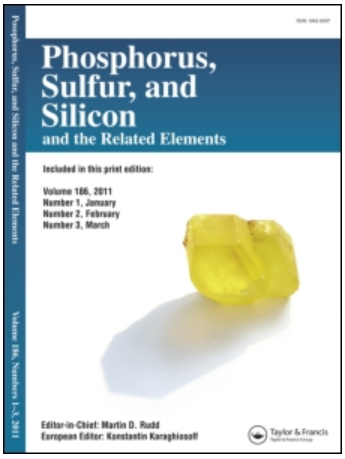

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SYNTHETIC, N.M.R. SPECTROSCOPIC AND X-RAY CRYSTALLOGRAPHIC INVESTIGATIONS ON THE PRODUCTS OF THE REACTIONS OF PHENYL (METHYL) PHOSPHONOTHIOIC DICHLORIDE AND THIOPHOSPHORYL CHLORIDE AND $PSCL_3$ WITH PRIMARY AMINES

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The syntheses in solution of (i) 2,4-dialkylamino-, (ii) 2,4-dimethyl-, and (iii) 2,4-diphenyl-2,4-dithiocyclodiphosph(V)azanes, $[R'P(S)NR]_2$ (R' = NHR, Ph, or Me; R = alkyl), derived from thiophosphoryl trichloride, methylphosphonothioic and phenylphosphonothioic dichlorides and primary alkylamines are described. N.m.r. spectroscopic properties for these cyclodiphosph(V)azanes and their monomeric precursors, $R'P(S)(NHR)_2$ (R' = NHR, Ph, or Me; R = alkyl), are presented and structural inferences are drawn from this data. The X-ray crystal structure of $[PhP(S)NBu^i]_2$ is reported.

INTRODUCTION

We have reported[1] on the syntheses, n.m.r. spectroscopic properties, and structures of phenylphosphonothioic di(monoalkylamides), $PhP(S)(NHR)_2$, and 1,3-dialkyl-2,4-diphenyl-2,4-dithiocyclodiphosph(V)azanes, $[PhP(S)NR]_2$. We have shown a relationship between (i) $\delta^{31}P$ of the di(monoalkylamides) and $\delta^{31}P$ of the corresponding cyclic dimers, and (ii) $\delta^{31}P$ and $\delta^{13}C$-1 for both the di(monoalkylamides) and the cyclic dimers (C-1 is the ipso carbon atom of the phenyl group attached to the phosphorus atom). Further investigations have been carried out on similar compounds derived from methylphosphonothioic dichloride, $MeP(S)Cl_2$, and thiophosphoryl chloride, $P(S)Cl_3$, and the data obtained from these three systems are compared.

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EXPERIMENTAL

The reaction of methylphosphonothioic dichloride, $MeP(S)Cl_2$, with alkylamines, NH_2R (R = Me, Et, Pr^i, Bu^i, Bu^s, Bu^t), in polar non-aqueous solvents. at room temperature yields methylphosphonothioic di(monoalkylamides), $MeP(S)(NHR)_2$, and 1,3-dialkyl-2,4-dimethyl-2,4-dithiocyclodiphosph(V)azanes, $[MeP(S)NR]_2$.

Monitoring the reaction of methylphenylphosphonothioic dichloride and isopropylamine by ^{31}P spectroscopy, at room temperature, only signals due to the starting material, $MeP(S)Cl_2$, the di(monoalkylamide), $MeP(S)(NHPr^i)_2$ and the cyclodiphosph(V(azane, $[MeP(S)NPr^i]_2$, were observed.

The reaction proceeds very quickly under a variety of concentration conditions. At lower concentrations of amine, dimeric cyclodiphosph(V)azanes predominate, whilst at higher amine concentration the di(monoalkylamide) is the predominant reaction product. It was found that the optimum ratio of methylphosphonothioic dichloride to isopropylamine is 1: 1.5 to obtain the highest yield of cyclodiphosph(V)azane.

Similarly, the reaction of thiophosphoryl chloride, $P(S)Cl_3$, with alkylamines, NH_2R (R = Me, Et, Pr^i, Bu^i, Bu^s, Bu^t, Hex^c, CH_2Ph), gives thiophosphoric tri(monoamides), $P(S)(NHR)_3$, and 1,3-dialkyl-2,4-dialkylamino-2,4-dithiocyclodiphosph(V)azanes, $[(RNH)P(S)NR]_2$, when boiled in acetonitrile for 2 to 6 hours under reflux conditions.

Each isolated compound had a satisfactory elemental analysis and mass spectrometric molecular mass. The cyclodiphosph(V)azanes obtained in this way are isomerically pure (t.l.c. and n.m.r. evidence) and *trans*-structures have been assigned.[2] (Some data for the cyclic derivatives of methylphosphonothioic dichloride are derived from measurements on reaction mixtures).

RESULTS AND DISCUSSION

Phosphorus-31 n.m.r. chemical shifts for the compounds $P(S)(NHR)_3$, $PhP(S)(NHR)_2$, $MeP(S)(NHR)_2$, $[(RNH)P(S)NR]_2$, $[PhP(S)NR]_2$, and $[MeP(S)NR]_2$ are shown in Table I. ^{31}P n.m.r. spectra were recorded using a F.T. spectrometer operating at 24.15 MHz and using 0.05 M solutions in chloroform with a deuterated

TABLE I

^{31}P N.m.r. Chemical Shift Data for $P(S)(NHR)_3$, $PhP(S)(NHR)_2$, $MeP(S)(NHR)_2$, $[(RNH)P(S)NR]_2$, $[PhP(S)NR]_2$, and $[MeP(S)NR]_2$. [Ref: 85% H_3PO_4; solvent, $CDCl_3$; 0.05 M solutions; downfield shifts positive; field strength, 24.15 MHz]

R =	Me	Et	Pr^i	Bu^i	Bu^s	Bu^t	Hex^c	CH_2PH
$P(S)(NHR)_3$	68.9	62.8	58.6	64.5	59.7	60.4	59.1	64.8
$[(RNH)P(S)NR]_2$	59.4	52.6	48.9	59.9	48.4	49.6	47.3	55.7
$PhP(S)(NHR)_2$	68.1	64.0	60.4	64.8	60.9	54.0	61.0	65.8
$[PhP(S)NR]_2$	80.1	76.3	71.5	81.9	81.8	61.2	71.4	78.2
$MeP(S)(NHR)_2$	69.3	63.9	60.1	65.7	66.9	53.2		
$[MeP(S)NR]_2$	78.6	79.6	80.7	84.3	84.1	84.6		

solvent as an external lock (8 mm tube in 10 mm). The shifts are measured relative to 85% H_3PO_4 (0 p.p.m.) and reported on the same scale in p.p.m.

A plot of ^{31}P n.m.r. chemical shifts for the cyclic dimers against those of the corresponding monomeric precursors is shown in Figure 1.

The ^{31}P n.m.r. chemical shifts of the monoalkylamides of the three series which have common alkyl groups are approximately similar, irrespective of the parent phosphorus chloride from which the amide is derived, [with the exception of $P(S)(NHBu^t)_3$]. All of these compounds contain a P=S bond, and all have an approximately tetrahedral shape in which the position of the atoms or groups attached to the phosphorus atom are not significantly constrained. We deduce that the electronic environments of the phosphorus nuclei in these compounds are likely to be similar as they give rise to consistent shielding and a small range of chemical shifts.

Major differences of ^{31}P n.m.r. chemical shift are observed for the dimers in each of the series even when they have common alkyl groups. This suggests that the factors which determine the ^{31}P n.m.r. chemical shifts are complex and not dependent simply upon the arrangement of atoms adjacent to the phosphorus atom but

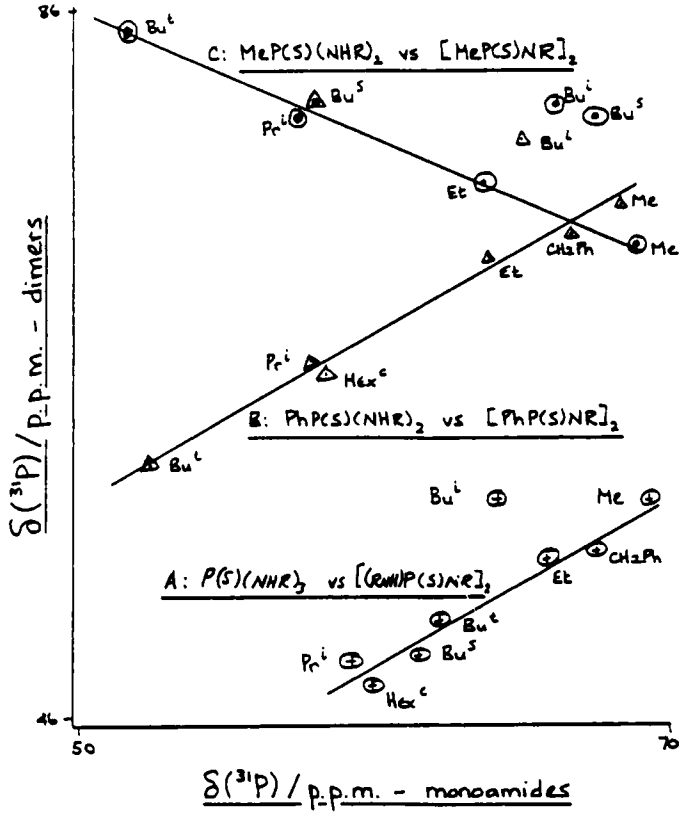

FIGURE 1 Plot of δ ^{31}P-dimers against δ ^{31}P-monoalkylamides for A: $[(RNH)P(S)NR]_2$ and $P(S)(NHR)_3$; B: $[PhP(S)NR]_2$ and $PhP(S)(NHR)_2$; C: $[MeP(S)NR]_2$ and $MeP(S)(NHR)_2$.

on stereo-electronic effects in the molecule as a whole which are more significant than in the corresponding monomeric compounds. We have demonstrated a similar effect in *N*-arylcyclodiphosph(V)azanes.[3]

It should be noted that the electron delocalisation within the four-membered ring system may have a direct influence on the deshielding of the phosphorus nuclei of the cyclodiphosph(V)azanes. This effect would not be observed in the corresponding di(monoalkylamides).

It is not out of place to mention that such $n. \rightarrow \Pi^*$ transitions have been observed in the ultraviolet spectra of many dimeric cyclodiphosph(V)azanes.[4,5]

The positions of the atoms attached to phosphorus in the cyclic dimers are constrained by the planarity of the $(P—N)_2$ ring (*trans*-structures) and by the spatial arrangement of the exocyclic atoms and groups. For example, in trans-$[PhP(S)NEt]_2$, the phenyl group adopts a position in which it eclipses the P=S bond.[6]

Curves A and B (Figure 1) are nearly parallel and describe similar changes in the shielding of the phosphorus nuclei in both the amides and the dimers. In these cases, the amount of deshielding appears to be directly related to the number of hydrogen atoms attached to the α-carbon atom of the alkyl group (i.e. the carbon atom attached to the nitrogen atom). For the derivatives of $MeP(S)Cl_2$ (Curve C) the change in the chemical shifts of the cyclic dimers is less pronounced and is opposite in sense to the changes for the alkylamino-P (Curve A) and phenyl-P (Curve B) derivatives. In the latter two series, the atom attached to phosphorus is sp^2 hybridised, and planar (or near planar) for nitrogen, with probable p_π–d_π contributions to the bond to the phosphorus atom due to interaction with vacant *d*-orbitals on the phosphorus. When a methyl group is attached to phosphorus, the methyl carbon is sp^3 hybridised and its bonds are directed tetrahedrally.

It should be noted that the ^{31}P n.m.r. chemical shift for the iso-butyl dimer derivative is anomalous in all three series. The crystal structure of $[PhP(S)NBu^i]_2$ has been investigated to determine whether conformational effects are responsible for the anomaly. Initial considerations suggest that there are marked similarities in the structural and dimensional parameters of this molecule when compared with previously determined structures e.g. *trans*-$[PhP(S)NEt]_2$[6]. Molecular diagrams for $[PhP(S)NBu^i]_2$ are shown at Figure 2. More detailed investigations into this phenomenon are continuing.

Further, the sec-butyl dimer derivatives of $PhP(S)Cl_2$ and $MeP(S)Cl_2$ are also anomalous whilst $[(Bu^sNH)P(S)NBu^s]_2$ lies on the predicted position on the curve for α-branched alkyl groups.

We have reported[1] a straight line relationship between δ ^{31}P and δ ^{13}C-1 n.m.r. chemical shifts for both $PhP(S)(NHR)_2$ and $[PhP(S)NR]_2$. A similar relationship has also been observed for $MeP(S)(NHR)_2$ in which the correlation between δ ^{31}P and δ ^{13}C showed a straight line relationship. These indicate that the inductive effect of the alkyl groups attached to nitrogen is one of the controlling factors in the electron flow towards the phosphorus atom. These curves (Figure 3) again reflect the regularity of the behaviour of the di(monoalkylamide) derivatives and confirm that derivations from regularity only occur in some cyclic dimers. These results will be discussed in more detail elsewhere.

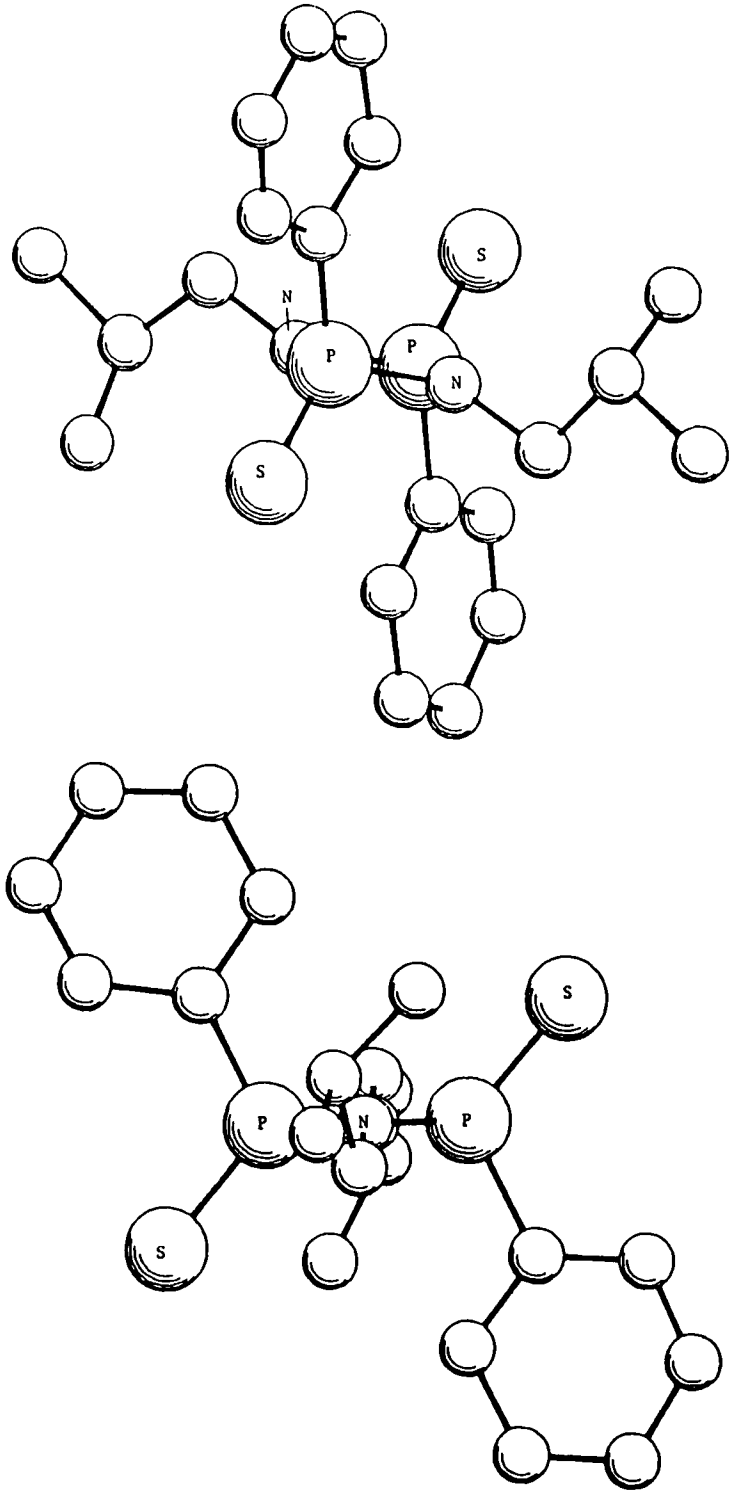

FIGURE 2 Molecular diagrams of $[PhP(S)NBu^i]_2$.

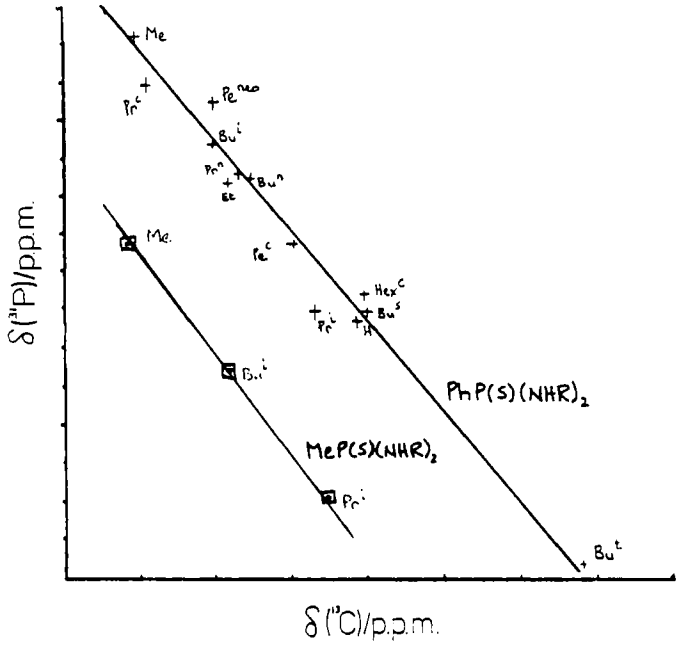

FIGURE 3 Plot of δ ^{31}P against δ ^{13}C for (i) PhP(S)(NHR)$_2$, and (ii) MeP(S)(NHR)$_2$.

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