# Phosphorus-31 Nuclear Magnetic Resonance Parameters for Amino Compounds with the α-Tetraphosphorus Trisulphide Skeleton

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Phosphorus-31 NMR spectra have been recorded and assigned for α-$P_4S_3X_2$ **1** and α-$P_4S_3X(Y)$ **2** (X = $NMe_2$, $NEt_2$, NMePh, NEtPh, or $NPh_2$; Y = I), and for a mixed-amino compound **2** (X = $NPh_2$, Y = $NEt_2$). All compounds were unstable and were not isolated. For the symmetric molecules **1** (X = NRR′) the $^2J$(PP) couplings were generally much less positive, the $^1J$(PP) couplings were much more negative, and the bridgehead chemical shifts were to lower frequency, than for other α-$P_4S_3$ compounds reported previously. New predictive relationships between NMR parameters for unsymmetric compounds and those for symmetric compounds have been found. The $^1J$(PP) couplings along opposite edges of the $P_4$ cage of the unsymmetric compounds α-$P_4S_3X(Y)$ deviated from values for the corresponding symmetric compounds (α-$P_4S_3X_2$ and α-$P_4S_3Y_2$) by similar but opposite amounts. Chemical shifts of the two bridgehead phosphorus nuclei similarly showed approximately equal and opposite deviations from the shifts found for the symmetric compounds.



Symmetric **1** or unsymmetric **2** α-$P_4S_3X(Y)$ compounds, where X and Y are halide, pseudohalide, or similar groups, provide excellent molecules with which to study the variation of P–P NMR coupling constants and $^{31}$P chemical shifts for a cage of phosphorus nuclei, as the substituents X and Y are varied and consequently the electronic and geometrical environments of the nuclei are changed. Owing to the physical interconnections of the nuclei in the cage, the variations in different coupling constants, or in different chemical shifts, have been found to be strongly interdependent; initial work involving four unsymmetric compounds α-$P_4S_3X(Y)$ **2** (X ≠ Y) showed that all six P–P coupling constants, for each, could be predicted from couplings found for the symmetric compounds α-$P_4S_3X_2$ and α-$P_4S_3Y_2$.[1] Such predictions subsequently proved useful in solving the $^{31}$P NMR spectra of strongly coupled spin systems in the isothiocyanate halides **2** (X = NCS Y = Cl or I).[2]

The series of compounds have now been extended to include amino derivatives **1** (X = NRR′) or **2** (X = NRR′, Y = I) where NRR′ = $NMe_2$, $NEt_2$, NMePh, NEtPh, or $NPh_2$. A mixed amino compound **2** (X = $NPh_2$, Y = $NEt_2$) has also been studied. These amino compounds showed more extreme values of coupling constants (and of bridgehead chemical shifts) than those of compounds reported previously,[1] necessitating the reformulation in more detail of the rules connecting NMR parameters for unsymmetric compounds with those for symmetric compounds.

Secondary amino derivatives with the α-$P_4S_3$ skeleton [**1**; X = $N(CH_2)_5$ or $N(CH_2CH_2)_2O$] were first observed[3] as discrete species in solution, showing $^{31}$P NMR spectra characteristic of the expected AA′MM′ spin system, but the compounds, made by reaction of α-$P_4S_3I_2$ with the appropriate free amine, were not obtained pure, and a full analysis of their spectra was not published. Typically of compounds containing the α-$P_4S_3$ skeleton, the amino derivatives in general decompose in solution over several days at room temperature, giving intractable solid products believed to be polymers.[1-3] This decomposition is greatly hastened by removal of solvent; in the present work, product solutions were evaporated to a maximum concentration of 0.3 mol $dm^{-3}$ of total $P_4S_3$ compounds, and NMR spectra were measured within the following 24 h. While the compounds consequently could not be separated and hence identified by other analytical methods, their spectra provided unequivocal identification: the parameters obtained, taken together with those from previous work,[1] formed regular series for which some rationalisation is possible.


**Scheme 1** NMR spin system labelling for symmetric **1** and unsymmetric **2** molecules containing the α-$P_4S_3$ skeleton

## Discussion

*Assignment of Spectra.*—$^{31}$P-{$^1$H} NMR spectra of symmetric molecules **1** were analysed by hand as AA′XX′ spin systems, and those of unsymmetric molecules **2** (X ≠ Y) as first-order spin systems, the hand analysis being followed in each case by iterative fitting using NUMARIT.[4] Coupling to $^{14}$N was ignored in the computer simulations, though peaks broadened or distorted by $^{31}$P–$^{14}$N scalar-coupling relaxation effects were omitted from the iterative fitting insofar as the chemical shift and $^{31}$P–$^{31}$P coupling information which they contained was redundant.

For the unsymmetric compounds, multiplets due to bridgehead atoms $P_A$ or $P_C$ were distinguished from those due to $P_B$ or $P_D$ because they contained a larger splitting associated with $^2J(P_AP_C)$, rather than a smaller one associated with $^3J(P_BP_D)$. By comparison, chemical shifts could then be assigned for the symmetric compounds. Multiplets due to $P_B$ or $P_D$ for the unsymmetric compounds were distinguished from each other by the different sizes of their largest splittings, due to couplings $^1J(P_AP_B)$ or $^1J(P_CP_D)$, and were assigned by comparison of these couplings with values for the symmetric compounds having substituents identical to those carried by $P_B$ or $P_D$ respectively. This method gave the correct assignment for all the unsymmetric amino compounds described here, while

**Table 1** Phosphorus-31 NMR parameters (chemical shift δ, coupling constant* $J$/Hz) for amino α-$P_4S_3$ compounds

| NRR′ | $T$/K | δ($P_A$) | δ($P_B$) | | | $^2J(P_AP_{A'})$ | $^1J(P_AP_B)$ | | $^2J(P_AP_{B'})$ | | $^3J(P_BP_{B'})$ | Root mean square deviation (Hz) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (*i*) Symmetric compounds α-$P_4S_3(NRR')_2$ **1** | | | | | | | | | | | | |
| $NMe_2$ | 297 | 76.55 | 144.69 | | | 43.4 | −329.7 | | 12.2 | | −10.7 | 1.4 |
| | | | | | | (1.4) | (0.6) | | (0.5) | | (0.8) | |
| | 210 | 73.43 | 142.63 | | | 44.9 | −331.51 | | 10.47 | | −13.5 | 0.17 |
| | | | | | | (0.2) | (0.07) | | (0.06) | | (0.1) | |
| $NEt_2$ | 297 | 72.97 | 139.66 | | | 41.6 | −332.9 | | 11.8 | | −12.4 | 0.72 |
| | | | | | | (0.8) | (0.3) | | (0.2) | | (0.5) | |
| | 210 | 69.89 | 136.27 | | | 41.6 | −334.30 | | 11.37 | | −13.4 | 0.17 |
| | | | | | | (0.2) | (0.07) | | (0.06) | | (0.1) | |
| NMePh | 297 | 85.11 | 135.25 | | | 48.3 | −330.6 | | 11.98 | | −12.7 | 0.28 |
| | | | | | | (0.2) | (0.1) | | (0.09) | | (0.2) | |
| NEtPh | 297 | 81.77 | 135.66 | | | 47.4 | −332.0 | | 12.0 | | −11.8 | 0.34 |
| | | | | | | (0.2) | (0.1) | | (0.1) | | (0.2) | |
| $NPh_2$ | 297 | 90.24 | 133.07 | | | 61.4 | −340.64 | | 9.29 | | −11.0 | 0.19 |
| | | | | | | (0.1) | (0.08) | | (0.05) | | (0.1) | |
| | | δ($P_A$) | δ($P_B$) | δ($P_C$) | δ($P_D$) | $^2J(P_AP_C)$ | $^1J(P_AP_B)$ | $^1J(P_CP_D)$ | $^2J(P_AP_D)$ | $^2J(P_BP_C)$ | $^3J(P_BP_D)$ | |
| (*ii*) Amino iodides α-$P_4S_3(NRR')I$ **2** (X = NRR′, Y = I) | | | | | | | | | | | | |
| $NMe_2$ | 297 | 90.19 | 145.70 | 114.12 | 124.62 | 56.8 | −322.0 | −251.5 | 11.8 | 18.6 | −0.2 | 0.71 |
| | | | | | | (0.6) | (0.4) | (0.4) | (0.4) | (0.5) | (0.4) | |
| | 210 | 88.83 | 145.77 | 113.08 | 124.10 | 55.95 | −325.12 | −255.28 | 11.68 | 20.93 | −0.19 | 0.04 |
| | | | | | | (0.02) | (0.03) | (0.02) | (0.02) | (0.02) | (0.02) | |
| $NEt_2$ | 297 | 89.01 | 139.92 | 112.17 | 125.09 | 55.33 | −325.9 | −252.18 | 11.40 | 21.87 | −0.15 | 0.11 |
| | | | | | | (0.07) | (0.1) | (0.07) | (0.07) | (0.07) | (0.09) | |
| | 210 | 88.25 | 139.29 | 112.26 | 125.12 | 54.35 | −328.34 | −256.84 | 11.44 | 22.24 | −0.15 | 0.04 |
| | | | | | | (0.03) | (0.03) | (0.03) | (0.03) | (0.03) | (0.03) | |
| NMePh | 297 | 96.75 | 137.22 | 116.95 | 126.10 | 59.00 | −322.87 | −252.47 | 12.13 | 22.34 | −0.29 | 0.08 |
| | | | | | | (0.05) | (0.05) | (0.05) | (0.05) | (0.05) | (0.05) | |
| NEtPh | 297 | 96.05 | 136.44 | 114.64 | 129.13 | 58.85 | −325.28 | −251.65 | 11.45 | 22.53 | −0.12 | 0.08 |
| | | | | | | (0.05) | (0.05) | (0.05) | (0.05) | (0.05) | (0.05) | |
| $NPh_2$ | 297 | 101.30 | 128.31 | 117.93 | 137.46 | 65.39 | −334.89 | −250.58 | 10.45 | 21.57 | −2.62 | 0.09 |
| | | | | | | (0.06) | (0.07) | (0.06) | (0.07) | (0.06) | (0.06) | |
| (*iii*) Mixed-amino compound α-$P_4S_3(NPh_2)(NEt_2)$ **2** (X = $NPh_2$, Y = $NEt_2$) | | | | | | | | | | | | |
| | 297 | 85.24 | 123.65 | 77.33 | 147.50 | 51.94 | −341.67 | −331.38 | 10.14 | 10.21 | −12.36 | 0.06 |
| | | | | | | (0.04) | (0.04) | (0.04) | (0.04) | (0.04) | (0.07) | |

* Standard deviation (σ) in parentheses.

comparing chemical shifts instead of $^1J$ coupling constants would have given the wrong assignment for α-$P_4S_3(NPh_2)I$, since the order δ($P_D$) > δ($P_B$) was the opposite, very surprisingly, of that expected from the shifts for the symmetric compounds. Results are shown in Table 1.

*The Coupling* $^2J(P_AP_C)$.—Except for α-$P_4S_3(NPh_2)_2$, the symmetric amino compounds **1** (X = NRR′) showed much smaller values of the bridge coupling $^2J(P_AP_C)$ (Table 1) than had previously been encountered.[1] The previously stated rule that $^2J(P_AP_C)$ for the unsymmetric compounds could be predicted as the average of the values found for the two corresponding symmetric compounds [1] was found to hold more approximately for the amino compounds (Table 2; refs. 1, 5 and 6). For each of the amino iodides **2** (X = NRR′, Y = I), the experimental value was about 2 Hz lower than the valuc predicted in this way, probably showing that this bridge coupling was slightly more influenced by the amino ligand than by the iodide.

*The Coupling* $^3J(P_BP_D)$.—This coupling, across the formally non-bonded edge of the approximate $P_4$ tetrahedron, was exceptionally large and negative for the amino compounds (Table 1), only the dicyanide **1** (X = CN) showing a more negative value.[1] The variability of size and sign of this coupling over the currently known series of α-$P_4S_3$ compounds is probably because it is the result of a combination of through-bonds and through-space coupling mechanisms, which make contributions to it of opposite sign. The previous rule that $J(P_BP_D)$ in the unsymmetric compounds could also be predicted as an average of the values for the symmetric compounds was found to hold quite well for the new amino derivatives (Table 2).

*The Couplings* $^2J(P_AP_D)$ *and* $^2J(P_BP_C)$.—Like the bridge coupling $^2J(P_AP_C)$, these couplings for the symmetric amino compounds (Table 1) were much smaller than any found previously.[1] In the unsymmetric compounds, $^2J(P_AP_D)$ and $^2J(P_BP_C)$, unlike $^2J(P_AP_C)$ or $^3J(P_BP_D)$, are along edges of the approximate $P_4$ tetrahedron which are unsymmetrically disposed with respect to the two ligands. Consequently, $J(P_AP_D)$ would be expected to be more influenced by one ligand, and $J(P_BP_C)$ more by the other. For the four unsymmetric compounds dealt with previously,[1] it was reported that this was not so and that both couplings in an unsymmetric compound approximated to the average of the couplings for the corresponding symmetric compounds. Examination of parameters for the 14 compounds now known (Table 2) shows that this conclusion lacked generality: for the amino iodides, the separation of values of $J(P_AP_D)$ and $J(P_BP_C)$ was similar to that between corresponding couplings for the symmetric amino compound and α-$P_4S_3I_2$, while this separation for α-$P_4S_3$(NCS)I was greater than between the symmetric compounds. The coupling $J(P_AP_D)$ would be expected to be influenced more by the ligand (Y) attached to $P_D$, and $J(P_BP_C)$ by the ligand (X) attached to $P_B$. For cases where $J(P_AP_D)$ and $J(P_BP_C)$ were

**Table 2** Relationships between NMR parameters for unsymmetric compounds α-$P_4S_3X(Y)$ **2** and those for corresponding symmetric compounds α-$P_4S_3X_2$ and α-$P_4S_3Y_2$ **1**

| X | CN | CN | CN | Br | $PPh_2$ | NCS | NCS | SPh | $NPh_2$ | NMePh | NEtPh | $NMe_2$ | $NEt_2$ | $NPh_2$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Y | I | Br | Cl | I | I | I | Cl | I | I | I | I | I | I | $NEt_2$ |
| Solvent | $CS_2$ | $CS_2$ | $CS_2$ | $CS_2$ | $C_6H_5Me$ | $CS_2$ | $CS_2$ | $C_6H_5Me$ | $C_6H_5Me$ | $C_6H_5Me$ | $C_6H_5Me$ | $C_6H_5Me$ | $C_6H_5Me$ | $C_6H_5Me$ |
| Origin of data | *a* | *a* | *a* | *a* | *b* | *c* | *c* | *d* | *e* | *e* | *e* | *e* | *e* | *e* |
| (*i*) Couplings (Hz) influenced similarly by X and Y | | | | | | | | | | | | | | |
| $^2J(P_AP_C)(XY)$ | 80.6 | 78.2 | 76.0 | 72.4 | 71.9 | 69.8 | 65.9 | 66.7 | 65.4 | 59.0 | 58.9 | 56.8 | 55.3 | 51.9 |
| Av. $^2J(P_AP_{A'})(X_2, Y_2)$[f] | 80.6 | 78.2 | 76.1 | 72.4 | 73.0 | 70.0 | 65.5 | 67.1 | 67.7 | 61.1 | 60.7 | 58.7 | 57.8 | 51.5 |
| Difference | 0.0 | 0.0 | −0.1 | −0.1 | −1.1 | −0.2 | +0.3 | −0.4 | −2.3 | −2.1 | −1.8 | −1.9 | −2.4 | +0.4 |
| $^3J(P_BP_D)(XY)$ | −1.7 | −1.1 | −2.0 | 9.9 | −4.7 | 3.7 | 4.4 | −0.2 | −2.6 | −0.3 | −0.1 | −0.2 | −0.1 | −12.4 |
| Av. $^3J(P_BP_{B'})(X_2, Y_2)$ | −2.5 | −1.3 | −2.0 | 10.5 | −2.3 | 4.4 | 4.9 | 2.1 | −0.4 | −1.2 | −0.8 | −0.2 | −1.1 | −11.7 |
| Difference | +0.8 | +0.3 | 0.0 | −0.6 | −2.4 | −0.7 | −0.5 | −2.3 | −2.2 | +0.9 | +0.7 | +0.1 | +1.0 | −0.7 |
| (*ii*) Couplings (Hz) influenced dissimilarly by X and Y | | | | | | | | | | | | | | |
| $^2J(P_AP_D)(XY)$ | 26.0 | 25.4 | 25.9 | 20.1 | 22.4 | 19.2 | 19.7 | 17.6 | 10.4 | 12.1 | 11.4 | 11.8 | 11.4 | 10.1 |
| $^2J(P_BP_C)(XY)$ | 28.6 | 26.3 | 25.5 | 21.7 | 27.2 | 25.4 | 23.1 | 24.8 | 21.6 | 22.3 | 22.5 | 18.6 | 21.9 | 10.2 |
| $^2J(P_AP_{B'})(X_2)$ | 32.1 | 32.1 | 32.1 | 19.7 | 27.5 | 23.3 | 23.3 | 21.7 | 9.3 | 12.0 | 12.0 | 12.2 | 11.8 | 9.3 |
| $^2J(P_AP_{B'})(Y_2)$ | 21.6 | 19.7 | 20.0 | 21.6 | 21.6 | 21.6 | 20.0 | 21.6 | 21.6 | 21.6 | 21.6 | 21.6 | 21.6 | 11.8 |
| Av. $^2J(P_AP_{B'})$, $^2J(P_BP_C)(XY)$ | 27.3 | 25.9 | 25.7 | 20.9 | 24.8 | 22.3 | 21.4 | 21.2 | 16.0 | 17.2 | 17.0 | 15.2 | 16.6 | 10.2 |
| Av. $^2J(P_AP_{B'})(X_2, Y_2)$ | 26.8 | 25.9 | 26.1 | 20.6 | 24.5 | 22.4 | 21.7 | 21.7 | 15.4 | 16.8 | 16.8 | 16.9 | 16.7 | 10.5 |
| Difference | +0.5 | −0.1 | −0.4 | +0.3 | +0.3 | −0.1 | −0.3 | −0.4 | +0.6 | +0.4 | +0.2 | −1.7 | 0.0 | −0.3 |
| $^1J(P_AP_B)(XY) - {}^1J(P_AP_B)(X_2)$ | −1.6 | +0.4 | +1.4 | −2.3 | +4.7 | −4.7 | −1.6 | −0.2 | +5.7 | +7.7 | +6.7 | +7.7 | +7.0 | −1.0 |
| $^1J(P_CP_D)(XY) - {}^1J(P_AP_B)(Y_2)$ | +1.6 | +0.8 | +1.2 | +1.6 | −4.0 | +3.9 | +2.4 | +3.0 | −3.8 | −5.7 | −4.8 | −4.7 | −5.4 | +1.5 |
| Av. $^1J(P_AP_B)$, $^1J(P_CP_D)(XY)$ | −249.1 | −253.9 | −257.6 | −249.4 | −276.8 | −253.1 | −262.1 | −263.2 | −292.7 | −287.7 | −288.5 | −286.7 | −289.0 | −336.5 |
| Av. $^1J(P_AP_B)(X_2, Y_2)$ | −249.2 | −254.5 | −258.9 | −249.0 | −277.1 | −252.7 | −262.5 | −264.6 | −293.7 | −288.7 | −289.4 | −288.2 | −289.9 | −336.8 |
| Difference | 0.0 | +0.6 | +1.3 | −0.4 | +0.3 | −0.4 | +0.4 | +1.4 | +1.0 | +1.0 | +0.9 | +1.5 | +0.8 | +0.2 |
| (*iii*) Chemical shifts of bridgehead phosphorus atoms | | | | | | | | | | | | | | |
| $\delta(P_A)(XY) - \delta(P_A)(X_2)$ | +4.4 | +3.5 | +1.8 | 0.0 | +8.0 | +6.1 | +4.7 | +11.3 | +11.1 | +11.6 | +14.3 | +13.6 | +16.0 | −5.0 |
| $\delta(P_C)(XY) - \delta(P_A)(Y_2)$ | −4.3 | −4.6 | −4.2 | +0.3 | −9.5 | −4.7 | −4.5 | −11.4 | −11.0 | −12.0 | −14.3 | −14.8 | −16.8 | +4.4 |
| Av. $\delta(P_A)$, $\delta(P_C)(XY)$ | 128.8 | 129.8 | 129.9 | 130.5 | 125.8 | 125.4 | 127.2 | 119.2 | 109.6 | 106.8 | 105.3 | 102.2 | 100.6 | 81.3 |
| Av. $\delta(P_A)(X_2, Y_2)$ | 128.7 | 130.4 | 131.1 | 130.4 | 126.6 | 124.7 | 127.1 | 119.2 | 109.6 | 107.0 | 105.4 | 102.7 | 101.0 | 81.6 |
| Difference | +0.1 | −0.6 | −1.2 | +0.2 | −0.7 | +0.7 | +0.1 | 0.0 | 0.0 | −0.2 | 0.0 | −0.6 | −0.4 | −0.3 |
| (*iv*) Chemical shifts of phosphorus atoms carrying substituents | | | | | | | | | | | | | | |
| $\delta(P_B)(XY) - \delta(P_B)(X_2)$ | −3.0 | −5.8 | −7.4 | −0.8 | −4.7 | +1.3 | +0.4 | +2.3 | −4.8 | +2.0 | +0.8 | +1.0 | +0.3 | −9.4 |
| $\delta(P_D)(XY) - \delta(P_B)(Y_2)$ | +6.0 | +4.0 | +2.6 | +0.1 | +7.7 | +1.9 | +0.5 | +6.0 | +14.6 | +3.2 | +6.2 | +1.7 | +2.2 | +7.8 |
| Av. $\delta(P_B)$, $\delta(P_D)(XY)$ | 81.1 | 91.8 | 95.5 | 137.8 | 108.6 | 125.9 | 143.1 | 129.3 | 132.9 | 131.7 | 132.8 | 135.2 | 132.5 | 135.6 |
| Av. $\delta(P_B)(X_2, Y_2)$ | 79.6 | 92.7 | 98.0 | 138.1 | 107.1 | 124.3 | 142.6 | 125.2 | 128.0 | 129.1 | 129.3 | 133.8 | 131.3 | 136.4 |
| Difference | +1.5 | −0.9 | −2.4 | −0.3 | +1.5 | +1.6 | +0.5 | +4.1 | +4.9 | +2.6 | +3.5 | +1.4 | +1.2 | −0.8 |

[a] Ref. 1. [b] Ref. 5 α-$P_4S_3(PPh_2)I$ has $J(P_AP_C)$ 71.9, $J(P_BP_D)$ −4.7, $J(P_AP_D)$ 22.4, $J(P_BP_C)$ 27.2, $J(P_AP_B)$ −302.7, $J(P_CP_D)$ −250.8, $J(P_AP_X)$ 74.0, $J(P_CP_X)$ −3.3, $J(P_BP_X)$ −210.1 and $J(P_DP_X)$ 8.0 Hz, $\delta(P_A)$ 132.17, $\delta(P_C)$ 119.48, $\delta(P_B)$ 86.62, $\delta(P_D)$ 130.60 and $\delta(P_X)$ −3.12; α-$P_4S_3(PPh_2)_2$ has $J(P_AP_{A'})$ 72.0, $J(P_BP_{B'})$ −14.9, $J(P_AP_{B'})$ 27.48, $J(P_AP_B)$ −307.4, $J(P_AP_X)$ 81.4, $J(P_AP_{X'})$ −4.0, $J(P_BP_X)$ −211.2 and $J(P_BP_{X'})$ 4.1 Hz, $\delta(P_A)$ 124.18, $\delta(P_B)$ 91.31 and $\delta(P_X)$ −2.07. [c] Ref. 2. [d] Ref. 5. α-$P_4S_3(SPh)I$ has $J(P_AP_C)$ 66.7, $J(P_BP_D)$ −0.2, $J(P_AP_D)$ 17.6, $J(P_BP_C)$ 24.8, $J(P_AP_B)$ −282.6 and $J(P_CP_D)$ −243.9 Hz, $\delta(P_A)$ 120.83, $\delta(P_C)$ 117.57, $\delta(P_B)$ 129.77 and $\delta(P_D)$ 128.86; data for α-$P_4S_3(SPh)_2$ are from ref. 6. [e] This work. [f] α-$P_4S_3I_2$ in $C_6H_5Me$ has $J(P_AP_{A'})$ 73.9, $J(P_BP_{B'})$ 10.2, $J(P_AP_{B'})$ 21.6 and $J(P_AP_B)$ −246.8 Hz, $\delta(P_A)$ 128.94 and $\delta(P_B)$ 122.90; data for α-$P_4S_3Y_2$ (Y = Cl, Br or I) in $CS_2$ are from Ref. 1.

appreciably different for an unsymmetric compound, this was true only for α-$P_4S_3$(CN)I, α-$P_4S_3$($PPh_2$)I, α-$P_4S_3$(NCS)I, and α-$P_4S_3$(NCS)Cl. Very surprisingly, for all the amino iodides, the opposite was true: $J(P_AP_D)$ was more influenced by the amino ligand (X) attached to $P_B$, and $J(P_BP_C)$ by the iodide ligand attached to $P_D$. The amino ligands were presumably influencing electronically primarily the bridgehead partner, $P_A$, in the coupling $J(P_AP_D)$. This control of $J(P_AP_D)$ by the bridgehead atom was found for cases where the bridgehead chemical shift $\delta(P_A)$ was low and where the bridge coupling $J(P_AP_C)$ deviated from an average value (see above): all three parameters may reflect a special influence of amino ligands on bond angles and hence on the electronic distribution, at the adjacent bridgehead. Extensive correlations of both couplings and chemical shifts with bond angles in similar molecules have been found previously.[7] The cyanide halides **2** (X = CN; Y = Cl, Br or I), reported originally,[1] were fortuitously cases in which the cyanide ligand attached at $P_B$ influenced $J(P_BP_C)$ directly and $J(P_AP_D)$ indirectly, *via* the bridgehead $P_A$, to a similar extent: hence a generalisation of too limited scope was reached.

From the present collection of data (Table 2) an interesting correlation may be seen: whether $J(P_AP_D)$ and $J(P_BP_C)$ became nearer together or further apart in value for an unsymmetric compound, compared with the two symmetric compounds, the average of $J(P_AP_D)$ and $J(P_BP_C)$ for the unsymmetric compound was equal to the average of the couplings for the symmetric compounds, to within *ca.* 0.5 Hz for most cases. A similar relationship is presented below for $^1J(P_AP_B)$ and $^1J(P_CP_D)$.

*The Couplings* $^1J(P_AP_B)$ *and* $^1J(P_CP_D)$.—In contrast to the other, exceptionally small, couplings to the bridgehead atoms, the $^1J$ couplings for the symmetric amino compounds (Table 1) had by far the largest (negative) values so far found for α-$P_4S_3$ derivatives. For the unsymmetric compounds, the previous rule that $^1J(P_AP_B)$ approximates to the value for the symmetric compound with the same ligands as that attached to $P_B$, was found still to hold, and was used for the assignment of chemical shifts (see above). However, the differences (5.7–7.7 Hz) in $J(P_AP_B)$ between symmetric amino compounds and amino iodides (Table 2) were greater than had been found previously, and it was observed that changes of $J(P_AP_B)$ to less negative values for the amino iodides were paralleled by similar though smaller changes in $J(P_CP_D)$, from the value for α-$P_4S_3I_2$, to more negative values. Thus the average of $J(P_AP_B)$ and $J(P_CP_D)$ for the unsymmetric compound was equal to the average of the couplings for the symmetric compounds, to within 1.5 Hz in all of the cases studied (Table 2). It is not surprising that $J(P_AP_B)$ should be affected to some extent by the ligand attached on the distant side of the cage, at $P_D$, but it is most remarkable that the effects of the two ligands upon the respectively opposite edges of the $P_4$ approximate tetrahedron should balance out in this way. The effect does not seem to be connected in a simple way to the similar (though less surprising) balancing of changes in $^2J(P_AP_D)$ and $^2J(P_BP_C)$ (see above), since cases for which deviations are largest for one pair of couplings are not those with the largest deviations in the other pair. Some connection of deviations in couplings sharing a common nucleus, *e.g.* $^1J(P_AP_B)$ and $^2J(P_AP_D)$, or $^1J(P_AP_B)$ and $^2J(P_BP_C)$, would have seemed at first sight more likely than connections between $^1J(P_AP_B)$ and $^1J(P_CP_D)$.

Especially where the presence of further NMR-active nuclei in the ligands complicates the spin system, the spectra of unsymmetric α-$P_4S_3$ compounds are generally easier to solve than those of the symmetric compounds. Using the relationships reported here, it should now be possible, from parameters from one symmetric compound and an unsymmetric compound, to predict all the $^{31}P$–$^{31}P$ couplings of the other corresponding symmetric compound, as a starting point for assignment of its spectrum. This method has already enabled the assignment of the $^{31}P$ NMR spectrum of α-$P_4S_3(PPh_2)_2$ **1** (X = $PPh_2$) (Table 2, footnote *b*).[5]

*The Chemical Shifts*.—The bridgehead chemical shifts $\delta(P_A)$ for the symmetric amino compounds were the least positive so far found, with the more basic aliphatic amino ligands leading to the most shielded bridgehead nuclei (Table 1). An inductive effect resulting from donation of negative charge from nitrogen to phosphorus might be hypothesised, except that the atoms $P_B$ carrying the amino ligands showed clearly an opposite trend in chemical shifts (Table 1). It is more likely (see above) that the bond angles at both $P_B$ and $P_A$ were being affected directly or indirectly by the nature of the $P_B$–N bonding.

In going from a symmetric amino compound to the corresponding amino iodide, the chemical shift of the neighbouring bridgehead, $\delta(P_A)$, moved substantially, by 11–16 ppm, to higher frequency, as shielding was removed (Table 2). There was a corresponding move to lower frequency of the other bridgehead shift, $\delta(P_C)$, in going from the symmetric diiodide to the amino iodide. One might expect a decrease in shielding in the whole α-$P_4S_3$ cage, relative to the symmetric amino compound, and an increase relative to the symmetric iodide, in going to the amino iodide, but, as for the pairs of coupling constants, *e.g.* $J(P_AP_B)$ and $J(P_CP_D)$, discussed above, it is most remarkable that these changes in bridgehead chemical shifts were not only of opposite sign, as expected, but of practically equal magnitude. The average of $\delta(P_A)$ and $\delta(P_C)$ for the unsymmetric compounds equalled the average of the bridgehead shifts for the two corresponding symmetric compounds, to within 1 ppm for 13 out of the 14 known unsymmetric compounds (Table 2). Considering that the shifts used in these calculations were obtained for compounds in at least two different solutions in each case, and that shifts for $P_4S_3$ derivatives are well known to be difficult to reproduce because of strong solvent interactions, this represents a very surprising coincidence. The sum of all four $^{31}P$ chemical shifts for an unsymmetric compound, as a measure of total shielding, did not take an average value between the sums for the corresponding symmetric compounds nearly so exactly: although deviations of $\delta(P_B)$ and $\delta(P_D)$ were mostly smaller than for $\delta(P_A)$ and $\delta(P_C)$, they balanced much more poorly, if at all, since for many cases deviations in $\delta(P_B)$ and $\delta(P_D)$ had the same sign (Table 2).

For α-$P_4S_3(NPh_2)$I, $\delta(P_B)$ was 4.76 ppm to lower frequency of $\delta(P_B)$ for α-$P_4S_3(NPh_2)_2$, while $\delta(P_B)$ was various smaller amounts to higher frequency of the values for the symmetric amino compounds, for all the other amino iodides (Table 2). Correspondingly, the shift $\delta(P_D)$ of the phosphorus atom carrying iodine was to exceptionally high frequency (137.46 ppm) for α-$P_4S_3(NPh_2)$I. The previous highest such shift was that for α-$P_4S_3$(CN)I, at 131.03 ppm. Large and opposite deviations in $\delta(P_B)$ and $\delta(P_D)$ for α-$P_4S_3(NPh_2)$I meant that these shifts crossed over in value, compared with the symmetric compounds, but the very different sizes of $^1J(P_AP_B)$ and $^1J(P_CP_D)$ (Table 1) makes it certain that this assignment is the correct one. In going from the symmetric amino compounds to α-$P_4S_3(NPh_2)(NEt_2)$, $\delta(P_B)$ and $\delta(P_D)$ became further apart in value, with the former again moving to lower frequency.

NMR *Parameters for* α-$P_4S_3(NPh_2)_2$.—Although $NPh_2$ was a less basic ligand than the other amino groups used, $^1J(P_AP_B)$ was even more negative and $^2J(P_AP_{B'})$ was even less positive, than for the other symmetric amino compounds. However, the parameter which was responsible for the failure of the data for α-$P_4S_3(NPh_2)_2$ to fit the kind of linear relationships established for the other symmetric compounds[1] was the bridge coupling $^2J(P_AP_{A'})$. This was not in the exceptionally low range of values found for the other amino compounds, and was similar to the value found for α-$P_4S_3(SPh_2)_2$,[6] for which none of the other NMR parameters was exceptional in value. While the way in which $NPh_2$ influenced $J(P_AP_{A'})$ thus appeared idiosyncratic, this influence was attenuated in unsymmetric compounds in just the same way for compounds containing $NPh_2$ as for the other amino derivatives, as discussed above. Only deviations of $\delta(P_B)$ for $NPh_2$ compounds were peculiar in this respect.

## Experimental

All operations were carried out under nitrogen by Schlenk methods. AnalaR toluene was dried over sodium. The compound $SiMe_3(NMe_2)$ (Aldrich) was used as received, $SiMe_3(NEt_2)$ was made from $SiMe_3Cl$, and $SiMe_3(NPh_2)$ was made by a transamination reaction between $SiMe_3(NEt_2)$ and $HNPh_2$.[8]

NMR spectra of solutions in toluene in 5 or 10 mm diameter tubes were measured using a Bruker WM300WB spectrometer operating at 121.5 MHz for $^{31}P$. An inverse-gated $^{1}H$ decoupling sequence was used to eliminate broadening of $^{31}P$ signals by unresolved $^{1}H$ coupling, while avoiding intensity distortion by the nuclear Overhauser effect. Precision capillaries containing $(CD_3)_2CO$ were used for locking, and chemical shifts, obtained by substitution experiments using the same capillaries, are reported relative to $H_3PO_4$–water.

Solutions in toluene of the new amino derivatives **1** were obtained by reaction of a suspension of $\alpha$-$P_4S_3I_2$, either with a secondary amine HX (X = $NEt_2$, NMePh, or NEtPh) or with the corresponding trimethylsilylamine $SiMe_3X$ (X = $NMe_2$, $NEt_2$, or $NPh_2$). Free $HNPh_2$ was insufficiently basic to react without the addition of $NEt_3$ to abstract HI, when considerable decomposition occurred. Use of $HNEt_2$ instead of $SiMe_3(NEt_2)$ allowed more complete conversion into $\alpha$-$P_4S_3(NEt_2)_2$, but also led to the formation of more unidentified by-products. The amino iodides **2** (X = NRR′, Y = I) were made by ligand redistribution between symmetric amino compounds **1** and $\alpha$-$P_4S_3I_2$, or by taking lower stoichiometric quantities of the secondary amine. The mixed-amino compound $\alpha$-$P_4S_3(NPh_2)(NEt_2)$ was made by treating a solution containing $\alpha$-$P_4S_3(NPh_2)I$ with $SiMe_3(NEt_2)$.

*Typical Procedure using Free Secondary Amine: Preparation of Solution containing* $\alpha$-$P_4S_3(NEtPh)_2$ *and* $\alpha$-$P_4S_3(NEtPh)I$.—The amine HNEtPh (4 $cm^3$, 31.8 mmol) was diluted to 50 $cm^3$ with toluene, then dried over KOH. A portion (10 $cm^3$) of this solution was added slowly by syringe-pipette to a stirred suspension of $\alpha$-$P_4S_3I_2$ (1.01 g, 2.13 mmol) in toluene (15 $cm^3$) at room temperature, in a Schlenk tube protected by a nitrogen flow. During the addtion (1 min) most of the suspended $\alpha$-$P_4S_3I_2$ dissolved; after 5 min a white precipitate of (amine hydroiodide) started to form. The mixture was filtered (positive nitrogen pressure, Whatman GF/D glass microfibre filter) after stirring for 94 h, and the yellow solution concentrated under vacuum at room temperature to 8 $cm^3$. The $^{31}P$ NMR spectrum showed that $\alpha$-$P_4S_3(NEtPh)_2$ and $\alpha$-$P_4S_3(NEtPh)I$ were the main products, along with a low concentration of $P_4S_3$. Another by-product in low yield, showing a singlet at $\delta$ 25.60, became a major component remaining in solution, when the mixture was allowed to stand for 2 weeks. This was probably $\overline{SP(S)(NEtPh)SP(S)(NEtPh)}$, the $NMe_2$ analogue of which has been reported with $\delta$ 23.9.[9]

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