Phosphorus–Nitrogen Compounds. Part 51.[1] Carbon-13 and Phosphorus-31 Nuclear Magnetic Resonance Properties of Phenylphosphonothioic Di(monoalkylamides). Determination of Aromatic Substituent Constants by ^{13}C Nuclear Magnetic Resonance Spectroscopy†

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Carbon-13 and phosphorus-31 n.m.r. spectra have been obtained for a series of phenylphosphonothioic di(monoalkylamides), PhP(S)(NHR)$_2$ (R = H, Me, Et, Pr^n, Pr^i, cyclopropyl, Bu^n, Bu^i, Bu^s, Bu^t, neopentyl, cyclopentyl, cyclohexyl, or CH$_2$Ph). Inductive and resonance substituent coefficients have been evaluated using the dual-substituent parameter method from the relative shieldings of the *meta*- and *para*-carbon nuclei in the phenyl ring. An attempt is also made to correlate data arising from different n.m.r. measurements to chemical behaviour, and to explore the relationship between carbon-13 and phosphorus-31 n.m.r. chemical shift data for the above group of compounds.

The thermal condensation of phenylphosphonothioic di(monoalkylamides), PhP(S)(NHR)$_2$ (**1**), under an inert atmosphere leads to a variety of different products.[2–10] When R = Me, Et, Pr^n, Bu^n, Bu^i, cyclopropyl, or CH$_2$Ph the corresponding 1,3-dialkyl-2,4-diphenyl-2,4-dithiocyclodi-λ^5-phosphazane, [PhP(S)NR]$_2$ (**2**), is obtained.[2,4,5,7–10] When R = H, Pr^i, Bu^s, or Bu^t the dealkylated cyclotri-λ^5-phosphazane, [PhP(S)NH]$_3$ (**3**), is the product,[5,10] whilst with R = cyclohexyl a most unusual fused bicyclic compound, (**4**), is formed.[6,10]

Some carbon-13 n.m.r. chemical shift data have been reported for compounds of the type PhP(X)Z$_2$ (X is doubly bonded group, *e.g.* O or S; Z is singly bonded group, *e.g.* halogen) which contain at least one phenyl group attached to a four-co-ordinate phosphorus atom.[11–17]

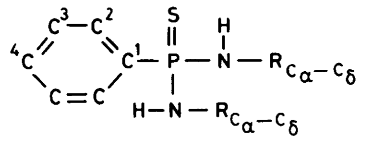
There has been considerable interest in the use of carbon-13 n.m.r. spectroscopy to probe the inductive and resonance effects of substituents in aromatic ring systems.[13,16,18,19] The dual-substituent parameter (d.s.p.) approach[20] best describes the structural effect on the carbon-13 n.m.r. chemical shift of the *meta*- and *para*-carbon nuclei relative to the chemical shift for benzene. This shift difference, *S*, at a given ring position represents the change in the shielding due to the substituent and is the sum of the inductive (σ_I) and resonance (σ_R^0) effects that the substituent exerts, according to equation (1) (*a* and *b* are

$$S = a\sigma_I + b\sigma_R^0 \tag{1}$$

constants). Carbon-13 n.m.r. spectroscopy would appear to be a useful tool for investigating the substituent effects of phosphorus-containing groups (see, for example, refs. 13, 16, and 21—23). We have measured carbon-13 n.m.r. chemical shifts for compounds (**1a**)—(**1n**) so that changes in the electron distribution of the benzene ring can be assessed. Substituent inductive and resonance constants were calculated from the chemical shift differences using the d.s.p. approach.

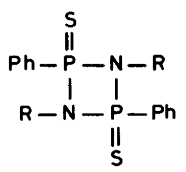
Results

The ^{31}P and ^{13}C n.m.r. data for the phenylphosphonothioic di(monoalkylamides) (**1a**)—(**1n**) are shown in Table 1.

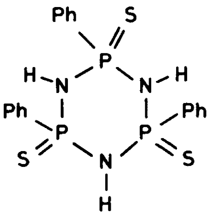


(**1**)

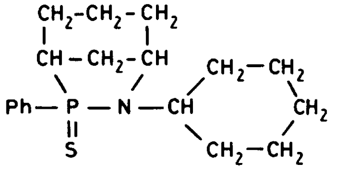
R = H (**a**), Me (**b**), Et (**c**), Pr^n (**d**), Pr^i (**e**), Bu^n (**f**), Bu^i (**g**), Bu^s (**h**), Bu^t (**i**), neopentyl (**j**), CH$_2$Ph (**k**), cyclopropyl (**l**), cyclopentyl (**m**), cyclohexyl (**n**).



(**2**)



(**3**)



(**4**)

Phosphorus-31 n.m.r. absorptions of the pure substances were observed as sharp, single peaks except for compound (**1h**) (R = Bu^s); two peaks separated by 0.03 p.p.m. were observed when the resolution of the spectrum was enhanced. These two peaks are probably due to the presence of diastereoisomers arising from the chiral-carbon atom in the alkyl side chain.

The proton-decoupled carbon-13 n.m.r. spectrum for PhP(S)(NHEt)$_2$, (**1c**) is shown at Figure 1, and for the aryl carbon nuclei [C(1) to C(4)] absorptions is representative of all of the di(monoalkylamide) compounds (**1**). Doublets are observed for C(1), C(2), C(3), and C(4) due to coupling with the phosphorus

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Table 1. Carbon-13[a] and phosphorus-31[b] n.m.r. parameters for $PhP(S)(NHR)_2$ (**1**)

Compound	$C(1)^c$		$C(2)^c$		$C(3)^c$		$C(4)^c$		C_α		C_β		C_γ		
	δ	$^1J[P\text{–}C(1)]$	δ	$^2J[P\text{–}C(2)]$	δ	$^3J[P\text{–}C(3)]$	δ	$^4J[P\text{–}C(4)]$	δ^c	$^2J(P\text{–}C_\alpha)^d$	δ^c	$^3J(P\text{–}C_\beta)^d$	δ^c	$^4J(P\text{–}C_\gamma)^d$	$\delta(^{31}P)$
(**1a**)	136.96(d)	121.63	130.39(d)	13.19	128.51(d)	14.65	131.66(d)	2.93							60.7
(**1b**)	134.00(d)	120.85	130.92(d)	9.76	128.28(d)	13.43	131.45(d)	2.45	27.12(d)	2.08					68.1
(**1c**)	135.06(d)	119.63	130.88(d)	10.98	128.32(d)	12.21	131.45(d)	2.45	36.12(d)	1.75	17.00(d)	8.13			64.0
(**1d**)	135.05(d)	119.62	130.93(d)	11.73	128.32(d)	13.19	131.49(d)	2.93	43.16(d)	2.19	24.70(d)	8.00	11.39(s)	<0.1	64.3
(**1e**)	136.44(d)	119.63	130.98(d)	10.98	128.24(d)	12.21	131.38(d)	2.44	43.74(s)	<0.6	25.58(d)	6.11[c]			60.4
											25.52(d)	4.88[c]			
(**1f**)[e]	135.13(d)	119.63	130.95(d)	10.98	128.34(d)	12.21	131.49(d)	3.67	41.09(s)	<0.6	33.64(d)	7.32[c]	20.02(s)	<0.6	64.3
(**1g**)	135.03(d)	119.63	130.98(d)	10.98	128.33(d)	13.43	131.51(d)	3.66	48.84(d)	2.38	29.70(d)	8.06	20.19(s)	<0.1	64.8
													20.14(s)	<0.1	
(**1h**)	136.98(d)	119.63	130.88(d)	10.98	128.04(d)	13.43	131.10(d)	3.67	48.82(d)	0.91	22.63(d)	3.60	10.27(s)	<0.1	60.9
											31.81(d)	6.43			
(**1i**)	139.93(d)	120.84	130.91(d)	10.98	128.06(d)	13.43	130.89(d)	2.44	53.05(d)	1.83	31.70(d)	4.47			54.0
(**1j**)	135.08(d)	120.16	131.17(d)	11.72	128.32(d)	13.19	131.40(d)	2.93	52.94(d)	2.68	33.71(d)	8.67	27.30(s)	<0.1	66.6
(**1k**)	135.03(d)	120.86	130.92[f]		128.38[f]		131.70[f]		45.50(d)	0.97					65.8
(**1l**)	134.15(d)	119.63	131.51(d)	10.99	128.13(d)	13.43	131.70(d)	2.44	23.86(d)	0.61	7.27(d)	5.37			66.6
											6.98(d)	5.62			
(**1m**)	136.00(d)	119.63	131.05(d)	10.99	128.26(d)	13.43	131.38(d)	2.44	53.49(d)	2.08	35.22(d)	5.19	23.31(t)	0.48	62.2
											35.06(d)	5.31			
(**1n**)[g]	136.90(d)	119.63	130.91(d)	10.98	128.22(d)	12.20	131.33(d)	2.44	50.65(d)	1.46	36.07(d)	3.50	25.23(s)	<0.1	61.0

[a] δ in p.p.m. with reference to $SiMe_4$, J values in Hz, solvent $CDCl_3$; c = complex multiplet(s), t = triplet, d = doublet, and s = singlet. [b] δ in p.p.m. relative to 85% H_3PO_4, solvent $CHCl_3$, external lock D_2O, downfield shifts are positive. [c] Resolution = 0.61 Hz. [d] Resolution = 0.061 Hz. [e] $\delta(C_\delta)$ 13.77(s) p.p.m., $^5J(P\text{–}C_\delta)$ <0.6 Hz. [f] Tentative assignment (see text). [g] $\delta(C_\delta)$ 25.53(c) p.p.m., $^5J(P\text{–}C_\delta)$ <0.1 Hz.

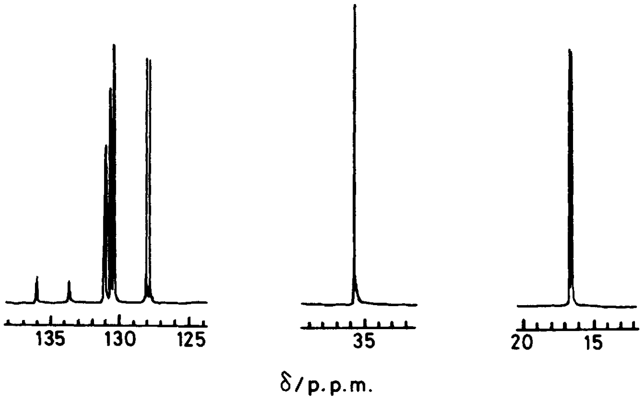

Figure 1. $^{13}C-\{^1H\}$ N.m.r. spectrum of $PhP(S)(NHEt)_2$ (**1c**) in $CDCl_3$

nucleus and the coupling constants are shown in Table 1. The coupling between the phosphorus nucleus and the alkyl carbon nuclei is generally less pronounced and, for a spectrometer resolution of 0.61 Hz, was only observed for C_α in (**1b**), (**1g**), (**1i**), and (**1j**), and not for the other compounds in the series. Repeat alkyl carbon-13 n.m.r. spectra were obtained at much higher resolution (10-fold) for all of the compounds using a narrower sweep width and by accumulating each part of the total n.m.r. signal separately. The coupling constant values obtained are shown in Table 1.

Under the higher resolution conditions, compound (**1b**) shows a coupling constant $[^2J(P-C_\alpha)]$ for the phosphorus and α-carbon atoms of 2.08 (±0.061) Hz [compared with 2.44 (±0.61) Hz at the lower resolution]. For compound (**1c**), $^2J(P-C_\alpha)$ was calculated as 1.75 (±0.061) Hz from the splitting of the α-carbon signal. This is in contrast to the lower-resolution spectrum of this compound for which no C_α splitting was observed. We have shown that carbon-13 n.m.r. spectra recorded at high enough spectral resolution reveal a splitting of the C_α signal to give an, albeit small, coupling constant in the other compounds comprising this series.

All of the compounds containing a β-carbon atom in the alkyl side chain showed $P-C_\beta$ coupling, but no four- or five-bond coupling was observed between the phosphorus nucleus and C_γ or C_δ respectively.

Discussion

The phosphorus-31 n.m.r. chemical shifts for the compounds (**1**) span a limited spectral range {δ = 60.4 to 68.1 p.p.m. [excluding (**1i**), R = Bu^t]}, which is comparable with the range for the corresponding cyclodi-λ^5-phosphazanes, $[PhP(S)NR]_2$ (**2**) [δ = 71.4 to 81.9 p.p.m.].[24] The shielding of the phosphorus nucleus in compounds (**1**) is at its greatest when the alkyl side chain is branched at the α-carbon atom [(**1e**), (**1h**), (**1i**), (**1m**), and (**1n**)] or when there are no carbon atoms attached to the nitrogen atom [(**1a**)], and the phosphorus-31 n.m.r. chemical shift range for these compounds is 60.4 to 62.2 p.p.m. [excluding (**1i**)]. These are the very compounds which do not form a cyclic dimer on thermal condensation but, instead, form the dealkylated cyclotri-λ^5-phosphazane, $[PhP(S)NH]_3$ (**3**), or in the case of R = cyclohexyl, the unusual fused bicyclic compound (**4**).

Less shielding is observed in compounds (**1b**)—(**1d**), (**1f**), (**1g**), and (**1j**)—(**1l**) and many of these have similar chemical shift values ranging from 64.0 to 68.1 p.p.m. All of these compounds thermally condense to the cyclic dimer, $[PhP(S)NR]_2$ (**2**), when heated under inert conditions. We have also shown[24] that (**1j**), R = neopentyl, will undergo thermal condensation to give the 'normal' cyclodi-λ^5-phosphazane (**2**) (R = neopentyl) and that no dealkylated cyclic trimer $[PhP(S)NH]_3$ (**3**) is present in the reactant–product mixture. We now believe that the crucial factors which determine whether compounds (**1**) will dealkylate to form the cyclic trimer are (*i*) branching at the α-carbon atom and (*ii*) the presence of a hydrogen atom at the β-carbon atom, of the alkyl side chain, rather than bulk or steric factors relating to the alkyl side chain. The hydrogen atom attached to the β-carbon atom of an α-branched alkyl side chain is in close proximity to the amido-nitrogen atom which allows, presumably, a molecular rearrangement to occur leading to the elimination of an alkene from the parent molecule.

The formation of the dealkylated trimer (**3**) is obviously due to a 1,2 elimination giving rise to an alkene. It is well established[25] that alkylation of the α-carbon drastically promotes this reaction, whilst alkylation of the β-carbon has a relatively minor effect. This is borne out by the fact that the thermolysis of (**1g**) gives rise to the normal dimer (**2**), whilst (**1e**), (**1h**), and (**1i**) give the dealkylated compound (**3**). The need for the presence of a hydrogen atom attached to the β-carbon atom is demonstrated because (**1j**) undergoes thermolysis to give the dimeric compound (**2**).

One particular anomaly to note is the behaviour of the cyclopropylamine derivative (**1l**). Although this compound is branched at the α-carbon atom, it gives the 'normal' corresponding cyclodi-λ^5-phosphazane under thermolysis conditions. However, (**1l**) does have a phosphorus-31 n.m.r. chemical shift which is further downfield than for other 'α-branched' compounds and is of the same order as these of the 'non-α-branched' compounds. Furthermore, it is most unlikely that the cyclopropyl derivative is able to sustain the formation of cyclopropene and so it has a tendency to behave more like the derivatives with unbranched alkyl groups.

The assignment of carbon-13 n.m.r. chemical shifts to specific carbon nuclei within the molecular structure of compounds (**1**) is based on the available comparable data for mononuclear phosphorus compounds containing a phenyl substituent at the phosphorus atom,[11–16] and our analysis of the complex spectra arising from $^{13}C-^1H$ coupled measurements. Absorptions due to the *ipso*-carbon nucleus [C(1)] are of generally low intensity and are difficult to detect for some of the compounds even after extended accumulation times. The low intensity of the C(1) signal has also been observed for other systems and can be ascribed to lack of nuclear Overhauser enhancement and, possibly, to slow relaxation of the directly bonded phosphorus atom.[26] The intensity, as indicated by the peak height, of the absorption due to C(4) is much lower than that due to C(2) and C(3).

Rigorous assignment of the C(2) and C(3) chemical shifts would appear to be more contentious. Some workers[11,12,*] have assigned the chemical shifts of the C(2), C(3), and C(4) carbons in order of decreasing phosphorus–carbon coupling constant, J(P–C), in a downfield direction. Hence, the phenyl-carbon nucleus with the most upfield chemical shift (δ *ca.* 128 p.p.m.) is regarded as C(2). Conversely, the carbon-13 n.m.r. chemical shifts listed by Ewing,[13] and reported by Modro,[16] and Albright *et al.*[14] for similar substances which have a phosphorus-containing moiety attached to the phenyl ring indicate C(3) as being the furthest upfield of the phenyl carbon nuclei. We have confirmed the latter system of assignment on the basis of proton-coupled carbon-13 n.m.r. spectra.

It is not surprising that $^4J[P-C(4)]$ has been observed previously to result in a singlet,[11,12] which suggests that the spectrometer resolution was not high enough to detect the

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[*] *Note added in proof.* Since submission of this paper, J. C. Shaw and C. W. Allen (*Inorg. Chem.*, 1986, **25**, 4632) have come to the same conclusion as we have on the assignment of the C(2) and C(3) resonances.

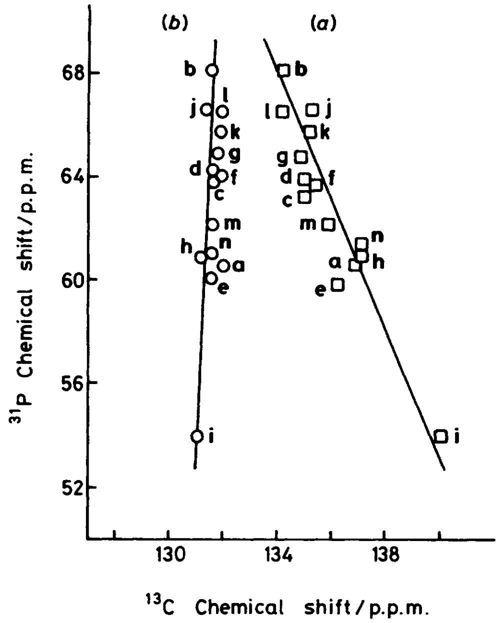

Figure 2. Plot of phosphorus-31 n.m.r. chemical shift against carbon-13 n.m.r. chemical shift for (*a*) C(1) and (*b*) C(4) in compounds (**1a**)—(**1n**)

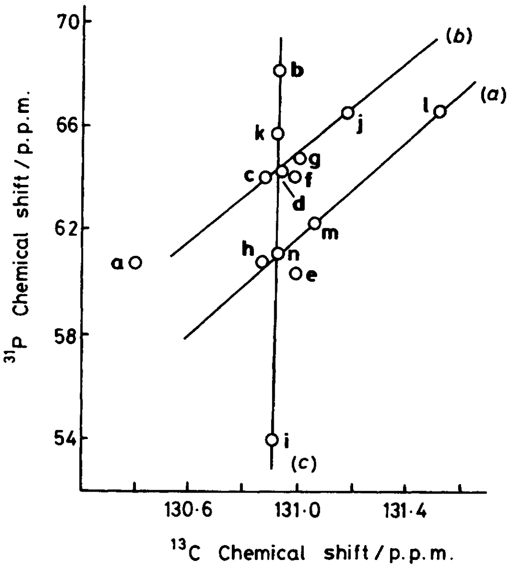

Figure 3. Plot of phosphorus-31 n.m.r. chemical shift against carbon-13 n.m.r. chemical shift for C(2) in compounds (**1a**)—(**1n**); (*a*) cyclo derivatives, (*b*) β-branched alkyl groups, (*c*) α-branched alkyl groups

splitting of the C(4) signal. By contrast, in more recent work[27] measurable doublets have been obtained for the C(4) carbon nucleus in phenyl-substituted cyclophosphazenes.

Inspection of the data in Table 1 shows that successive substitution of hydrogen atoms by methyl groups decreases the shielding of the α-carbon nucleus of the alkyl chain by approximately equal amounts. For example, the shielding of the α-carbon nucleus in compounds (**1b**), (**1c**), (**1e**), and (**1i**) is 27.12, 36.12, 43.74, and 53.05 p.p.m. respectively. It is apparent that as the three hydrogen atoms attached to the methyl carbon atom in compound (**1b**) are sequentially replaced the structural change –C–H to –C–Me caused an average deshielding of approximately 9 p.p.m. This phenomenon has been termed the 'α effect' and it appears to be general for many classes of compound although its magnitude does differ in various families. A similar trend is observed when a β-hydrogen atom is substituted by a methyl group, *i.e.* –C–C–H becomes –C–C–Me. This can be seen by comparing the β-carbon shieldings for compounds (**1**) when R = Et, (**1c**), Pr^n, (**1d**), Bu^i, (**1g**), and neopentyl, (**1j**). The β effect is of smaller magnitude than the α effect and averages 5.5 p.p.m. This is in contrast to the data for saturated hydrocarbons where both the α and β effects are approximately equal at 9 p.p.m.[28,29]

We have suggested previously, in preliminary reports,[30,31] that a linear relationship exists between the phosphorus-31 n.m.r. chemical shift and the carbon-13 n.m.r. chemical shift for the C(1) carbon nucleus in certain di(monoalkylamide) compounds (**1**). A complete plot for all the compounds (**1**) is shown in Figure 2, giving a negative slope such that the phosphorus nucleus becomes more shielded as the C(1) carbon nucleus becomes less shielded, and *vice versa*. The equation for the plot is $y = -2.45x + 396$. The graph appears to have four distinct parts: (*i*) alkyl group contains one carbon atom only [*i.e.* R = Me, (**1b**)]; (*ii*) alkyl group in which only one carbon atom is attached to the C_α carbon atom [*i.e.* R = Et, (**1c**); Pr^n, (**1d**); Bu^n, (**1f**); Bu^i, (**1g**); CH$_2$Ph, (**1k**); or neopentyl, (**1j**)]; progressive shielding is observed within this group with increased β branching of the alkyl group, the plot for (**1l**), R = cyclopropyl, also occurs in this region, and the anomalous behaviour of the cyclopropyl derivative has been referred to previously; (*iii*) alkyl groups in which two carbon atoms are attached to the C_α carbon atoms [*i.e.* R = Pr^i, (**1e**); Bu^s, (**1h**); cyclopentyl (**1m**); cyclohexyl, (**1n**)]; interestingly, the plot for (**1a**), R = H, also occurs in this region, and the predictive value of the graph is evidenced by the fact that the chemical shift of the phosphorus-31 n.m.r. absorption for (**1a**) was deduced from the graph having first measured the carbon-13 n.m.r. chemical shift of the C(1) carbon nucleus. (The predicted value was later confirmed by an actual measurement and the two values agreed to within 0.5 p.p.m.); (*iv*) alkyl group in which three carbon atoms are attached to the C_α carbon atoms [*i.e.* R = Bu^t, (**1i**)].

There is a further linear relationship between the phosphorus-31 n.m.r. chemical shift and the carbon-13 n.m.r. chemical shift of the C(4) carbon nucleus (Figure 2). It is not immediately clear why there should be a such a significant difference in the slopes of the two graphs. A plot of phosphorus-31 n.m.r. chemical shift against carbon-13 n.m.r. chemical shift for the C(2) carbon nucleus gives rise to three interesting, but hitherto unexplained relationships (Figure 3).

No apparent relationship emerged from the plot of phosphorus-31 n.m.r. chemical shift against carbon-13 n.m.r. chemical shift for the C(3) carbon nucleus. This is consistent with the observation that the smallest variation in carbon-13 n.m.r. chemical shift occurs at C(3) in monosubstituted benzenes.[16,29]

The assignment of carbon-13 chemical shift values for compound (**1k**), R = CH$_2$Ph, is tentative. The spectrum is very complex owing to the overlap of resonances due to one Ph–P and two Ph–CH$_2$ phenyl groups. However, we report the values for the Ph–P carbon nuclei with some degree of confidence as our values coincide with those that could be predicted by extrapolation from the plots in Figures 2 and 3. In fact, careful expansion and enhancement of the spectrum in the region predicted for the C(1) carbon nucleus allowed the observation of a doublet of very low intensity (for the Ph–P moiety) which had not been seen in the normal spectrum.

In compounds (**1**) the phosphorus nucleus (and the nuclei and groups of nuclei attached to it) appears to exert a strong perturbation on the carbon nuclei of the phenyl ring causing, in most cases, a significant deshielding with respect to the carbon-13 n.m.r. signal for benzene of 128.7 p.p.m.[32] It is thought[33] that substituents which are attached to benzene rings modify the aryl

π system causing a change in the carbon-13 n.m.r. chemical shifts, and that the size of the shift change is related to the extent of the interaction between the substituent and the ring system. The variations in chemical shift at the C(1) and C(2) positions cannot be used to assess substituent effects because they reflect both polar and magnetic effects.[34] However, the variation in the chemical shifts of the C(3) and C(4) carbon nuclei can be used to obtain substituent effect constants as they are essentially free of substituent magnetic effects.[34]

Inductive and resonance substituent constants for groups attached to the phenyl ring in compounds (**1**) have been calculated from d.s.p. fits for the C(3) and C(4) carbon-13 n.m.r. chemical shifts according to equations (2) and (3),[35] where S_3

$$S_3 = 1.54\sigma_I - 1.61\sigma_R^0 \qquad (2)$$

$$S_4 = 3.98\sigma_I + 19.79\sigma_R^0 \qquad (3)$$

and S_4 are the carbon-13 n.m.r. chemical shifts in p.p.m. relative to the chemical shift for benzene for C(3) and C(4) respectively. The values obtained are shown in Table 2. The magnitude (0.14—0.17) of the resonance parameter, σ_R^0, for all of the substituents is similar to that for the nitro or acetyl group, suggesting that these phosphorus-containing substituents are mesomerically strongly electron-withdrawing groups. These resonance effects are virtually certain to be due to p_π–d_π interactions between the aromatic system and the quinquevalent four-co-ordinate phosphorus nucleus.

Table 2. Calculated S parameters and inductive and resonance effect constants for a series of groups, $P(S)(NHR)_2$, attached to a phenyl ring

Substituent	S_3	S_4	σ_I	σ_R^0
$P(S)(NH_2)_2$	−0.23	2.92	0.00	0.15
$P(S)(NHMe)_2$	−0.19	2.98	0.03	0.14
$P(S)(NHEt)_2$	−0.15	2.98	0.05	0.14
$P(S)(NHPr^n)_2$	−0.15	3.02	0.05	0.14
$P(S)(NHPr^i)_2$	−0.23	2.91	0.00	0.15
$P(S)(NHBu^n)_2$	−0.13	3.02	0.06	0.14
$P(S)(NHBu^i)_2$	−0.14	3.04	0.06	0.14
$P(S)(NHBu^s)_2$	−0.43	2.63	−0.12	0.16
$P(S)(NHBu^t)_2$	−0.41	2.42	−0.11	0.15
$P(S)(NHCH_2Bu^t)_2$	−0.15	2.93	0.05	0.14
$P(S)(NHCH_2Ph)_2$	−0.09	3.23	0.09	0.14
$P(S)(NH\overline{CHCH_2CH}_2)_2$	−0.34	3.23	−0.04	0.17
$P(S)[NH\overline{CH(CH_2)_2CH}_2]_2$	−0.21	2.91	0.01	0.14
$P(S)[NH\overline{CH(CH_2)_4CH}_2]_2$	−0.25	2.86	0.00	0.14
Range	0.34	0.81	0.21	0.03

Comparing the inductive effect constant, σ_I, for these substituents with values for other similar series of substituents shows that the electron-attracting properties of the substituents decrease in the order:[24] $P(S)Cl_2 > \overline{P(S)NRP(S)PhNR} > P(S)(NHR)_2 > H > P(S)Ph_2 > P(S)(Ph)NHR$. Also, within any series of compounds, there is a trend to lower σ_I values with increased α branching of the alkyl substituent, R. For the substituents in Table 2, lower values are obtained when R = Pr^i, (**1e**), Bu^s, (**1h**), cyclopropyl, (**1l**), cyclopentyl (**1m**), and cyclohexyl, (**1n**), and most marked for R = Bu^t, (**1i**), than for other substituents. Compounds (**1**) containing these substituents were found grouped together [except for (**1i**)] in the plot of phosphorus-31 n.m.r. chemical shift against carbon-13 n.m.r. chemical shift for C(1), C(2), and C(4), Figures 2 and 3 (with the exception of R = cyclopropyl which usually can be relied on to be anomalous). The compound $PhP(S)(NH_2)_2$ (**1a**), was also found to lie close to these latter compounds and it is not surprising that the $P(S)(NH_2)_2$ substituent has a σ_I value very similar to those of the substituents containing a secondary alkyl group. Furthermore, all of these compounds undergo thermal dealkylation to give the cyclic trimer (**3**).

It is important to note that the cause of the substituent effect is transmitted from the alkyl group, through nitrogen and phosphorus, to the phenyl ring, suggesting that modifications to the substituent which occur at some interatomic distances from the phenyl ring can still affect the substituent effect. Where σ_I values are very close to zero or negative in compounds (**1**), dealkylation to the cyclic trimer (**3**) occurs, whilst substituents which have more positive values retain their alkyl group and condense to the corresponding cyclodi-λ^5-phosphazane (**2**) on thermolysis. This observation may well serve as a useful predictor for other similar reactions.

Experimental

The phenylphosphonothioic di(monoalkylamides), (**1**), were prepared by the reaction of 0.40 mol of ammonia or of an alkylamine NH_2R (R = H, Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s,

Table 3. Characterisation details for $PhP(S)(NHR)_2$ (**1**)

		M.p./°C		M		Elemental analysis/percentage composition							
						Calc.				Found			
Compound	Yield/%	Obs.	Lit.	Calc.[a]	Obs.	C	H	N	P	C	H	N	P
(**1a**)	74	43	43[10]	172	172	41.9	5.3	16.3	18.0	41.6	5.1	16.0	18.0
(**1b**)	69	68	68[2]	200	200	48.0	6.6	14.0	15.5	48.1	6.7	13.8	15.4
(**1c**)	86	87	87[b]	228	228	52.6	7.5	12.3	13.6	52.7	7.4	12.5	13.7
(**1d**)	79	54	54[b]	256	256	56.2	8.3	10.9	12.1	56.3	8.3	11.0	12.0
(**1e**)	81	51	51[b]	256	256	56.2	8.3	10.9	12.1	56.2	8.3	10.9	12.1
(**1f**)	69	47	47[b]	284	284	59.1	8.9	9.9	10.9	59.2	8.9	9.9	10.8
(**1g**)	79	85	84[c]	284	284	59.1	8.9	9.9	10.9	59.0	8.9	10.0	11.0
(**1h**)	55	14—16	15[b]	284	284	59.1	8.9	9.9	10.9	59.1	9.0	9.9	11.0
(**1i**)	64	104	103[b]	284	284	59.1	8.9	9.9	10.9	59.1	9.0	9.8	10.6
(**1j**)	55	94		312	312	61.5	9.4	9.0	9.9	61.5	9.1	9.1	9.9
(**1k**)	82	80	80	352	352	68.2	6.0	8.0	8.8	68.0	6.2	8.0	8.7
(**1l**)	94	118	119[10]	252	252	57.1	6.8	11.1	12.3	57.7	6.9	10.9	12.1
(**1m**)	86	80	79—80[c]	308	308	62.3	8.2	9.1	10.0	62.7	8.5	8.9	9.9
(**1n**)	78	110	110[b]	336	336	64.2	8.7	8.3	9.2	64.4	8.5	8.2	9.5

[a] Based on the mass of the most abundant isotope. [b] E. H. M. Ibrahim, Ph.D. Thesis, University of London, 1967. [c] J. D. Healy, Ph.D. Thesis, University of London, 1974.

Bu^t, neopentyl, CH_2Ph, cyclopropyl, cyclopentyl, or cyclohexyl) with phenylphosphonothioic dichloride, $PhP(S)Cl_2$ (0.10 mol, 21.1 g), in polar solvents such as acetonitrile or ethanol-free chloroform at room temperature. In most cases, an immediate reaction was observed with the formation of a pale yellow precipitate. In those cases where little or no precipitate was observed on mixing the reactants, the reaction mixture was boiled under reflux for up to 6 h. Compounds (**1**) were obtained in good to excellent yields (55—94%) and were recrystallised to constant melting point from chloroform [with the exception of $PhP(S)(NHBu^s)_2$ (**1h**) which is a liquid at room temperature; purification of this compound was achieved by passing a solution in light petroleum (b.p. 40—60 °C) through an alumina column and subsequent removal of the solvent by evaporation under a vacuum]. All compounds showed satisfactory micro-analysis and molecular mass determinations (VG 7070 mass spectrometer) before n.m.r. spectra were recorded (Table 3).

The ^{31}P n.m.r. spectra were recorded on a JEOL JNM FX 60 Fourier-transform spectrometer operating at 24.15 MHz, and 0.05 (± 0.01) mol dm^{-3} solutions in chloroform with D_2O as an external lock (8-mm tube in 10-mm tube). Spectra were measured under broad-band proton-decoupling conditions and the ^{31}P n.m.r. chemical shifts (δ) are expressed in p.p.m. with reference to external 85% orthophosphoric acid; downfield shifts are positive. The ^{13}C n.m.r. spectra were obtained using a JEOL FX 200 spectrometer operating at 50.1 MHz in the pulsed Fourier-transform mode. Spectra were recorded under broad-band proton-decoupling conditions (except where indicated), using approximately 0.5-cm^3 solutions in deuteriated chloroform (for locking). The chemical shifts were measured relative to $SiMe_4$ (0 p.p.m.) as the internal reference.

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