Phosphorus-31 and Selenium-77 Nuclear Magnetic Resonance Spectra of Sulphur- or Arsenic-substituted Derivatives of Tetraphosphorus Triselenide; Fitting of Chemical Shifts and Coupling Constants to Molecular Parameters for Cage Compounds containing a Phosphorus–Selenium–Phosphorus Linkage

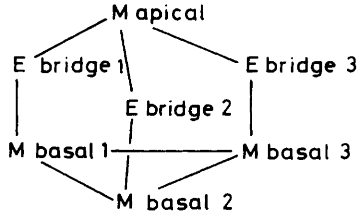
Bruce W. Tattershall *
Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE1 7RU
Roger Blachnik * **and Hans Peter Baldus**
Anorganische Chemie, FB Biologie/Chemie, Universität Osnabrück, D-4500 Osnabrück, Germany

Phosphorus-31 and selenium-77 n.m.r. spectra have been measured and assigned to give chemical shifts and coupling constants for PP_3S_2Se (**1**), PP_3SSe_2 (**2**), PP_2AsSe_3 (**4**), $PPAs_2Se_3$ (**5**), PAs_3Se_3 (**6**), AsP_3Se_3 (**7**), AsP_2AsSe_3 (**8**), and $AsPAs_2Se_3$ (**9**), where the symbol written first in each formula represents the apical phosphorus or arsenic atom. In each case, the presence of ^{77}Se in natural abundance allowed the molecule without ^{77}Se, and molecules with one ^{77}Se atom, to be studied. For molecules containing both basal phosphorus and basal arsenic atoms, spectra were seen of isotopomers with the ^{77}Se atom connected either to basal phosphorus [(**4b**), (**5b**), (**8b**), and (**9b**)] or to basal arsenic [(**4c**), (**5c**), (**8c**), and (**9c**)]. Complete chemical shift and coupling data were thus obtained for, *inter alia*, five molecules [(**1b**), (**2b**), (**3b**), (**4b**), and (**5b**)] containing a $^{31}P-^{77}Se-^{31}P$ linkage; the three shifts and three couplings which characterise this linkage could be fitted statistically by linear relationships involving two molecular parameters. Multiple regression analysis showed that two other coupling constants involving the basal phosphorus atom P_A could be fitted to these same molecular parameters.

Phosphorus–selenium cage molecules offer the advantage, over their sulphur-containing analogues, of the possibility of measurement of several more coupling constants and chemical shifts, for those isotopomers which contain the spin-$\frac{1}{2}$ nucleus ^{77}Se. Hence more data may be contributed to aid our eventual understanding of the dependence of coupling constants and chemical shifts on geometric and electronic properties of such molecules.

Phosphorus-31 n.m.r. chemical shifts and coupling constants have been published[1] for the main phosphorus spectra (*i.e.* of molecules containing no ^{77}Se) of the compounds (**1**)—(**9**) which are the subject of this paper: PP_3S_2Se (**1**), PP_3SSe_2 (**2**), PP_3Se_3 (**3**), PP_2AsSe_3 (**4**), $PPAs_2Se_3$ (**5**), PAs_3Se_3 (**6**), AsP_3Se_3 (**7**), AsP_2AsSe_3 (**8**), and $AsPAs_2Se_3$ (**9**), where the first element symbol represents the apical atom. Following the well established dependence of phosphorus chemical shifts on bond angles, for non-bridgehead phosphorus atoms, one of us found[1] that the chemical shifts of bridgehead, basal phosphorus atoms (Scheme) in twelve molecules [(**3a**), (**4a**), (**5a**), (**7a**), (**8a**), and (**9a**) (Table 1), and six corresponding sulphur-bridged molecules] could be fitted by a linear relationship involving two estimated angles at the basal phosphorus atom; one of these was the endocyclic angle of the basal three-membered ring, while the other was the exocyclic angle between the plane of this ring and the bridging selenium or sulphur atom. This linear dependence of chemical shift on two molecular parameters clearly resembled the dependence on two 'substituent constants' of the two chemical shifts and four coupling constants for α-$P_4S_3R_2$ (R = halide, pseudohalide, or alkylthio) molecules, found by the other of us.[2]

Considering only the five molecules of the original work[1] which contained a selenium bridge between basal and apical phosphorus atoms [(**1a**), (**2a**), (**3a**), (**4a**), and (**5a**)], we then found that the basal phosphorus to apical phosphorus coupling constant, J_{AM}, also fitted a linear relationship with the estimated basal bond angles, though more poorly (multiple correlation coefficient $R = 0.992$, *cf.* $R = 0.997$ for the basal phosphorus chemical shift of the same molecules), as did the apical phosphorus chemical shifts ($R = 0.984$). It was very surprising that two angles at the basal phosphorus atom should serve so well as parameters for fitting these further n.m.r. properties, involving other atoms of the molecules, and it seemed likely that two parameters for molecule *i*, X_i and Y_i, could be found which would be even better for fitting these and further n.m.r. properties of the molecule, if the requirement were removed that they should represent some predefined physical properties, such as bond angles. Using the least-squares method devised previously[2] for α-$P_4S_3R_2$ compounds, vectors X_i and Y_i for the molecules, and A_p, B_p, and C_p for the n.m.r. properties, could be found as best fits to equation (1), where N_{pi} is a measured



Scheme. Cage positions in derivatives of tetraphosphorus triselenide

$$N_{pi} = A_pX_i + B_pY_i + C_p \qquad (1)$$

n.m.r. property *p* (a chemical shift or coupling constant) for compound *i*.

To overdetermine the problem for the five available compounds, more than five n.m.r. properties needed to be measured for each. Each n.m.r. property *p* had to have a broadly similar meaning for each molecule *i*: *e.g.* it should be a coupling between nuclei in comparable geometrical positions, over the same number of bonds. By measuring and interpreting the ^{31}P and ^{77}Se n.m.r. spectra of the isotopomers [(**1b**), (**2b**), (**3b**), (**4b**),

Table 1. Occupancy of cage positions and n.m.r. spin system labelling for derivatives of tetraphosphorus triselenide

		Cage positions[a]								
Species	Formula	apical	basal 1	basal 2	basal 3	bridge 1[b]	bridge 2[b]	bridge 3[b]	Spin system	Relative abundance[c]
(1a)	PP_3S_2Se	P_M	P_A	P_F	P_F	^0Se	S	S	AF_2M	0.924
(1b)		P_M	P_A	P_F	P_F	$^{77}Se_X$	S	S	AF_2MX	0.076
(2a)	PP_3SSe_2	P_M	P_A	P_A	P_F	^0Se	^0Se	S	A_2FM	0.854
(2b)		P_M	P_A	P_B	P_F	$^{77}Se_X$	^0Se	S	ABFMX	0.140
(3a)	PP_3Se_3	P_M	P_A	P_A	P_A	^0Se	^0Se	^0Se	A_3M	0.789
(3b)		P_M	P_A	P_B	P_B	$^{77}Se_X$	^0Se	^0Se	AB_2MX	0.194
(4a)	PP_2AsSe_3	P_M	P_A	P_A	As	^0Se	^0Se	^0Se	A_2M	0.789
(4b)		P_M	P_A	P_B	As	$^{77}Se_X$	^0Se	^0Se	ABMX	0.129
(4c)		P_M	P_A	P_A	As	^0Se	^0Se	$^{77}Se_X$	A_2MX	0.065
(5a)	$PPAs_2Se_3$	P_M	P_A	As	As	^0Se	^0Se	^0Se	AM	0.789
(5b)		P_M	P_A	As	As	$^{77}Se_X$	^0Se	^0Se	AMX	0.065
(5c)		P_M	P_A	As	As	^0Se	^0Se	$^{77}Se_X$	AMX	0.129
(6a)	PAs_3Se_3	P_M	As	As	As	^0Se	^0Se	^0Se	M	0.789
(6c)		P_M	As	As	As	^0Se	^0Se	$^{77}Se_X$	MX	0.194
(7a)	AsP_3Se_3	As	P_A	P_A	P_A	^0Se	^0Se	^0Se	A_3	0.789
(7b)		As	P_A	P_B	P_B	$^{77}Se_X$	^0Se	^0Se	AB_2X	0.194
(8a)	AsP_2AsSe_3	As	P_A	P_A	As	^0Se	^0Se	^0Se	A_2	0.789
(8b)		As	P_A	P_B	As	$^{77}Se_X$	^0Se	^0Se	ABX	0.129
(8c)		As	P_A	P_A	As	^0Se	^0Se	$^{77}Se_X$	A_2X	0.065
(9a)	$AsPAs_2Se_3$	As	P_A	As	As	^0Se	^0Se	^0Se	A	0.789
(9b)		As	P_A	As	As	$^{77}Se_X$	^0Se	^0Se	AX	0.065
(9c)		As	P_A	As	As	^0Se	^0Se	$^{77}Se_X$	AX	0.129

[a] See Scheme. [b] ^0Se represents any natural isotope of Se other than ^{77}Se. [c] Natural abundance of this isotopomer, relative to total for all isotopomers of this isomer; pairs of diastereomeric isotopomers are counted as single species.

and (**5b**)], which contained one atom of ^{77}Se as the bridge between basal and apical phosphorus atoms, we could find six n.m.r. properties dependent mostly on the electronic properties of the atoms of the ^{31}P–^{77}Se–^{31}P linkage, and hence likely to be good candidates for fitting in this way. These were (Table 1): δ_A, δ_M, δ_X, J_{AM}, J_{AX}, and J_{MX}.

Consequently, we set out to measure the ^{77}Se n.m.r. spectra and all visible ^{77}Se satellite spectra in the ^{31}P n.m.r. spectra of compounds (**1**)—(**5**) containing ^{77}Se in natural abundance, as saturated solutions in CS_2. Since they were present in the same solutions, we made similar measurements for compounds (**6**)—(**9**). Our more intensive study of P_4Se_3 (**3**) has been published separately.[3]

Experimental

Solid reaction mixtures containing compounds (**1**)—(**3**) or (**3**)—(**9**) were prepared by melting together P_4Se_3 with P_4S_3 or with As_4Se_3 respectively.[1] N.m.r. spectra of solutions, made by stirring excesses of these solid mixtures with dry CS_2, were measured at 121.5 MHz for ^{31}P and 57.3 MHz for ^{77}Se, as described previously.[3]

Because of low solubilities, long accumulations of n.m.r. data were necessary: for the phosphorus selenide sulphides, a 5-mm diameter tube and typically 30 000 scans for the ^{31}P spectrum and 50 000 scans for the ^{77}Se spectrum were required. For the phosphorus arsenic selenides, ^{77}Se spectra could not be distinguished from noise when a 5-mm tube was used; by use of a 10-mm diameter tube, good ^{31}P spectra were obtained after 84 000 scans (in 40 h) and usable ^{77}Se spectra after 118 000 scans (in 64 h).

Assignment of N.M.R. Spectra

Main Phosphorus Spectra.—The spectra of molecules (**1a**), (**2a**), (**3a**), (**4a**), and (**5a**) were fitted iteratively using NUMARIT (S.E.R.C. n.m.r. Program Library, Daresbury) to obtain more precise shifts and couplings than previously published.[1] Initial parameters were found by subspectral analysis for (**1a**) (AF_2M spin system, Table 1, treated as AB_2M) and (**2a**) (A_2FM treated as A_2BM), and by the first-order approximation for (**4a**) and (**5a**). Molecules (**6a**), (**7a**), (**8a**), and (**9a**) gave single-line spectra. Results are shown in Tables 2 and 3.

Molecules containing one ^{77}Se *Nucleus*.—In each case, corresponding ^{31}P chemical shifts and ^{31}P–^{31}P couplings for the main spectrum (see above) could be used as initial parameters for fitting using NUMARIT. Couplings to ^{77}Se were estimated by other means, as described below. The $^1J(^{31}P$–$^{31}P)$ and (^{31}P–^{77}Se) couplings were assumed to be negative.[4] Results are shown in Tables 2 and 3.

Spectrum of $PP_3S_2{}^{77}Se$ (**1b**).—The internal chemical shift δ_{AF} ($= \nu_A - \nu_F$) for this AF_2MX spin system (Table 1) was sufficiently large that the first-order approximation could be taken in assigning the ^{77}Se spectrum, yielding initial values for ν_X, J_{AX}, J_{FX}, and J_{MX}; $^2J_{FX}$ was assumed to be negative by analogy with molecule (**2b**) (see below). In a normal transform of the ^{31}P n.m.r. spectrum, all 16 transitions of this satellite spectrum in the P_A region, and 13 out of 16 transitions in the P_M region, were clearly visible, but because of the small value of J_{FX} (-7.09 Hz), those in the P_F region were completely overlaid by the main spectrum. By careful use of resolution enhancement (line-narrowing) techniques, four of the 16 P_F transitions could be resolved, allowing all shifts and couplings to be refined.

Spectrum of $PP_3{}^{77}Se^0Se$ (**2b**).—For this ABFMX spin system (Table 1) the $^{77}Se_X$ multiplet was asymmetric [Figure (*g*)] and not readily interpreted on a first-order basis. To allow an initial computer simulation, values of J_{AB}, J_{AX}, J_{BX}, J_{FX}, and J_{MX} were assumed to be the same as the corresponding coupling constants of $PP_3{}^{77}Se^0Se_2$ (**3b**).[3] Partial fitting of the spectrum in the P_F and P_M regions [Figure (*c*), (*a*)], where the initial simulation could be recognised, led to a revised value of -6.4 Hz for $^2J_{FX}$, and a recognisable ^{77}Se simulation. A corresponding positive value of J_{FX} gave a simulated ^{77}Se spectrum with asymmetry which was the mirror image of that observed, confirming the negative sign of this coupling.

The P_A, P_B region [Figure (*e*)], which consisted of eight AB subspectra, could still not easily be recognised. However, if the very small ^{77}Se isotope effect on ^{31}P shifts and couplings was ignored,[3] then $\delta_{AB} = 0$, $J_{AF} = J_{BF}$, and $J_{AM} = J_{BM}$, so these subspectra were all expected to have the same effective internal shift, $\delta_{AB}^* = (J_{AX} - J_{BX})/2$, and hence the same separation of their more intense, central lines, $(J_{AB}^2 + \delta_{AB}^{*2})^{\frac{1}{2}} - |J_{AB}|$. A repeated separation, similar to that predicted in this way, was found between eight pairs of the more intense peaks of the observed satellite spectrum, allowing assignment of the subspectra. Ten of the 16 small outside peaks of these subspectra could then be identified.

Finally a computer fit of all regions could be carried out, with assignment of 26 out of 32 transitions in the P_A, P_B region, 10 out of 16 in the P_F region, 12 out of 16 in the P_M region, and 23 out of 24 in the ^{77}Se spectrum.

Spectrum of $PP_2As^{77}Se^0Se_2$ (**4b**).—The apical phosphorus (P_M) multiplet of this ABMX spin system, which could be distinguished by its greater intensity (Table 1) from that of the isotopomeric molecule (**4c**), could be treated as a first-order doublet (J_{MX}) of triplets (J_{AM}) to yield an initial value of J_{MX}.

Only the eight stronger central peaks of the four AB subspectra in the P_A, P_B region could readily be seen. There were three repeated separations between these: $(J_{AM} + J_{BM})/2$, $(J_{AX} + J_{BX})/2$, and the separation between the central peaks of any one subspectrum. Of these, the first was approximately known from the main spectrum of compound (**4a**). If J_{BX} was approximately zero [*cf.* $PP_3{}^{77}Se^0Se_2$, (**3b**), $J_{BX} = -0.4$ Hz],[3] then the second repeated separation approximated to $J_{AX}/2$ and the third repeated separation was necessarily smaller than this, since δ_{AB}^* for each subspectrum [*cf.* (**2b**), above] also approximated to $J_{AX}/2$. Hence the subspectra could unambiguously be assigned, allowing initial values for J_{AX}, δ_{AB}^*, and thus, from the observed separation of the central lines within any subspectrum, J_{AB} to be found. The positions of the weaker, outside peaks of the AB subspectra could then be predicted. With the aid of this prediction, and only for a spectrum obtained by very long data collection (see Experimental section), six of these eight small peaks were found, allowing a computer fit of the ^{31}P spectrum and a simulation of the ^{77}Se multiplet. The latter could then be identified in the ^{77}Se spectrum of the mixture and included in the fit.

Spectrum of $AsP_3{}^{77}Se^0Se_2$ (**7b**).—The ^{31}P n.m.r. spectrum of compound (**7b**) was the P_A, P_B part for an AB_2X spin system, and consisted of two overlapping AB_2 subspectra. These had δ_{AB}^* of equal magnitude but opposite sign, so the subspectra were mirror images of each other; since $J_{AX} \gg J_{BX}$, their A parts pointed outwards. If the eight principal transitions of an AB_2 subspectrum are numbered sequentially from the A part, then transitions 3—7 could be seen as separate peaks for each subspectrum. This allowed initial values for J_{AX} and J_{BX} to be found directly. In the most intense spectrum obtained, four of the remaining six, smaller transitions could finally be assigned with certainty, allowing J_{AB} to be determined, a computer fit to be carried out, and the ^{77}Se n.m.r. multiplet to be identified.

Spectrum of $AsP_2As^{77}Se^0Se_2$ (**8b**).—The P_A, P_B region for this ABX spin system presented similar problems to that of the ABMX spin system of (**4b**), and was dealt with in the same way.

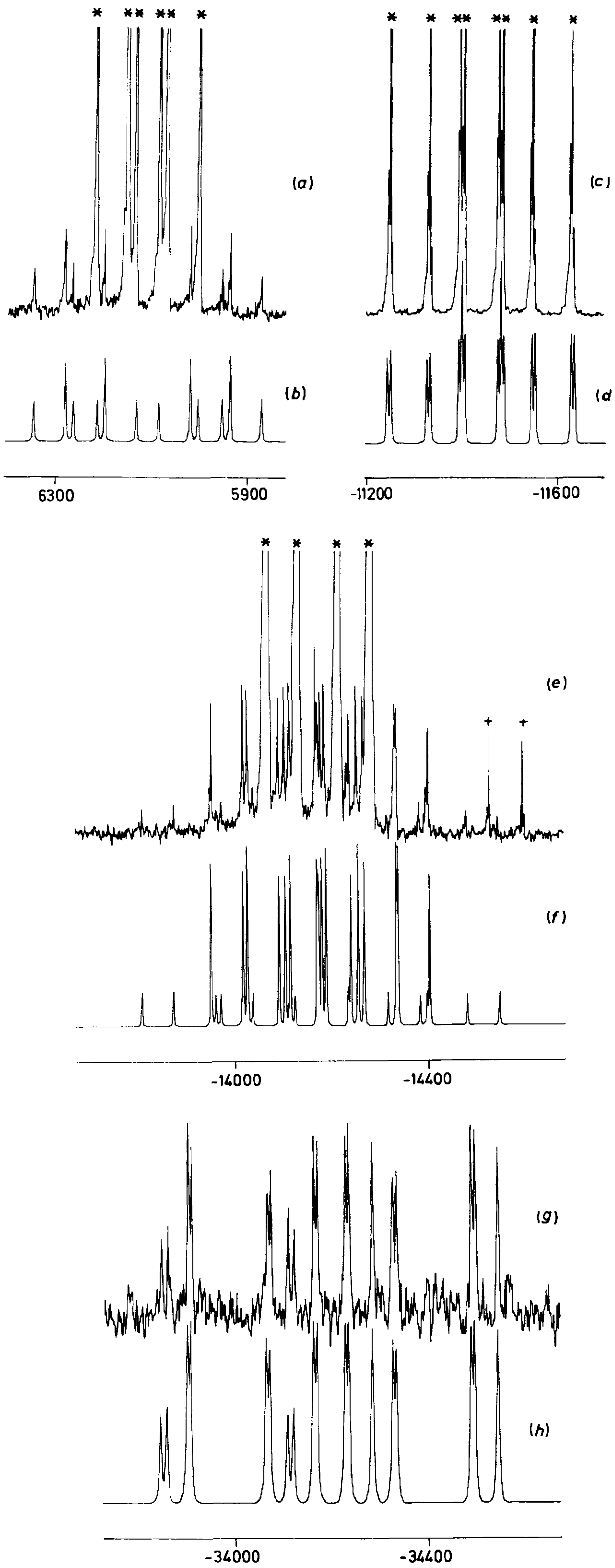


Figure. Observed [(*a*), (*c*), (*e*), (*g*)] and calculated [(*b*), (*d*), (*f*), (*h*)] ^{31}P and ^{77}Se n.m.r. spectra of $PP_3S^{77}Se^0Se$ (**2b**). (*a*), (*b*) P_M region (Table 1); (*c*), (*d*) P_F region; (*e*), (*f*) P_A, P_B region; (*g*), (*h*) ^{77}Se spectrum. *, Main phosphorus spectrum [$PP_3S^0Se_2$, (**2a**)]; +, impurity peaks due to P_4S_3. Scales are in Hz relative to D_3PO_4–D_2O for ^{31}P and saturated H_2SeO_3–H_2O for ^{77}Se. The ^{31}P spectrum is after 25 000 scans, the ^{77}Se spectrum after 49 000 scans

Table 2. Coupling constants[a] for derivatives of tetraphosphorus triselenide

Species[b]	Apical P –basal P	Basal P –basal P	Apical P –Se	Basal P –Se (^1J)	Basal P –Se (^2J)
$\mathrm{P_4S_3}$[c]	$J_{\rm FM}$ 70.58 (0.04)				
(1a)	$J_{\rm AM}$ 61.32 (0.05) $J_{\rm FM}$ 75.69 (0.04)	$J_{\rm AF}$ −144.05 (0.04)			
(1b)	$J_{\rm AM}$ 61.16 (0.07) $J_{\rm FM}$ 75.58 (0.07)	$J_{\rm AF}$ −144.05 (0.07)	$J_{\rm MX}$ −265.22 (0.09)	$J_{\rm AX}$ −331.82 (0.07)	$J_{\rm FX}$ −7.09 (0.07)
(2a)	$J_{\rm AM}$ 65.83 (0.03) $J_{\rm FM}$ 81.77 (0.03)	$J_{\rm AF}$ −150.62 (0.03)			
(2b)	$J_{\rm AM}$ 65.88 (0.12) $J_{\rm BM}$ 65.84 (0.14) $J_{\rm FM}$ 81.79 (0.13)	$J_{\rm AB}$ −142.86 (0.08) $J_{\rm AF}$ −150.63 (0.11) $J_{\rm BF}$ −150.57 (0.15)	$J_{\rm MX}$ −260.75 (0.10)	$J_{\rm AX}$ −323.7 (0.2)	$J_{\rm BX}$ −2.60 (0.11) $J_{\rm FX}$ −6.44 (0.11)
(3a)[d]	$J_{\rm AM}$ 71.33 (0.06)				
(3b)[d]	$J_{\rm AM}$ 71.4 (0.2) $J_{\rm BM}$ 71.2 (0.2)	$J_{\rm AB}$ −149.51 (0.09)	$J_{\rm MX}$ −256.5 (0.2)	$J_{\rm AX}$ −316.4 (0.3)	$J_{\rm BX}$ −0.4 (0.2)
(4a)	$J_{\rm AM}$ 81.67 (0.08)				
(4b)	$J_{\rm AM}$ 81.8 (0.2) $J_{\rm BM}$ 81.5 (0.1)	$J_{\rm AB}$ −166.09 (0.10)	$J_{\rm MX}$ −247.6 (0.2)	$J_{\rm AX}$ −312.4 (0.2)	$J_{\rm BX}$ −0.9 (0.3)
(4c)	$J_{\rm AM}$ 81.8		$J_{\rm MX}$ −287.5		$J_{\rm AX}$ *e*
(5a)	$J_{\rm AM}$ 96.874 (0.006)				
(5b)	$J_{\rm AM}$ 96.7 (0.2)		$J_{\rm MX}$ −239.0 (0.2)	$J_{\rm AX}$ −307.4 (0.2)	
(5c)	$J_{\rm AM}$ 97.0		$J_{\rm MX}$ −278.5		$J_{\rm AX}$ *e*
(6c)			$J_{\rm MX}$ −269.8		
(7b)		$J_{\rm AB}$ −137.62 (0.04)		$J_{\rm AX}$ −338.47 (0.11)	$J_{\rm BX}$ 4.70 (0.08)
(8b)		$J_{\rm AB}$ −153.5 (0.1)		$J_{\rm AX}$ −338.1 (0.4)	$J_{\rm BX}$ 8.3 (0.3)
(8c)					$J_{\rm AX}$ *e*
(9b)				$J_{\rm AX}$ −335.8	
(9c)					$J_{\rm AX}$ ±9.1

[a] Coupling constants are in Hz; standard deviations (σ) are shown beneath entries which were obtained by computer fitting. [b] For definition of species, see Table 1. [c] Included for comparison. [d] Ref. 3. [e] Insufficiently resolved (see assignment of n.m.r. spectra).

In the most intense spectrum obtained, three out of four of the less intense transitions could finally be assigned.

Spectra of $\mathrm{PPAs_2{}^{77}Se^0Se_2}$ (**5b**), $\mathrm{PAs_3{}^{77}Se^0Se_2}$ (**6c**), *and* $\mathrm{AsPAs_2{}^{77}Se^0Se_2}$ (**9b**).—These were almost, (**5b**), or completely first-order spin systems which presented no special difficulty. The apical ($\mathrm{P_M}$) multiplet of compound (**5b**) was distinguished by its lower intensity (Table 1) from that of its isotopomer (**5c**) [*cf.* (**4b**), above].

Spectra of Molecules containing ^{77}Se *bonded to Basal Arsenic*, (**4c**), (**5c**), (**8c**), *and* (**9c**).—In each case, the coupling ($^2J_{\rm AX}$) between ^{77}Se and a basal phosphorus atom not directly bonded to it was sufficiently small that the $\mathrm{P_A}$ multiplet was completely obscured by the main phosphorus spectrum [of (**4a**), (**5a**), *etc.*], so $J_{\rm AX}$ could be obtained only, if at all, from the ^{77}Se spectra. For molecules containing an apical phosphorus atom [(**4c**) and (**5c**)], the $\mathrm{P_M}$ multiplet yielded $J_{\rm MX}$, allowing the ^{77}Se multiplet to be identified by the size of this coupling.

The ^{77}Se multiplets of $\mathrm{AsP_2As^0Se_2{}^{77}Se}$ (**8c**) and $\mathrm{AsPAs_2{}^0Se_2{}^{77}Se}$ (**9c**) lacked any coupling which could be measured in the corresponding ^{31}P spectra, but were assigned on the basis of chemical shift. All three chemical shifts ($\nu_{\rm A}$, $\nu_{\rm M}$, and $\nu_{\rm X}$) for the phosphorus arsenic selenides moved progressively to higher frequency with replacement of phosphorus by arsenic at a basal position (Table 3). Replacing phosphorus by arsenic at the apical position had a similar effect on the basal phosphorus shift ($\nu_{\rm A}$), so this shift for molecules containing apical phosphorus [(**4a**), (**5a**)] was similar to that for the isomeric molecules with all of their phosphorus atoms in basal positions [(**7a**), (**8a**)].[1] This was not so for the ^{77}Se shifts ($\nu_{\rm X}$): replacement of phosphorus by arsenic at the apical

Table 3. Chemical shifts and iterative fitting data for derivatives of tetraphosphorus triselenide

	Chemical shifts[b]			No. of transitions assigned in:		Root mean square (r.m.s.) deviation (Hz)
Species[a]	Apical P	Basal P	^{77}Se	P spectrum	Se spectrum	
P_4S_3[c]	ν_M 67.99	ν_F −120.05		14		0.11
(1a)	ν_M 60.2025 (0.0003)	ν_A −129.0925 (0.0003) ν_F −107.1876 (0.0003)		24		0.09
(1b)	ν_M 60.2083 (0.0005)	ν_A −129.0857 (0.0004) ν_F −107.1855 (0.0009)	ν_X −652.9	33	16	0.18
(2a)	ν_M 50.2598 (0.0002)	ν_A −116.7124 (0.0002) ν_F −94.1871 (0.0002)		24		0.06
(2b)	ν_M 50.2646 (0.0007)	ν_A −116.7066 (0.0006) ν_B −116.7087 (0.0007) ν_F −94.1853 (0.0007)	ν_X −596.7	48	23	0.26
(3a)[d]	ν_M 37.4036 (0.0005)	ν_A −104.5089 (0.0005)		14		0.14
(3b)[d]	ν_M 37.4091 (0.0011)	ν_A −104.5038 (0.0013) ν_B −104.5049 (0.0011)	ν_X −540.6	45	24	0.50
(4a)	ν_M 57.7402 (0.0006)	ν_A −87.3057 (0.0006)		8		0.12
(4b)	ν_M 57.7456 (0.0007)	ν_A −87.2980 (0.0011) ν_B −87.3049 (0.0007)	ν_X −527.3	22	11	0.18
(4c)	ν_M 57.7485	ν_A *e*	ν_X −531.9	*f*		
(5a)	ν_M 75.249 66 (0.000 03)	ν_A −74.091 79 (0.000 03)		4		0.003
(5b)	ν_M 75.2552 (0.0010)	ν_A −74.0847 (0.0010)	ν_X −501.0	8	4	0.18
(5c)	ν_M 75.2562	ν_A *e*	ν_X −505.1	*f*		
(6a)	ν_M 87.8032			*f*		
(6c)	ν_M 87.8091		ν_X −469.5	*f*		
(7a)		ν_A −89.1313		*f*		
(7b)		ν_A −89.1238 (0.0004) ν_B −89.1293 (0.0004)	ν_X −619.1	14	12	0.09
(8a)		ν_A −71.4724		*f*		
(8b)		ν_A −71.4642 (0.0014) ν_B −71.4699 (0.0009)	ν_X −599.4	7	6	0.12
(8c)		ν_A *e*	ν_X −604.5	*f*		
(9a)		ν_A −58.1347		*f*		
(9b)		ν_A −58.1277	ν_X −568.6	*f*		
(9c)		ν_A *e*	ν_X −574.9	*f*		
As_4Se_3[c]			ν_X −536.3	*f*		

[a] For definition of species, see Table 1. [b] Chemical shifts are in p.p.m.; standard deviations (σ) are shown only beneath entries which were obtained by computer fitting; ^{77}Se shifts are not reported to full experimental precision because isotopomers had ^{77}Se in differing chemical environments, so relative chemical shifts would be influenced by solvent effects. [c] Included for comparison. [d] Ref. 3. [e] Not observed. [f] No computer fit done.

position caused a larger shift of the ^{77}Se absorption than replacement at a basal position, and in the opposite direction, so isomeric molecules with and without apical phosphorus formed two parallel series of shifts which did not overlap, molecules with apical phosphorus absorbing to higher frequency than those with apical arsenic. Extending these series to P_4Se_3 and As_4Se_3 respectively (Table 3), As_4Se_3 did absorb at slightly higher frequency than P_4Se_3. Within the series of molecules with apical phosphorus, the ^{77}Se shifts already assigned to **(4c)** and **(5c)** (above) were close to and less than those due to the isotopomeric molecules (**4b**) and (**5b**), in which the ^{77}Se nucleus was bonded to basal phosphorus. It was therefore anticipated that the sought ^{77}Se resonances of (**8c**) and (**9c**) would be near to the multiplets assigned to (**8b**) and (**9b**) in the series of molecules with apical arsenic. The only major remaining unassigned features of the ^{77}Se spectra of the mixtures occurred at these expected frequencies, so were assigned to (**8c**) and (**9c**).

Although all four molecules (**4c**), (**5c**), (**8c**), and (**9c**) should show first-order multiplets in their ^{77}Se spectra, the compromise between signal-to-noise ratio and resolution which we obtained in our best spectra was sufficient to resolve clearly a $^2J_{AX}$ splitting only for (**9c**), where the expected doublet was found ($|^2J_{AX}| = 9.1$ Hz). For (**5c**), one leg of the J_{MX} doublet was barely resolved (splitting 2.1 Hz), but not the other leg, so $|^2J_{AX}|$ may be assumed to be $\leqslant 2.1$ Hz. The relatively less-abundant molecules (**8c**) and (**4c**) were expected to show a triplet and a doublet of triplets respectively; in each case, although there clearly was some splitting, triplets could not be recognised, so we cannot report J_{AX} for these molecules.

Discussion

Trends in Chemical Shifts and Coupling Constants.—As might be expected, all of the shifts and coupling constants (Tables 2 and 3) for the molecules studied formed regular series, with replacement of selenium by sulphur, or of phosphorus by arsenic. Two possible approaches to rationalising these series are: to try to correlate them with expected geometric and hence electronic properties of the molecules, upon which they might be expected to depend; or to take a completely empirical approach by examining their correlations with each other, and hence their dependence upon a minimum number of arbitrary molecular parameters.

Complete structural data from crystallography are available only for P_4Se_3 (**3**). The basal bond angles have been estimated geometrically for the phosphorus arsenic selenides (**4**)—(**9**), assuming additivity of covalent radii, and constant bond angles at apical phosphorus or apical arsenic respectively.[1] Basal angles in the phosphorus sulphide selenides (**1**) and (**2**) have been found from the basal ^{31}P chemical shifts by applying the linear relationships already established for the phosphorus arsenic selenides and sulphides.[1] That these estimated angles were substantially correct is amply reinforced by the good correlations reported below of these angles with the further n.m.r. properties which we have now measured. So far, we know of no molecular orbital nor molecular mechanics calculations on the molecules, which could lead to better predictions of geometry.

Chemical Shifts.—A single linear relationship allowed the chemical shift of a basal phosphorus nucleus to be calculated from the bond angles at it, irrespective of whether it was bonded to a selenium or to a sulphur atom: the usual dependence of chemical shift upon the electronegativity of bonded atoms was not found.[1] The ^{77}Se chemical shifts reported here can similarly not be rationalised as depending mainly on electronegativity effects. While the ^{77}Se resonances moved to lower frequency on replacement of more electronegative phosphorus by less electronegative arsenic at the apical position, just as $As(SeCF_3)_3$ absorbs at lower ^{77}Se frequency than $P(SeCF_3)_3$,[5] they moved to higher frequency when a phosphorus atom was replaced at a basal position. This shift to higher frequency was slightly greater for selenium nuclei not bonded directly to the substituted basal position than for the selenium nucleus which was.

These trends may, however, readily be explained if it is assumed that the differences in electronegativity between phosphorus and arsenic in the basal positions of these molecules have a small effect on the chemical shift of a neighbouring selenium nucleus, compared with the effect of the bond angle at the selenium, and that an increase in this angle leads to more positive chemical shifts, as it does for ^{31}P in cyclic phosphines. If apical bond angles remain relatively constant during basal substitution, as previously assumed,[1] then replacement of a basal phosphorus atom by the larger arsenic will increase the bond angles at the selenium bridges as well as the 'exocyclic' angles at the other two basal positions. Thus chemical shifts of the selenium nuclei and of any remaining basal phosphorus nuclei should become more positive, as observed. If the bond angles at all three selenium bridges are assumed to increase equally, then since the influence of a change in bond angle on ^{77}Se chemical shift works in the opposite direction to the smaller electronegativity effect, the smaller change in shift of a selenium nucleus directly bonded to the substituted basal position, and hence feeling the electronegativity effect most strongly, is rationalised.

Replacement of apical phosphorus by the larger arsenic will also increase the 'exocyclic' angles at the basal positions, but if the bond angles about apical arsenic are similar to those about apical phosphorus, as is true for As_4S_3 compared with P_4S_3, then the angles at bridging selenium must decrease. Thus the observed change of ^{77}Se chemical shift, to lower frequency, is rationalised. Here the influence of changing bond angle augments the effect of changing electronegativity, so the greater changes in ^{77}Se chemical shift, compared with those resulting from replacement at a basal position, are partly explained. Changes in ^{77}Se chemical shift to more negative values as other bridging selenium atoms were replaced by sulphur, in the phosphorus sulphide selenides, may similarly be explained as being due to a decrease in bond angle at selenium.

Of all the trends in chemical shifts for these molecules, only those for the apical phosphorus nuclei of molecules (**1**)—(**6**) cannot be rationalised using this argument of dependence on bond angles. The hypothesis that the apical angles remain constant during basal substitution could be abandoned without invalidating the previous arguments: an increase in atomic size at a basal position would be accommodated by some increase in apical angles as well as in angles at selenium and at the other basal positions. This rationalises the move of apical ^{31}P chemical shift to higher frequency as arsenic is introduced at the basal positions, which is counter to the move expected on electronegativity grounds. However, it is not clearly possible to invoke an increase in apical bond angles to explain the observed move of the apical chemical shift to more positive values on replacement of selenium bridges by sulphur bridges. Here alone, the electronegativity of the neighbouring chalcogenide bridges has been assumed to be the dominant factor;[1] this remains an anomaly.

Table 4. Molecular parameters used for multiple regression analyses of n.m.r. properties of molecules containing a P_A–^{77}Se–P_M bridge

	Estimated bond angles/° at basal phosphorus P_A[b]		Molecular parameters[c]	
Species[a]	*endo*	*exo*	X_i	Y_i
(**1b**)	60.0	101.0	0.2058	−0.9841
(**2b**)	60.0	104.0	0.1257	−0.4844
(**3b**)	60.0	105.4	0.0000[d]	0.0000[d]
(**4b**)	61.6	105.4	0.5158	0.4685
(**5b**)	62.8	105.4	1.0000[d]	1.0000[d]

[a] For definition of species, see Table 1. [b] From Ref. 1; angles are endocyclic and exocyclic respectively with respect to the basal three-membered ring. [c] From least-squares fitting to equation (1) in this work, followed by normalisation. [d] Set during normalisation.

Table 5. Analyses of multiple regression of n.m.r. properties on molecular parameters[a]

N.m.r. property[b]	No. of species	Regression on basal bond angles				Regression on X_i and Y_i [equation (1)]			
		Coeff. of *endo*	Coeff. of *exo*	Constant	R^c	A_p	B_p	C_p	R^c
ν_A	5	11.59	5.392	−1 369.8	0.997	4.065	26.67	−103.8	0.9986
ν_M	5	12.49	−5.018	−181.2	0.98	50.34	−12.61	37.6	0.9999
ν_X	5	17.24	23.94	−4 109.6	0.991	−59.71	99.86	−541.9	0.9999
J_{AB}	4	−10.64	−1.187	614.5	0.9989	−23.04	−10.39	−149.3	0.9995
J_{AM}	5	9.147	2.003	−690.3	0.992	12.83	12.54	70.6	0.998
J_{AX}	5	3.540	3.339	−881.9	0.995	−5.606	14.48	−316.3	0.9998
J_{BX}	4	0.229	1.415	−164.2	0.96	−5.716	5.632	−0.6	0.995
J_{MX}	5	6.425	1.858	−838.6	0.998	7.108	10.47	−256.4	0.9999

[a] Table 4. [b] As defined in Table 1, except for species (**1b**) and (**2b**): see footnotes to Table 6. [c] Multiple correlation coefficient.

Table 6. Comparison of experimental and predicted n.m.r. properties

Species[a]	Origin[b]	ν_A	ν_M	ν_X	J_{AB}	J_{AM}	J_{AX}	J_{BX}	J_{MX}
(**1b**)[c]	E	−129.1	60.2	−652.9	−144.0	61.2	−331.8	−7.1	−265.2
	A	−130.0	61.4	−656.7	−143.8	60.8	−332.3	−7.5	−265.5
	X	−129.2	60.3	−652.4	−143.8	60.9	−331.7	−7.3	−265.3
(**2b**)[d]	E	−116.7	50.3	−596.7	−146.7	65.9	−323.7	−4.5	−260.7
	A	−113.8	46.4	−584.8	−147.4	66.9	−322.3	−3.2	−259.9
	X	−116.2	50.0	−597.7	−147.2	66.2	−324.0	−4.1	−260.6
(**3b**)	E	−104.5	37.4	−541.7[e]	−149.5	71.4	−316.4	−0.4	−256.5
	A	−106.3	39.4	−551.3	−149.1	69.7	−317.6	−1.3	−257.3
	X	−103.8	37.6	−541.9	−149.3	70.6	−316.3	−0.6	−256.4
(**4b**)	E	−87.3	57.7	−527.3	−166.1	81.8	−312.4	−0.9	−247.6
	A	−87.7	59.3	−523.7	−166.1	84.3	−311.9	−0.9	−247.0
	X	−89.2	57.6	−525.9	−166.1	83.1	−312.4	−0.9	−247.9
(**5b**)	E	−74.1	75.3	−501.0		96.7	−307.4		−239.0
	A	−73.8	74.3	−503.0		95.3	−307.7		−239.3
	X	−73.1	75.3	−501.7		96.0	−307.4		−238.9

[a] For definition of species, see Table 1. [b] E = Experimental; A = predicted using estimated basal bond angles (Table 4) and regression coefficients (Table 5); X = predicted using X_i and Y_i (Table 4), A_p, B_p, and C_p (Table 5), and equation (1). [c] J_{AF} and J_{FX} (Table 2) used in place of J_{AB} and J_{BX} respectively. [d] Averages of J_{AB} and J_{AF} and of J_{BX} and J_{FX} used (see Discussion). [e] Average of values for solution of phosphorus selenide sulphides and for solution of phosphorus arsenic selenides.

Coupling Constants.—The increases, hypothesised above, of bond angles at selenium and at basal phosphorus P_A, in a P_A–$^{77}Se_X$–P_M bridge, on replacing another basal phosphorus atom by arsenic, or a sulphur bridge by a selenium bridge, led not only to less negative chemical shifts ν_A and ν_X, but also to more positive couplings, $^2J_{AM}$, between apical and basal phosphorus nuclei, to less negative ^1J couplings to ^{77}Se, $^1J_{AX}$ and $^1J_{MX}$, and to more negative couplings, $^1J_{AB}$, between basal phosphorus nuclei. Since all of these couplings could be correlated to the same molecular parameters as could the chemical shifts (see below), it is likely that changing bond angles were the main causes of changes in the couplings, as they were for the chemical shifts.

Statistical Analysis of N.M.R. Properties.—Multiple regression analyses were performed of the three chemical shifts (ν_A, ν_M, and ν_X) and the five coupling constants (J_{AB}, J_{AM}, J_{AX}, J_{BX}, and J_{MX}) shown by four or five of the molecules containing a P_A–$^{77}Se_X$–P_M bridge [(**1b**), (**2b**), (**3b**), (**4b**), and (**5b**)], on the two estimated[1] angles (Table 4) at the basal phosphorus atom P_A. In order to maintain compatibility with both $PP_3{}^{77}Se^0Se_2$ (**3b**) and $PP_3S_2{}^{77}Se$ (**1b**), the $^1J_{PP}$ and $^2J_{PSe}$ couplings taken for $PP_3S^{77}Se^0Se$ (**2b**) were averages of the couplings to basal phosphorus bonded to selenium and to basal phosphorus bonded to sulphur, *i.e.* the average of J_{AB} and J_{AF} was taken instead of J_{AB}, and of J_{BX} and J_{FX} instead of J_{BX}. The analyses found (Table 5) remarkably high multiple correlation coefficients in each case. A comparison of the experimental shifts and couplings with values calculated from the regression parameters is included in Table 6.

Molecular parameters X_i and Y_i were next calculated by least-squares fitting of the experimental data to equation (1) (see Introduction), using the three chemical shifts, as above, but only the three coupling constants (J_{AM}, J_{AX}, and J_{MX}) available for all five molecules. In the absence of an imposed physical meaning for X_i and Y_i, there are an infinite number of exactly equally good fits to equation (1), since *e.g.* if all parameters X_i are multiplied by an arbitrary constant, then all coefficients A_p may be divided by that constant. Thus, sets of values X_i and Y_i, once found, may each be normalised by multiplication by any scale factor, and each can be relative to any scale origin, since changes in their origins can be taken up by changes in the set of constants C_p. In practice, the least-squares fit was simplified by elimination of the constant term C_p, by standardisation of the n.m.r. properties N_{pi} to means of zero and standard deviations of unity; X_i and Y_i were then fixed for $PP_3{}^{77}Se^0Se_2$ (**3b**) to 1.0 and 0.0 respectively in the fitting process. The resulting vectors X_i and Y_i were then normalised for convenience each to a value of 0.0 for molecule (**3b**) and a maximum value of 1.0 (Table 4). Vectors A_p, B_p, and C_p were then found by multiple regression analysis of the original n.m.r. properties N_{pi} on these normalised molecular parameters. The multiple correlation coefficients (Table 5) and the match of observed *versus* predicted n.m.r. properties (Table 6) were clearly slightly better than for multiple regression on estimated bond angles. The n.m.r. properties available for only four molecules (J_{AB} and J_{BX}), which could not be included in the least-squares fit for obtaining X_i and Y_i, were included in the multiple regression analyses on them, and served as extra tests of the validity of X_i and Y_i as useful molecular parameters. In fact it was the fit of J_{BX} whose significance improved the most in moving from regression on basal angles to regression on X_i and Y_i.

Acknowledgements

Dr. M. N. S. Hill (University of Newcastle) is thanked for obtaining the n.m.r. spectra.

References

1 R. Blachnik, U. Wickel, and P. Schmitt, *Z. Naturforsch., Teil B*, 1984, **39**, 1135.
2 B. W. Tattershall, *J. Chem. Soc., Dalton Trans.*, 1987, 1515.
3 B. W. Tattershall and R. Blachnik, *J. Chem. Soc., Dalton Trans.*, 1988, 2055.
4 W. McFarlane and J. A. Nash, *Chem. Commun.*, 1969, 913.
5 W. Gombler, *Z. Naturforsch., Teil B*, 1981, **36**, 535.

Received 16*th May* 1988; *Paper* 8/01921E