
(7) $[NPhH\{PMe_2(SMe)\}]\ I$	40 483 300 ± 15	62.2	10 133 568 ± 2	21.4	10.5	−2.13	−84.5	9.0	−12.9	−1.3		$CHCl_3$	*g*
(8) $[NPhH\{PMe_2(SeMe)\}]\ I$	40 482 835 ± 8	50.5	10 133 570 ± 2	21.6	14.0	−2.84	−82.5	7.4	−12.9	−1.2		CH_2Cl_2	*h*
(9) $[Me_2P(\dot{B}H_2)\dot{N}Ph]_n$	40 483 317 ± 15	62.4	10 133 878 ± 8	52.0	17.0	−3.34			−9.0	?		CH_2Cl_2	*i*
(10) $NPhH(PBu^t_2)$	40 483 115 ± 8	57.4	10 133 510 ± 1	15.7	59.6	−12.10	−80.5	−10.9			11.3	$C_6H_3Me_3$-1,3,5	
(11) $NPhH(PBu^t_2O)$	40 483 150 ± 15	58.3	10 133 560 ± 2	20.6	11.5	−2.33	−80.5	10.5			14.0	$CH_2Cl_2 + C_6H_3Me_3$-1,3,5	
(12) $NPhH(PBu^t_2S)$	40 484 476 ± 25	91.0	10 133 513 ± 2	16.0	22.2	−4.50	−78.5	7.8			15.0	$CHCl_3 + C_6H_3Me_3$-1,3,5	
(13) $NPhH(PBu^t_2Se)$	40 484 570 ± 15	93.3	10 133 467 ± 2	11.5	27.2	−5.58	−78.5	5.0			15.5	$CHCl_3 + C_6H_3Me_3$-1,3,5	
(14) $[NPhH(PMeBu^t_2)]\ I$	40 483 580 ± 15	68.9	10 133 328 ± 2	−2.3	13.4	−2.72	−77.0		−14.1	−1.2	15.3	$[^2H_6]Me_2SO$	*j*
(15) $[NPhH\{PBu^t_2(SeMe)\}]\ I$	40 484 618 ± 15	94.5	10 133 490 ± 2	13.6	23.8	−4.83	−81.0	7.3			13.0	$[^2H_6]Me_2SO$	
(16) $NPh(PBu^t_2)(SnMe_3)$	40 483 155 ± 30	58.4	10 133 317 ± 15	−3	80.0	−16.23					11.3	$C_6H_6 + CH_2Cl_2$	
(17) $NPh(PMe_2)(SnMe_3)$	40 481 802 ± 3	25.0	10 133 397 ± 2	4.5	71.9	−14.59			5.7	−2.1		C_6H_6	*k*
(18) $NPh(PMe_2S)(SnMe_3)$	40 483 155 ± 5	58.4	10 133 650 ± 2	29.5	24.8	−5.03			−12.2	±0.2		C_6H_6	*l*
(19) $P(NMe_2)_2(NPhH)$	40 484 998 ± 8	103.9	10 133 753 ± 2	39.8	53.8	−10.9	−79.0	−2.4				C_6H_6	
(20) $P(NMe_2)(NPhH)_2$	40 484 045 ± 15	84.5	10 133 757 ± 2	40.1	52.8	−10.7	−79.5	−2.9				C_6H_6	*m*
(21) $P(NPhH)(MeNCH_2CH_2NMe)$	40 484 837 ± 15	99.9	10 133 907 ± 2	54.9	84.2	−17.0	−78.5	−2.3				C_6H_6	*n*
(22) $P(NPhH)(MeNCH_2CH_2NMe)S$	40 483 470 ± 15	66.2	10 133 835 ± 2	47.8	2.6	−0.53	−83.0	14.3				$C_6H_6 + CHCl_3$	*n*
(23) $P(NPhH)(MeNCH_2CH_2NMe)Se$	40 483 273 ± 15	61.3	10 133 888 ± 2	53.1	7.8	−1.58	−85.8	15.4				C_6H_6	*n*
(24) $[PMe(NPhH)(MeNCH_2CH_2NMe)]\ I$	40 482 703 ± 15	47.2	10 133 688 ± 2	−33.4	−3.3	0.67	−79.8		−15.1	−1.2		CH_2Cl_2	*n,o*
(25) $NH_2\{P(CF_3)_2\}$					52.6	−10.7		−14.2					*p*
(26) $N(PF_2)(PF_3)$					−53.2,[s] 93.8	10.8,[s] −19.0							*p*
(27) $PF_3(NH_2)_2$					−81.5	16.5		14.5					*p*
(28) $NH_2(PF_2)$		417.5		21.4	72.5	−14.7	−80.4	18.8					*q*
(29) $NH(PF_2)_2$		144.4		86.3	78.9	−16.0	−74.7	13.6					*r*
(30) $N(PF_2)_3$		150.3		139.0	87.0	−17.7							*r*
(31) $NH(PF_2)(SiH_3)$					69.0	−14.0	−73.1	18.8					

[a] Coupling constants are accurate to ±0.2 Hz. Chemical shifts are to low field of the reference. [b] $\Xi(X)$ is the resonant frequency of X corrected to a polarizing field strength at which $SiMe_4$ would give a proton resonance at exactly 100 MHz. [c] Relative to 85% H_3PO_4 for which $\Xi(^{31}P)$ is taken to be 40 480 790 Hz. [d] Relative to aqueous $[NMe_4]I$ for which $\Xi(^{15}N)$ is taken to be 10 133 351 Hz. [e] $\Xi(^{13}C) = 25.145\ 499$, whence $\delta(^{15}C)$19.7 p.p.m. relative to $SiMe_4$; $^1J(^{31}P-^{13}C) = -12.5$, $^1J(^{13}C-H)$ 127.5 Hz. [f] This compound has not been fully characterized and the solution contained some of (2) (see text). [g] $^3J(^{31}PSCH)$ 14.1 Hz. [h] $^3J(^{31}PSeCH)$ 12.9 Hz. [i] Polymeric; no N–H signal was observed, the *P*-methyl proton resonance was broad and no coupling to ^{15}N was resolved. [j] $^3J(^{31}PSeCH)$ 15.8 Hz. [k] $^1J(^{119}Sn-^{15}N)$ 9.5 ± 3 Hz, $^1K(SnN)$ 2.1 nm^{-3}, $^2J(^{119}Sn\cdots H)$ 54.0 Hz; $\Xi(^{119}Sn)$ 37 293 035 ± 50 Hz, whence $\delta(^{119}Sn)$ 63.5 p.p.m. relative to $SnMe_4$. [l] $^1J(^{119}Sn-^{15}N)$ −47.5 ± 4 Hz, $^1K(SnN) = -10.6\ nm^{-3}$, $^2J(^{119}Sn\cdots H) = 54.3$ Hz; $\Xi(^{119}Sn)$ 37 293 125, whence $\delta(^{119}Sn)$ 66 p.p.m. relative to $SnMe_4$.

[m] $^2J(^{15}NP-^{15}N)$ 2.2 ± 0.5, $^3J(^{15}N-P-N-H)$ −3.5 ± 0.5 Hz. [n] Contains a $\overline{PNMe\cdot CH_2CH_2\cdot N}Me$ ring. [o] Coupling to protons associated with the ring: $|^3J(^{31}PNCH_2)|$ 9.1, $|^3J(^{31}PNCH_3)|$ 10.5 Hz. [p] From ref. 12. [q] From ref. 10. [r] From ref. 11. [s] The first value refers to P^V, the second to P^{III}.

indeed would be expected for one-bond coupling constants which are as close to zero as these. It may be noted here that the small range of variation of $^1J(^{15}N-H)$ in these species indicates that changes in $\psi(0)^2$ and/or α_s^2 for the nitrogen atom are unlikely to be important.

Replacement of the two methyl groups on phosphorus by Bu^t increases $^1J(^{31}P-^{15}N)$ by 10 ± 3 Hz, *i.e.* the reduced coupling constant becomes more negative. The greater bulk of Bu^t compared with Me will lead to larger C–P–C interbond angles with greater *s* character for the P–C bonds and therefore less for the P–N bond. Hence β(PN) will be smaller and the coupling constant will be more negative. The relative constancy of the change in ^1K(PN) irrespective of whether this coupling is large or small supports the contention that it is an alteration in β(PN) which is dominant.

The coupling ^1K(PN) is appreciably more negative in the cyclic compound (21) than in the analogous acyclic molecules (1) and (10), and the values of this coupling constant in (19) and (20) indicate that this cannot be due primarily to there being three electronegative atoms bound to phosphorus. Another possibility is the strain in the PNCCN ring. Examination of models indicates that this will enlarge the ring N–P–N interbond angle at phosphorus and hence reduce the *s* character of the phosphorus–exocyclic nitrogen bond so that ^1K(PN) becomes more negative. In this context it would clearly be of interest to have values of the coupling constant between phosphorus and the ring nitrogens. In contrast, for the species (22)—(24) ^1K(PN) is rather more positive than for the acyclic analogues. This can again be attributed to interbond-angle deformation because the constraints of the ring reduce the angle at phosphorus to less than that normally found in phosphorus(V) derivatives so that the *s* character of the P–N(exocyclic) bond is increased.

It is also instructive to compare the P–N coupling constants with values of ^1K(PP) which have been reported in the literature. For phosphorus(III) compounds this coupling constant is fairly large and negative, and also is very sensitive to changes in the bulk of the substituents on phosphorus. For example, in the series P_2Me_4, $Me_2PPBu^t_2$, $P_2Bu^t_4$ the values are −9.1, −16.2, and −22.9 nm^{-3} respectively.[8] Additionally, there is evidence that the dihedral angle between the electron lone pairs on phosphorus is important.[17,18] Changes of the substituents on phosphorus appear to have much smaller effects on ^1K(PN), but the data for species (1) and (16) and (3) and (18) indicate that ^1K(PN) is sensitive to changes in the substituents on nitrogen. The transformation $P^{III}-P^{III} \longrightarrow P^{III}-P^{V}$ has a relatively small effect on ^1K(PP) while the transformation $P^{III}-P^{V} \longrightarrow P^{V}-P^{V}$ has a large effect. Thus the behaviour of ^1K(PN) is analogous to the second of these cases and suggests that the nitrogen atom behaves as though it had no electron lone pair. This situation would arise if the nitrogen atom were sp^2 hybridized, and we therefore suggest that the remaining two electrons are participating either in $p_\pi-p_\pi$ bonding with the phenyl group on nitrogen or in $p_\pi-d_\pi$ bonding with phosphorus. The latter type of behaviour is now well established for many species with phosphorus–nitrogen bonds and would not affect the Fermi-contact contribution to ^1K(PN) directly, although it would stabilize certain rotamers and could affect the coupling constant in the manner outlined above. The relatively large differences in ^1K(PN) in the series (2)—(5) may stem from changes in rotamer populations which would effect the extent of π bonding. Such π bonding could also lead to significant contributions to ^1K(PN) from spin–orbital and orbital–orbital coupling, and it is not possible at present to assess the importance of these. However, there are indications that these interactions should be important only for coupling between very electronegative elements (*e.g.* fluorine) and certainly our results can be explained without invoking these mechanisms.

When the co-ordination number of phosphorus increases from three to four the geminal coupling $^2J(^{31}PCH)$ usually becomes more negative (*e.g.* compare values of +2.7 and −13.0 Hz in PMe_3 and PMe_3S respectively [4]) and this behaviour is usually attributed to the same cause as the accompanying variations in $^1J(^{31}P-^{13}C)$. This behaviour is also observed for $^2J(^{31}PCH)$ in the present work, but the corresponding changes in $^2J(^{31}PNH)$ are in the opposite direction, and it is reasonable to attribute this difference to the presence of the intervening nitrogen atom rather than to a difference in the behaviour of phosphorus. A general theory due to Jameson [19] shows that geminal couplings are given by a relation of the form (1), in which the terms are defined

$$^2K(XMY) = GS_XS_Y \qquad (1)$$

so that ^1K(MX) and ^1K(MY) would be proportional to S_X and S_Y respectively, and G depends on the hybridization and substituents of M and may be of either sign. The behaviour of $^1J(^{31}P-^{13}C)$ and $^2J(^{31}P-^1H)$ when M is sp^3-hybridized carbon is consistent with S_H being positive and G being negative, and with S_P being negative in three-co-ordinate and positive in four-co-ordinate phosphorus species. If M = N then the observed changes in $^2J(^{31}P-H)$ can be understood if it is assumed that G is positive. This is reasonable in view of our suggestion above that in these species the nitrogen atom may be sp^2 rather than sp^3 hybridized. In certain vinyl derivatives of phosphorus the direction of the change in $^2J(^{31}PCH)$ which accompanies the transformation $P^{III} \longrightarrow P^{V}$ is opposite to that normally found, and here again we are dealing with an intervening atom which is sp^2 hybridized.[20]

An important consequence of the rather wide range of variation of $^1J(^{31}P-^{15}N)$, especially in derivatives of four-co-ordinate phosphorus, is that for certain sets of

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compounds the ranges for phosphorus-(III) and for -(V) species may overlap; thus some care may be needed if this parameter is to be used for structural work.

The phosphorus chemical shifts call for no comment but the nitrogen shieldings display interesting features. In the derivatives of four-co-ordinate phosphorus there is a shift to low field as the electronegativity of the substituents on phosphorus increases in series such as (2)—(5) or (11)—(13), and the t-butyl compounds all have nitrogen chemical shifts to high field of the corresponding methyl one. This last feature can be attributed to the β effect of the methyl groups in the t-butyl compounds and also possibly to reduced p_π–p_π bonding between nitrogen and phosphorus which would tend to increase the amount of p_π–p_π bonding to the phenyl rings in the latter.

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