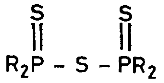
Multinuclear Magnetic Resonance Studies. Part 3.[1] Compounds with Phosphorus–Oxygen–Phosphorus or Phosphorus–Sulphur–Phosphorus Bridges

By **Robin K. Harris** * and **Elizabeth M. McVicker**, School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ
Gerhard Hägele, Institut für Anorganische Chemie der Universität Düsseldorf, 4 Düsseldorf, Universitätsstrasse, West Germany

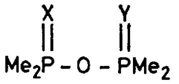
Phosphorus-31 and carbon-13 spectra are reported for four compounds containing P–S–P bridges, $[R_2P(S)]_2S$ (R = Me, Pr^i, Bu^t, or Ph), and two with P–O–P links, $Me_2P(X)–O–(Y)PMe_2$ (X = Y = S; X = O, Y = S). Phosphorus-31 relaxation data are also given for the former compounds. ' Carbon-13 satellites ' in ^{31}P resonance have yielded values for J_{PP} in some cases.

WE have extended our recent studies of diphosphorus [1-3] compounds, which involved the use of ^{31}P, ^{13}C, and ^{1}H n.m.r. to obtain coupling constants and chemical shifts in diphosphanes and dithioxodi-λ^5-phosphanes,[1,3] to diphosphorus compounds (1) and (2) with a sulphur bridge and an oxygen bridge respectively. In addition, we have measured the ^{31}P spin–lattice relaxation times and nuclear Overhauser enhancements for the di-λ^5-phosphathianes (1) in order to gain further insight into the various intramolecular motions of the compounds.



$$R_2\overset{\overset{\displaystyle S}{\|}}{P}-S-\overset{\overset{\displaystyle S}{\|}}{P}R_2$$

(1) R = Me, Pr^i, Bu^t, or Ph



$$Me_2\overset{\overset{\displaystyle X}{\|}}{P}-O-\overset{\overset{\displaystyle Y}{\|}}{P}Me_2$$

(2) X = Y = O or S
X = O, Y = S

The proton spectra of (1; R = Me or Bu^t), and of all three compounds (2), have been studied previously by Hägele *et al.*,[4] who used computer simulation to determine (P,H) coupling constants and $^2J_{PP}$. Using procedures described previously,[1,3] however, it has been possible to measure $^2J_{PP}$ directly, by observing the ^{13}C satellite lines in the ^{31}P–{^1H} spectra of some of these compounds. The spin–lattice relaxation rate of the ^{31}P nuclei in diphosphanes and dithioxo-λ^5-diphosphanes is controlled [2] by the (P,H) dipole–dipole interaction and the spin-rotation mechanism, with a further possible contribution from (P,P) dipolar effects. This last mechanism is unlikely to be important in the relaxation of compounds (1) and (2), as the (P,P) internuclear distance is much greater than for the diphosphanes. Furthermore, a greater flexibility in these molecules is envisaged, due to the intervening O or S atom, relieving some of the steric interactions between substituents on the phosphorus atoms and providing an addition internal-rotation process.

SPECTRAL ANALYSIS FOR THE SYMMETRICAL COMPOUNDS

When proton-noise decoupling is applied to (1) and (2), most molecules contain two equivalent ^{31}P nuclei as the only effective magnetic nuclei. They therefore gave only a single line in the ^{31}P spectrum. Compounds (2; X $\neq$ Y) provide exceptions to this generalisation. However, in molecules with a ^{13}C nucleus (in natural abundance in our experiments) the symmetry is removed and an ABX spin system is formed, where A is the ^{31}P nucleus directly bound to ^{13}C and B is the phosphorus two bonds removed. The chemical-shift difference, $\Delta\nu_{AB} = \nu_A - \nu_B$, between A and B is very small (being caused only by isotopic effects) and deceptively simple spectra are observed. Under circumstances where $\Delta\nu_{AB}$ is very small, and $|L|$ ($L = J_{AX} - J_{BX}$) is much less than $|J_{AB}|$, several approximations [1] can be made to obtain the coupling constants $|J_{AB}|$, $|J_{AX}|$, and $|J_{BX}|$, together with the relative signs of J_{AX} and J_{BX}. Normally only three lines are observed in the X (*i.e.* ^{13}C) part of such a deceptively simple ABX spectrum: a doublet separated by $|N|$ ($N = J_{AX} + J_{BX}$), and two inner lines which often overlap to give a singlet, centred at ν_X. There are two other lines, symmetrical about ν_X, which are usually too weak to be seen,[5] but if $|L| > |J_{AB}|$ these lines, which will be referred to as the outer lines, may have appreciable intensity. In some of the ^{13}C spectra of the compounds (1) the outer lines had almost double the intensity of the inner lines (those near ν_X), a condition occurring if sin ($\phi_+ - \phi_-$) > cos ($\phi_+ - \phi_-$), where ϕ is defined † by equations (1)—(3).

$$D_{\pm}\cos 2\phi_{\pm} = \tfrac{1}{2}\,\Delta\nu_{AB} \pm \tfrac{1}{4}\,L \qquad (1)$$

$$D_{\pm}\sin 2\phi_{\pm} = \tfrac{1}{2}\,J_{AB} \qquad (2)$$

$$D_{\pm} = \tfrac{1}{2}[(\Delta\nu_{AB} \pm \tfrac{1}{2}\,L)^2 + J_{AB}{}^2]^{\frac{1}{2}} \qquad (3)$$

When $|\Delta\nu_{AB}| \ll |J_{AB}|,|L|$, the condition simplifies to $|L| > 2|J_{AB}|$.

Where feasible we have also studied the AB region of the spectra, *i.e.* the ^{13}C satellites in ^{31}P resonance, as described previously.[1]

RESULTS

Di-λ^5-phosphathianes (1).—The ^{31}P spectra of the alkyl-substituted compounds showed eight-line patterns [1] (*i.e.* two ab subspectra) for the ^{13}C satellites from the α carbons, as seen in Figure 1. From this it was possible to obtain all the parameters, including the isotopic chemical-shift differences $\Delta\nu_{AB}$. Satellite lines from the β carbons of R = Pr^i or Bu^t were obscured by the main ^{31}P peak due to the [per-^{12}C]isotopomer.

The ^{13}C spectra gave six-line patterns for the α carbons, with the outer lines having greater intensity than the inner lines; thus $|L| > 2|J_{PP}|$. A triplet pattern was observed

---

† The formulae are derived from ref. 5 but with N and L redefined.

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

[2] R. K. Harris and E. M. McVicker, *J.C.S. Faraday II*, 1976, 2291.

[3] S. Aime and R. K. Harris, *J. Mag. Resonance*, 1974, **13**, 236.

[4] G. Hägele, W. Kuchen, and H. Steinberger, *Z. Naturforsch.*, 1974, **B29**, 349.

[5] R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.*, 1961, **39**, 216; R. J. Abraham, ' Analysis of High-resolution NMR Spectra,' Elsevier, Amsterdam, 1971.

for the β carbons for R = Pr^i or Bu^t, consistent with $\Delta\nu_{AB}$ *ca.* 0 and $|L| \ll |J_{AB}|$ for a deceptively simple ABX spectrum. Non-equivalence of methyl groups occurred for R = Pr^i, as noted previously [1] for diphosphanes and dithioxo-λ^5-diphosphanes. Figure 2 illustrates the six-line pattern for the α carbon in [Pr$^i_2$P(S)]$_2$S; the central band can just be resolved into two peaks under optimum conditions.

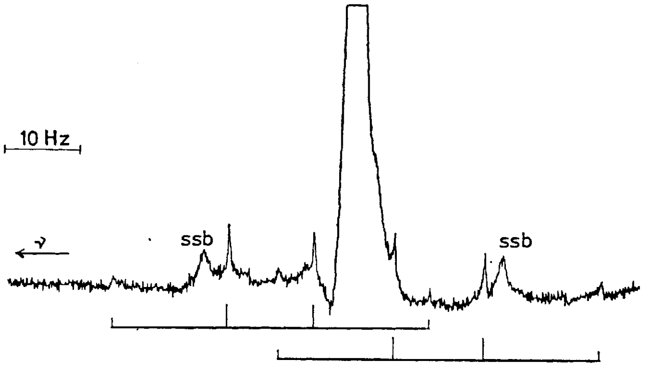


FIGURE 1 40.5-MHz ^{31}P-{^{1}H} spectrum of [Pr$^i_2$P(S)]$_2$S, showing '^{13}C satellite' ab subspectra from the methine carbon. Spinning sidebands are marked ssb

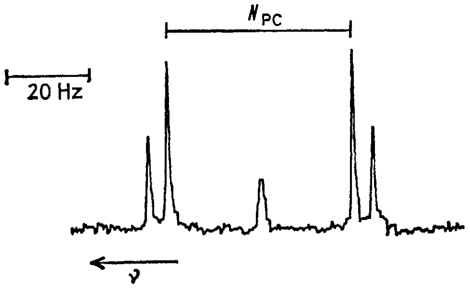


FIGURE 2 25-MHz ^{13}C-{^{1}H} spectrum for the methine carbon of [Pr$^i_2$P(S)]$_2$S. The central line can just be split under higher resolution

No ^{13}C satellite spectra were observed for compound (1; R = Ph) as this sample was very dilute. Interpretation of the ^{13}C spectrum was not definitive, as even after an overnight accumulation the signals for C^1 (bonded directly to phosphorus) were not clear. There is a quintet at δ_c 128.99 p.p.m. presumably due to the *meta* carbon, and a complex of lines at δ_c 132.64 p.p.m. This complex pattern appears to be a superimposition of a quintet (presumably due to the *ortho* carbon) and a triplet due to the *para* carbon, the two chemical shifts being equal within experimental error.

The ^{31}P and ^{13}C n.m.r. data obtained are given in Tables 1 and 2, and the T_1 and nuclear Overhauser enhancements (η) for compounds (1) are given in Table 3. Using (see, for example, ref. 2) equation (4), where $\eta_{max.}$ is the maximum

$$\eta = \eta_{max.}\, T_1/T_{1dd} \quad (4)$$

Overhauser enhancement (1.24 for ^{31}P-{^{1}H}), the dipolar contribution, T_{1dd}, to T_1 was evaluated. The spin-lattice relaxation time from other mechanisms, T_{1o}, was then found, since $T_1^{-1} = T_{1dd}^{-1} + T_{1o}^{-1}$.

TABLE 1

Phosphorus-31 n.m.r. data for di-λ^5-phosphathianes, [R$_2$P(S)]$_2$S

R	δ_P/p.p.m.	$\|^2J_{PP}\|$/Hz	$(\nu_A - \nu_B)$ [a]/Hz
Me	61.09 (60.7 [b])	14.8 (14.6 [b])	−0.45
Pr^i	106.47	15.7	−1.2
Bu^t	121.29 (120.3 [b])	14.6 (12.5 [b])	−0.9
Ph	61.9		

[a] ν_P for ^{13}C–P minus ν_P for ^{12}C–P in the [^{13}C]isotopomer. [b] Ref. 4.

TABLE 2

Carbon-13 n.m.r. data for [R$_2$P(S)]$_2$S

R		δ_C/p.p.m.	$\|N_C\|$/Hz	$^1J_{PC}$ [a]/Hz	$^3J_{PC}$/Hz
Me		32.88	56.3	56.0	*ca.* 0.3 [b]
Pr^i	α	35.31	45.0 (±0.2)	45.0 (±0.2)	*ca.* 0.1 [b]
	β	18.92	2.9		
	β	17.45	1.6		
Bu^t	α	47.07	37.0 (±0.2)	36.9 (±0.2)	<0.1
	β	28.95	<2.0		
Ph [c]	C^1	136.21			
	C^4	132.64	3.0		
	C^2	132.64	11.8	$2D_+ + 2D_- = 27.8$	
	C^3	128.99	13.8	$2D_+ + 2D_- = 26.8$	

[a] Assumed to be positive.[6] [b] The values deduced are probably within experimental error of zero. [c] The assignments for this molecule are not unambiguous.

TABLE 3

Phosphorus-31 relaxation data for [R$_2$P(S)]$_2$S at *ca.* 35 °C

R	Solvent	T_1/s	η	T_{1dd}/s	T_{1o}/s
Me	CCl$_4$	17.8	0.48	46	29
Pr^i	CDCl$_3$	14.6	0.94	19	61
Bu^t	CDCl$_3$	17.0	0.81	26	49
Ph	CDCl$_3$	23.6	0.52	56	41

Compounds (2).—The spectral characteristics for these compounds are as follows.

Me$_2$P(S)–O–(S)PMe$_2$. A five-line ^{13}C spectrum was recorded for the methyl group, but satellite lines in the ^{31}P spectrum were too weak to be detected. Taking the literature value of $|^2J_{PP}|$(34 Hz),[3] carbon–phosphorus coupling constants were calculated assuming the separation of the outer lines of the carbon spectrum (98.5 Hz) to be [1] $(L_{PC}^2 + {}^4J_{PP}^2)^{\frac{1}{2}}$.

TABLE 4

Phosphorus-31 and ^{13}C n.m.r. data for the oxygen-bridged compounds, Me$_2$P(X)–O–(Y)PMe$_2$

Compound	δ_P/p.p.m.	$\|J_{PP}\|$/Hz	δ_C/p.p.m.	$^1J_{PC}$ [a]/Hz	$^3J_{PC}$/Hz
X = Y = O	51.1 [b]	30.52 [b]			
X = Y = S	93.39 (90.9 [b])	34.0 [b]	26.86	72.2 [c]	1.7 [c,d]
X = O, Y = S	54.26 (54.9 [b]) 92.05 (91.9 [b])	30.7	18.97 26.53	93.3 72.5	*e* *e*

[a] Assumed to be positive. [b] Ref. 4. [c] Calculated using the value of $|^2J_{PP}|$ given in ref. 4. [d] Has the same sign as $^1J_{PC}$ (assumed to be positive). [e] Less than the spectrometer resolution (*ca.* 0.4 Hz).

Me$_2$P(S)–O–(O)PMe$_2$. This unsymmetrical compound gave first-order ^{31}P spectra, as the chemical-shift difference between P(S) and P(O) was much larger than $|^2J_{PP}|$. The chemical shifts and $|^1J_{PC}|$ for each part of the molecule were

---

[6] W. McFarlane, *Proc. Roy. Soc.*, 1968, **A306**, 185; W. McFarlane and J. A. Nash, *Chem. Comm.*, 1969, 913.

similar to those in the corresponding symmetrical compounds. Splittings due to ${}^3J_{PC}$ were too small to be resolved.

The results for the above two compounds are given in Table 4, together with some literature data on (2; X = Y = O).

DISCUSSION

The ${}^{31}P$ chemical shifts show the expected increase with substituent bulk for the di-λ^5-phosphathianes (1). The replacement of the sulphur bridge by oxygen causes a substantial increase (*ca.* 30 p.p.m.) in resonance frequency, as expected on simple electronegativity considerations. However, the P=O groups resonate well to low frequency of the corresponding P=S moieties, and the assignment of the ${}^{31}P$ spectrum of (2; X = O, Y = S) is therefore unambiguous. Presumably, the shifts are greatly influenced by d_π-p_π back donation. Long-range effects of replacing P=S by P=O on the ${}^{31}P$ resonance of the other moiety are small (<2 p.p.m.). The values of $\Delta\nu_{AB}$ (the shift between ${}^{31}P$-${}^{13}C$ and ${}^{31}P$-${}^{12}C$) show that for the symmetrical compounds it may be neglected in the calculation involving $D_\pm$, as found for diphosphanes and dithioxo-λ^5-diphosphanes.[1]

The ${}^{13}C$ chemical shifts of (1; R = Me) and (2; X = Y = S) are to high frequency of that for $[Me_2P(S)]_2$ (δ_C 16.93 p.p.m.),[1] presumably due to the electronegativity of the bridging atoms. However, both the replacements of -S- by -O- and P=S by P=O cause low-frequency shifts, so that the resonance of (2; X = Y = O) would be expected to be close to that of $[Me_2P(S)]_2$. In the case of (1; R = Pr^i) the β-methyl groups of a given Pr^i are non-equivalent, due to molecular asymmetry.

The one-bond (P,C) coupling constants decrease in magnitude with the bulk of substituent in compounds (1), as found for the dithioxo-λ^5-diphosphanes.[1] We assume that ${}^1J_{PC}$ is positive [6] in all the cases presented here. Values of ${}^1J_{PC}$ increase rapidly with the number of oxygens around phosphorus, from 56 Hz for (1; R = Me) to 93 Hz for the P=O group of (2; X = O, Y = S). This is as expected if Bent's rule [7] applies and the couplings are Fermi-contact dominated, since greater *s* character (and hence a more positive coupling constant) is concentrated in bonds towards the more electropositive groups, in this case the methyls. In fact there is a good linear relation (admittedly with only four points) between ${}^1J_{PC}$ and δ_C for the tetramethyl compounds, thus indicating that bonding variations affect both parameters similarly.

For the di-λ^5-phosphathianes (1) there is a remarkable lack of variation in (P,P) coupling constants. Other data in the literature refer to compounds with fluorine substituents. Where one fluorine is placed on each phosphorus, stereoisomerism is possible and different values of ${}^2J_{PP}$ for *meso* and *rac* forms were reported.[8] When both R substituents are fluorine a temperature variation in ${}^2J_{PP}$ has been found;[9] in the analogous compound of P^{III}, F_2P-S-PF_2, the temperature variation is more drastic,[10] changing from +274 Hz at 39 °C to +392 Hz at 120 °C. These features must be attributed to alteration of the P-S-P bond angle, and the consistency of $|{}^2J_{PP}|$ in (1) implies that at ambient temperature the angle P-S-P remains relatively unchanged by the substituents on phosphorus.

The magnitudes of the two-bond (P,P) coupling constants through oxygen are roughly twice those through sulphur, but they are not altered significantly by changing the substituents X and Y from S to O. Although the signs of ${}^2J_{PP}$ were not determined in our work, it seems probable that they are positive [11] for all our compounds. However, Charlton and Cavell [9] reported a negative sign for $[F_2P(S)]_2S$, with the value of ${}^2J_{PP}$ increasing algebraically as the bridging group changes from sulphur to oxygen (as for our compounds). Increasing the electronegativity of Z should lead to decrease in *s* character in the P-Z-P bond, thus decreasing $|J_{PP}|$ if a simple model is envisaged. However, the *s*-electron density at the phosphorus nuclei should be increased by the increase in electronegativity of Z. Thus, these effects will tend to compensate. Moreover, the lack of an effect of changing substituents X and Y militates against Z electronegativity being the dominant influence, and it is likely that further factors are important, such as changes in the P-Z-P bond angle and P · · · P distance caused by variation in the substituent sizes. Geminal coupling constants, even ${}^2J_{HH}$, are notoriously difficult to rationalise in simple terms.

The nuclear Overhauser enhancement for the di-λ^5-phosphathianes (1) (Table 3) shows a spread of values, from η = 0.48 to 0.94, as a result of changes in the balance of the relaxation mechanisms. The values of T_1 also show appreciable variations, as is the case for the dithioxo-λ^5-diphosphanes,[2] but it is difficult to pick out consistent trends (probably because the solution conditions were not standardised). The (P,H) dipolar relaxation rate increases markedly in efficiency from (1; R = Me) to (1; R = Pr^i), as for the corresponding dithioxo-λ^5-diphosphanes; T_{1dd} increases again for $[Bu^t_2P(S)]_2S$, perhaps because of the lack of any protons nearer than three chemical bonds to the phosphorus nuclei. In general, the larger the group R the more likely it is that the dipolar term dominates, but the pattern is by no means clear-cut, probably because increases in correlation times for overall motion are accompanied by increased possibilities of internal rotation and by decreases in the number of close (P,H) distances.[2] The (P,P) dipolar interaction is unlikely to effectively compete with the (P,H) interaction, and T_{1o} is probably dominated by the spin-rotation mechanism, as for the dithioxo-λ^5-diphosphanes;[2] the additional flexibility inherent in the P-S-P bridge does not appear to give very marked changes in relaxation behaviour. It is possible that chemical-

---

[7] H. A. Bent, *Chem. Rev.*, 1961, **61**, 275.

[8] R. K. Harris, J. R. Woplin, M. Murray, and R. Schmutzler, *J.C.S. Dalton*, 1972, 1590.

[9] T. L. Charlton and R. G. Cavell, *Inorg. Chem.*, 1972, **11**, 1583.

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

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

shift anisotropy also provides a contributory mechanism for T_{1o}.

EXPERIMENTAL

Compounds (1; R = Me or Bu^t) were placed in n.m.r. tubes (outside diameter, 5 mm) in solution with CCl_4, then degassed and sealed. The deuterium lock was provided by $CDCl_3$ in a concentric 12-mm tube. The derivative (1; R = Ph) was placed in a 12-mm tube with $CDCl_3$ as solvent. The compound (1; R = Pr^i) was found in the same sample[1] as $[Pr^i_2P(S)]_2$ and was not isolated. Compounds containing an oxygen bridge were moisture sensitive and the samples were made up in a dry-box with $CDCl_3$ as solvent, then degassed and sealed. The concentrations of the various compounds were not determined. Spectra were recorded in the Fourier-transform mode at 40.5 MHz for ^{31}P and at 25.2 MHz for ^{13}C using a Varian XL100 spectrometer and an on-line 620/*l* computer. Proton-noise decoupling was used throughout. Spin–lattice relaxation times were measured using the inversion-recovery pulse sequence as modified by Freeman and Hill[12] (including pulse delays of $>5\ T_1$), and measurements of the nuclear Overhauser enhancement were made using gated decoupling.[13] The reported T_1 values are averages from three measurements, and nuclear Overhauser data are averages from at least five experiments. Spin–lattice relaxation times were reproducible to within 10%, generally to better than 5%. The reproducibility of the nuclear Overhauser results was better than ±0.08.

Spectra were mostly recorded at ambient probe temperature (*ca.* 35 °C). No account was taken of temperature variations caused by gating the decoupler for the nuclear Overhauser measurements. Typical conditions for the ^{13}C spectra were: between 500 and 6 000 pulses, with acquisition times of 1—4 s and appropriate variations in pulse angles from 10 to 80 ° depending on the relaxation times. For the ^{13}C satellites in ^{31}P resonance 1 000 pulses with 20-s pulse intervals, *ca.* 75° pulse angles, and sweep widths of 100—250 Hz were typical. Carbon-13 and phosphorus-31 chemical shifts are reported with respect to $SiMe_4$ and external 85% H_3PO_4 respectively, using the high-frequency-positive convention and the absolute-frequency indirect method of measurement.[14] Values of δ_C are likely to be accurate to ±0.5 p.p.m., but their relative accuracy is higher.

The compounds were prepared as described in ref. 4, except for (1; R = Pr^i) which was present as an impurity in another sample, as mentioned above, and (1; R = Ph) which was obtained[15] by condensation of $PPh_2S(SH)$ involving loss of H_2S.

We thank Dr. M. Fild for the sample containing $[Pr^i_2P(S)]_2S$, and the Northern Ireland Department of Education for the award of a research studentship (to E. M. McV.).

[7/334 *Received*, 25*th February*, 1977]

---

[12] R. Freeman and H. D. W. Hill, *J. Chem. Phys.*, 1971, **54**, 3367.

[13] R. Freeman, H. D. W. Hill, and R. Kaptein, *J. Mag. Resonance*, 1972, **7**, 327.

[14] R. K. Harris, M. I. M. Wazeer, O. Schlak, and R. Schmutzler, *J.C.S. Dalton*, 1974, 1912; R. K. Harris and B. J. Kimber, *J. Mag. Resonance*, 1975, **17**, 174.

[15] H. Steinberger, Diplomarbeit, University of Düsseldorf, 1970.