Phosphorus–Nitrogen Compounds. Part 56.[1] The Solution Synthesis of some *trans*-1,3-Dialkyl-2,4-diphenyl-2,4-dithiocyclodi-λ⁵-phosphazanes and their Proton, Carbon-13, and Phosphorus-31 Nuclear Magnetic Resonance Spectra†

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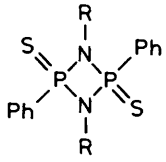
A series of *trans*-1,3-dialkyl-2,4-diphenyl-2,4-dithiocyclodi-λ⁵-phosphazanes, $[PhP(S)NR]_2$ (R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, neopentyl, CH_2Ph, or cyclohexyl) has been synthesized by a solution method and their proton, carbon-13, and phosphorus-31 n.m.r. spectra obtained. The relationships between phosphorus-31 and carbon-13 n.m.r. chemical shift data are explored; interpretation of proton n.m.r. data has led to the assignment of *trans* structures for the cyclodi-λ⁵-phosphazane molecules. 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.

trans-1,3-Dialkyl-2,4-diphenyl-2,4-dithiocyclodi-λ⁵-phosphazanes, $[PhP(S)NR]_2$ (**1**) (R = Me, Et, Pr^n, Bu^n, Bu^i, cyclopropyl, or CH_2Ph) are obtained by the thermal condensation of the corresponding phenylphosphonothioic di(monoalkylamide), $PhP(S)(NHR)_2$, under an inert atmosphere.[2–6] The thermolysis of phenylphosphonothioic di(monoalkylamides) which contain α-branched alkyl carbon atoms (*i.e.* R = Pr^i, Bu^s, or Bu^t) leads to the dealkylated cyclotri-λ⁵-phosphazane, $[PhP(S)NH]_3$[3,6] (except when R = cyclopropyl when a normal cyclodi-λ⁵-phosphazane is formed); when R = cyclohexyl a most unusual fused bicyclic molecule is obtained.[6,7]

We have recently published a preliminary report[8] on a method for the synthesis of the hitherto unavailable cyclodi-λ⁵-phosphazanes with α-branched alkyl carbon atoms by the reaction of phenylphosphonothioic dichloride with alkylamines in polar, non-aqueous solvents at room temperature. We now report more fully on the synthesis of the α-branched cyclodi-λ⁵-phosphazanes (**1**) (R = Pr^i, Bu^s, Bu^t, or cyclohexyl), and on the n.m.r. properties of the 1,3-dialkyl derivatives of the cyclodi-λ⁵-phosphazanes.

We believe that the exclusive formation of the *trans* dimers at room temperature arises from the following. Phenylphosphonothioic dichloride, $PhP(S)Cl_2$, reacts with the alkylamine to give initially the monosubstituted derivative, PhP(S)(NHR)Cl. This reacts rapidly with base to give *via* proton abstraction and chloride ion elimination a quinquevalent three-co-ordinate intermediate, PhP(S)(NR). We have not, so far, been able to identify this at room temperature or below by its ^{31}P n.m.r. spectrum, and believe that it might well be solvated. At room temperature this monomer dimerises to give exclusively the *trans* dimer. Higher temperatures are required to give the less favoured *cis* isomer. If sufficient alkylamine is present the intermediate monomer reacts to give the phenylphosphonothioic di(alkylamide). The variable yields of dimers are presumably linked to electronic and steric factors in the above quite complex reaction sequence.

We have measured proton, carbon-13, and phosphorus-31 n.m.r. chemical shifts and coupling constants (where appropriate) for compounds (**1**) where R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, neopentyl, CH_2Ph, and cyclohexyl, and compared



(**1**)

R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, neopentyl, CH_2Ph, cyclohexyl (all *trans*), or *cis*-Et

these to the same properties in the corresponding phenylphosphonothioic di(monoalkylamide) precursors. 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[9–12] and some carbon-13 n.m.r. chemical shift data have been reported for compounds which contain at least one phenyl group attached to a four-co-ordinate phosphorus atom.[9,10,13–18] The dual-substituent parameters (d.s.p.) approach[19] best describes the structural effect on the carbon-13 n.m.r. chemical shift of the C(3) and C(4) carbon nuclei (of the phenyl groups) 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

$$S = a\sigma_I + b\sigma_R^0 \quad (1)$$

constants). Carbon-13 n.m.r. spectrocopy would appear to be a useful tool for investigating the substituent effects of phosphorus-containing groups (see, for example, refs. 9, 10, 18, and 20—23), and we have calculated substituent inductive and resonance constants in compounds (**1**) from chemical shift differences using the dual-substituent parameter approach. This has enabled us to assess changes in the electron distribution of the phenyl ring systems within compounds (**1**).

Results

Proton n.m.r. data for the 1,3-dialkyl-2,4-diphenyl-2,4-dithiocyclodi-λ⁵-phosphazanes (**1**), measured at 199.5 MHz, are

† Presented, in part, at the 4th International Symposium on Inorganic Ring Systems, Paris, September 1985.

Table 1. Proton n.m.r. data[a] for *trans*-$[PhP(S)NR]_2$

R	Phenyl protons *o*	Phenyl protons *m*, *p*	CH_3	CH	α-CH_2[b]	β-CH_2	γ-CH_2	δ-CH_2
Me	8.30	7.58	2.52					
Et	8.36	7.56	0.98		2.96			
Et (*cis*)	7.95	7.52	1.10		3.26			
Pr^n	8.38	7.56	0.72		2.92	1.42		
Pr^i	8.46	7.55	1.00	3.60				
Bu^n	8.36	7.56	0.94		2.94	1.38[c]	1.38[c]	
Bu^i	8.36	7.58	0.66	1.42	3.00			
Bu^s	8.42	7.58	0.72	3.06	0.98[d]	1.48		
Bu^t	8.40	7.60	0.70					
CH_2Ph[e]	8.16	7.42			4.28 (A)			
					3.90 (B)			
Neopentyl	8.38	7.56	0.67		2.45			
Cyclohexyl	8.04	7.54		2.08		1.92	1.62	1.24

[a] Chemical shifts (δ/p.p.m.) at 199.5 MHz; solvent, $CDCl_3$. [b] Centre of multiline signal arising from asymmetric protons [except R = *cis*-Et (symmetric) and R = CH_2Ph where the signals are resolvable]. [c] Complex overlap of lines. [d] Methyl group attached to α-carbon atom. [e] CH_2*Ph* Phenyl protons centred at δ 7.04 p.p.m.

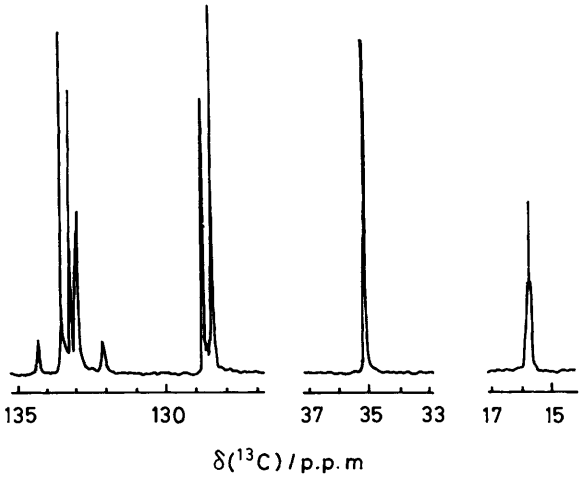


Figure 1. ^{13}C N.m.r. spectrum of *trans*-$[PhP(S)NEt]_2$

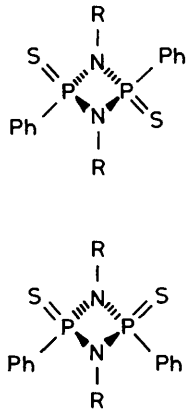


Figure 2. *cis* and *trans* forms of $[PhP(S)NR]_2$

shown in Table 1, and the carbon-13 and phosphorus-31 n.m.r. data in Table 2. The phosphorus-31 n.m.r. absorptions of the pure substances were observed as sharp, single peaks (except for R = Bu^s which presented two peaks very close together) and the chemical shift values span a spectral range of 20.7 p.p.m. from 61.2 to 81.9 p.p.m.

The proton-decoupled carbon-13 n.m.r. spectrum for $[PhP(S)NEt]_2$ is shown in Figure 1, and for the aryl carbon [C(1)—C(4)] absorptions is fairly typical of all of the cyclic dimer compounds. Doublets are observed for C(1), C(2), and C(3) due to coupling with the nearest phosphorus nucleus, but no coupling was observed for C(4) (except when R = Pr^i). In the case of R = Bu^s, the spectrum was not completely resolved due to the presence of many signals arising from the two enantiomeric forms. The corresponding phenylphosphonothioic di(monoalkylamides), $PhP(S)(NHR)_2$, all show[18] a small coupling constant, ^4J[P–C(4)], and the general non-appearance of this coupling in the cyclic dimer series of compounds is probably due to insufficient resolution of the absorptions by the spectrometer (*i.e.* the number of data points that can be detected for a given sweep width is too low). We would also have expected to have seen more complex spectra than those that were obtained, if account is taken of the predicted effect of long-range virtual coupling with the more distant phosphorus nucleus in the molecule.

It is remarkable that no coupling was detected between the phosphorus nucleus and the α-carbon nucleus in the alkyl side chain. Following previous trends,[18] this coupling constant would be predicted as being numerically small (*i.e.* less than four times the spectrometer resolution of 0.61 Hz) and is therefore below the level of resolution under the conditions used. The carbon-13 n.m.r. absorption of the β-alkyl carbon nucleus is observed as a triplet due to the coupling (three bond) of the carbon nucleus with both phosphorus nuclei in the $(P–N)_2$ ring.

Discussion

Cyclodi-λ^5-phosphazanes which contain four-co-ordinate phosphorus atoms may exhibit geometrical isomerism. Such compounds may exist in either a *trans* or a *cis* form and this is shown diagrammatically for compound (**1**) in Figure 2. Nearly all of the reported cyclodi-λ^5-phosphazanes of the type $[PhP(S)NR]_2$ (R = alkyl or aryl) have been assigned a *trans* structure and *cis* isomers have been isolated for R = Et[3,24,25] and claimed for R = Ph[26,27] only. There is some tentative evidence for the formation of the *cis* isomer when R = Me from proton n.m.r. results.[2]

Table 2. Carbon-13[a] and phosphorus-31[b] n.m.r. data for *trans*-$[PhP(S)NR]_2$

R	C(1) δ	C(1) $^1J(PC^1)$	C(2) δ	C(2) $^2J(PC^2)$	C(3) δ	C(3) $^3J(PC^3)$	C(4) δ	C_α[c] δ	C_β δ	C_β $^3J(PC_\beta)$	C_γ[d] δ	C_δ	δ(^{31}P)
Me	131.7 (d)	109.9	133.5 (d)	14.7	128.7 (d)	14.7	133.2	24.6					80.1
Et	133.2 (d)	109.9	133.4 (d)	14.6	128.6 (d)	15.9	133.0	35.1	15.7 (t)	3.7			76.3
Et (*cis*)	135.8 (q)	116.0	131.4 (d)	13.4	128.6 (d)	15.9	132.7	35.3	15.5				80.4
Pr^n	133.2 (d)	109.9	133.4 (d)	14.7	128.6 (d)	14.7	133.0	40.2	19.7 (t)	2.4	10.8		75.4
Pr^i	134.9 (d)	108.4	133.1 (d)	14.7	128.3 (d)	15.8	132.5 (d)[e]	46.0	23.6 (t)	3.6			71.5
									22.6 (t)	6.1			
Bu^n	132.5(d)	113.4	133.7 (d)	13.4	128.6 (d)	14.7	133.0	38.4	30.5 (t)	2.4	17.5	9.9	78.6
Bu^i	132.5 (d)	113.5	133.7 (d)	13.4	128.6 (d)	14.7	133.0	48.9	28.8 (t)	2.4	20.1,20.3		81.9
Bu^s[f]	133.3 (d)	113.4	133.4 (d)	14.7	128.3		133.0	48.2	32.6 (t)	6.1	15.4		81.8
Bu^t	138.4 (d)	113.5	133.7 (d)	13.4	128.1 (d)	14.6	133.0	54.7	33.7 (t)	4.9			61.2
CH_2Ph	132.7	113.5	133.1	14.7	128.6 (d)	15.9	133.0	44.4					78.2
Neopentyl	134.2 (d)	108.4	133.1 (d)	14.7	128.3 (d)	15.9	133.0	53.7	34.7 (t)	8.5	26.9		74.1
Cyclohexyl	134.9 (d)	109.9	131.0 (d)	10.3	128.3 (d)	16.1	131.8	51.0	30.9		24.2	14.6	71.4

[a] Approximately 10% solution in $CDCl_3$ measured at 50.1 MHz; chemical shifts (δ) in p.p.m; d = doublet, t = triplet, q = quartet. [b] 0.05 (±0.1) mol dm^{-3} solutions in $CHCl_3$ measured at 24.15 MHz. [c] $^1J(PC_\alpha)$ not observed. [d] $^2J(PC_\gamma)$ not observed. [e] $^4J(PC^4) = 2.5$. [f] The spectrum was not completely resolved and some assignments are tentative (see text).

In cyclodi-λ^5-phosphazanes which contain an α-CH_2 group in the *N*-alkyl side chain, $[PhP(S)NCH_2R']_2$, the proton spectrum of the methylene protons has assisted in the determination of the geometrical isomer type that the molecule exhibits using the rules proposed previously[3] for $[PhP(S)NEt]_2$. In the compounds obtained during this work, the α-CH_2 protons signal is very complex with many lines being observed. These α-CH_2 protons are non-identical in that they exhibit magnetic non-equivalence and this gives rise to an AB or an AX spectrum with each line being further split into three by coupling to two adjacent phosphorus nuclei. Each line is now further split into $n + 1$ lines due to the coupling to the n protons on the adjacent β-carbon nucleus in the alkyl side chain. Thus, the cyclodi-λ^5-phosphazanes prepared in this work which contain an α-CH_2 group have been assigned *trans* structures on the basis of the multiline signals observed for the α-CH_2 protons.

Conversely, *cis* structures would be expected to give much simpler spectra as both of the α-CH_2 protons are equivalent and no intrinsic asymmetry would occur, thus giving an A_2 spectrum. For example, 12 lines would be predicted in the α-CH_2 proton n.m.r. spectrum for *trans*-$[PhP(S)NCH_2Ph]_2$, and 11 lines are actually observed; numerical coincidence of coupling constants can cause the spectra to be simplified, but this does not invalidate the present argument.

According to the rules proposed earlier,[24] the chemical shifts of the phenyl proton signals may also be used to provide evidence of the *trans* structure for these molecules. It is suggested that structural features would lead to different shielding effects for the *ortho*-phenyl protons in the *cis*- and *trans*-dimer molecules and that the *ortho* protons in the *trans* molecule would resonate further downfield than the *ortho* protons in either the *cis* molecule or the monomeric precursor, $PhP(S)(NHR)_2$. All of the compounds (**1**) (except for R = CH_2Ph and cyclohexyl) have *ortho*-proton signals which resonate 0.36—0.42 p.p.m. further downfield than the corresponding protons in the phenylphosphonothioic di(monoalkylamides).[28] In compound (**1**), when R = cyclohexyl, the *ortho*-phenyl proton signal resonates only 0.04 p.p.m. downfield from the corresponding resonance in the di(monocyclohexylamide) and it would be tempting to assign a *cis* structure to the molecule. However, the benzyl derivative $[PhP(S)NCH_2Ph]_2$ shows a downfield shift of only 0.16 p.p.m. and this latter molecule has been assigned a *trans* structure on the basis of its α-CH_2 proton spectrum. Hence, very small downfield shifts in the *ortho*-phenyl protons resonance in the dimer compared with the di(monoalkylamide) may not always signal a *cis* structure.

The assignment of a *trans* structure to $[PhP(S)NMe]_2$ can only be made on the basis of phenyl signal shifts as there are no α-CH_2 groups present. However, a previous *X*-ray analysis confirms the *trans* structure of this compound.[3]

The proton n.m.r. resonances for terminal methyl groups appear as triplets in all of the compounds (**1**) (except when R = Me, Pr^i, or Bu^i) due to the coupling between the methyl protons and the protons of an adjacent CH_2 group. The methyl proton signals when R = Pr^i or Bu^i occur as two doublets (coupling to an adjacent CH proton together with non-equivalence of the terminal methyl groups).

Jefferson *et al.*[29] observed that the methyl protons within the isopropyl group of $(ClPNPr^i)_2$ will be non-equivalent in the *trans* isomer (centre of symmetry) and equivalent in the *cis* isomer which has a plane of symmetry giving methyl group equivalence. Since more than one methyl proton signal is observed in the compounds (**1**) when R = Pr^i and Bu^i, a *trans* structure has been assigned. In fact, this multiple proton n.m.r. line-shape (together with a similar non-equivalence in the carbon-13 spectrum) observed for the isopropyl derivative confirms the *trans* structure deduced from *ortho*-phenyl proton chemical shifts.

A plot of phosphorus-31 n.m.r. chemical shifts for compounds (**1**) against those of the corresponding monomeric precursors, $PhP(S)(NHR)_2$ gives a straight line relationship (Figure 3) for R = Me, CH_2Ph, and α-branched alkyl groups, in which the plots for R = Bu^s and *cis*-Et appear to be anomalous. Extrapolation of these points to the 'di(monoalkylamide) axis' gives the predicted position showing that the anomaly (*i.e.* the deviation from the line for α-branched alkyl groups) is probably due to the chemical shift of the cyclic dimer. There appears to be another, less pronounced, curve (of opposite sign) for β-branched alkyl groups; R = Bu^i is the anomalous one here. In analogous plots for $P(S)(NHR)_3$ (R = alkyl) and the corresponding cyclodi-λ^5-phosphazane, $[(RNH)P(S)NR]_2$, the position of the R = Bu^i derivative is also anomalous.[25] Similarly, the plot of δ(^{31}P) for $MeP(S)(NHR)_2$ against δ(^{31}P) for $[MeP(S)NR]_2$ shows anomalous behaviour when R = Bu^i or when R = Bu^s.[30] Possible reasons for this anomaly have been discussed previously,[30] but there is still no clear

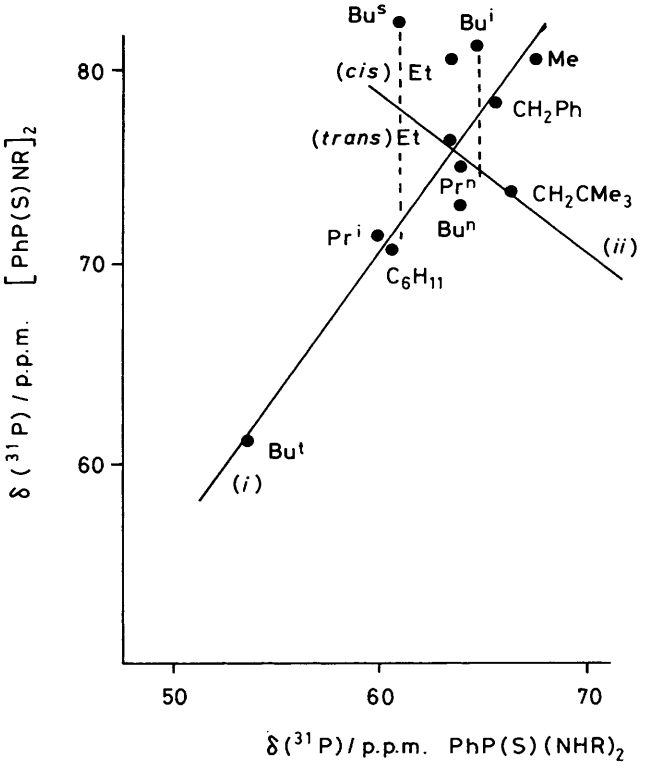


Figure 3. Plot of $\delta(^{31}P)$ for $PhP(S)(NHR)_2$ against $\delta(^{31}P)$ for $[PhP(S)NR]_2$ (R = alkyl): (*i*) = α-branched alkyl groups, (*ii*) = β-branched alkyl groups

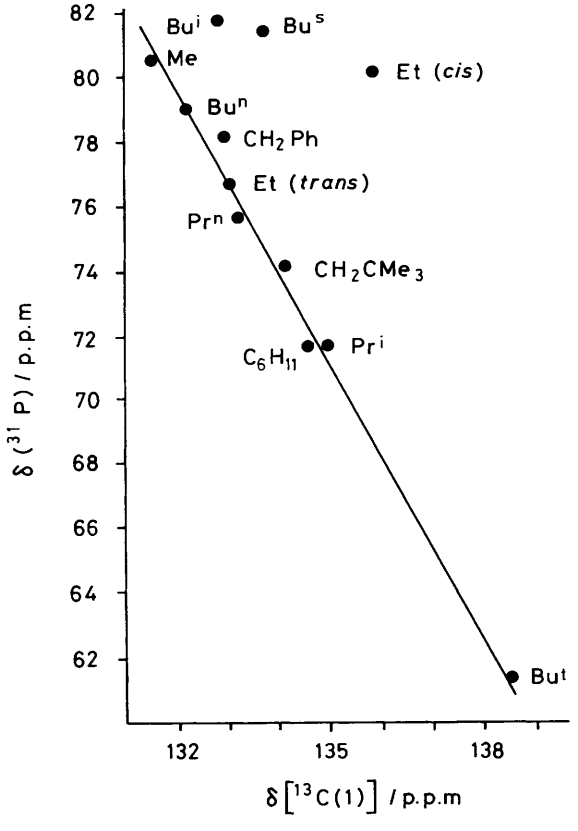


Figure 4. Plot of $\delta(^{31}P)$ against $\delta[^{13}C(1)]$ for $[PhP(S)NR]_2$

explanation for this behaviour. There are at present insufficient data to decide whether a third curve will apply to γ-substituted alkyl groups.

When $\delta(^{31}P)$ chemical shifts are plotted against $\delta[^{13}C(1)]$ for compounds (**1**), a linear relationship is seen (Figure 4). All of the compounds (except for R = Bu^s, Bu^i, and *cis*-Et; *cf.* Figure 3) lie on or near to a negative gradient straight line where phosphorus shielding increases as C(1) shielding decreases, and *vice versa.*

Inspection of the carbon-13 n.m.r. data in Table 2 shows that successive substitution of hydrogen by methyl groups decreases the shielding of the α-carbon atom of the alkyl chain by approximately equal amounts. For example, the shieldings of the α-carbon atoms in compounds (**1**) (R = Me, Et, Pr^i, or Bu^t) are 24.64, 35.08, 45.96, and 54.71 p.p.m. respectively. It is apparent that as the three hydrogen atoms of the methyl are sequentially replaced, the structural change CH to CMe causes a deshielding of *ca.* 10 p.p.m. This phenomenon has been termed the α-effect and it appears to be general for many classes of compounds 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.* CCH becomes CCMe. The β-effect is of smaller magnitude than the α-effect and is *ca.* 6 p.p.m. This is similar to the data obtained from phenylphosphonothioic di(monoalkylamides), $PhP(S)(NHR)_2$,[18] but is in contrast to the data for saturated hydrocarbons where both the α- and β-effects are approximately equal at 9 p.p.m.[31,32]

The assignment of carbon-13 n.m.r. chemical shifts to specific carbon nuclei in molecules which contain phenyl groups has been discussed in detail elsewhere.[18]

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),[33] where S_3

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

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

and S_4 are the carbon-13 n.m.r. chemical shifts in p.p.m. relative to the chemical shift for benzene (128.7 p.p.m.[34]) for the C(3) and C(4) carbon nuclei respectively. The values obtained are shown in Table 3.

The magnitude of the resonance parameters, σ_R^0 (0.16—0.25) for all of the substituents are similar or greater than those for nitro or acetyl groups,[10] suggesting that these phosphorus-containing substituents are mesomerically strongly electron-withdrawing groups. It should be noted that the cyclodi-λ^5-phosphazane (**1**) derivatives are more strongly withdrawing than the corresponding monomeric precursor derivatives.[18] This provides yet more evidence for the interaction between the delocalised electrons of the aryl system with the $(P–N)_2$ ring system in the dimer molecules; this interaction is not available in the monomeric precursor compounds. These resonance effects are most likely to be due to p_π–d_π interactions between the quinquevalent phosphorus atom and the aromatic system.

Table 3. Calculated σ_I and σ_R^0 constants for the phosphorus-containing substituent, P(S)N(R)P(S)(Ph)NR, attached to a phenyl ring

R	σ_I	σ_R^0	R	σ_I	σ_R^0
Me	0.19	0.18	Bu^i	0.10	0.19
Et (*trans*)	0.12	0.19	Bu^s	−0.05	0.23
Et (*cis*)	0.11	0.18	Bu^t	−0.18	0.25
Pr^n	0.12	0.19	Neopentyl	−0.05	0.22
Pr^i	−0.09	0.21	CH_2Ph	0.25	0.16
Bu^n	0.10	0.19	Cyclohexyl	−0.13	0.18

Table 4. Characterisation details for $[PhP(S)NR]_2$ (1)

R	Yield (%)	M.p./°C Obs.	M.p./°C Lit.	*M* Calc.[a]	*M* Obs.	Analysis (%) Found C	H	N	P	Calc. C	H	N	P	Yield of $PhP(S)(NHR)_2$ also isolated (g)
Me	14	216	216—217[b]	338	338	49.2	4.7	8.2	18.8	49.7	4.8	8.3	18.3	5.3
Et	18	142	142[c]	366	366	52.1	5.6	7.7	16.7	52.4	5.5	7.7	16.9	6.2
Pr^n	6	135	137[d]	394	394	54.8	6.6	6.9	15.8	54.8	6.1	7.1	15.7	9.8
Pr^i	13	128		422	422	54.8	6.4	7.2	15.6	54.8	6.1	7.1	15.7	9.2
Bu^n	10	96	94—96[d]	422	422	56.9	6.7	6.6	14.7	56.8	6.7	6.6	14.7	22.6
Bu^i	42	196	195[d]	422	422	56.6	6.9	6.9	14.7	56.8	6.7	6.6	14.7	12.2
Bu^s	8	201		422	422	56.6	6.6	6.8	14.2	56.8	6.7	6.6	14.7	3.7
Bu^t	2	263[e]		422	422	56.8	6.4	6.7	14.4	56.8	6.7	6.6	14.7	12.6
Neopentyl	32	274[e]		450	450	58.6	6.9	6.9	13.6	58.6	7.2	6.2	13.8	6.9
CH_2Ph	37	214	214[b]	490	490	63.7	4.9	5.8	12.8	63.7	4.9	5.7	12.6	12.7
Cyclohexyl	35	249		474	474	60.6	6.6	5.8	12.9	60.7	6.8	5.9	13.1	16.6
Et (*cis*)	*f*	133	134[g]	366	366	52.6	5.7	7.4	16.7	52.4	5.5	7.7	16.9	

[a] Based on the most abundant isotope. [b] Ref. 2. [c] Ref. 24. [d] Ref. 6. [e] Sublimes. [f] None observed in room temperature reaction; higher reaction temperatures are required for its synthesis. [g] C. P. Thakur, Ph.D. Thesis, University of London, 1970.

Comparing the inductive effect constant, σ_I, for these substituents with other similar series of substituents, shows that the electron-attracting properties of the substituents decrease in the order:[18,28] $P(S)Cl_2 > \overline{P(S)N(R)P(S)(Ph)NR} > P(S)(NHR)_2 > H > P(S)Ph_2 > P(S)Ph(NHR)$. Also, within any of these series of substituents there is a trend to lower σ_I values with increased α-branching of the alkyl substituent, R.

Experimental

The alkylamine NH_2R (R = Me, Et, Pr^n, Pr^i, Bu^n, Bu^i, Bu^s, Bu^t, neopentyl, CH_2Ph, or cyclohexyl) (0.30 mol) was dissolved in acetonitrile (100 cm^3) and added dropwise over 1—3 h to a stirred ice–salt-cooled solution of phenylphosphonothioic dichloride, $PhP(S)Cl_2$, containing 0.10 mol (21.2 g) in 200 cm^3 of the same solvent. The mixture was stirred at room temperature for a period of time varying from 1 to 24 h. Precipitated alkylamine hydrochloride, RNH_3Cl, was then filtered off from the mixture under a partial vacuum and the filtrate reduced to one half of its volume by rotary evaporator and left to stand. Further precipitated alkylamine hydrochloride was removed by filtration and the remaining solvent in the filtrate removed by rotary evaporation. The resulting product (either a solid or a viscous oil) was extracted with boiling benzene, filtered hot and the filtrate left to stand. The cyclodi-λ^5-phosphazane, $[PhP(S)NR]_2$, was crystallised from the solution first and was filtered off. On further standing the phenylphosphonothioic di(monoalkylamide), $PhP(S)(NHR)_2$, crystallised from the filtrate and was removed by filtration. The compounds (1) were recrystallised to constant melting point and all compounds showed satisfactory microanalysis and molecular mass determinations (VG 7070 mass spectrometer) (Table 4) before n.m.r. spectra were recorded.

Phosphorus-31 n.m.r. spectra were recorded using a JEOL JNM FX60 Fourier-transform spectrometer operating at 24.15 MHz and using 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.

Carbon-13 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 decoupled conditions, using *ca.* 0.5 cm^3 solutions in deuteriated chloroform (for locking). ^{13}C N.m.r. chemical shifts were measured relative to $SiMe_4$ (0 p.p.m.) as the internal reference.

Proton n.m.r. spectra were recorded at 199.5 MHz on a JEOL JNM FX 200 spectrometer. Samples were dissolved in deuteriated chloroform and $SiMe_4$ was used as the internal reference.

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