

A Nuclear Magnetic Resonance Study of some Bis(phosphinoyl)amines and Bis(phosphinothioyl)amines

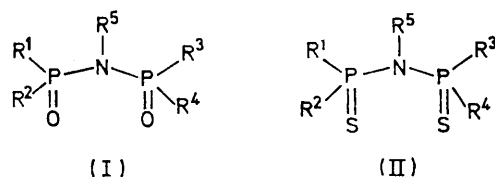
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^1H , ^{31}P , and ^{13}C N.m.r. spectra have been obtained for a number of bis(phosphinoyl)amines (I) and bis(phosphinothioyl)amines (II). The spectra have been analysed to give chemical shifts and coupling constants, which are presented and discussed here. The sign of $^2J_{\text{PNP}}$ has been determined by heteronuclear spin tickling in several cases and found to be positive.

THERE has been considerable interest recently¹⁻¹⁴ in compounds containing the P(X)NP(Y) system, where X and Y may be O, S, Se, or a lone pair. Studies of n.m.r. spectra have shown that there is considerable

high values are observed whenever X and/or Y are lone pairs.^{1,3-6,11,14} In some cases the sign of $^2J_{\text{PP}}$ has been measured.^{4,6,15}

We present here n.m.r. data for two series of compounds, viz. bis(phosphinoyl)amines (I) and bis(phosphinothioyl)amines (II). We have examined compounds a-i in both series except for (Ii), (IIc), and (IIe). Some of these compounds contain symmetrical spin systems, giving rise to spectra of a type that has been described.¹⁶ The remaining compounds are unsymmetrical and give spectra which are to a good approximation first-order.



	R ¹	R ²	R ³	R ⁴	R ⁵
a;	Cl	Cl	Cl	Cl	Me
b;	NMe ₂	Cl	Cl	Cl	Me
c;	NMe ₂	NMe ₂	Cl	Cl	Me
d;	NMe ₂	Cl	NMe ₂	Cl	Me
e;	NMe ₂	NMe ₂	NMe ₂	Cl	Me
f;	NMe ₂	NMe ₂	NMe ₂	NMe ₂	Me
g;	Cl	Cl	Cl	Cl	Ph
h;	NMe ₂	Cl	Cl	Cl	Ph
i;	NMe ₂	Cl	NMe ₂	Cl	Ph

variation in $^2J_{\text{PP}}$, though the factors affecting this coupling constant are not well understood; however,

¹ J. F. Nixon, *J. Chem. Soc. (A)*, 1969, 1087.

² R. Keat, W. Sim, and D. S. Payne, *J. Chem. Soc. (A)*, 1970, 2715.

³ R. Keat, *J. Chem. Soc. (A)*, 1970, 2732.

⁴ R. W. Rudolf and R. A. Newmark, *J. Amer. Chem. Soc.*, 1970, **92**, 1195.

⁵ I. A. Nuretdinov, V. V. Negrebetskii, A. Z. Yankelevich, A. V. Kessenikh, E. I. Loginova, L. K. Nikonorova, and N. P. Grechkin, *Doklady Chem.*, 1971, **196**, 161.

EXPERIMENTAL

The preparations of the compounds (and in some cases preliminary n.m.r. data) have been reported elsewhere.^{3,9,11,17} For the present work saturated solutions were made in

⁶ I. A. Nuretdinov, V. V. Negrebetskii, A. Z. Yankelevich, A. V. Kessenikh, L. K. Nikonorova, and E. I. Loginova, *Bull. Acad. Sci. U.S.S.R. (Chem. Sect.)*, 1971, **20**, 2460.

⁷ H. G. Metzinger, *Org. Magnetic Resonance*, 1971, **3**, 485.

⁸ H. W. Roesky and H. Wiezer, *Chem. Ber.*, 1971, **104**, 2258.

⁹ I. Irvine and R. Keat, *J.C.S. Dalton*, 1972, 17.

¹⁰ T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, 1972, **11**, 1583.

¹¹ R. Keat, *J.C.S. Dalton*, 1972, 2189.

¹² H. W. Roesky and W. Schaper, *Z. Naturforsch.*, 1972, **27b**, 1137.

¹³ G. Gzieslik, G. Flakerud, R. Höfer, and O. Glmsner, *Chem. Ber.*, 1973, **106**, 399.

¹⁴ R. Keat, *J.C.S. Dalton*, 1974, 876.

¹⁵ G. Bulloch, R. Keat, and W. McFarlane, unpublished results.

¹⁶ R. K. Harris, *Canad. J. Chem.*, 1964, **42**, 2275.

¹⁷ G. Bulloch, R. Keat, and N. H. Tennent, *J.C.S. Dalton*, in the press.

CDCl_3 and a few drops of tetramethylsilane were added. All the samples were degassed by the freeze-pump-thaw technique using a vacuum line, and sealed in the degassed condition. ^1H and ^{31}P Spectra were obtained for samples in 5 mm (o.d.) tubes, whereas for the ^{13}C spectra 12 mm o.d. tubes were employed.

^1H Spectra were recorded with a Varian HA-100 spectrometer, by using the frequency sweep mode at the full expansion of 50 Hz sweep width. The ^1H resonance of Me_4Si provided a signal for field-frequency locking. The ^{31}P and ^{13}C spectra were recorded under conditions of proton noise decoupling on a Varian XL-100 spectrometer, in continuous wave (CW) mode for ^{31}P and Fourier transform (FT) mode for ^{13}C . The deuterium resonance of CDCl_3 was used for the XL-100 field-frequency locking. Some ^{31}P spectra were obtained by multiscan averaging via a Varian 620/i computer (which was also used for the Fourier transformation process). The $^1\text{H}\{-^{31}\text{P}\}$ experiments were carried out on the HA-100 instrument by using a double-tuned probe.¹⁸ The 40 MHz frequency was generated by a Schlumberger (FSX 3005) frequency synthesizer and amplified by an r.f. amplifier (type HB 805, R.F. Communication Inc.). The $^1\text{H}\{-^{14}\text{N}\}$ experiment was carried out with the XL-100 spectrometer, equipped with a ^{14}N decoupler module; the 7 MHz frequency was generated by the Schlumberger frequency synthesizer and passed through the HB 805 r.f. amplifier.

The ^{31}P and ^{13}C resonance frequencies were measured by using an El Dorado/Varian MHz frequency counter; the frequency of the lock signal was similarly measured. The ^{31}P and ^{13}C frequencies were then scaled to be appropriate for a field at which the ^1H resonance of Me_4Si occurs at exactly 100 MHz. The chemical shifts (Tables 2 and 4) were then obtained by subtracting the appropriate frequencies for ^{31}P in 85% H_3PO_4 (40,480,720 Hz)* and for ^{13}C in Me_4Si (25,145,004 Hz),²⁰ with conversion to a p.p.m. scale. Drifts in the master oscillator result in possible errors in the shifts of a few Hz, though relative shifts between different compounds are probably more accurate.

Spectral Analysis.—The ^1H , $^{31}\text{P}\{-^1\text{H}\}$, and $^{13}\text{C}\{-^1\text{H}\}$ spectra for the unsymmetrical compounds were first-order and all the parameters could be obtained by direct measurement. It was possible to resolve the long-range (P,H) coupling ($^5J_{\text{PH}}$) in two compounds, (IIb) and (IIh). The rotation about the P-N bonds is fast on the n.m.r. time-scale, so that any geometry effects can be ignored. In compound (Ie) one P atom is asymmetric and causes the two dimethylamino-groups on the other P atom to be chemically nonequivalent. For compounds (Id), (IIId), and (IIIi) both phosphorus atoms are asymmetric; the samples used were mixtures of stereoisomers. The n.m.r. spectra showed that the relative concentrations of the isomers were ca. 3 : 1, ca. 2 : 1, and ca. 5 : 7 : 1, respectively. In each case the predominant isomer had the higher frequency ^1H signal from the terminal NMe_2 protons but this does not necessarily imply that these isomers have the same configuration. For (IIIi) a pure sample of the isomer that was dominant in the mixture was obtained and examined.

The relative signs of $^2J_{\text{PP}}$ and $^3J_{\text{PH}}$ were determined for (Ib), (IIb), and (IIIh) by $^1\text{H}\{-^{31}\text{P}\}$ experiments and found to

* McFarlane¹⁹ gives 40,480,740 Hz for this frequency.

¹⁸ J. R. Woplin, Ph.D. Thesis, University of East Anglia, 1971; E. G. Finer, R. K. Harris, M. R. Bond, R. Keat, and R. A. Shaw, *J. Mol. Spectroscopy*, 1970, **33**, 72.

¹⁹ W. McFarlane, *Ann. Rev. N.M.R. Spectroscopy*, 1968, **1**, 135.

be the same. The sign of $^3J_{\text{PNCH}}$ may be assumed to be positive,²¹ giving the sign of $^2J_{\text{PNP}}$ as positive.

The ^1H spectra of the symmetrical compounds were analysed according to the spin system $[\text{AX}_6]_2$ or $[\text{AX}_{12}]_2$ (ignoring the methyl or phenyl groups on the bridging nitrogen) with $J_{\text{XX}'} (= ^3J_{\text{HH}}) = 0$ (see Figure 1). The two intense lines separated by $N (= J_{\text{AX}} + J_{\text{AX}'})$ could be easily picked out; thus N could be obtained accurately. The inner lines could be resolved only for compounds (Id), (IIIf), and (IIIi) (predominant isomer) but were several times broader than the N lines. An attempt was made to observe the first outer lines for these compounds, using high powers in the r.f. field B_1 ,²² but this procedure was successful only in two cases, (IIIf) and (IIIi); in these instances J_{PP} was

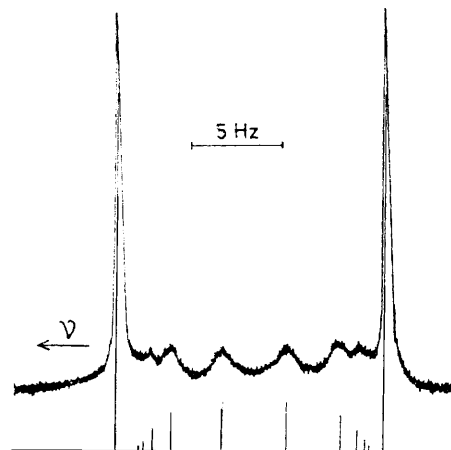


FIGURE 1 100 MHz ^1H N.m.r. spectra of (IIIi), $\text{PhN}[\text{P}(\text{S})\text{CINMe}_2]_2$, for the dimethylamino-group. A pure sample of one of the stereoisomers was used. A calculated stick-plot spectrum is shown

readily obtained (see ref. 16). The nature of the outer lines observed using high B_1 powers (*i.e.* their relationship to the inner lines) was confirmed by $^1\text{H}\{-^1\text{H}\}$ experiments. The value of J_{PP} for (Id) was calculated using the separations of the first and second pairs of inner lines, with the expressions given in ref. 16. The other symmetrical compounds, (If) and (IIId), showed only a broad hump, without structure, between the N lines (see Figure 2). This phenomenon has been observed¹⁸ for several other symmetrical spin systems containing phosphorus. The effect of ^{14}N quadrupolar relaxation on these lines was investigated by heating the samples and by irradiating at 7.2 MHz. There was no appreciable change. The compound (IIId) was a mixture of (\pm)- and *meso*-isomers. The reason for the lack of resolution of the inner lines in this case may be overlap of lines from the two isomers, but this was not a problem for the purified isomer of (IIIf). To determine the value of J_{PP} for (If) and (IIId) attempts were made to obtain ^{13}C spectra and to observe the ^{13}C satellites in the ^{31}P spectrum.²³ The latter proved impossible because of the very small value of (P,C) couplings in these systems. The separation of the two ab patterns in the ^{31}P spectrum due to ^{13}C satellites is $\frac{1}{2}N_{\text{PC}}$ (ca. 2 Hz) and the separation between the two intense lines in an ab subspectrum is $L_{\text{PC}}^2/8J_{\text{PP}}$; hence the principal satellite peaks are obscured under the

²⁰ B. J. Kimber, unpublished work.

²¹ W. McFarlane, *Proc. Roy. Soc. (A)*, 1968, **306**, 185.

²² E. G. Finer and R. K. Harris, *Mol. Phys.*, 1967, **12**, 457.

²³ E. G. Finer and R. K. Harris, *Mol. Phys.*, 1967, **13**, 65.

broad base of the ^{31}P peak due to molecules containing the abundant ^{13}C isotope. The ^{13}C spectra involved attempts to observe the outer 'combination' lines in the X region of ABX ($\nu_A \sim \nu_B$) spin systems. All the symmetrical compounds studied here gave a triplet structure in

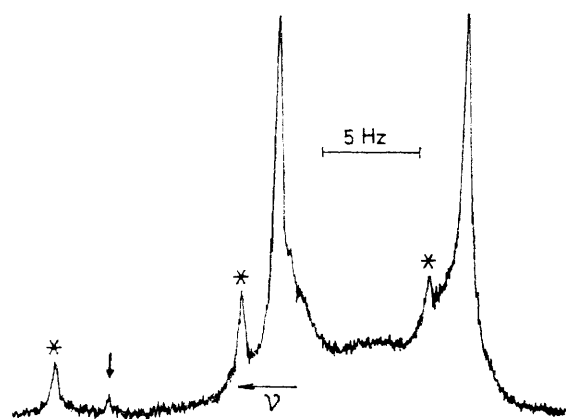
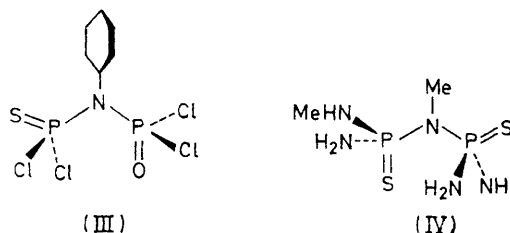


FIGURE 2 100 MHz ^1H N.m.r. spectrum of (If), $\text{MeN}[\text{P}(\text{O})(\text{NMe}_2)_2]$, showing the broad unresolved band between the 'N lines' due to the terminal NMe_2 protons (see the text). The lines with asterisks are due to the bridging NMe protons. The arrowed line is a spinning sideband

the proton noise-decoupled ^{13}C spectrum. The 'combination' lines were too weak to be observed, because J_{PP} is appreciably greater than $|^2J_{\text{PC}} - ^4J_{\text{PC}}|$. [For compound (IIe), the combination lines are 3.5% of the intensity of one

chemical shifts fall in the appropriate regions reported for similar groups.²⁵ The bridging methyl protons give resonances at higher frequency than those for the terminal methyl protons. The δ_{NMe} values decrease significantly with the increasing substitution of Cl by NMe_2 groups, in spite of the fact that the site of the substitution is four bonds removed from the observed protons. Similarly the value of δ_{NMe_2} is consistently greater for the PCINMe_2 group than for the $\text{P}(\text{NMe}_2)_2$ group. There is also a tendency for δ_{NMe_2} to increase with the extent of substitution by Cl at the second phosphorus atom. However, the situation is complicated by the existence of an asymmetry effect for compounds (Id), (Ie), and (IIe). This complication may be influenced by rotational isomerism or by geometry variations for individual rotamers.



Some evidence of conformational variations is provided by X-ray results^{26,27} for $\text{Cl}_2\text{P}(\text{O})\cdot\text{NPh}\cdot\text{P}(\text{S})\text{Cl}_2$ (III) and $(\text{H}_2\text{N})_2\text{P}(\text{S})\cdot\text{NMe}\cdot\text{P}(\text{S})(\text{NH}_2)\text{NHMe}$ (IV). In

TABLE I^a
 ^1H N.m.r. parameters for compounds of types (I) and (II)

Compound	δ_{NMe_2}	δ_{NMe}	$^5J_{\text{PH}}$	$^3J_{\text{PH}}$ to terminal NMe_2		$^3J_{\text{PH}}$ to bridging NMe		
				PCINMe_2	$\text{P}(\text{NMe}_2)_2$	PCl_2	PCINMe_2	$\text{P}(\text{NMe}_2)_2$
(Ia)		3.376				13.65		
(Ib)	2.858	3.217	<i>d</i>	12.80		15.35	11.17	
(Ic)	2.736	3.110	<i>d</i>		10.12	16.42		8.22
(Id) ^b	α	2.825	<i>d</i>	(13.41) ^c			12.01	
	β	2.816	<i>d</i>	(13.56) ^c			11.59	
(Ie)	R^1	2.767	<i>d</i>	13.88	9.83		12.71	8.32
	R^2	2.678						
	R^3	2.780						
(If)	2.688	2.756	<i>d</i>		9.62			9.55
(IIa)		3.634				14.75		
(IIb)	2.900	3.370	0.3	14.10		15.62	12.98	
(IIe) ^b	α	2.890 ^c	<i>d</i>	(15.45) ^c			12.50	
	β	2.880 ^c	<i>d</i>	(15.35) ^c			12.78	
(IIe)	2.726	2.919	0.2		11.25			10.48
(IIh)	2.980		0.4	14.25				
(IIi) ^b	α	2.800	0.7	14.12				
	β	2.761	<i>d</i>	(15.08) ^c				

^a Chemical shifts are δ -values (positive to high frequency of Me_4Si), accurate to ± 0.005 p.p.m. Coupling constants are in Hz (± 0.03 Hz). The values of $^3J_{\text{PH}}$ are assumed to be positive; $^5J_{\text{PH}}$ was determined to be of the same sign as $^3J_{\text{PH}}$ by spectral analysis for (IIe) and (IIe). ^b Isomer mixture; α is the major component and β the minor component. ^c Strictly speaking this is $N = ^3J_{\text{PH}} + ^5J_{\text{PH}}$. ^d Not observed.

of the N_{PC} doublets; this was calculated²⁴ using $N = L$ and the value of J_{PP} obtained from the ^1H spectrum.] Hence only the N_{PC} values are obtained from ^{13}C measurements on the symmetrical compounds.

RESULTS AND DISCUSSION

Table I lists the proton chemical shifts and the (P,H) coupling constants for the compounds studied. The

²⁴ R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.*, 1961, **39**, 216.

each case the environment of the bridging nitrogen atom is planar; the S and O atoms are also nearly in this plane but in each case one of the chalcogen substituents

²⁵ G. Mavel, *Ann. Reports N.M.R. Spectroscopy*, 1973, **5B**, 1; E. A. Robinson and D. S. Lavery, *Spectrochim. Acta*, 1972, **28A**, 1099.

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

²⁷ M. I. Ziegler and J. Weiss, *Z. anorg. Chem.*, 1968, **361**, 136.

is approximately *cis* to the *N*-substituent whereas the other is approximately *trans*. Of course, crystal packing forces may be important, and the reported structures may not be relevant to the solution situation.

The difference in substituent electronegativity has a profound effect on $^3J_{PH}$. The coupling decreases in the order of $PCl_2 > PCl(NMe_2) > P(NMe_2)_2$. The effect is similar for coupling involving the bridging and terminal methyl groups, though for analogous situations coupling to the terminal methyls is always the larger. The substitution effect implies that the contact term is probably dominant for these couplings. The couplings are also sensitive to the groupings at the distant P atom. For example, in the oxide series, the coupling constant for the ^{31}P of the $PCINMe_2$ group to the bridging NMe protons increases from 11.17 to 12.01 to 12.71 Hz as the nature of the second phosphorus group changes from PCl_2 to $PCl(NMe_2)$ to $P(NMe_2)_2$. This is also observed for other couplings. The (P,H) couplings are larger for the sulphides than for the corresponding oxides. We would expect a larger coupling for the oxides according to Bent's rule, but the anomaly may be due to differing hybridizations in the two systems. This is consistent with the literature report²⁵ that $^3J_{PH}$ in $P(S)(NMe_2)_3$ is larger than that in $P(O)(NMe_2)_3$.

Table 2 lists the ^{31}P chemical shifts and (P,P) coupling

TABLE 2

^{31}P N.m.r. parameters^a for compounds of types (I) and (II)

Compound	$\delta_{P(X)O_2}$	$\delta_{P(X)Cl(NMe_2)}$	$\delta_{P(X)(NMe_2)_2}$	$ ^2J_{PP} ^b$
(Ia)	10.6			<i>c</i>
(Ib)	12.4	16.1		15.9
(Ic)	14.6		18.9	11.0
(Id)	α	21.8		20
	β	20.9		<i>c</i>
(Ie)		23.9	18.9	14.5
(If)			20.4	<i>c</i>
(Ig)	7.4 ^d			<i>c</i>
(Ih)	8.4 ^d	14.5 ^d		40 ^d
(IIa)	47.5			<i>c</i>
(IIb)	48.8	70.8		19.8
(IIc)	α	73.5		<i>c</i>
(IId)	β	74.8		<i>c</i>
(IIe)			77.7	11.5
(IIg)	43.5 ^e			<i>c</i>
(IIh)	45.5	69.1		43.3
(IIi)	α	70.2		24.5
	β	69.4		<i>c</i>

^a Chemical shifts are in p.p.m. relative to 85% H_3PO_4 (positive to high frequency). Coupling constants are in Hz. ^b Estimated errors ± 0.2 Hz, except for the result for (Id) (obtained from 1H resonance spectral analysis) which is much more uncertain. ^c Not determined. ^d Data from measurements at 24.3 MHz with a Perkin-Elmer R10 spectrometer. ^e Data from ref. 11.

constants for the compounds studied here. The ^{31}P chemical shifts for the oxides and the sulphides with $R^5 = Me$ fall in two distinct regions (δ_P 10–24 and 45–78 p.p.m., respectively), as has been observed²⁵ for related compounds of the type R_3PX ($X = O$ or S).

* This is a mean value for nearest neighbour nitrogen, rather than a specific value for the NMe_2 group.

²⁵ (a) J. H. Letcher and J. R. Van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 75; (b) J. R. Van Wazer and J. H. Letcher, *ibid.*, p. 169.

The variations within each series are not easy to understand. The changes for the groups $OPCl_2$, $OPClNMe_2$, and $OP(NMe_2)_2$ (when the grouping at the distant phosphorus is kept constant in one of the three possible ways for the series) are non-additive, markedly so for two of the three cases. The series $OPCl_n(NMe_2)_{3-n}$ also shows²⁵ such non-additivity clearly. The non-additivity is invariably such that the mixed compounds have higher values of δ_P (in our notation) than the parent compounds, as is indeed the case for the present examples. Such behaviour is well known for ^{31}P shifts and has been discussed in detail by Letcher and Van Wazer.^{28a} The cause of this type of variation has been given as a mixture of σ - and π -effects, depending on substituent electronegativity and the total occupation of d orbitals at phosphorus, respectively. In the case of Cl and NMe_2 substituents the electronegativities are sufficiently close (given as 3.15 and 3.10, respectively, by Van Wazer and Letcher,^{28b} and as 3.07 and 2.83* respectively by Cotton and Wilkinson²⁹) that σ -contributions to the non-additivity are probably relatively small, so that π -effects dominate, with the NMe_2 group acting as the better π -donor. The total occupation of d_π orbitals at phosphorus may be at a maximum for one of the mixed compounds,²⁸ thus explaining the non-additivity. In the case of the compounds studied here these effects cannot be evaluated quantitatively because ternary mixed species are involved and the related tri- and tetra-phosphorus compounds are not available. A notable feature is the sensitivity of the variations to substitution at the distant phosphorus atom. This may be due, in part, to conformational and other geometric changes. In general the value of δ_P increases with the number of NMe_2 substituents at the distant P atom. The most marked variation of δ_P with the distant substituents occurs for the mixed $OPClNMe_2$ group.

The chemical shift variations for the sulphides are similar to those for the oxides, but the situation is not so clear cut since it was not possible to study the full series of compounds. The effect of substituting Ph for Me at the bridging nitrogen is to reduce δ_P slightly.

The sulphides show slightly larger (P,P) coupling constants than the oxides. For (Ib) \rightarrow (IIb) there is an increase of *ca.* 4 Hz, and for (Ih) \rightarrow (IIe) an increase of *ca.* 3.3 Hz. This is in contrast to the reported¹⁰ J_{PP} values for tetrafluoro-compounds, where J_{PP} for the dioxide (+32.2) is much higher than that for the disulphide (+1.5 Hz).

The *N*-phenyl compounds have significantly larger values of J_{PP} than the corresponding *N*-methyl compounds [compare (Ih) with (Ib) or (IIh) with (IIb)], in agreement with the data³⁰ (Table 3) for $Cl_2P(O) \cdot NR \cdot P(O)ClX$. This finding is surprising in view of the fact that for $Cl_2P(:O) \cdot NPh \cdot P(:S)Cl_2$ the phenyl plane is at an angle of 87.5° to the PNP plane in the crystal,²⁶ so that the phenyl group presumably does not

²⁸ F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York and London, 1972, p. 103.

³⁰ R. Keat, unpublished results.

influence PNP π -bonding greatly. The effect of the phenyl group on J_{PP} therefore must be due to size or electronegativity differences between Ph and Me. It is possible that there are conformational differences between

TABLE 3

J_{PP} /Hz for $\text{Cl}_2\text{P}(\text{O})\cdot\text{NR}\cdot\text{P}(\text{O})\text{ClX}$

X	R = Me	R = Ph
Ph	9.3	24
CH_3		26
CH_2Cl	14.0	28
CHCl_2		35

(III) and (IV) (due to the presence of Ph in the former) in solution, giving rise to the variations in J_{PP} . It should be noted that the tetrafluorodiphosphine (trivalent phosphorus) compounds show the opposite trend: for $(\text{F}_2\text{P})_2\text{NR}$, J_{PP} is +437 Hz for R = Me^{1,4} and 371 Hz (presumably positive) for R = Ph.¹

spectral analysis. For (If) a value of 10.0 Hz is predicted; a spectrum calculated on this basis (with $^5J_{PH} = 0$) does not appear to be in good agreement with that observed, but this is probably due to band-shape anomalies.¹⁸ The above procedure produces group parameters for the PCl_2 , PCINMe_2 , and $\text{P}(\text{NMe}_2)_2$ groups of 3.47, 4.58, and 3.17 Hz¹, respectively, for the oxide series; these values certainly do not show a smooth substituent effect. An 'anomaly' arises for the mixed group PCINMe_2 , as in the case of the ^{31}P chemical shifts. Unfortunately the observed value of J_{PP} for (Id) has a relatively large error (± 3 Hz) due to the rather large line-widths, but this cannot affect the conclusion that the group PCINMe_2 has an anomalously high effect on J_{PP} .

The signs of J_{PP} for three compounds [(Ib), (IIb), and (IIIh)] were determined to be positive. Since all the J_{PP} values fall in the same range, it can be assumed that

TABLE 4^a
¹³C N.m.r. data for compounds of types (I) and (II)

Compound	δ_{C}		$^2J_{\text{PC}}$ to terminal NMe_2		$^2J_{\text{PC}}$ to bridging NMe		
	NMe_2	NMe	$\text{P}(\text{X})\text{ClNMe}_2$	$\text{P}(\text{X})(\text{NMe}_2)_2$	$\text{P}(\text{X})\text{Cl}_2$	$\text{P}(\text{X})\text{Cl}(\text{NMe}_2)$	$\text{P}(\text{X})(\text{NMe}_2)_2$
(Ia)		36.65					
(Ic)	37.20	36.67			0.73		
(Id)	α 37.76	36.57	4.15 ^c		<i>b</i>		<i>b</i>
	β 37.46	36.26	4.00 ^c			1.50	
(Ie)	37.42	<i>b</i>		5.00		1.00	
	37.36			5.00		<i>b</i>	<i>b</i>
	37.54		3.25				
(If)	37.48	36.84		4.75 ^c			2.05
(IIId)	α 38.71	36.73	4.00 ^c			3.05	
	β 39.21	37.47	4.00			3.50	
(IIIe)	38.67	36.29		4.75 ^c			<i>b</i>

^a Chemical shifts in p.p.m. (± 0.05 p.p.m.) relative to the ^{13}C signal for Me_4Si (positive to high frequency). Coupling constants in Hz (± 0.05 Hz). ^b Not determined. ^c These values are actually $N_{\text{PC}} = ^2J_{\text{PC}} + ^4J_{\text{PC}}$.

It is also interesting that the symmetrical dichloro-compound (Id) has a larger J_{PP} value than the unsymmetrical dichloro-compound (Ic). This indicates that J_{PP} is not merely a function of a substituent property (e.g. electronegativity), summed over the various groups attached to the phosphorus atoms. As observed for fluorodiazadiphosphetides³¹ the coupling constant can be expressed as in equation (i), where a_{P} and $a_{\text{P}'}$ are

$$^2J_{\text{PP}'} = a_{\text{P}} \cdot a_{\text{P}'} \quad (\text{i})$$

group parameters for $\text{P}(\text{X})\text{Cl}_n(\text{NMe}_2)_{2-n}$. The three relevant parameters for each series can be calculated by using the known J_{PP} values. For the oxide series, the three group parameters were obtained from the results for (Ib), (Ic), and (Ie). By using these parameters the value of J_{PP} was predicted for (Id) (21.0 Hz) and was found to be in reasonable agreement with the experimental value (20 Hz); the latter is not very accurate owing to the width of the lines and the nature of the

³¹ R. K. Harris, M. I. M. Wazeer, O. Schlak, and R. Schmutzler, *J.C.S. Dalton*, 1974, 1912.

³² L. F. Johnson and W. C. Jankowski, 'Carbon-13 N.M.R. Spectra,' Wiley-Interscience, New York, 1972.

they are all positive. This has also been found for a number of related compounds,^{6,15} but a negative value (-4.5 Hz) has been reported⁶ for one related compound, $(\text{MeO})_2\text{P}(\text{S})\cdot\text{NMe}\cdot\text{P}(\text{Se})(\text{OPr}^i)\text{NEt}_2$.

Table 4 lists the ^{13}C chemical shifts and (P,C) coupling constants for some of the compounds studied. The methyl carbon chemical shifts fall in the same region as for other NMe compounds.³² The two-bond (P,C) couplings are small,³³ especially to the carbons in the bridging methyl groups. Comparison of the NMe_2 data for the symmetrical and unsymmetrical compounds indicates that $^4J_{\text{PC}}$ is also small.

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³³ R. D. Ballard, F. B. Ogilvie, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1970, **92**, 1908.