The First Hydrides of a Phosphorus Sulfide Cage: Nuclear Magnetic Resonance Evidence for α-Tetraphosphorus Trisulfide Hydride Compounds

Bruce W. Tattershall* and Nigel L. Kendall

Department of Chemistry, The University of Newcastle, Newcastle upon Tyne NE1 7RU, UK

The hydrides $\alpha\text{-}P_4S_4(H)R$ (R = H, I, NMePh or SPh) have been prepared in solution by the reaction of $\alpha\text{-}P_4S_3I_2$ or of the corresponding $\alpha\text{-}P_4S_3(I)R$ with $SnBu^n_3H$, and identified by ^{31}P NMR spectroscopy. The compounds were unstable and not isolated. *Ab initio* molecular orbital calculations of geometry have been carried out for $\alpha\text{-}P_4S_3H_2$, $\alpha\text{-}P_4S_3(NMe_2)_2$ and $\alpha\text{-}P_4S_3H(NMe_2)$.

The cage molecule $\alpha\text{-}P_4S_3I_2$ is a useful starting material for substitution reactions of halide, pseudohalide, or similar ligands, at phosphorus,[1,2] leading to the symmetric ($R^1 = R^2$) or unsymmetric ($R^1 \neq R^2$) compounds $\alpha\text{-}P_4S_3R^1R^2$ 1. The possibility of attaching a hydrogen ligand to the $\alpha\text{-}P_4S_3$ cage is of chemical interest, as well as offering an insight into the steric influence of substituents on the cage NMR parameters. Hydrides of homonuclear polyphosphorus cages are known, but tend to be insoluble;[3] in particular, P_7H_3, with a structure like P_4S_3 but with sulfur replaced by PH, was insoluble in all of a wide range of solvents tried. Its ^{31}P NMR spectrum could be measured only as the compound was being formed, and before complete precipitation had occurred.[4] As far as we are aware, no corresponding phosphorus sulfide hydrides have been reported. Syntheses starting from $\alpha\text{-}P_4S_3I_2$ have until now involved substituents more electronegative than phosphorus, although a group of unstable compounds containing the PPh_2 ligand has been studied.[5] While hydrogen is weakly protonic in phosphine, we considered the use of a hydride-transfer reagent for reduction of $\alpha\text{-}P_4S_3I_2$ to $\alpha\text{-}P_4S_3H_2$, although there was the possibility that sulfide ligands might be replaced, with breakdown of the cage structure, in addition to the replacement of iodide. Ionic reagents, for example tetrahydroborate, raise problems of insolubility in solvents unreactive towards $\alpha\text{-}P_4S_3I_2$, so we have employed $SnBu^n_3H$ in solution in toluene, in which $\alpha\text{-}P_4S_3I_2$ has a small but useful solubility.

We now report that the new compounds $\alpha\text{-}P_4S_3R^1R^2$ 1 ($R^1 = H$; $R^2 = H$, I, NMePh or SPh) can be prepared in this way and identified in solution, without isolation, by ^{31}P NMR spectroscopy. Geometric constraints of the bicyclic (or *nido*-cage) structures of $\alpha\text{-}P_4S_3$ compounds cause the values of the six P–P endocyclic NMR coupling constants to fall into well defined ranges, and to change systematically with exocyclic substitution. Not only does the observation of such couplings in its ^{31}P NMR spectrum allow a new compound to be assigned the $\alpha\text{-}P_4S_3$ structure, but a series of new compounds $\alpha\text{-}P_4S_3R^1R^2$ can be established containing the same new ligand R^1 and particular previously investigated ligands R^2. General relationships have been found to hold, for endocyclic coupling constants and for ^{31}P chemical shifts, between values for these parameters in the symmetric compounds $\alpha\text{-}P_4S_3R^1_2$ and $\alpha\text{-}P_4S_3R^2_2$, and those in the corresponding unsymmetric compounds $\alpha\text{-}P_4S_3R^1R^2$.[2] When the ligand R^1 additionally contains a NMR-active nucleus showing couplings to the cage phosphorus atoms, as in the present case, where $R^1 = H$, ^{31}P NMR spectroscopy provides very strong evidence for the identity of the compounds, even though their stability is such that they may be observed only along with other components in solution.

Results and Discussion

Addition of a solution of 2 molar equivalents of $SnBu^n_3H$ to a suspension of $\alpha\text{-}P_4S_3I_2$ in toluene gave a pale yellow solution and a mid-yellow precipitate. The ^{31}P NMR spectrum of the solution showed that no $\alpha\text{-}P_4S_3I_2$ remained. There was a low concentration of $\alpha\text{-}P_4S_3H_2$ (3% yield, see below), a comparable amount of PH_3 (although some would have been lost to the gas phase), and traces of P_2H_4 and of several unidentified by-products. When toluene was removed by pumping on the reaction mixture at 15 °C, and the residue stirred with the same quantity of CS_2, a similar concentration of $\alpha\text{-}P_4S_3H_2$ was obtained. This showed that the precipitate from the reaction contained little $\alpha\text{-}P_4S_3H_2$, since it is unlikely that the compound would have a similar low solubility in both solvents. Probably the solid was a polymeric product, as is frequently encountered in $\alpha\text{-}P_4S_3$ chemistry, and accounted for most of the $\alpha\text{-}P_4S_3I_2$ taken. The compound $\alpha\text{-}P_4S_3H_2$ disappeared completely from solution in CS_2 over 17 h at 0 °C, after which ^{31}P NMR spectroscopy showed only traces of P_4S_3 and of $\alpha\text{-}P_4S_4$, while after the same time in toluene, a good ^{31}P NMR spectrum of $\alpha\text{-}P_4S_3H_2$ still could be obtained.

Use of a 1:1 molar ratio of $SnBu^n_3H$ and $\alpha\text{-}P_4S_3I_2$ (in suspension in toluene) gave a significantly higher concentration of $\alpha\text{-}P_4S_3(H)I$ (10–30% yield), along with unreacted $\alpha\text{-}P_4S_3I_2$ and traces of $\alpha\text{-}P_4S_3H_2$ and P_4S_3. By then changing the solvent as before, a solution of $\alpha\text{-}P_4S_3(H)I$ in CS_2 was obtained of sufficient concentration and stability for the expected ^1H NMR multiplet to be observed.

Possible causes of low yields of the hydrides were polymer-chain growth by intermolecular elimination of HI between $\alpha\text{-}P_4S_3(H)I$ and the existing polymer, and the use of a two-phase system necessitated by the low solubility of $\alpha\text{-}P_4S_3I_2$ in solvents inert to $SnBu^n_3H$. We sought to avoid these by use of an $\alpha\text{-}P_4S_3$ compound in which one functional site was protected by a solubilising group. A solution in toluene, containing $\alpha\text{-}P_4S_3(NMePh)_2$, $\alpha\text{-}P_4S_3I(NMePh)$ and $\alpha\text{-}P_4S_3I_2$ in molar ratio 16:64:20,[2] was treated with a deficiency of $SnBu^n_3H$. The $\alpha\text{-}P_4S_3I_2$ reacted completely and the $\alpha\text{-}P_4S_3I(NMePh)$ partially, giving a solution containing $\alpha\text{-}P_4S_3(NMePh)_2$, $\alpha\text{-}P_4S_3I(NMePh)$, $\alpha\text{-}P_4S_3H(NMePh)$, $\alpha\text{-}P_4S_3(H)I$ and $\alpha\text{-}P_4S_3H_2$ in molar ratio 37:32:22:7:2. After 72 h at 20 °C, all three phosphorus hydride components had decomposed completely.

Protection by a PhS group was less convenient, since $\alpha\text{-}P_4S_3I(SPh)$ was formed only in low yield on sequential addition of 1 molar equivalent of each of PhSH and NEt_3 to a suspension of $\alpha\text{-}P_4S_3I_2$, the principal toluene-soluble product being $\alpha\text{-}P_4S_3(SPh)_2$. Subsequent addition of $SnBu^n_3H$ therefore gave a solution containing mainly $\alpha\text{-}P_4S_3(SPh)_2$, with $\alpha\text{-}P_4S_3H(SPh)$ as one of three minor products. Another of these

was an unsymmetrical compound with ^{31}P NMR parameters [δ_1 127.38, δ_2 120.54, δ_3 111.11, δ_4 105.72; J_{12} $-5.61(7)$, J_{13} $-278.38(7)$, J_{14} 22.6(1), J_{23} 19.17(6), J_{24} $-282.14(9)$, J_{34} 60.40(7) Hz; no change on ^1H decoupling] very similar to those of α-$P_4S_3(SPh)_2$,[6] and was postulated to be α-$P_4S_3(SSPh)(SPh)$. Successive ^{31}P NMR accumulations started 16 and 24 h after the first, showed α-$P_4S_3H(SPh)$ to be disappearing slowly with time, relative to the other products.

Assignment of NMR Spectra.—Phosphorus-31 NMR spectra were obtained with and without inverse-gated ^1H decoupling. The decoupled spectra were analysed by hand as AA'MM' (α-$P_4S_3H_2$; Scheme 1, II) or first-order spin systems, the hand analysis being followed in each case by iterative fitting using NUMARIT.[7] Phosphorus atoms carrying hydride ligands were identified through causing large additional splittings in the proton-coupled spectra, the analysis and fitting of which followed immediately for the unsymmetric hydride compounds. The results are given in Table 1.

The multiplet due to P_D (Scheme 1, I) in α-$P_4S_3H(NMePh)$ was broadened due to $^3J(H_3C-N-P_D)$ couplings as well as by ^{14}N scalar coupling relaxation, and was not fitted for the
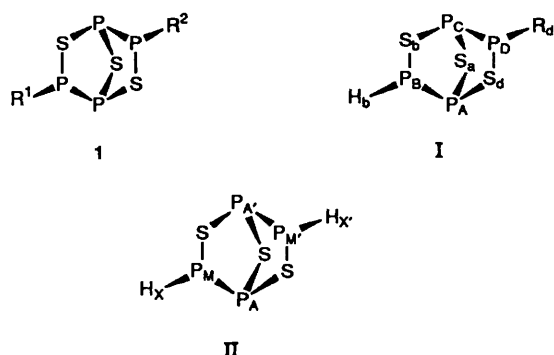
Scheme 1 General structure of α-P_4S_3 compounds α-$P_4S_3R^1R^2$ **1**, labelling of nuclei in α-P_4S_3 hydrides α-$P_4S_3(H)R$ (**I**) and NMR spin system for α-$P_4S_3H_2$ (**II**)

proton-coupled spectrum; all other 48 ^{31}P transitions were included, so only $^4J(P_DH_b)$ was unobtainable. Splittings corresponding to $^3J(P_CH_b)$ were not resolved in the ^{31}P NMR spectra of any of the unsymmetric compounds, since broadening caused by use of a precision capillary containing $(CD_3)_2CO$ for locking was sufficient to obscure this splitting. Only for α-$P_4S_3(H)I$ was a ^1H NMR spectrum obtained; as this could be measured without the use of a locking capillary, peaks were narrower and the $^3J(P_CH_b)$ splitting could be measured.

Assignment and fitting of the proton-coupled ^{31}P NMR spectrum of α-$P_4S_3H_2$ yielded P–P couplings identical to those found from the ^1H-decoupled spectrum, to within the precision of the fit, demonstrating the correctness of the assignment. Starting from the assumption of negative signs for $^1J(P–P)$ coupling constants, the signs of other coupling constants were found in the assignment and fitting procedure. They were assumed to be the same, by analogy, in the unsymmetric compounds.

Table 2, which is in the format adopted for previously reported unsymmetric α-P_4S_3 compounds,[2] shows that endocyclic NMR parameters for α-$P_4S_3(H)R$ (R = I, NMePh or SPh) are related to those for α-$P_4S_3H_2$ and the corresponding α-$P_4S_3R_2$ by the rules developed already.[2] This confirms well the identification of the new compounds.

Theoretical Calculations of Molecular Geometries.—By analysis of the ^{31}P NMR spectra of α-$P_4S_3I_2$ and its analogues in which sulfur atoms are progressively replaced by selenium,[8] it was possible to show dependencies of $^2J(PP)$ couplings and of phosphorus chemical shifts on bond angles in the α-P_4E_3 cage, since some prediction could be made of how these would change. In order to find out whether similar distortions in bond angles at phosphorus or sulfur can explain changes in NMR parameters for compounds α-$P_4S_3R^1R^2$, when only the identities of the ligands R^1 and R^2 are changed, it would be necessary to have some detailed structural measurements. Amongst such compounds a crystal-structure determination has been performed only for α-$P_4S_3I_2$,[9] since it has not yet been possible to obtain crystals of any others. We have now, therefore, calculated optimum geometries for α-$P_4S_3H_2$,

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Table 1 NMR parameters for hydrides α-$P_4S_3(H)R$

R	H	I	I	NMePh	SPh
Solvent	PhMe	PhMe	CS₂	PhMe	PhMe

(a) Coupling constants (Hz)[a]

(i) $^{31}P-^{31}P$

$^2J(P_AP_C)$	72.5(2)	74.84(8)	74.78(3)	60.27(3)	67.67(4)
$^1J(P_AP_B)$	$-253.1(2)$	$-246.42(8)$	$-245.68(3)$	$-251.61(3)$	$-247.47(3)$
$^1J(P_CP_D)$		$-249.64(9)$	$-247.58(3)$	$-326.21(3)$	$-287.60(3)$
$^2J(P_AP_D)$	38.4(1)	29.59(9)	29.84(3)	32.68(3)	32.53(3)
$^2J(P_BP_C)$		30.94(8)	30.86(3)	22.45(3)	27.73(3)
$^3J(P_BP_D)$	$-17.5(2)$	$-8.25(8)$	$-8.57(3)$	$-16.75(4)$	$-13.30(3)$

(ii) $^{31}P-^1H$

$^2J(P_AH_b)$	4.4(2)	5.04(7)	4.84(3)	5.31(2)	5.00(8)
$^3J(P_CH_b)$	$-1.0(1)$	-0.04^b	$-1.22(4)$	0.00^b	-0.02^b
$^1J(P_BH_b)$	177.8(2)	182.24(7)	178.99(3)	178.98(2)	180.03(8)
$^4J(P_DH_b)$	4.2(1)	11.12(8)	11.17(3)		7.01(9)

(b) Chemical shifts[c]

$\delta(P_A)$	107.41	123.73	125.57	108.60	109.83
$\delta(P_B)$	31.55	24.17	26.52	18.71	18.46
$\delta(P_C)$		112.11	114.56	77.14	103.35
$\delta(P_D)$		129.83	131.27	136.39	131.88
$\delta(H_b)$			4.45		

[a] Standard deviations (σ) in parentheses; $^{31}P-^{31}P$ coupling constants are from fitting inverse-gated ^1H-decoupled spectra. [b] Unresolved splittings. [c] Phosphorus shifts are from fitting inverse-gated ^1H-decoupled spectra and are uncorrected for solvent diamagnetic susceptibility.

Table 2 Relationships between NMR parameters for unsymmetric compounds α-P$_4$S$_3$(H)R and those for corresponding symmetric compounds α-P$_4$S$_3$H$_2$ and α-P$_4$S$_3$R$_2$

R	I	NMePh	SPh*
(i) Couplings (Hz) influenced similarly by H and R			
$^2J(\text{P}_\text{A}\text{P}_\text{C})(\text{HR})$	74.8	60.3	67.7
Av. $^2J(\text{P}_\text{A}\text{P}_\text{A'})(\text{H}_2, \text{R}_2)$	73.2	60.4	66.2
Difference	+1.6	−0.2	+1.5
$^3J(\text{P}_\text{B}\text{P}_\text{D})(\text{HR})$	−8.3	−16.8	−13.3
Av. $^3J(\text{P}_\text{B}\text{P}_\text{B'})(\text{H}_2, \text{R}_2)$	−3.6	−15.1	−11.8
Difference	−4.6	−1.7	−1.5
(ii) Couplings (Hz) influenced dissimilarly by H and R			
$^2J(\text{P}_\text{A}\text{P}_\text{D})(\text{HR})$	29.6	32.7	32.5
$^2J(\text{P}_\text{B}\text{P}_\text{C})(\text{HR})$	30.9	22.4	27.7
$^2J(\text{P}_\text{A}\text{P}_\text{B'})(\text{H}_2)$	38.4	38.4	38.4
$^2J(\text{P}_\text{A}\text{P}_\text{B'})(\text{R}_2)$	21.6	12.0	21.2
Av. $^2J(\text{P}_\text{A}\text{P}_\text{D})$, $^2J(\text{P}_\text{B}\text{P}_\text{C})(\text{HR})$	30.3	27.6	30.1
Av. $^2J(\text{P}_\text{A}\text{P}_\text{B'})(\text{H}_2, \text{R}_2)$	30.0	25.2	29.8
Difference	+0.3	+2.4	+0.4
$^1J(\text{P}_\text{A}\text{P}_\text{B})(\text{HR}) - {}^1J(\text{P}_\text{A}\text{P}_\text{B})(\text{H}_2)$	+6.7	+1.5	+5.7
$^1J(\text{P}_\text{C}\text{P}_\text{D})(\text{HR}) - {}^1J(\text{P}_\text{A}\text{P}_\text{B})(\text{R}_2)$	−2.8	+4.4	−4.3
Av. $^1J(\text{P}_\text{A}\text{P}_\text{B})$, $^1J(\text{P}_\text{C}\text{P}_\text{D})(\text{HR})$	−248.0	−288.9	−267.5
Av. $^1J(\text{P}_\text{A}\text{P}_\text{B})(\text{H}_2, \text{R}_2)$	−250.0	−291.9	−268.2
Difference	+1.9	+2.9	+0.7
(iii) Chemical shifts of bridgehead phosphorus atoms			
$\delta(\text{P}_\text{A})(\text{HR}) - \delta(\text{P}_\text{A})(\text{H}_2)$	+16.3	+1.2	+2.4
$\delta(\text{P}_\text{C})(\text{HR}) - \delta(\text{P}_\text{A})(\text{R}_2)$	−16.8	−8.0	−3.4
Av. $\delta(\text{P}_\text{A})$, $\delta(\text{P}_\text{C})(\text{HR})$	117.9	92.9	106.6
Av. $\delta(\text{P}_\text{A})(\text{H}_2, \text{R}_2)$	118.2	96.3	107.1
Difference	−0.3	−3.4	−0.5
(iv) Chemical shifts of phosphorus atoms carrying substituents			
$\delta(\text{P}_\text{B})(\text{HR}) - \delta(\text{P}_\text{B})(\text{H}_2)$	−7.4	−12.8	−13.1
$\delta(\text{P}_\text{D})(\text{HR}) - \delta(\text{P}_\text{B})(\text{R}_2)$	+6.9	+1.1	+6.9
Av. $\delta(\text{P}_\text{B})$, $\delta(\text{P}_\text{D})(\text{HR})$	77.0	77.5	75.2
Av. $\delta(\text{P}_\text{B})(\text{H}_2, \text{R}_2)$	77.2	83.4	78.3
Difference	−0.2	−5.8	−3.1

* α-P$_4$S$_3$(SPh)$_2$ in PhMe has $J(\text{P}_\text{A}\text{P}_\text{A'})$ 59.9(3), $J(\text{P}_\text{B}\text{P}_\text{B'})$ −6.1(2), $J(\text{P}_\text{A}\text{P}_\text{B'})$ 21.2(1) and $J(\text{P}_\text{A}\text{P}_\text{B})$ −283.3(2) Hz, $\delta(\text{P}_\text{A})$ 106.72 and $\delta(\text{P}_\text{B})$ 125.02.

α-P$_4$S$_3$H(NMe$_2$) and α-P$_4$S$_3$(NMe$_2$)$_2$ by *ab initio* methods at the RHF/3-21G* level, using GAUSSIAN 92.[10] Amino and hydrido ligands respectively cause the values of several of the ^{31}P NMR parameters of their α-P$_4$S$_3$ compounds to have values at opposite extremes of their known ranges, and thus offer the best opportunity of finding relationships between NMR parameters and geometry. Although it has not been prepared, α-P$_4$S$_3$H(NMe$_2$) was selected for calculation instead of α-P$_4$S$_3$H(NMePh) to shorten the computation time, since it is known that NMe$_2$ and NMePh ligands give rise to similar ^{31}P NMR parameters for α-P$_4$S$_3$ compounds.[2]

The whole geometry of α-P$_4$S$_3$H$_2$ was optimised using a 3-21G* basis set after intermediate optimisation at the STO-3G level. For α-P$_4$S$_3$(NMe$_2$)$_2$, the ligand geometry was optimised at the STO-3G level while the P$_4$S$_3$ cage geometry was fixed at that found for α-P$_4$S$_3$H$_2$, then the cage geometry was optimised at this level with the ligand geometry fixed. Finally, optimisation at the 3-21G* level was undertaken, allowing the variation of geometric parameters defining the cage geometry and angles at nitrogen, although not at carbon. A C_2 symmetry was imposed for both molecules. A starting geometry for α-P$_4$S$_3$H(NMe$_2$) could be guessed from those of the symmetric molecules, and optimisation at first the STO-3G, then the 3-21G* level, was straightforward, using the same constraints on the geometry of the methyl groups. For both NMe$_2$ compounds, the *trans* isomer about the P$_\text{D}$-N bond was selected on the basis of preliminary calculations on simpler molecules.

Bond lengths within the α-P$_4$S$_3$ cage were found to vary little, and bond angles best reflect ligand influence. Selected geometric parameters for the three compounds are compared with those from the crystal-structure determination of α-P$_4$S$_3$I$_2$, in Table 3.

Values of NMR Coupling Constants and Chemical Shifts and their Relationships to Molecular Geometry.—The compound α-P$_4$S$_3$H$_2$ is distinguished by showing (Table 1) the most negative cross-ring coupling $^3J(\text{P}_\text{B}\text{P}_\text{D})$, the largest coupling $^2J(\text{P}_\text{A}\text{P}_\text{D})$ $[= {}^2J(\text{P}_\text{B}\text{P}_\text{C})]$ through a sulfur atom in the six-membered ring, and the least positive chemical shift $\delta(\text{P}_\text{B})$ $[= \delta(\text{P}_\text{D})]$, of any symmetric α-P$_4S_3$ compound so far encountered. The compound α-P$_4$S$_3$(CN)$_2$ resembles it most closely in these properties.[1] Low steric bulk is a property shared by neutral hydride and cyanide ligands, and may help to explain the NMR observations. Both ligands when attached to P$_\text{B}$ should be able to approach the neighbouring non-bonded atoms S$_\text{b}$, P$_\text{A}$ and S$_\text{a}$ (I, Scheme 1) more closely than other ligands investigated.[2]

The α-P$_4$S$_3$ skeleton may be considered as two half rings P$_\text{A}$P$_\text{B}$S$_\text{b}$P$_\text{C}$ and P$_\text{C}$P$_\text{D}$S$_\text{d}$P$_\text{A}$, joined at the hinge P$_\text{A}$S$_\text{a}$P$_\text{C}$. Changes in bond angles can then lead to the following independent distortions: *(a)* change in length of the hinge by alteration of the angle at S$_\text{a}$, along with change in at least one angle in each half ring, so as to change its bite; *(b)* trapezoidal distortion of a half ring, e.g. by a decrease in angle P$_\text{A}$-P$_\text{B}$-S$_\text{b}$ with a concomitant increase in P$_\text{B}$-S$_\text{b}$-P$_\text{C}$; *(c)* change in the book angles, e.g. S$_\text{b}$-P$_\text{C}$-P$_\text{D}$; and *(d)* twisting of the half rings. In a symmetric compound $(\text{R}^1 = \text{R}^2)$ twisting *(d)* can take place without distorsions *(a)* *(b)* or *(c)*, provided that the two half rings twist in a concerted way, e.g. so that all four atoms P$_\text{B}$, S$_\text{b}$, P$_\text{D}$ and S$_\text{d}$ move clockwise when viewed along the bisector of angle P$_\text{A}$-S$_\text{a}$-P$_\text{C}$, while the hinge atoms remain stationary.

In analysing the coupling constants for the mixed α-P$_4$E$_3$I$_2$ cages (E = S or Se),[8] discussion was restricted to distortions of type *(a)*, but distortions of type *(b)* are also possible causes of variations in the coupling constants $^2J(\text{P}_\text{A}\text{P}_\text{D})$ and $^2J(\text{P}_\text{B}\text{P}_\text{C})$ because they also involve changes in angle at the transmitting sulfur atoms S$_\text{d}$ or S$_\text{b}$. The present calculations of geometry show that for the α-P$_4$S$_3$ cage the angle at S$_\text{a}$ is practically constant, and cannot account for the wide variation in values of $^2J(\text{P}_\text{A}\text{P}_\text{C})$. Angles at S$_\text{d}$ or S$_\text{b}$ also vary only slightly, according to the ligand attached at the adjacent P$_\text{D}$ or P$_\text{B}$. They cannot account for variations in $^2J(\text{P}_\text{A}\text{P}_\text{D})$ or $^2J(\text{P}_\text{B}\text{P}_\text{C})$ respectively, and certainly not for the influence of a ligand attached at P$_\text{B}$ upon the value of $^2J(\text{P}_\text{A}\text{P}_\text{D})$, between nuclei on the opposite side of the molecule.[2] Hence, where no endocyclic substitution is being considered, distortions of types *(a)* and *(b)* are ruled out by the near constancy of angles at sulfur. The book angle S$_\text{b}$-P$_\text{C}$-P$_\text{D}$ does change between compounds, but is only 1.6° different between the selected compounds α-P$_4$S$_3$H$_2$ and α-P$_4$S$_3$(NMe$_2$)$_2$: comparison with the value for α-P$_4$S$_3$I$_2$ shows that the variation of this angle in type *(c)* distortions is unlikely to account for variations in $^2J(\text{P}_\text{A}\text{P}_\text{C})$ or in $\delta(\text{P}_\text{C})$.

We conclude, therefore, that ring twisting distortions of type *(d)* are the most important factors in controlling several of the NMR parameters. They may be quantified as the torsion angles P$_\text{A}$-P$_\text{B}$-S$_\text{b}$-P$_\text{C}$ and P$_\text{C}$-P$_\text{D}$-S$_\text{d}$-P$_\text{A}$, which are nearly twice as large in α-P$_4$S$_3$(NMe$_2$)$_2$ as in α-P$_4$S$_3$H$_2$ (Table 3). The extra twisting in α-P$_4$S$_3$(NMe$_2$)$_2$ is such as to decrease the non-bonded distance S$_\text{b}$-S$_\text{d}$ while increasing P$_\text{B}$-P$_\text{D}$ to a lesser extent. In α-P$_4$S$_3$H(NMe$_2$) these torsion angles become more equal, with their average being practically equal to the average of the angles in the two symmetric molecules. This parallels the general relationship between the $^2J(\text{P}_\text{A}\text{P}_\text{D})$ and $^2J(\text{P}_\text{B}\text{P}_\text{C})$ coupling constants (Table 2).

The influence of a ligand on the twisting of the half ring on the opposite side of the molecule results from necessarily concerted twisting of the two half rings, in order nearly to maintain the short non-bonded distances P$_\text{B}$-S$_\text{d}$ and P$_\text{D}$-S$_\text{b}$. The induced twist in the opposite half ring, together with unchanged bond angles, contributes to the crossing over of characteristic values

Table 3 Geometric parameters[a]

	α-P$_4$S$_3$H$_2$[b]	α-P$_4$S$_3$H(NMe$_2$)[b]	α-P$_4$S$_3$(NMe$_2$)$_2$[b]	α-P$_4$S$_3$I$_2$[c]
(*i*) Bond lengths (Å)				
P$_A$–S$_a$	2.106	2.101		
P$_C$–S$_a$		2.097	2.093	2.094
P$_A$–S$_d$	2.120	2.121		
P$_C$–S$_b$		2.122	2.123	2.132
P$_B$–S$_b$	2.141	2.138		
P$_D$–S$_d$		2.136	2.136	2.115
P$_A$–P$_B$	2.197	2.199		
P$_C$–P$_D$		2.214	2.216	2.208
P$_B$–H$_b$	1.399	1.399		
P$_D$–R$_d$		1.729	1.731	2.477
(*ii*) Bond angles (°)				
P$_A$–S$_a$–P$_C$	99.36	99.38	99.35	100.35
P$_B$–S$_b$–P$_C$	106.28	106.27		
P$_A$–S$_d$–P$_D$		107.28	107.17	107.05
S$_d$–P$_A$–P$_B$	99.18	97.94		
S$_d$–P$_A$–S$_a$	102.44	102.57		
P$_B$–P$_A$–S$_a$	100.24	100.24		
S$_b$–P$_C$–P$_D$		98.74	97.61	93.18
S$_b$–P$_C$–S$_a$		102.99	103.13	102.93
P$_D$–P$_C$–S$_a$		100.38	100.42	101.57
P$_A$–P$_B$–S$_b$	102.19	101.85		
P$_A$–P$_B$–H$_b$	94.06	94.34		
S$_b$–P$_B$–H$_b$	97.94	98.00		
P$_C$–P$_D$–S$_d$		100.75	100.30	102.20
P$_C$–P$_D$–R$_d$		96.97	97.39	96.56
S$_d$–P$_D$–R$_d$		101.11	101.33	102.34
(*iii*) Selected torsion angles (°)[d]				
P$_A$–P$_B$–S$_b$–P$_C$	6.75	8.82		
P$_C$–P$_D$–S$_d$–P$_A$		9.72	11.75	5.97
P$_B$–S$_b$–P$_C$–P$_D$	77.07	79.21		
P$_D$–S$_d$–P$_A$–P$_B$		79.63	81.81	78.20
lp–P$_A$–P$_C$–lp	4.7	8.3	11.9	5.7
lp–P$_B$–P$_D$–lp	44.3	45.5	46.7	46.2
(*iv*) Selected non-bonded distances (Å)				
S$_b$–S$_d$	3.794	3.723	3.654	3.665
P$_B$–P$_D$	4.045	4.082	4.123	3.923
P$_B$–S$_d$	3.288	3.259		
P$_D$–S$_b$		3.291	3.265	3.153

[a] Atom labelling as in **I** (Scheme 1). [b] From *ab initio* geometry optimisation at the RHF/3-21G* level. [c] Average values over both molecules unsymmetrically situated in the crystallographic unit cell, ref. 9. [d] Torsion angle A–B–C–D is the angle between projections of vectors BA and CD on a plane perpendicular to BC; lp–A–B–lp is the torsion angle between a notional lone pair (see text) on A and a notional lone pair on B.

of the ^2J coupling constants, *e.g.* to the production of a large coupling $^2J(P_AP_D)$ as a result of a hydride ligand attached at P$_B$ (Table 1). The twisting effect of the ligand NMe$_2$ on its half ring in α-P$_4$S$_3$H(NMe$_2$), opposing the untwisting effect of the hydride ligand on its side, results in distortions which decrease the book angle S$_d$–P$_A$–P$_B$ while increasing S$_b$–P$_C$–P$_D$, to an almost equal and opposite extent. Their values therefore cross over, compared with those in the symmetric compounds, while their average remains constant. This helps to explain the averaging rules[2] for the NMR parameters mainly involving the bridgehead atoms,$^2J(P_AP_C)$ and the pair $\delta(P_A)$ and $\delta(P_C)$. For α-P$_4$S$_3$H(NMePh) reported here, while $^2J(P_AP_C)$ conforms well to the rules, the $\delta(P_A)$, $\delta(P_C)$ pair does not (Table 2), in contrast *e.g.* to α-P$_4$S$_3$(H)I or to α-P$_4$S$_3$I(NMePh).[2] This is not rationalised by the present calculations.

Localised lone-pair molecular orbitals do not result from *ab initio* calculations of the type performed, but calculation of the direction of a notional lone-pair orbital on phosphorus, which in a simple valence shell electron pair repulsion conceptualisation would be at an equal angle to each of the three bonding contacts, is useful in describing the molecular geometry in a way which may have relevance to the origin of coupling constants.

Thus, the torsion angle lp–P$_A$–P$_C$–lp (lp = lone pair) is influenced by the ring twisting effects discussed above, and has more than twice the value in α-P$_4$S$_3$(NMe$_2$)$_2$ as in α-P$_4$S$_3$H$_2$. This corresponds to the exceptionally small value of the coupling constant $^2J(P_AP_C)$ in α-P$_4$S$_3$(NMe$_2$)$_2$ (43.4 Hz)^2 (*cf.* α-P$_4$S$_3$H$_2$ 72.5, α-P$_4$S$_3$I$_2$ 73.9 Hz). The torsion angle takes an exactly average value in α-P$_4$S$_3$H(NMe$_2$) (Table 3), consistent with the average value of the coupling constant for α-P$_4$S$_3$H(NMePh) (Table 2).

The torsion angle lp–P$_B$–P$_D$–lp is similar in value in α-P$_4$S$_3$I$_2$, α-P$_4$S$_3$(NMe$_2$)$_2$ and α-P$_4$S$_3$H$_2$, and does not account for the positive value of $J(P_BP_D)$ in the iodide, probably due to a through-space coupling mechanism, compared with the negative values for the other two compounds. The smaller angle (108.2°) in the iodide (compared with 113.7 or 114.6° respectively) between the lone pairs and the P$_B$–P$_D$ direction, may be a contributing factor to this. If it is assumed that the negative couplings $J(P_BP_D)$ are mostly through bonds, then the torsion angles P$_B$–S$_b$–P$_C$–P$_D$ and P$_D$–S$_d$–P$_A$–P$_B$ should be significant structural parameters. These obey similar averaging rules to the book angles S$_d$–P$_A$–P$_B$ and S$_b$–P$_C$–P$_D$, dealt with above, which are also involved in a through-bonds coupling route.

For α-$P_4S_3H_2$ the reduced bond angles to the hydride ligands would contribute to the low chemical shift $\delta(P_B)$.[8] It is well known that introduction of either hydride or cyanide ligands on acyclic phosphorus causes the ^{31}P NMR chemical shift to move to lower frequency. For cyanide this is unlikely to be a diamagnetic anisotropy effect associated with the CN π electron density, since ^{31}P chemical shifts in α-P_4S_3 cyanide compounds obey the same correlation rules as for other ligands.[1] For both hydride and cyanide, the major factors contributing to the unusual ^{31}P chemical shifts are likely to be electronic ones in the phosphorus–ligand bonding, although it is interesting that both PH_3 and $P(CN)_3$ have smaller bond angles at phosphorus than does PCl_3, and an effect of bond angles on chemical shift may be important.

The values of ^{31}P–^1H couplings (Table 1) were quite consistent for the four compounds reported here, only $^4J(P_DH_b)$ showing much variation with the changes in geometry discussed above. The coupling $^4J(P_DE_b)$ was numerically greater than $^3J(P_CE_b)$ here (E = H), as for α-P_4S_3 isothiocyanates (E = ^{15}N)[11] and for α-P_4S_3 diphenylphosphino compounds (E = P).[2,5] The coupling $^1J(P_BH_b)$ had values similar to those in PH_3 (186.4),[12] P_2H_4 (186.5)[13] or Li_2HP_7 (166 Hz).[14]

Experimental

All operations were carried out under nitrogen by Schlenk methods. AnalaR toluene was dried over sodium, and CS_2 by distillation from P_4O_{10}. The compound $SnBu^n_3H$ (Aldrich) was used as received. Phosphorus-31 NMR spectra were measured using a Bruker WM300WB spectrometer operating at 121.5 MHz, 10 mm diameter tubes and precision capillaries containing $(CD_3)CO$ for locking. Chemical shifts, obtained by substitution experiments using the same capillaries, are reported relative to H_3PO_4–H_2O. Proton NMR spectra were measured with a Bruker AC200 spectrometer and 5 mm diameter tubes.

Preparation of a Solution of α-$P_4S_3H_2$.—The compound α-$P_4S_3I_2$ (0.50 g, 1.06 mmol) was suspended in toluene (10 cm^3) by stirring, first at 60 °C, then while cooling to 20 °C. Dropwise addition of $SnBu^n_3H$ (0.57 cm^3, 2.11 mmol) in toluene (5 cm^3) over 45 min was followed by further stirring for 15 min, giving an almost colourless solution and a poorly settling lemon yellow precipitate. Phosphorus-31 NMR integration relative to PCl_3O–$CDCl_3$ in a capillary showed the concentration of α-$P_4S_3H_2$ in the solution to be 2.1 mmol dm^{-3} (3.0% yield, based on α-$P_4S_3I_2$).

Preparation of a Solution containing α-$P_4S_3H(NMePh)$.— The compound α-$P_4S_3I_2$ (1.00 g, 2.11 mmol) was suspended in

toluene (15 cm^3) as above, then a solution of NHMePh (0.46 cm^3, 4.22 mmol) in toluene (10 cm^3), dried over KOH, was added over 10 min. Stirring was continued for 18 h, then the mid-yellow solution was removed from the solid products and $SnBu^n_3H$ (0.30 cm^3, 1.12 mmol) in toluene (5 cm^3) was added dropwise to it over 30 min, giving a very poorly settling suspension. Estimation of relative concentrations of α-P_4S_3 compounds (see Results and Discussion section) in the solutions before and after the addition of $SnBu^n_3H$ was by integration of multiplets due to bridgehead phosphorus nuclei in the ^{31}P-$\{^1H\}$ NMR spectra.

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