Multinuclear Magnetic Resonance Studies. Part 2.[1,†] Diphosphanes and Dithioxodi-λ^5-phosphanes

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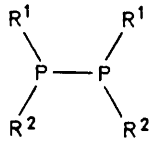
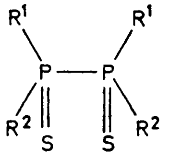
Carbon-13 and phosphorus-31 n.m.r. spectra have been obtained for a number of tetra-alkyldiphosphanes and tetra-alkyldithioxodi-λ^5-phosphanes of general formulae $(R^1R^2P)_2$ and $[R^1R^2P(S)]_2$ respectively. Some analogous compounds with phenyl substituents have also been studied. Satellite resonances in ^{31}P resonance due to ^{13}C-containing isotopomers have been examined. The data are treated, together with ^1H n.m.r. studies where appropriate, to obtain (P,P) and (P,C) coupling constants, as well as ^{13}C and ^{31}P chemical shifts. These n.m.r. parameters are discussed in terms of steric interactions and stereoisomerism. The values of $|^1J_{PP}|$ for both series of compounds increase markedly as the size of the substituents increases, and this effect correlates with an increase in δ_P.

WITH the advent of Fourier-transform n.m.r. spectroscopy, it has become more feasible to study a range of nuclei, whereas in the past only ^1H, ^{19}F, and, to some extent, ^{31}P work was common. In particular the use of ^{13}C n.m.r. has become widespread. Normally such spectra are recorded under proton-decoupled conditions and each type of ^{13}C nucleus gives rise to a single peak. Splittings due to spin–spin coupling are usually only present when there are nuclei of spin $\frac{1}{2}$ other than ^{13}C and ^1H in the compound being studied. Such is the case for phosphorus-containing compounds, and this paper is concerned with the ^1H, ^{13}C, and ^{31}P n.m.r. spectra of a series of substituted diphosphanes, (I), and dithioxodi-λ^5-phosphanes, (II).‡ The data for tetramethyldiphosphane (I; $R^1 = R^2 = Me$) were published earlier.[1] Such compounds have been of interest (*a*) to n.m.r. spectroscopists because of the problems of spectral analysis for symmetrical spin systems [3,4] and because of the wide (and as yet unexplained) variation [5] in the values of $^1J_{PP}$, and (*b*) to structural chemists because of the problem of internal rotation about the P–P bond.[6] For the diphosphanes (I) themselves, the values of $|^1J_{PP}|$ are normally very large,[5] and the ^1H spectra are ' deceptively simple ',[7] yielding detailed information only when stringent experimental conditions are employed.[8] However, this is not usually [5,9] the case for the dithioxodi-λ^5-phosphanes (II), and spectral analysis by inspection is straightforward when there is only a single type of ^1H present, since it may be assumed that long-range (H,H) coupling is negligible. For compounds of both types (I) and (II) analysis of the ^1H spectra becomes difficult [10] if there is more than one type of proton in the compound. The objects of the present investigation have been to widen the range of compounds investigated, to use ^{13}C and ^{31}P spectra to obtain data on $^1J_{PP}$ for cases where analysis of the ^1H spectra is very difficult, and to increase the number of nuclear spin parameters available by measuring δ_C, δ_P, and (P,C) coupling constants. A comparison of the data for compounds of types (I) and (II) produces information regarding the effects of lone-pair electrons and sulphur atoms on the spin parameters.


(I)


(II)

Compounds (I) and (II) with $R^1 \neq R^2$ can exist as stereoisomers, *meso* and *rac*.[11] In fact only one isomer was present [12] in the sample of (I; $R^1 = Me$, $R^2 = Bu^t$) which we studied. This situation has also been reported by other workers.[13] The samples of (I; $R^1 = Me$, $R^2 = Et$) and (I; $R^1 = Me$, $R^2 = Pr^i$), however, consisted of a mixture of isomers.[12] One of the results of the present work was the finding that measurement of $|N_{PC}| = |J_{PC} + J_{PC'}|$ enables an assignment of the stereoisomers to be made unambiguously, and also provides evidence regarding the favoured rotamer of the *rac* isomer. We reported the basis of this use of $|N_{PC}|$ in a preliminary publication,[12] and the arguments will not be repeated here, although we shall assume the assignments of isomers as reported.[12]

Compound (II; $R^1 = Me$, $R^2 = Et$) was obtained as two separate samples of the *meso* and *rac* isomers, although each sample was contaminated with a small

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† See also Part 1 of a related series.[2]

‡ For the use of λ^n to indicate the ' connecting number ' *n* see IUPAC rules ' Nomenclature of Organic Chemistry: Section D.'

[1] Part 1, S. Aime and R. K. Harris, *J. Mag. Res.*, 1974, **13**, 236.

[2] W. Althoff, M. Fild, and H. P. Rieck, *Z. Naturforsch.*, in the press.

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

[4] P. Diehl, R. K. Harris, and R. G. Jones, *Progr. N.M.R. Spectroscopy*, 1967, **3**, 1.

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

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

[7] R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.*, 1961, **39**, 216.

[8] E. G. Finer and R. K. Harris, *Mol. Phys.*, 1967, **12**, 457.

[9] R. K. Harris and R. G. Hayter, *Canad. J. Chem.*, 1964, **42**, 2282.

[10] G. Hägele, R. K. Harris, and J. M. Nichols, *J.C.S. Dalton*, 1973, 79.

[11] J. B. Lambert, G. F. Jackson, and D. C. Mueller, *J. Amer. Chem. Soc.*, 1968, **90**, 6401; 1970, **92**, 3093.

[12] R. K. Harris, E. M. McVicker, and M. Fild, *J.C.S. Chem. Comm.*, 1975, 886.

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

amount of the other isomer. Only one signal was found in the ^{31}P spectrum of the sample of (II; $R^1 = Me$, $R^2 = Bu^t$) supplied by G. Hägele, showing that there was only one isomer present, as previously suggested[10] from the proton spectrum. We do not have evidence as to the nature of the isomer present. A recent publication[13] reports the preparation of both stereoisomers. The sample of (II; $R^1 = Me$, $R^2 = Ph$) studied in the present work consisted of a single stereoisomer of m.p. *ca.* 140 °C, the *rac* isomer.

SPECTRAL ANALYSIS

All the compounds discussed here are symmetrical, so that for the [per-^{12}C]isotopomers the phosphorus nuclei are equivalent and the ^{31}P spectra obtained under conditions of proton-noise decoupling consisted of a single absorption, allowing the determination of the phosphorus chemical shift, δ_P. The ^{31}P single-resonance spectra were in most cases rather complex, and give no information that is not better obtained by other methods (*e.g.* from ^1H spectra). The ^1H spectra for cases in which R^1 and R^2 are identical and contain only a single type of proton have been adequately discussed before.[3] Such compounds give $[AX_n]_2$ spin systems. The cases with $R^1 = R^2 = Me$ have been discussed previously, both for the diphosphane (I)[8] and the di-λ^5-phosphane (II).[9] The only additional case studied here is (I; $R^1 = R^2 = Bu^t$) since the compound (II; $R^1 = R^2 = Bu^t$) could not be prepared. Cases for which $R^1 \neq R^2$ but when R^1 and R^2 contain a single type of proton each are also[10] amenable to analysis as $[AR_tX_n]_2$ spin systems in suitable cases (*e.g.* $R^1 = Me$, $R^2 = Bu^t$), but for the remaining compounds the ^1H spectra are relatively uninformative. However, for most of the molecules of type (I) observation of weak outer lines in the ^1H spectra under conditions of high radiofrequency (r.f.) power[8] yielded values of $|^1J_{PP}|$.

This paper is principally concerned with the species which contain a single ^{13}C nucleus. The effects on the ^1H spectra for $R^1 = R^2 = Me$ have been discussed earlier,[14] and the relative signs of J_{PP} and $N_{PH} = J_{PH} + J_{PH}'$ were obtained by ^1H-{^{31}P} double-resonance experiments. We have made a similar determination for (I; $R^1 = R^2 = Bu^t$). Although the weak outer ab lines (see below) in the ^{31}P spectrum were not observable directly, it is easy to locate them for double-resonance purposes, if J_{PP} is known, as they will be near $\nu_P \pm J_{PP}$.

Introduction of a ^{13}C nucleus into (I) or (II) removes the symmetry of the spin system, and under proton-decoupled conditions an ABX spin system[15] exists for the ^{13}C and ^{31}P nuclei. The ^{31}P spectrum of a given ^{13}C-containing species will, of course, appear as a set of ' satellite ' lines near the peak due to the [per-^{12}C]isotopomer, comprising two ab subspectra. The chemical-shift difference $\Delta\nu_{AB} = \nu_A - \nu_B$ arises entirely from isotopic effects (being the difference in resonance frequencies of phosphorus adjacent to ^{12}C and ^{13}C nuclei). It will contain contributions from both one-bond and two-bond isotopic shifts, *i.e.* $\Delta\nu_{AB} = \Delta\nu_1 - \Delta\nu_2$ (where nucleus A is defined as bonded to ^{13}C), and is likely to be small compared to the coupling constants in the system. The shift differences for the ab subspectra[16] are $\Delta\nu_{ab} = \Delta\nu_{AB} \pm \frac{1}{2}L_{PC}$, where $L_{PC} = J_{PC} - J_{PC}'$. The distance between the centres of the two subspectra will be $\frac{1}{2}|N_{PC}| = \frac{1}{2}|J_{PC} + J_{PC}'|$. Frequently it will be a good approximation to ignore $\Delta\nu_{AB}$. The ab shift differences are then $\Delta\nu_{ab} = \pm\frac{1}{2}L_{PC}$ and the separation, S, of the inner lines of each ab subspectrum will be $(\frac{1}{4}L^2_{PC} + J^2_{PP})^{\frac{1}{2}} - |J_{PP}|$. If, in addition, $|L_{PC}| \leqslant |J_{PP}|$, the ab subspectra will be closely coupled, and it is probable that the outer lines will be too weak to observe. [We have only observed them in the case of (II; $R^1 = R^2 = Me$).] In such cases S will closely approximate to $|L^2_{PC}/8J_{PP}|$. If all the four inner lines are observed, and $|J_{PP}|$ is known (*e.g.* from the proton spectrum), measurement of the satellites in the ^{31}P spectrum therefore gives L_{PC}, N_{PC}, and (from the mean frequency of the four transitions, together with the resonance frequency of the [per-^{12}C]-isotopomer) $\Delta\nu_1 + \Delta\nu_2$. However, in the cases where $|L_{PC}| \leqslant |J_{PP}|$, the value derived for L_{PC} will not be very accurate. Strictly speaking the inner ab separations should be unequal, and this will be observed when $|\Delta\nu_{AB}|$ is not negligible compared to $|L_{PC}|$. In such a case $\Delta\nu_{AB}$ can also be obtained, and hence $\Delta\nu_1$ and $\Delta\nu_2$ separated, but this was not the case for any of the compounds discussed here except (II; $R^1 = R^2 = Me$), where the difference in splittings was only small. It may be noted that normally N_{PC} is known from the ^{13}C spectrum, and this information is of use in assigning the satellite lines in the ^{31}P spectrum, otherwise ambiguities exist.

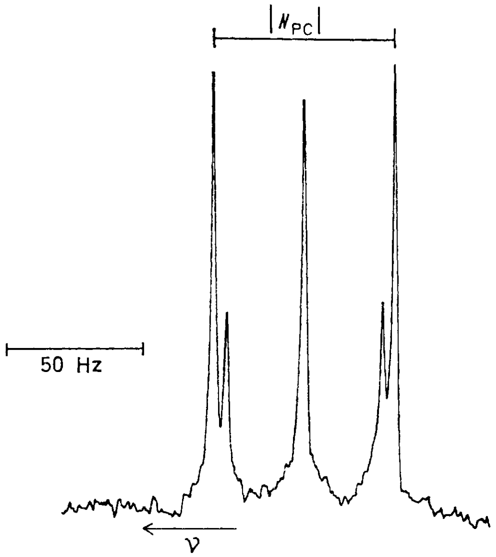

FIGURE 1 25 MHz ^{13}C-{^1H} n.m.r. spectrum of *rac*-$[PhMeP(S)]_2$, $^{13}CH_3$ part, recorded in the Fourier-transform mode (1 000 transients) for a solution in $CDCl_3$, showing the characteristic five-line pattern

The X region of an ABX spin system normally consists of six lines.[15] The two strongest are separated by $|N_{PC}|$ in the present instances. However, when $\Delta\nu_{AB}$ is small, two of the other lines will be very near ν_X and are likely to be unresolved. A quintet pattern will therefore be seen (see Figure 1). The separation of the remaining pair of lines is (ignoring $\Delta\nu_{AB}$) $4D$, where D is given by equation (1).

$$2D = (\tfrac{1}{4}L^2_{PC} + J^2_{PP})^{\frac{1}{2}} \qquad (1)$$

Therefore, provided $\Delta\nu_{AB}$ can be ignored, $|J_{PP}|$ is obtained by subtracting the splitting in the AB region, mentioned above, from half the splitting between the weak lines in the X region. Frequently, however (especially when $|J_{AB}| \geqslant$

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[14] E. G. Finer and R. K. Harris, *Mol. Phys.*, 1967, **13**, 65.

[15] R. J. Abraham, ' The Analysis of High Resolution NMR Spectra,' Elsevier, Amsterdam, 1971.

$|L_{PC}|$), these lines will be too weak to observe, and a ' deceptively simple ' triplet will be seen, from which only $|N_{PC}|$ and ν_C can be obtained. Under the approximation $|L_{PC}| < 1.1\,|J_{PP}|$, expression (1) reduces to $2D = |J_{PP}| + (L^2_{PC}/8|J_{PP}|)$ to within 1%.

For the spectral analysis by multinuclear magnetic resonance of systems of the type studied here it is convenient to make a classification of the available experimental data. Four pieces of information are involved. One of them, $|N_{PC}|$, is normally available from the ^{13}C-{^{1}H} spectra. A second, $|J_{PP}|$, may be available from ^{1}H measurements, from ^{1}H-{^{31}P} double resonance, or from spectral analysis for a different [^{13}C]isotopomer than the one under consideration. Such situations we will classify as case 1. If $|J_{PP}|$ is not available, the situation will be referred to as case 2. The other two items of importance are (*i*) whether the ^{13}C-{^{1}H} spectrum is a five- or a three-line pattern (an unresolved singlet being included in the latter category), and (*ii*) whether the inner ab splittings for the ^{13}C satellites of the ^{31}P-{^{1}H} spectrum are available or not. (The splitting may be too small to measure properly, or the satellites may be obscured by the peak due to the [per-^{12}C]isotopomer, or the lines may be unassignable for other reasons.) We define the following sub-cases:

(*a*) five-line ^{13}C pattern; satellite splitting available
(*b*) five-line ^{13}C pattern; satellite splitting not available
(*c*) three-line ^{13}C pattern; satellite splitting available
(*d*) three-line ^{13}C pattern; satellite splitting not available

Thus case 1(*a*) refers to a situation where $|J_{PP}|$ is available, there is a five-line ^{13}C pattern, and the satellite splitting is available: such a situation is overdetermined for $|J_{PP}|$ and $|L_{PC}|$. In cases 1(*b*), 1(*c*), and 2(*a*) the parameters $|J_{PP}|$ and $|L_{PC}|$ may be obtained, but their accuracy will depend greatly on the measurement of satellite splittings; however, estimates of J_{PC} and J_{PC}' separately can then be made, including their relative signs. For the other cases $|L_{PC}|$ cannot be determined. All the cases under discussion ignore the existence of $\Delta\nu_{AB}$, but all are equally applicable whether or not the approximation $|L_{PC}| \ll |J_{PP}|$ holds. The spectral-analysis cases for compounds (II) studied here are given in Table 5.

In principle the values of J_{PC} and J_{PC}' are not distinguished by the spectral analysis. In practice assignments are made by comparison with literature data, but it should be remembered that there is a residual ambiguity.

RESULTS

Diphosphanes.—Seven of these compounds were studied, and some literature data are available for three others. The phosphorus chemical shifts and $|J_{PP}|$ values (the latter derived in most instances from ^{1}H spectra) are given in Table 1, together with previously reported data. The carbon chemical shifts and coupling constants are summarised in Table 2. The very large (P^{III}, P^{III}) coupling constants of the diphosphanes mean that the approximation $|L_{PC}| \ll |J_{PP}|$ holds, and the ^{13}C spectra show only a deceptively simple triplet. Unfortunately, for diphosphanes other than tetramethyl and tetraphenyl, the phosphorus chemical shift was very sensitive to temperature; indeed on one occasion the signal of $Pr^i_2PPPr^i_2$ moved by 4 Hz while the spectrum was being recorded, although the sample had been in the probe under constant conditions for several hours. Over a temperature range of +50 to −40 °C the chemical shift changed from −7.11 (in benzene) to −17.70 p.p.m. (in dichloromethane); values for the two solvents are very close at probe temperature, −11.58 in C_6D_6 and −11.64 p.p.m. in CD_2Cl_2. Due to the instability of the chemical shift with temperature, the phosphorus lines from molecules with no ^{13}C nuclei were quite broad (W = 0.8—1 Hz), and the central lines of the ab subspectra were difficult to resolve, or (where N_{PC} was small) they were obscured by the base of the main ^{31}P line. Thus the separations $|L^2_{PC}/8J_{PP}|$ are not known with sufficient accuracy to obtain meaningful values of $|L_{PC}|$, although it is clear that $|L_{PC}| <$ *ca.* 40 Hz in each case. The spectral analyses (except for Me_2PPMe_2) therefore fall into the categories 1(*d*) or 2(*d*), mentioned above. Assignment of the signals in the ^{13}C spectra was straightforward for the tetrasubstituted diphosphanes, but low-power {^{1}H} decoupling was used to distinguish the deceptively simple triplets of the methyl groups in Me and Et of 1,2-diethyl-1,2-dimethyldiphosphane, as the $|N_{PC}|$ separation cannot be assumed to decrease with the number of intervening bonds. The quaternary carbon signal of the Bu^t group in $Bu^tMePPMeBu^t$ was identified using low-power {^{1}H} decoupling, since this carbon has a very small N_{PC} value and its signal was almost overlapped by the

TABLE 1

Phosphorus-31 n.m.r. data for symmetrical diphosphanes, $(R^1R^2P)_2$

R^1R^2	δ_P/p.p.m. [a,b]	$\lvert J_{PP}\rvert$ [b-e]/Hz	$\frac{1}{2}(\Delta\nu_1 + \Delta\nu_2)$ [f] /Hz
H_2		(108 [g])	
Me_2	−57.58 [h] (−59.5 [i])	(179.7 [j])	(−1 [j])
Et_2	−32.70 (−34.3 [k])	221 (±1)	−0.2 (β) −0.7 (α)
Pr^i_2	−11.58	302 ± 1	−0.5 (α)
Bu^t_2	40.0 (40 [l])	449 ± 1 (451 ± 3 [m])	−0.2 (β) −0.7 (α)
MeEt *rac* [n]	−46.55 (−46.2,[k] −48.1 [o])	204 [c]	−1 (α-Me)
meso [n]	−44.75 (−44.7,[k] −45.9 [o])		
$MePr^i$ *rac* [n]	−38.49 [p]	246 [c]	
meso [n]	−31.47 [p]		
$MeBu^t$ *rac* [n]	−31.26 (−31.8 [q])	294 (290 ± 3 [m])	−1.2 (β of Bu^t)
Ph_2	−14.12 (−15.2 [r])		−0.5 (α)
MePh [s]	(−38.2,[k] −36.9 [t]) (−41.7,[k] −40.5 [t])	(215 [t]) (234 [t])	
HPh [s]	(−66 [u]) (−70 [u])	(191.5 [u]) (190.8 [u])	

[a] For the [per-^{12}C]isotopomers (data from this work are given for benzene solutions). [b] Literature data are given in parentheses. [c] Note the reservations on accuracy mentioned in the text. Possible ambiguities in the assignments for R^1 = Me, R^2 = Et or Pr^i have been ignored. [d] The sign has been shown to be negative for $(Me_2P)_2$, and we have also demonstrated this for $(Bu^t_2P)_2$. It has also been established recently[13] for $Me_2PPBu^t_2$, $(Bu^t_2P)_2$, and $(Bu^tMeP)_2$ by ^{1}H-{^{31}P} studies. [e] Data obtained in this study were derived from ^{1}H spectra. [f] Mean isotopic chemical shift (see the text), accurate to ±0.5 Hz. [g] R. M. Lynden-Bell, *Trans. Faraday Soc.*, 1961, **57**, 888. [h] Ref. 1, but δ_P is corrected following remeasurement[61] of the resonance frequency of 85% H_3PO_4. [i] Ref. 24. [j] Ref. 8. [k] Ref. 57 and K. Moedritzer, L. Maier, and L. D. C. Groenweghe, *J. Chem. and Eng. Data*, 1962, **7**, 307. [l] K. Issleib and M. Hoffmann, *Chem. Ber.*, 1966, **99**, 1320. [m] Ref. 13. [n] Ref. 12. [o] Ref. 11. [p] The isomer concentrations are *ca.* 1 : 2, the signal at δ_P −38.49 p.p.m. being the more intense. [q] Ref. 58. [r] W. Kuchen and H. Buchwald, *Chem. Ber.*, 1958, **91**, 2871. [s] The two sets of data for these compounds are for the *meso* and *rac* isomers, but the assignments are uncertain. [t] Refs. 30 and W. McFarlane and D. S. Rycroft, *J.C.S. Faraday II*, 1974, 377. [u] Ref. 21.

methyl signals of the t-butyl group. Assignment of the carbon signals of $(Ph_2P)_2$ was made on intensity ratios for C^1 and the *para*-carbons, the *para*-carbon having no resolved coupling to phosphorus; $|N_{PC}|$ for the *ortho*-carbon was taken to be larger than that for the *meta*, since ${}^2J_{PC}$ and ${}^3J_{PC}$ are expected [16] to have the same sign and ${}^4J_{PPCCC}$ will be small.

TABLE 2

Carbon-13 n.m.r. data for symmetrical diphosphanes, $(R^1R^2P)_2$

R^1R^2	Position		δ_C/p.p.m.	$\lvert N_{PC}\rvert$/Hz
Me_2			10.29	8.6 [a]
Et_2	α-C		16.92	8.5
	β-C		12.12	21.5
Pr^i_2	α-C		21.69	12.0
	β-C		22.49	18
			21.85	20
Bu^t_2	α-C		35.15	24
	β-C		33.39	19
Ph_2	α-C		136.4	10.6
	ortho-C		134.86	26.3
	meta-C		128.76	6.9
	para-C		129.27	<1.0
MeEt	*rac* [b]	Me	6.90	15.6
		Et (α)	20.09	<2
		Et (β)	11.67	22.5
	meso [b]	Me	8.05	9.3
		Et (α)	19.37	6.5
		Et (β)	11.63	20.5
$MePr^i$	*rac* [b]	Me	3.84	25.5
		Pr^i (α)	26.09	<1.0
		Pr^i (β)	21.22	24.2
			20.69	20.0
	meso [b]	Me	5.75	9.7
		Pr^i (α)	25.09	9.3
		Pr^i (β)	21.65	22.0
			20.26	15.8
$MeBu^t$	*rac* [b]	Me	2.61	33.7
		Bu^t (α)	28.43	0.8
		Bu^t (β)	28.71	21.3

[a] Ref. 1; shown to be negative. [b] Ref. 12.

The carbon spectra for $(Pr^i_2P)_2$ and the two isomers of $(Pr^iMeP)_2$ showed two sets of signals for the methyls of the isopropyl groups, differing by up to 1.4 p.p.m. at ambient probe temperature (*ca.* 36 °C). The non-equivalence of methyl groups in an isopropyl substituent bonded to an asymmetric phosphorus has been found previously [17-20] and has been attributed to population differences between the conformers associated with hindered rotation about the P–C bond and/or to an intrinsic shift difference. The methyl non-equivalence is unlikely to be due to the isopropyl substituents on each phosphorus being fixed in different orientations with respect to the lone-pair electrons since this would give rise to two ^{13}C signals for the tertiary carbons. As was the case for $PPr^iCl(NMe_2)$,[19] heating caused the non-equivalence to disappear for $(Pr^i_2P)_2$. Our ^{13}C signals coalesced above *ca.* 75 °C; the way in which this occurred was characteristic of an exchange phenomenon rather than a simple variation in δ_C values towards an average. We believe that the change is therefore probably not due to the equalisation of rotamer populations but arises from interconversion of the methyl sites due to inversion at phosphorus. Presumably inversion is faster than for diphosphanes (I; $R^1 \neq R^2$) with R^1 = H or Me, for which racemisation has been shown [11,21] to occur on the n.m.r. time scale at *ca.* 150 °C, because the steric effect of the isopropyl groups in $(Pr^i_2P)_2$ increases the CPC and CPP angles and therefore lowers the inversion barrier.

The main purpose of studying the proton spectra of the diphosphanes was to obtain $|J_{PP}|$ (see below) but the additional information derived (usually only qualitative) is given in Table 3 for the sake of completeness. With the exception of tetramethyldiphosphane and tetra-t-butyldiphosphane, the proton spectra were complicated by (H,H) coupling or other effects (see below), but for all the molecules except tetraphenyldiphosphane it was possible to find at least one outer line on each side of the central region of the spectrum, using very high r.f. powers.[8] For $(Bu^t_2P)_2$, an $[AX_{18}]_2$ spin system, the intensity of each $\chi = 1$ outer line [3] is only *ca.* 0.001% of the total ^1H intensity, but observation still proved possible. However, the interpretation of the weak lines was not always unambiguous, since for $R^1 = R^2$ = Et or Pr^i and for R^1 = Me, R^2 = Et or Pr^i there are complications arising from direct (H,H) coupling, from the existence of different Me groups, or the presence of isomers, giving a number of weak lines in each case. The values of $|J_{PP}|$ which we quote were obtained under the assumption that the above complications may be ignored. Direct measurements of the separation between corresponding weak lines on either side of the main peaks due to the [per-^{12}C]isotopomer were used to give $|J_{PP}|$, since the separation of the $\chi = 1$ pair of outer lines approximates to $2J_{PP}$ when $|L_{PH}| \ll |J_{PP}|$. This approach results in a lack of variation for J_{PP} between isomers, but this should not be taken as proven. On the other hand, model calculations of line positions and intensities for $\chi > 1$ and $\chi = 1$, $\Omega \neq 0$ outer lines (see refs. 3 and 10) show that these lines are probably merged with the $\chi = 1$, $\Omega = 0$ outer lines (the observed widths are substantial, *ca.* 4 Hz).

TABLE 3

Hydrogen-1 n.m.r. data for symmetrical diphosphanes, $(R^1R^2P)_2$

R^1R^2	δ_H/p.p.m.	Coupling information
Me_2	1.06 [a]	N_{PH} 14.15 Hz [a]
Et_2	1.07 (CH_3)	Complex [b]
	1.42 (CH_2)	Complex
Pr^i_2	*ca.* 1.03 (CH_3)	Complex
	1.98 (CH)	Complex
Bu^t_2	1.35 (1.41 [c])	N_{PH} 12.5 Hz (12.5,[c, d] 12.3 [e])
MeEt	*ca.* 0.96 (α- and β-Me)	Complex
	ca. 1.37 (CH_2)	Complex
$MePr^i$	0.67 (α-Me)	N_{PH} 9.1 Hz
	ca. 0.9 (β-Me)	Complex
	ca. 1.3 (CH)	Complex
$MeBu^t$	0.90 (α-Me)	N_{PH} 8.2 Hz (8.1 [e])
	0.98 (β-Me)	N_{PH} 12.6 Hz (12.8,[c] 12.7 [e])

[a] Ref. 8. [b] Basically a quintet, J_{HH} *ca.* 7 Hz and N_{PH} *ca.* 14 Hz (deceptively simple). [c] G. Hägele, W. Kuchen, and H. Steinberger, *Z. Naturforsch.*, 1974, **B29**, 349. [d] The reference in footnote *c* also gives L_{PH} 12.5 Hz. [e] Ref. 13.

1,2-Diethyl-1,2-dimethyldiphosphane occurred as two diastereoisomers,[11,12] in the ratio 6 : 7 as measured by relative intensities of the carbon signals; the *rac* form is the

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[16] T. Bundgaard and H. J. Jakobsen, *Acta Chem. Scand.*, 1972, **26**, 2548.

[17] W. McFarlane, *Chem. Comm.*, 1968, 229.

[18] R. D. Baechler and K. Mislow, *J.C.S. Chem. Comm.*, 1972, 185.

[19] J. E. Bissey, H. Goldwhite, and D. G. Rowsell, *Org. Mag. Res.*, 1970, **2**, 81.

[20] M. Fild and W. Althoff, *J.C.S. Chem. Comm.*, 1973, **933**.

[21] J. P. Albrand and D. Gagnaire, *J. Amer. Chem. Soc.*, **1972**, **94**, 8630.

more abundant. The carbon and phosphorus spectra of both isomers were clearly distinguishable. Our assignment in the ^{31}P region is based on the relative intensities reported in ref. 11 since the instability of the chemical shift with respect to temperature made it difficult for us to measure intensities with sufficient accuracy. The assignment given is consistent with that for $R^1 = Me$, $R^2 = Pr^i$. The proton spectrum was complex due to the superposition of the CH_3 regions of the methyl and ethyl substituents of both isomers, and due to proton coupling within the ethyl group. The situation was somewhat simpler for (I; $R^1 = Me$, $R^2 = Pr^i$) since the stereoisomers were present in very different concentrations, the *rac* form predominating by *ca.* 2 : 1.

TABLE 4

Phosphorus-31 n.m.r. data for symmetrical dithioxodi-λ^5-phosphanes, $[R^1R^2P(S)]_2$

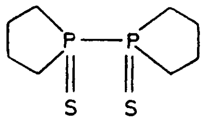
R^1R^2	δ_P [a]/p.p.m.	$\lvert J_{PP}\rvert$ [b]/Hz	$\frac{1}{2}(\Delta\nu_1 + \Delta\nu_2)$ [c] /Hz
Me_2	35.07 (34.7,[d] 35,[e] 33.4[f])	(18.7[g])	−0.8
Et_2	51.27 (49.4,[h] 52.5[e])	53.5	−0.2
Pr^n_2	46.65	53.2	−0.4 (α-C) −0.2 (β-C)
Pr^i_2	64.61	*ca.* 95	−0.4 (α-C)
MeEt[h] (*rac*)	44.00 (43.80)[i]	37.5 ± 0.5	−0.4 (CH_2)
(*meso*)	43.50 (43.70)[i]		
$MeBu^t$	63.55[j]	(118,[k] 109 ± 5[l] 103 ± 5[l])	
MePh (*rac*)	37.55 (37.0[e])*	(21.0[m])	
n	61.62 (62.2[o])		−0.4 (α-C)

[a] Values given for the [per-^{12}C]isotopomers. [b] Values obtained in this work were derived from the analysis of five-line ^{13}C patterns, except for $R^1R^2 = Pr^i_2$ (see the text). [c] Mean isotopic chemical shift (see the text), accuracy ±0.2 Hz. [d] Ref. 60. [e] K. Moedritzer, L. Maier, and L. D. C. Groenweghe, *J. Chem. and Eng. Data*, 1962, **7**, 307. [f] Ref. 10. [g] Ref. 9. [h] E. Fluck and K. Issleib, *Chem. Ber.*, 1965, **98**, 2674. [i] Two solutions were studied: one was rich in the *meso* isomer, the other rich in the *rac* isomer. There are small variations in the shifts. The data in parentheses refer to the solution that is weak in the isomer designated. [j] This shift was incorrectly given as 48.05 p.p.m. in ref. 10. [k] Ref. 10. [l] Ref. 13. Established as negative by ^1H-{^{31}P} double resonance. The two values are for the two isomers. Judging by the other data in ref. 13, the isomer discussed in ref. 10 and used in the present work is the one with the higher value of $\lvert J_{PP}\rvert$, but its stereoisomeric assignment is unknown. [m] Ref. 23. The effect of the phenyl protons was ignored in the analysis which resulted in this value. [n] Compound (III). [o] R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 421.

* The ^{31}P chemical shift of the rather insoluble *meso* isomer is 1.05 p.p.m. to low frequency of that of the *rac* isomer (R. K. Harris and A. Okruszek, unpublished work).

The sign of $^1J_{PP}$ was determined relative to $N_{PH} = {}^3J_{PH} + {}^4J_{PH}$ in tetra-t-butyldiphosphane by ^1H-{^{31}P} double resonance, since the ^{13}C satellites were easily observed (there are 12 equivalent methyl groups in each molecule). The sign of N_{PH} was taken to be positive since the four-bond coupling will be very small, and three-bond J_{PCCH} couplings are predominantly positive.[22] Irradiation of the phosphorus spectrum with frequencies near $\nu_P + {}^1J_{PP}$ affected the low-frequency line of the N doublets of the ^{13}C satellites and irradiation near $\nu_P - {}^1J_{PP}$ affected the high-frequency line; hence $^1J_{PP}$ is confirmed as negative in $Bu^t_2PPBu^t_2$, as expected since it is negative [14] in Me_2PPMe_2. While this paper was in course of preparation the sign of $^1J_{PP}$ in $(Bu^t_2P)_2$ and some related compounds was also reported as negative.[13]

Dithioxodi-λ^5-phosphanes.—Seven of these compounds were studied, including the cyclic system (III). Tables 4 and 5 summarise the phosphorus and carbon n.m.r. parameters obtained for the dithioxodi-λ^5-phosphanes.



(III)

TABLE 5

Carbon-13 n.m.r. data for symmetrical dithioxodi-λ^5-phosphanes $[R^1R^2P(S)]_2$

R^1R^2		δ_C /p.p.m.	Spectral analysis case [a]	$\lvert N_{PC}\rvert$ [b] /Hz	$^1J_{PC}$ /Hz	$^2J_{PPC}$ /Hz
Me_2		16.93	1(*a*)	60	48	12
Et_2	α	22.02	2(*a*)	53 ±0.5	43 ±0.5	10 ±0.5
	β	7.16	1(*d*)	3		
Pr^n_2	α	30.84	2(*a*)	50	41	9
	β	16.81	1(*d*)	2		
	γ	16.14[c]	1(*c*)	17		
Pr^i_2	α	30.92	1(*c*)	42.2 ±0.1	34 ±2	8 ±2
	β	18.69	1(*d*)	<1.0		
		18.89	1(*d*)	2.0		
MeEt[d]	*meso* Me (α)	15.10 (15.30)[e]	2(*a*)	59	42 ±1	17 ±1
	Et (α)	22.89 (23.08)[e]	2(*a*)	57	42 ±1	15 ±1
	Et (β)	6.23 (6.45)[e]	2(*d*)	3		
	rac Me (α)	15.22 (15.02)[e]	2(*a*)	57	41 ±1	16 ±1
	Et (α)	22.81 (22.63)[e]	2(*a*)	57	42 ±1	15 ±1
	Et (β)	6.59	2(*d*)	3		
$MeBu^t$	Me	17.93	1(*c*)	53	41.5 ±1.5	11.5 ±1.5
	Bu^t (α)	41.10	1(*c*)	42	36 ±1.5	6 ±1.5
	(β)	27.27	1(*d*)	2		
MePh *rac*	Me	17.33	1(*b*)	66	52.5	13.5
	Ph-C^1	127.58	1(*b*)	79.5	69.7	9.7
	ortho[f]	132.51	1(*d*)	13		
	meta[f]	128.54	1(*d*)	12		
	para	132.83	1(*d*)	<3		
g	CH_2 (α)	33.11	2(*d*)	55.7		
	CH_2 (β)	28.10	2(*d*)	7.6		

[a] See the text. [b] For the *para*-carbon of $R^1R^2 = MePh$ and for the signal at δ_C 18.69 p.p.m. for $R^1R^2 = Pr^i_2$ only singlets could be found. [c] $^3J_{PCCC}$ 15 ± 1 and $^4J_{PPCCC}$ 2 ± 1 Hz, with the same reservations as for $^1J_{PC}$ and $^2J_{PPC}$ (see the text). [d] Only data from samples enriched in the appropriate isomer are given, except where indicated. [e] See footnote *i* of Table 4. [f] These assignments may be interchanged. [g] Compound (III).

Measurement of $\lvert J_{PP}\rvert$ and (P,C) coupling constants was considerably simpler for some of the dithioxodi-λ^5-phosphanes compared to the diphosphanes, since a five-line ^{13}C spectrum was observed for the α-carbons in certain cases (see Table 5) and the phosphorus spectra did not show any substantial temperature variation, so the ^{13}C satellite lines were resolved more clearly (*W* for the phosphorus signals of

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[22] E. Duval and G. E. Béné, *Helv. Phys. Acta*, 1967, **40**, 501; R. R. Dean and W. McFarlane, *Chem. Comm.*, 1967, 840.

the [per-^{12}C]isotopomers was of the order of 0.4 Hz). When the ' combination ' lines of the carbon spectrum were observed then $|J_{PP}|$ and $|L_{PC}|$ could be determined without having to use the proton spectra, which were in most cases difficult to analyse because they no longer showed deceptively simple spectra ($|J_{PP}|$ is smaller than for the diphosphanes and the condition[3] $|L_{PH}| \ll |J_{PP}|$ is not usually fulfilled). We have not determined the sign of J_{PP}, although it has been reported[13] as negative for (II; R^1 = Me, R^2 = Bu^t).

Each sample of the *meso* and *rac* isomers of (II; R^1 = Me, R^2 = Et) contained a small amount of the other stereoisomer, and in $CDCl_3$ the ^{13}C and ^{31}P chemical shifts of the isomers were slightly different in the two solutions, so all the values are reported in Tables 4 and 5.

The sample of $[Pr^i_2P(S)]_2$ contained *ca.* 30% of the corresponding thiophosphoryl sulphide $[Pr^i_2P(S)]_2S$, and, although the carbon and phosphorus spectra of the two species were quite separate, the proton spectrum was very complex since the isopropyl groups of both compounds have non-equivalent methyl groups, as shown by the ^{13}C spectrum, and the ^{1}H signals all lay in the same region. This complexity meant that the methyl N_{PH} lines could not be found; however, two sets of outer[3] lines were detected with high r.f. powers, separated by 196 Hz. This separation is *ca.* $|^2J_{PP}|$ plus the separation of the first set of inner lines for the methyl groups, and although $S_i(1)$ is not known it is presumed to be small. Thus $|J_{PP}|$ is *ca.* 95—98 Hz, which is within the expected region by comparison with other values of the same series. In the ^{13}C spectrum of $[Pr^i_2P(S)]_2$ no ' combination ' lines were seen for either CH_3 or CH carbons so only values for $|N_{PC}|$ and $|L^2_{PC}/8J_{PP}|$ were found.

Compound (III) only gave triplets in the carbon spectrum, and due to the complexity of the proton spectrum no J_{PP} value was found. The two types of CH_2 carbon were distinguishable, since for the dithioxo-series the $|N_{PC}|$ values decrease with the distance of the carbon from the phosphorus nuclei, whereas where the phosphorus was trivalent this trend was not found.

In the case of (II; R^1 = Me, R^2 = Ph) it was not possible to assign unambiguously the *ortho*- and *meta*-carbon resonances.

In only one case was the spectral analysis problem in principle overdetermined. For (II; $R^1 = R^2$ = Me), $|J_{PP}|$ was available from the ^{1}H spectrum,[9] and was also measured directly from the ab subspectra of the ^{13}C satellites in the ^{31}P spectrum, because the outer lines were observable. A full ABX analysis was therefore employed to find $|L_{PC}|$. In fact the inner separations of the ab subspectra were detectably different, presumably due to the effect of differential isotopic shifts, but this fact was ignored in the analysis, an average splitting being used. For (II; R^1 = Me, R^2 = Ph) the approximation $|J_{PP}| \gg |L_{PC}|$ was also not valid, so the full equation (1) was used, together with $|J_{PP}|$ measured from the H spectrum[23] to obtain $|L_{PC}|$.

Low-temperature Experiments.—Previous work[6] had shown that cooling $(Bu^t_2P)_2$ to −50 °C suffices to slow internal rotation about the P–P bond so that the *gauche* rotameric form is ' frozen ' on the n.m.r. time scale. We cooled $(Bu^tMeP)_2$ to −60 °C in $CDCl_3$, $(Pr^i_2P)_2$ to −110 °C in CD_2Cl_2–vinyl chloride, and $(Ph_2P)_2$ to −80 °C in CD_2Cl_2 but observed no qualitative changes in the spectra. It appears that rotation about the P–P bond is relatively rapid for these compounds (and presumably for all the diphosphanes with smaller alkyl groups than Bu^t). The alternative explanation that the above compounds exist only as *trans* isomers appears to be unlikely. We also cooled $(Bu^t_2P)_2$ to −120 °C in CD_2Cl_2–vinyl chloride in an attempt to slow internal rotation about the P–C bond on the n.m.r. time scale, but without success.

DISCUSSION

Chemical Shifts.—Throughout both series of compounds the predominant influence on chemical shifts and coupling constants is the size of the substituent and the effect this has on the bond angles at phosphorus and therefore on hybridisation. The other two parameters which are known[24] to be important in determining the chemical shifts of phosphorus are the degree of π bonding between phosphorus and the substituent, and the electronegativity of the substituent. With a series of alkyl-substituted compounds there is no π bonding with the alkyl groups (although the extent of P–P π bonding may vary through the diphosphane series) and the electronegativity varies little, but with an aromatic substituent π bonding could occur, although for phenylphosphines this has been shown to be unlikely.[25] The same conclusion would also be valid for tetraphenyldiphosphane, as the difference in carbon chemical shifts of the *m*- and *p*-carbons, which has been taken[26] as a measure of the π-electron density at the *para* position (although no cases of phosphorus-containing compounds were discussed), is very small. In addition the ^{31}P chemical shift of Ph_2PPPh_2 is in line with those of the tetra-alkyldiphosphanes if the bulkiness of the phenyl group is considered. Comparisons within each series of compounds (I) and (II) may presumably be made without reference to the electronegativity of the second phosphorus atom.

The large increase in ^{31}P chemical shift caused by the substituent replacement Me $\longrightarrow$ Et $\longrightarrow$ Pr^i $\longrightarrow$ Bu^t for both series of compounds is presumably due to an increase in CPC bond angle, and thus a change in hybridisation at phosphorus. This leads to an increase in *s*-orbital character in the phosphorus bonds, but a decrease in *s* character of the lone-pair electrons, and hence a decrease in shielding of the phosphorus nucleus.[27] Any influence of γ-carbons on the ^{31}P shift, which has been demonstrated in the case of alkylphosphines,[28] and which may operate through the second phosphorus atom (analogous to effects reported on ^{13}C shifts),[29] cannot be disentangled from the deshielding effects of substituents β to the relevant phosphorus.

In the diphosphanes which have two different groups on each phosphorus, the ^{31}P chemical shift is approximately the mean of the two tetrasubstituted compounds

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[23] E. G. Finer, M.Sc. Thesis, University of East Anglia, 1966.

[24] V. Mark, C. H. Dungan, M. V. Crutchfield, and J. R. van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 227.

[25] B. E. Mann, *J.C.S. Perkin II*, 1972, 30.

[26] G. E. Maciel and J. J. Natterstad, *J. Chem. Phys.*, 1965, **42**, 2427.

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

[28] L. D. Quinn and J. J. Breen, *Org. Mag. Res.*, 1973, **5**, 17.

[29] J. B. Stothers, ' Carbon-13 NMR Spectroscopy,' Academic Press, 1972, ch. 5.

for $(EtMeP)_2$ and $(PhMeP)_2$,[30] but as the size of the second substituent is increased to t-butyl the ^{31}P chemical shift of the mixed compound becomes much nearer that of $(Me_2P)_2$ than $(Bu^t{}_2P)_2$, indicating that replacement of the second methyl by Bu^t causes somewhat severer alteration of the angle CPC than replacement of the first Me. [The chemical shift for $(Bu^tMeP)_2$ is, however, for only one of two possible isomers.] The temperature dependence of the chemical shifts may not be attributed only to changes in the angle CPC; there may be some contribution from changing populations of the conformational isomers.

Carbon-13 chemical shifts do not appear to be much altered by the presence of a phosphorus atom, in comparison to the alkanes, since the electronegativity of phosphorus is nearly that of hydrogen,[31] but the carbon directly bonded to phosphorus is clearly affected by changes in the angle CPC, since if the ^{13}C shift is plotted against the ^{31}P shift for tetra-alkyldiphosphanes a straight line is produced with the empirical relation (2).

$$\delta_P = -100 + 4\delta_{C(\alpha)} \qquad (2)$$

The usual[32] α- and β-deshielding effects are shown for ^{13}C shifts of the alkyl substituents, and presumably relate to changes in the CPC bond angle. There is also a γ-shielding effect operating through the phosphorus atom,[29] which may be seen by comparing the α-methyl carbon shifts of the series R^1 = Me, R^2 = Et, Pr^i, and Bu^t; this effect appears to be substantial, *ca.* 2.5 p.p.m. per substituent (contrast the data in ref. 33). A similar shift to low frequency may also be noted for δ_H of the methyl protons of $(Bu^tMeP)_2$ compared to $(Me_2P)_2$ (see Table 3; this fact is also mentioned by Hägele[34]).

For the dithioxodi-λ^5-phosphanes the presence of the sulphur atom deshields the phosphorus, giving a higher resonance frequency than for the corresponding diphosphanes, but the steric effect of the alkyl substituents is still the major influence on the chemical shifts. The two isomers of $[EtMeP(S)]_2$ were studied separately, the ^{31}P chemical shift of the *rac* isomer having the slightly larger value of δ_P. The ^{31}P chemical shift of the n-propyl-substituted dithioxodi-λ^5-phosphane is lower than that of $[Et_2P(S)]_2$, but this can be satisfactorily explained, at least partially, by the shielding effect of the γ-carbons.[28,33] The relation between this effect and the changes in bond angle by steric influence is not well established. The ^{31}P chemical shift of the mixed dithioxodi-λ^5-phosphane $[PhMeP(S)]_2$ lies to lower frequency than expected by comparison with the diphosphane $(PhMeP)_2$.

In general the ^{13}C chemical shifts of the α-carbons are to high frequency of those for the diphosphanes, presumably due to the electronegativity of sulphur. Moreover, the α-carbons are significantly less shielded (by *ca.* 15 p.p.m.) than the β-carbons, which is not true in the diphosphane series, nor does it occur for (III). Whereas it was noted for the diphosphanes that replacement of a methyl group in $(Me_2P)_2$ by a larger group caused a low-frequency shift for the methyl carbon, in $[PhMeP(S)]_2$ and $[Bu^tMeP(S)]_2$ the methyl group moves to slightly higher frequency compared to the tetramethyl compound. This may be due to steric influences causing geometry changes which enhance the deshielding effect of sulphur.

Coupling Constants.—For the diphosphane series $|J_{PP}|$ increases markedly and consistently as the size of the substituents increases. The value changes from 108 Hz for P_2H_4 to 449 Hz for $P_2Bu^t{}_4$. It has been shown in this and previous work,[13,14] however, that certain of the values for this series of compounds are negative, and it is highly likely that this is true for them all. Consequently, it is not possible to explain the variations in terms of simple *s*-character changes and their influence on the Fermi contact term. On the other hand, recent calculations[35] have indicated that the contact term is indeed dominant, to the extent that other contributions may be neglected, and have succeeded in reproducing values of J_{PP} of the correct sign and order of magnitude. If the Pople–Santry molecular-orbital theory[36] of coupling is considered it is clear that variations in *s*-electron density at phosphorus are unlikely to be sufficient to account for the large changes in J_{PP} observed, and therefore that changes in the mutual polarisability of the valence *s* orbitals on the phosphorus atoms must be invoked. Clearly, too, the physical feature causing these variations must be the steric influences of the substituents. As the size of the alkyl groups increases, so must the CPC angle. As has already been suggested,[13,37] this implies the alkyl carbon atoms will use more of the phosphorus 3*s* electrons, leaving a lower *s* character in the P–P bond and giving the mutual polarisability a more negative value, thus enhancing the negative magnitudes of J_{PP}.

It is possible that the variations of J_{PP} with the nature of the substituent may arise from changes in rotamer populations as well as PPC angle changes, since substantial amounts of the *trans* form have been suggested[38] for P_2Me_4 (in spite of the comments by McFarlane and McFarlane[13]), and a pronounced dihedral-angle dependence of J_{PP} has been shown both by calculations[35] and by other experimental results.[39] Our earlier analysis[12] of N_{PC} values is not necessarily inconsistent with some variation in rotamer populations, particularly for *meso* compounds. Dihedral-angle differences could be an important origin for the variations between stereoisomers, *e.g.* for $(PhMeP)_2$, which has[30] a difference of 19 Hz in the two values of J_{PP}.

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

[31] F. J. Weigert and J. D. Roberts, unpublished work quoted in ref. 29.

[32] D. M. Grant and E. G. Paul, *J. Amer. Chem. Soc.*, 1964, **86**, 2984.

[33] L. D. Quinn, M. D. Gordon, and S. O. Lee, *Org. Mag. Res.*, 1974, **6**, 503.

[34] G. Hägele, personal communication.

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

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

[37] E. G. Finer and R. K. Harris, *Chem. Comm.*, 1968, 110.

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

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

The values of J_{PP} for the tetra-alkyldiphosphanes show an approximately linear correlation with δ_P (Figure 2). This is presumably because both parameters are affected by the variations in bond angles caused by steric interactions. The data for the compounds (I) with $R^1 \neq R^2$ also fall close to the plot of Figure 2, but with complications due to the stereoisomerism. We have found that, at *ca.* −52 °C, $\delta_P = 36.9$ p.p.m. and $|J_{PP}| = 438$ Hz for $(Bu^t_2P)_2$; thus the effects of temperature also follow the correlation of Figure 2. (The temperature variation of J_{PP} is not, however, in the direction expected if the *trans*-rotamer becomes appreciably populated at room temperature.) The observed effects may reflect the narrowing of vibrational amplitudes at low temperature, or possibly arise from intermolecular interactions. It is possible to use Figure 2 for predictive purposes.

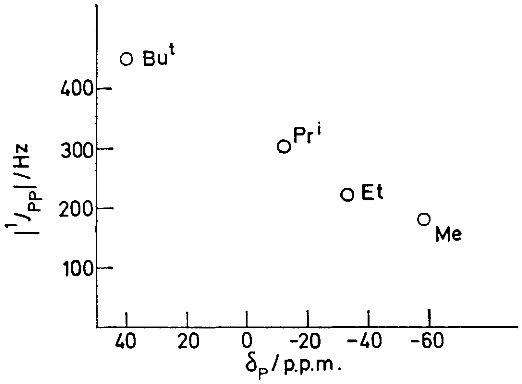

FIGURE 2 Plot of $|^1J_{PP}|$ against δ_P for tetra-alkyldiphosphanes, $(R_2P)_2$

The (P,P) coupling constants in the dithioxodi-λ^5-phosphane series are lower in magnitude than those for the diphosphanes themselves, but they show a similar trend with size of substituent. Most reported [5,40] signs of J_{PP} between two P^V atoms have been positive, but it was suggested earlier,[41] although not unambiguously,[*] that the sign of J_{PP} is negative for (II; $R^1 = R^2 = Me$). Recently [13] a negative sign has been conclusively demonstrated for (II; $R^1 = Me$, $R^2 = Bu^t$). It is likely, then, although not certain, that all the signs for the series are negative; such an assumption gives a reasonable correlation between J_{PP} for the two series (I) and (II), but leads to a prediction that J_{PP} for $[H_2P(S)]_2$ should be positive unless there are conformational changes. The values of $|J_{PP}|$ for the dithioxodi-λ^5-phosphanes are consistently lower than for the corresponding diphosphanes, and the variation with substituent bulk is somewhat smaller, the difference from $R^1 = R^2 = Me$ to $R^1 = R^2 = Pr^i$ being 122 Hz for (I) and *ca.* 75 Hz for (II) (if all the J_{PP} values are negative). That the effect is primarily one of substituent bulk is shown by the fact that J_{PP} for $[R_2P(S)]_2$ with $R = Pr^n$ is close to that for $R = Et$, but very different from that for $R = Pr^i$. If δ_P is plotted against J_{PP} for (II), the point for $[Pr^n_2P(S)]_2$ lies somewhat away from the correlation (which is otherwise reasonably good), showing that the influences on δ_P are not entirely those of changes in CPC bond angle; the deviation of δ_P for the Pr^n compound is consistent with a γ-shielding effect (not influencing J_{PP}). The effect of stereoisomerism on J_{PP} for (II; $R^1 = Me$, $R^2 = Et$) is not significant.[30]

Carbon–phosphorus coupling constants have been measured for several compounds recently, and it is clear that the sign and magnitude of J_{PC} depends on the co-ordination at phosphorus, the orientation to the lone pair or relevant bonds if P is trivalent, the number of bonds through which coupling occurs, and the hybridisation of carbon. For trivalent phosphorus, the sign of the one-bond coupling to phosphorus is normally negative,[42-44] and the negative sign of $^1J_{PC}$ has been rationalised theoretically [45,46] by consideration of spin densities at the nuclei (but see refs. 47 and 48). In the case of tetramethyldiphosphane it has been shown [14] by double resonance that N_{PC} is negative, and it may be presumed that $^1J_{PC} = -22$ Hz and $^2J_{PC} = 14$ Hz.

The use of N_{PC} for α-carbons to define stereoisomerism and rotameric forms[†] of compounds (I) with $R^1 \neq R^2$ has already been discussed.[12] It is concluded that for R^1 or R^2 *trans* to a lone pair $|N_{PC}|$ is relatively large (15.6—45.5 Hz) and increases consistently with the bulk of the substituents (presumably due to geometry changes or to unrecognised contributions from conformations with *trans* lone pairs). On the other hand values of $|N_{PC}|$ for α-carbons *gauche* to a lone pair are small (<2 Hz) and appear to be independent of substituent bulk. It is not known whether the pronounced dependence on dihedral angle is that of $^1J_{PC}$ or of $^2J_{PPC}$, but analogous variations of (P,C) coupling are known.[49-53] It is likely that the low value of $|N_{PC}|$ for α-carbons *gauche* to a lone pair may be due to near cancellation of values of $^1J_{PC}$ and $^2J_{PPC}$ which are close in magnitude but opposite in sign. The sizes of $^1J_{PC}$ and $^2J_{PPC}$ are often similar,[25] and in some cases $|^2J_{PCC}|$ is larger [54] than $|^1J_{PC}|$. Values of of $^2J_{PNC}$ for a carbon *cis* to the lone pair have been reported [53] as large and positive, but small and negative for a carbon *trans* to the lone pair. The increase of

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[*] The negative sign has now been confirmed (R. K. Harris and A. Okruszek, unpublished work).

[†] The rotamers were shown as perfectly staggered in ref. 12 for convenience, but the n.m.r. data do not exclude substantial deviations in dihedral angle.

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$|N_{\mathrm{PC}}|$ with substituent size need not be connected with lone-pair orientation, since similar variations of $|^{1}J_{\mathrm{PC}}|$ are shown by monophosphines; Mann reported [25] 23.5 Hz for $\mathrm{PBu^t_3}$ compared to 13.6 Hz for $\mathrm{PMe_3}$, and for the methyl carbon $|^{1}J_{\mathrm{PC}}|$ becomes 25.2 Hz in $\mathrm{PMeBu^t_2}$.

The values for N_{PC} of the β-carbons in the diphosphanes do not show the same marked dependence on stereochemistry as those for the α-carbons. In fact variations between the two non-equivalent methyl carbons of an isopropyl group are nearly as large as the total range, which is rather narrow (15.6—24.2 Hz). There is some evidence that values for groups *gauche* to a lone pair are slightly smaller than for those *trans* to a lone pair. The lack of dependence on stereochemistry for N_{PC} of β-carbons is probably due to averaging arising from the flexibility introduced by internal rotation about P–C bonds.

Values of N_{PC} for the α-carbons of the dithioxodi-λ^5-phosphanes (II) also do not show any pronounced dependence on stereochemistry. This may be due either to differences in rotamer populations from those for compounds (I) (arising because of the replacement of lone pairs by sulphur atoms) or because of a genuine lack of dependence of N_{PC} on geometry. In each case $|L_{\mathrm{PC}}| < |N_{\mathrm{PC}}|$ so that the signs of $^{1}J_{\mathrm{PC}}$ and $^{2}J_{\mathrm{PPC}}$ are the same. We assume $^{1}J_{\mathrm{PC}}$ to be positive, as found for other ($\mathrm{P^V}$,C) coupling constants.[42,55] It is not, of course, possible to assign the derived parameters to $^{1}J_{\mathrm{PC}}$ and $^{2}J_{\mathrm{PPC}}$ unambiguously from the spectra, but comparison [42,55] with literature data for $^{1}J_{\mathrm{PC}}$ suggests the assignments given in Table 5. Values of $^{1}J_{\mathrm{PC}}$ therefore range from 52.5 to 34 Hz [excluding the value of 69.7 Hz for the α-carbon of the phenyl group in (II; $\mathrm{R^1 = Me}$, $\mathrm{R^2 = Ph}$), which presumably owes its size to the increased *s* character at carbon]. A trend to lower values of $^{1}J_{\mathrm{PC}}$ as the substituents increase in size is apparent; this is the opposite of that expected on simple steric rehybridisation grounds if the contact term is dominant. The trend is also clear from the values of N_{PC} themselves, which are rather more accurate than those of $^{1}J_{\mathrm{PC}}$. The values of $^{2}J_{\mathrm{PPC}}$ for (II) fall in the range 6–17 Hz, generally being lower for the bulkier substituents (variations could be obscured by experimental errors). The sign would appear to be positive, whereas literature data indicate that $^{2}J_{\mathrm{PC}}$ for the P(:S)*O*C linkage is negative,[42] although $^{2}J_{\mathrm{P(:O)CC}}$ has been shown [56] to be positive when the carbon atoms are *sp* hybridised. We do not understand these apparent anomalies.

Values of $|N_{\mathrm{PC}}|$ for β-carbons are small [$\leqslant$3 Hz except for compound (III)], presumably indicating that $^{2}J_{\mathrm{PCC}}$ and $^{3}J_{\mathrm{PPCC}}$ are comparable in magnitude but opposite in sign. This fact prevented observation of the ^{13}C satellites in ^{31}P resonance and thus meant that L_{PC} could not be obtained. It seems likely that $^{2}J_{\mathrm{P(:S)CC}}$ is negative (in contrast to $^{2}J_{\mathrm{P(:S)PC}}$) in these compounds and $^{3}J_{\mathrm{P(:S)PCC}}$ is positive, but we have no proof of this statement. The only γ-carbon resonance, for $\mathrm{[Pr^n_2P(S)]_2}$, did not give this problem, so $^{3}J_{\mathrm{PCCC}}$ and $^{4}J_{\mathrm{PPCCC}}$ were separately obtained. Indeed, the high value of $N_{\mathrm{PC(\gamma)}}$ was used to distinguish the β- and γ-carbon resonances for this compound.

EXPERIMENTAL

Diphosphanes were synthesised by one of two routes. Tetramethyldiphosphane, $\mathrm{(EtMeP)_2}$, and $\mathrm{(Et_2P)_2}$ were prepared by reduction [57] of the corresponding dithioxo-compounds with $\mathrm{PBu^n_3}$, and purified by repeated distillation. Tetraphenyldiphosphane was purchased from Strem Chemicals Inc. Diphosphanes with bulky substituents such as $\mathrm{(Bu^tMeP)_2}$, $\mathrm{(Pr^iMeP)_2}$, $\mathrm{(Pr^i_2P)_2}$, and $\mathrm{(Bu^t_2P)_2}$ were prepared [20,58,59] from the chlorides, $\mathrm{PR^1R^2Cl}$, by dehalogenation with sodium in dioxan. The only compound not previously reported in the literature is $\mathrm{(Pr^iMeP)_2}$, b.p. 99—100 °C (20 mmHg).* Since the alkyldiphosphanes are readily oxidised in air, all operations were made under an atmosphere of dry oxygen-free nitrogen. Dithioxodi-λ^5-phosphanes were generally prepared from the appropriate Grignard reagent and $\mathrm{PCl_3S}$, or the organo-substituted thiophosphonic dichlorides, $\mathrm{PRCl_2S}$. The work-up procedure followed was that of Maier;[60] the compounds were recrystallised from ethanol–toluene mixtures, and their melting points compared with literature values. For the preparation of $\mathrm{[Pr^i_2P(S)]_2}$ the addition of sulphur to the parent diphosphane was used.

The samples of diphosphanes for n.m.r. were made up under a nitrogen atmosphere in a dry-box, using n.m.r. tubes (outside diameter, 12 mm). The solutions were prepared in benzene, with $\mathrm{C_6D_6}$ (*ca.* 0.5 cm^3) to provide a lock signal, or dichloromethane [with $\mathrm{CD_2Cl_2}$ (*ca.* 1.5 cm^3) for lock] when the spectra were to be recorded at low temperature. All the tubes were degassed by the freeze–pump–thaw technique, using liquid nitrogen or a slush-bath of 50% v/v carbon tetrachloride and chloroform for freezing. Dithioxodi-λ^5-phosphanes were dissolved in $\mathrm{CDCl_3}$, degassed, and sealed.

All spectra were recorded on a Varian XL100 spectrometer using the Fourier transform mode for carbon at 25.14 MHz, Fourier-transform or continuous wave (CW) with multiscan averaging at 40.5 MHz for phosphorus, and the CW mode at 100.06 MHz for protons. Both carbon and phosphorus spectra were proton-decoupled. Phosphorus and carbon chemical shifts were measured by the absolute-frequency indirect method described previously,[61] and are quoted with respect to 85% $\mathrm{H_3PO_4}$ and $\mathrm{SiMe_4}$ for ^{31}P and ^{13}C respectively. Proton shifts were measured in a similar fashion and are quoted with respect to $\mathrm{SiMe_4}$. All the shifts are quoted with the positive frequency convention, *i.e.* a positive sign implies the sample resonates to high frequency of the reference. To determine the relative signs of $^{1}J_{\mathrm{PP}}$ and N_{PH} in tetra-t-butyldiphosphane, a sample in benzene with 2 or 3 drops of $\mathrm{SiMe_4}$ in a 5-mm tube was used with a Varian HA 100 spectrometer, and irradiation at a phosphorus frequency was carried out using a modified Varian V4333 probe as described by Woplin.[41] The second

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

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frequency was provided by a Schlumberger type FSX 3005 decade frequency generator and passed through an attenuator and amplifier (type HB 805, RF communications Inc., Rochester, New York) to the probe.

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