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Interdependence of phosphorus-31–selenium-77 NMR coupling constants in bicyclic phosphorus selenide compounds†

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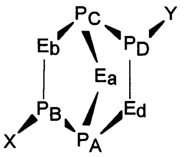
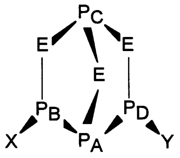
Bicyclic compounds *exo,exo*-α-$P_4Se_3X_2$ and *exo,exo*-α-P_4Se_3XI (X = CN, NMePh or NPr^i_2) and *endo,exo*-α-$P_4Se_3(CN)_2$ have been made in solution and their ^{31}P and ^{77}Se NMR spectra completely analysed. *Ab initio* calculations of ^{31}P and ^{77}Se NMR shieldings in *exo,exo*- and *endo,exo*-α-$P_4Se_3(CN)_2$ and in *exo,exo*-α-$P_4Se_3(CN)I$ confirmed these assignments. In an unsymmetric compound *exo,exo*-α-P_4Se_3XI the twelve ^{31}P–^{77}Se NMR coupling constants have values related to those in the corresponding symmetric compounds *exo,exo*-α-$P_4Se_3X_2$ and *exo,exo*-α-$P_4Se_3I_2$ by simple rules, useful for predicting couplings in *exo,exo*-α-$P_4Se_3X_2$ when the spectra of *exo,exo*-α-P_4Se_3XI and *exo,exo*-α-$P_4Se_3I_2$ have already been analysed.

Introduction

For compounds *exo,exo*-α-P_4S_3XY **1**, where X and Y are hydrogen or halogen or carbon-, nitrogen-, phosphorus- or sulfur-centred substituents, there are six endocyclic ^{31}P–^{31}P NMR coupling constants, corresponding to the edges of the approximate tetrahedron of phosphorus atoms in the α-P_4S_3 skeleton. It became apparent that the couplings in the unsymmetric compound **1xy** (X ≠ Y) were related to the corresponding couplings in the symmetric compounds *exo,exo*-α-$P_4S_3X_2$ **1xx** and *exo,exo*-α-$P_4S_3Y_2$ **1yy** by a set of balancing rules.[1] Thus, $^2J(P_AP_C)$ or $^3J(P_BP_D)$ in **1xy** were very nearly the averages of $^2J(P_AP_C)$ or $^3J(P_BP_D)$ respectively in **1xx** and **1yy** (taking into account the sign of $^3J(P_BP_D)$). Couplings $^1J(P_AP_B)$ or $^1J(P_CP_D)$ in **1xy** had similar values to $^1J(P_AP_B)$ in **1xx** or $^1J(P_CP_D)$ in **1yy** respectively, since the atoms involved in these couplings were nearer to one substituent X or Y, but deviations from the values in the symmetric compounds were nearly equal and opposite: the average of $^1J(P_AP_B)$ and $^1J(P_CP_D)$ in **1xy** was approximately the average of these couplings over **1xx** and **1yy**. Similar pairwise relationships were found for the chemical shifts $\delta(P_A)$, $\delta(P_C)$ and (less precisely) $\delta(P_B)$ and $\delta(P_D)$. For the remaining pair of ^{31}P–^{31}P couplings, $^2J(P_AP_D)$ and $^2J(P_BP_C)$, amino substituents $X = NR^1R^2$ were found to cause particularly low values of $^2J(P_AP_D)$, through the skeleton edge distant from their point of attachment at P_B, rather than of $^2J(P_BP_C)$, but the averaging rule still applied. This was attributed to a concerted twisting of the two five-membered rings of the skeleton, which transmitted the steric effect of the substituent and of its N–P bond.[2]



1 (E = S)
2 (E = Se)



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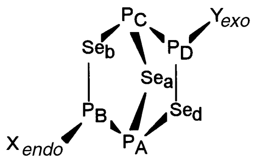

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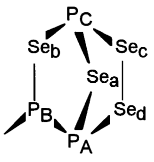

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While it is not possible, except by analogy with very similar compounds, to predict the direction or size of deviations of individual couplings or chemical shifts from the average values in **1xy**, this is not of practical importance because, except for a few cases of accidental near-equality of chemical shifts, the ^{31}P NMR spectra of the unsymmetric compounds **1xy** are relatively easy to analyse, starting from a first-order approximation. There are much greater difficulties in analysing the spectra of symmetric compounds *exo,exo*-α-$P_4S_3X_2$, for which the phosphorus nuclei of the skeleton constitute an AA′MM′ spin system, particularly where X also contains an NMR-active nucleus, such as ^{31}P, which is hard to decouple. Here the application of the above rules has been very useful. For example, for *exo,exo*-α-$P_4S_3(PPh_2)_2$ (spin system AA′FF′MM′) a fairly accurate prediction of coupling constants was necessary before sufficient transitions could be assigned correctly for an initial computer fit to succeed.[3] This was achieved using the rules with coupling constants known for *exo,exo*-α-$P_4S_3(PPh_2)I$ and *exo,exo*-α-$P_4S_3I_2$. The rules were found to apply also to the selenium analogues **2**, and similar rules were developed for molecules *exo,exo*-β-P_4E_3XY (E = S or Se) **3**.[4] Besides facilitating the analysis of spectra, observation that NMR parameters for three compounds **xx**, **xy** and **yy** balance under these rules is useful evidence that the same substituent X (or Y) is present in two of them.

Probably these rules all work because the constraints of the bicyclic (or *nido*-cage) structure cause an interdependency of changes in skeletal bond angles with exocyclic substitution, as well as an interdependency of changes in molecular orbital composition. The values of some ^{31}P–^{77}Se couplings appear to depend on bond angles in a similar way to ^{31}P–^{31}P couplings,[5] so it seemed possible that similar balancing rules might apply to ^{31}P–^{77}Se coupling constants in compounds *exo,exo*-α-P_4Se_3XY.

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† Electronic supplementary information (ESI) available: rotatable 3-D molecular structure diagrams in CHIME format. Also *ab initio* geometries and energies for α-$P_4Se_3(CN)_2$ and α-$P_4Se_3(CN)I$. See http://www.rsc.org/suppdata/dt/b0/b010068o/

These would be useful in a similar way, *i.e.* to provide starting values of coupling constants for assignment of ^{77}Se satellites in the ^{31}P NMR spectra of symmetric compounds. Here too, the appearance and hence recognisability of simulations depends critically upon the relative values of the coupling constants used, and reliance only on guesswork from trends can lead to a very protracted process of analysis by trial and error.

To establish rules, we set out to make compounds which, on the basis of the ^{31}P NMR spectra of their known sulfur analogues, should have skeletal geometries as dissimilar as possible. As substituent X we chose cyanide, which in compounds *exo*,*exo*-α-$P_4S_3(CN)Y$ leads to large couplings $^2J(P_AP_C)$ and $^2J(P_AP_D)$,[6] and NMePh which leads to small values of these couplings.[1] During this work the substituent NPr^i_2 was reported to show very strong π bonding to phosphorus,[7] so we used this to give even more extreme data. Using preparative methods well established for the sulfur analogues, we made solutions containing *exo*,*exo*-α-$P_4Se_3X_2$ and *exo*,*exo*-α-P_4Se_3XI, for X = CN, NMePh or NPr^i_2. The cyanide *exo*,*exo*-α-$P_4Se_3(CN)_2$ yielded crystals suitable for structure determination, which has been reported separately in comparison with *ab initio* predictions of molecular structure.[8] We now report complete analysis of the ^{31}P and ^{77}Se NMR spectra of these compounds, along with those of *endo*,*exo*-α-$P_4Se_3(CN)_2$ **4**, which we have identified as a by-product in the cyanide case. For the compounds *exo*,*exo*-α-P_4Se_3XY we report balancing rules involving, in pairs, all twelve ^{31}P–^{77}Se coupling constants, as well as operation of the previously reported rules involving the six ^{31}P–^{31}P coupling constants.

Results and discussion

Reactions and observed products

Aminophosphorus selenides. Solutions of compounds *exo*,*exo*-α-$P_4Se_3X_2$ and *exo*,*exo*-α-P_4Se_3XI **2**, where X = NMePh or NPr^i_2, were made by reaction of a suspension of α-$P_4Se_3I_2$ in C_6H_5Me with a slowly added solution of four molar equivalents of the amine HX. In either case reaction was not complete when the resulting solutions were sampled for NMR after 46 hours. The diamino compounds α-$P_4Se_3X_2$ were the major phosphorus-containing solutes in toluene, but when this solvent was removed, along with unchanged amine, by pumping at room temperature, and then the solid residue was stirred with CS_2, substantial concentrations of α-P_4Se_3XI appeared. This can be ascribed to higher solubility in CS_2 of the iodine-containing compounds, which had remained mixed with the $H_2X^+I^-$ by-product in the solid phase of the reaction mixture. It was not possible to use CS_2 as a solvent for the reaction because of its known insertion reaction with the amines used, but the aminophosphorus products, once formed, appeared unreactive towards it.

For the symmetric compounds α-$P_4Se_3X_2$, main ^{31}P NMR spectra were distorted by scalar ^{31}P–^{14}N coupling relaxation, and some ^{77}Se satellite peaks were rendered indistinguishable from noise. The effect was less in the more viscous solvent C_6H_5Me than in CS_2, particularly at low temperature, so the best-quality NMR parameters reported are for solutions in toluene. However, for examination of the 'balancing' of coupling constants, it was desirable to use data for α-$P_4Se_3X_2$, α-P_4Se_3XI and α-$P_4Se_3I_2$ in the same solvent, which was necessarily CS_2. Where satellite peaks were invisible, coupling information was taken from ^{77}Se NMR spectra, which because of long acquisition times could not be obtained at low temperature. Thus, the spectra selected for comparison were those obtained at ambient temperature, despite their lower quality.

Phosphorus selenide cyanides. Despite lower solubility, it appears that phosphorus selenide halides undergo halide replacement reactions under milder conditions than do the corresponding sulfur compounds. We therefore undertook the initial reaction of α-$P_4Se_3I_2$ with AgCN, using CS_2 as solvent, at ambient temperature over 5 days, rather than at 50 °C, as had been necessary for the corresponding reaction of α-$P_4S_3I_2$.[6,9] This resulted in a cleaner, though less complete reaction, giving a solution in which the only significant solutes were *exo*,*exo*-α-$P_4Se_3(CN)I$, *exo*,*exo*-α-$P_4Se_3(CN)_2$ and *endo*,*exo*-α-$P_4Se_3(CN)_2$, in molar ratio 48 : 29 : 23. Subsequent heating of the reaction mixture to 52 °C for one day caused further reaction of *exo*,*exo*-α-$P_4Se_3(CN)I$ **2** and *endo*,*exo*-α-$P_4Se_3(CN)_2$ **4**, to leave a solution of the symmetric *exo*,*exo*-dicyanide. ^{31}P, ^{77}Se and ^{13}C NMR spectra were obtained in CS_2 at ambient temperature, either using the initial solution containing all three components, or using the final solution of *exo*,*exo*-α-$P_4Se_3(CN)_2$.

Assignment and fitting of NMR spectra

Main ^{31}P spectra of *exo*,*exo*-compounds 2. Multiplets were assigned readily by methods used previously,[1] with broadening by ^{14}N scalar coupling relaxation or observation of low-frequency chemical shifts allowing assignment of multiplets associated with phosphorus carrying amino or cyano substituents respectively. Hand analysis was followed by iterative fitting using NUMARIT.[10] Comparison of resulting chemical shifts and coupling constants (Table 1) with data for corresponding sulfur compounds **1** (with X = NMePh,[1] NPr^i_2,[11] or CN[6]) leaves little doubt about the identity of the compounds.

Distortion of ^{31}P multiplets of the symmetric amino compounds *exo*,*exo*-α-$P_4Se_3X_2$ **2** (X = NMePh or NPr^i_2) by unresolved ^{14}N coupling made normal fitting inaccurate for solutions in CS_2 at room temperature. In the absence of ^{14}N coupling, the P_A and P_B multiplets would have been in a mirror-image relationship to each other, and ^{31}P–^{31}P coupling information could have been obtained equally from either. In fact, for X = NMePh, differently situated pairs of transitions were unresolved in the two multiplets, because of different broadening effects. If some unresolved transitions were included for one multiplet, then the other multiplet, which was distorted in a different way, clearly did not fit. While excluding all unresolved transitions left insufficient data for a fit of all four coupling constants at the same time, either the pair $^1J(P_AP_B)$ and $^2J(P_AP_D)$ or the pair $^2J(P_AP_C)$ and $^3J(P_BP_D)$ could be fitted while the other pair was held constant. Starting with values of coupling constants for the solution in toluene at 243 K, the pairs of couplings were fitted alternately, over five cycles of an iterative process, during which the root mean square deviation obtained converged to 0.62 Hz over the observed transitions. While this artificially constrained fitting could have converged to a false minimum, the couplings obtained seem sensible when compared with those from the low-temperature spectrum, or from satellite spectra.

^{77}Se isotopomers of unsymmetric compounds *exo*,*exo*-α-P_4Se_3XI. These constituted approximately first order spin systems, but the difficulties here were that ^{31}P multiplets containing small (<20 Hz) ^{31}P–^{77}Se splittings were obscured by the main spectrum, while those for P_B in the amino iodides were broadened so as to be indistinguishable from noise. In both cases, these ^{31}P–^{77}Se couplings could be obtained only from the ^{77}Se spectrum. For *exo*,*exo*-α-$P_4Se_3(NPr^i_2)I$ this was poor because of low concentration, but for the other compounds **2** (X = NMePh or CN, Y = I) all sixteen $^{77}Se_b$ transitions were visible and partially resolved, while 12/16 $^{77}Se_d$ peaks were well resolved. Some ^{14}N broadening of the Se_b multiplets allowed them to be assigned relative to Se_d. In fitting using NUMARIT, $^2J(P_BSe_d)$ was assumed to be positive, by analogy with P_3Se_4I **5**, for which this could be demonstrated by a dynamic NMR study.[12] A positive sign for $^2J(P_CSe_d)$ gave a significantly better fit for **2** (X = CN, Y = I) and a slightly better fit for **2** (X = NMePh, Y = I). Similarly, $^2J(P_ASe_b)$ was shown to

Table 1 NMR parameters for *exo*,*exo*- or *endo*,*exo*-*α*-P_4Se_3XY (**2** or **4**)

	2	**2**	**2**	**2**	**2**	**2**	**2**	**2**	**4**	**2**
X	NPr$^i_2$	NPr$^i_2$	NPr$^i_2$	NMePh	NMePh	NMePh	CN	CN	CN	I[a]
Y	NPr$^i_2$	NPr$^i_2$	I	NMePh	NMePh	I	CN	I	CN	I
Solvent	C_6H_5Me	CS_2	CS_2	C_6H_5Me	CS_2	CS_2	CS_2	CS_2	CS_2	CS_2
T/K	243	294	294	243	294	294	294	294	294	297
(a) Coupling constants (Hz)[b]										
(i) ^{31}P–^{31}P										
$^1J(P_AP_B)$	−341.32(8)	−342.5(3)	−334.05(4)	−329.28(6)	−327.5(4)	−320.93(2)	−252.11(5)	−255.93(2)	−254.74(3)	
$^1J(P_CP_D)$			−250.55(4)			−247.52(2)		−235.10(2)	−253.57(3)	−239.7
$^2J(P_AP_C)$	45.7(2)	44.5(4)	61.80(4)	58.9(1)	59.3(c)	69.72(2)	95.73(7)	91.96(2)	106.75(3)	87.2
$^2J(P_AP_D)$	11.82(6)	13.3(2)	10.46(4)	12.87(5)	13.3(2)	12.71(2)	34.63(3)	27.24(2)	62.57(3)	
$^2J(P_BP_C)$			24.41(4)			23.41(2)		28.34(2)	4.59(3)	21.4
$^3J(P_BP_D)$	−16.6(1)	−15.7(4)	−0.03(4)	−13.98(9)	−11.6(c)	−0.03(2)	−19.26(4)	−9.28(2)	13.42(3)	5.3
(ii) ^{31}P–$^{77}Se_a$										
$^1J(P_ASe_a)$	−265.5(6)	−262.8(4)	−285.9(2)	−261.5(2)	−259.44(7)	−278.60(3)	−263.2(1)	−256.5(2)	−241.0(2)	
$^1J(P_CSe_a)$			−260.5(1)			−262.80(3)		−285.8(2)	−208.8(2)	−279.6
$^2J(P_BSe_a)$	20.09(3)[d]	19.0[d]	31.1(6)	[c]	20.41(8)	28.52(4)	6.3(2)	9.1(2)	21.8(2)	
$^2J(P_DSe_a)$			0.1(6)			0.28(4)		0.3(2)	0.0(2)	6.0
(iii) ^{31}P–$^{77}Se_b$, ^{31}P–$^{77}Se_d$										
$^1J(P_ASe_d)$	−299.0(4)	−299.1(2)	−242.4(1)	−281.0(2)	−280.8(2)	−238.91(5)	−214.8(2)	−232.7(1)	−269.3(3)	
$^1J(P_CSe_b)$			−260.6(2)			−247.1(2)		−191.8(1)	−253.8(2)	−207.76
$^1J(P_BSe_b)$	−275.5(4)	−274.2(2)	[c]	−280.8(2)	−278.6(2)	−272.3(3)	−261.8(1)	−267.7(1)	−223.6(3)	
$^1J(P_DSe_d)$			−297.0(1)			−294.02(4)		−278.07(9)	−247.6(2)	−285.41
$^2J(P_ASe_b)$	−21.9(8)	−22.5(5)	−19.6(3)	−12.2(4)	−11.5(2)	−8.8(2)	11.9(1)	10.3(1)	12.5(6)	
$^2J(P_CSe_d)$			6(1)[d]			11.12(7)		14.6(1)	7.7(3)	13.0
$^2J(P_BSe_d)$	57.1(2)[d]	54.8[d]	52(1)[d]	61.8(3)	60.7(2)	60.40(8)	42.6(1)	40.3(1)	22.1(3)	
$^2J(P_DSe_b)$			53.1(2)			52.1(2)		50.1(1)	38.2(2)	48.55
(b) Chemical shifts (ppm)[e]										
$\delta(P_A)$	62.38	70.56	78.57	75.03	80.90	84.53	106.16	108.87	107.42	
$\delta(P_B)$	138.39	141.15	145.51	146.97	151.20	150.48	29.17	26.56	99.94	
$\delta(P_C)$			97.47			102.08		102.65	149.50	105.25
$\delta(P_D)$			130.07			133.22		132.33	13.34	126.15
$\delta(Se_a)$	−717.63[d]	−701.72	−645.32	[c]	−661.54	−625.69	−547.81	−571.19	−642.45	−598.65
$\delta(Se_b)$	−1003.04[d]	−980.40	−869.75	[c]	−986.06	−866.21	−870.78	−845.07	−1060.54	
$\delta(Se_d)$			−830.38			−842.11		−764.19	−732.52	−744.96
(c) Secondary isotope shifts (ppb)[f]										
$^1\Delta\ P_A(Se_a)$	4.8	6.0	6.1	6.7	7.7	6.1	5.7	5.1	5.9	
$^1\Delta\ P_C(Se_a)$			5.7			6.4		7.2	5.3	6
$^1\Delta\ P_B(Se_b)$	9.1	[c]	[c]	5.5	[c]	[c]	3.9	4.4	4.6	
$^1\Delta\ P_C(Se_b)$	8.2	[c]	5.8	5.7	5.0	4.4	3.8	3.7	4.8	
$^1\Delta\ P_A(Se_d)$			4.7			4.9		4.6	[c]	4.7
$^1\Delta\ P_D(Se_d)$			6.8			5.5		5.2	4.3	5.8
(d) Number of scans accumulated										
^{31}P	2560	56528	56528	3600	11856	11856	25896	22368	22368	
^{77}Se	112208[d]	43200	43200	[c]	113552	113552	158208	158208	158208	

[a] From ref. 12, for comparison. [b] Standard deviations (σ) in parentheses. [c] Not observed. [d] From ^{77}Se spectrum measured at 294 K. [e] ^{31}P Shifts relative to 85% H_3PO_4–water; ^{77}Se shifts relative to sat. H_2SeO_3–water. [f] Relative to main ^{31}P spectrum shifts, *i.e.* to average shifts for all selenium isotopomers, but excluding those containing any ^{77}Se.

be positive for **2** (X = CN, Y = I), as it is for **2** (X = Y = I). For the amido compound **2** (X = NMePh, Y = I), however, a negative value of $^2J(P_ASe_b)$ gave an insignificantly better fit, and this was confirmed in the diamido compound **2** (X = Y = NMePh), for which only a negative $^2J(P_ASe_b)$ led to a recognisable simulation of the $^{77}Se_b$ multiplet.

For all three unsymmetric compounds **2** with Y = I the $^{77}Se_a$ multiplet showed eight peaks, there being one practically zero ^{31}P–$^{77}Se_a$ coupling, which could have been $^2J(P_BSe_a)$ or $^2J(P_DSe_a)$. Since the non-zero one of these was about 30 Hz for the amido compounds, this must have been $^2J(P_BSe_a)$, otherwise it would have led to resolved satellite peaks for P_D, which were not observed. The near-zero coupling was $^2J(P_DSe_a)$. Insignificantly better fits were obtained for both **2** (X = CN, Y = I) and **2** (X = Y = CN), when $^2J(P_BSe_a)$ was made positive, but currently we lack satisfactory evidence for this sign.

^{77}Se isotopomers of symmetric compounds *exo,exo*-α-$P_4Se_3X_2$. These constituted AA′EE′X or ABEFX spin systems, depending on whether ^{77}Se was present at Se_a or at Se_b respectively. The $^{77}Se_a$ multiplets were 'deceptively simple' triplets ($^1J(P_ASe_a)$) of triplets ($^2J(P_BSe_a)$), from which starting values of these couplings could be obtained. The $^{77}Se_b$ multiplets were clearly the symmetric X parts of non-first-order spectra. We greatly simplified the task of obtaining initial values of ^{31}P–$^{77}Se_b$ couplings by applying the balancing rules which this paper sets out to demonstrate (see below). Starting from couplings known for α-P_4Se_3XI and for α-$P_4Se_3I_2$, we obtained simulated ^{31}P and ^{77}Se spectra which could be recognised, and from which computer fitting could proceed. *exo,exo*-α-$P_4Se_3(CN)_2$ **2** showed a ^{13}C multiplet at δ 116.68, with $^1J(P_B{}^{13}C) = -114.6(1)$ Hz. Since there were several possible fits to overlapping transitions, values of the remaining couplings $^2J(P_A{}^{13}C)$, $^3J(P_C{}^{13}C)$ and $^4J(P_D{}^{13}C)$ of 4.6, −4.6 and 4.2 Hz respectively were not reliable.

***endo,exo*-α-$P_4Se_3(CN)_2$ 4.** The main ^{31}P NMR spectrum of the *endo,exo* compound **4** was recognised by its high chemical shift $\delta(P_C)$ (Table 1) and identified provisionally by comparison with the spectrum of the sulfur analogue *endo,exo*-α-$P_4S_3(CN)_2$.[3,6] Its low chemical shift showed that P_D carried a cyano group. Besides its typical $^1J(PP)$ coupling to P_C, P_D showed couplings of 62.57 and 13.42 Hz to other phosphorus atoms. Of these, the smaller was likely to be $^3J(P_BP_D)$ and the larger to be $^2J(P_AP_D)$, since there is here no alignment of lone pair orbitals likely to lead to a large ^3J coupling. A positive sign for $^3J(P_BP_D)$ led to a better fit than did a negative sign (rms deviation 0.045 *versus* 0.099 Hz, over 31 transitions).

The $^{77}Se_a$ multiplet for **4** showed eight resolved peaks. The smallest resolved coupling (21.8 Hz) was assigned to $^2J(P_BSe_a)$ and the near-zero coupling to $^2J(P_DSe_a)$, by comparison with *exo,exo*-α-$P_4Se_3(CN)_2$ **2**, where the coupling to P_D (carrying *exo*-CN) was 6.3 Hz. A positive sign of $^2J(P_BSe_a)$ gave the best fit. The $^{77}Se_b$ and $^{77}Se_d$ multiplets, though of rather poor quality, were visibly asymmetric. These features could be reproduced if $^2J(P_ASe_b)$, $^2J(P_DSe_b)$, $^2J(P_BSe_d)$ and $^2J(P_CSe_d)$ were given positive signs, and this combination gave also the smallest rms deviations in fits including selected transitions in both the ^{31}P and the ^{77}Se spectra. The P_A multiplet was heavily overlaid by other components of the mixture, and no satellite peaks from splitting by $^{77}Se_d$ were unobscured. Consequently, no secondary isotope shift $^1\Delta P_A(Se_d)$ is reported (Table 1). In other cases, these isotope shifts gave a useful confirmation that satellite peaks had been assigned to the correct isotopomers.

Values of NMR coupling constants and chemical shifts

Parameters found for *exo,exo*-α-$P_4Se_3(NPr^i_2)_2$ **2** were similar to results for this compound made independently by a different route.[13] It showed the expected low value of $\delta(P_A)$, associated with strong π donation by the amido substituent.[11] $^1J(P_AP_B)$ was very negative and $^2J(P_AP_C)$ and $^2J(P_AP_D)$ were small, in agreement with previous correlations with substituent constants.[3] It may now be seen that **2** (X = Y = NPr^i_2) showed also low $\delta(Se_a)$ and very negative $^1J(P_ASe_d)$. Opposite extremes were seen in these parameters for the dicyanide **2** (X = Y = CN), corresponding to poor π-donor ability of the CN group. Besides being negative for amido substituents but positive for cyanide or iodide, $^2J(P_ASe_b)$ showed the biggest relative difference between the amides with X = Y = NPr^i_2 and with X = Y = NMePh, becoming more negative with increasing π-donor ability of X. In the amide iodides it is $^2J(P_ASe_b)$, through P_B carrying the amido substituent, which shows a value similar to that in the diamido compound, rather than $^2J(P_CSe_d)$.

In *endo,exo*-α-$P_4S_3(NHR)_2$ (R = Bu^t, Ph or Me), P_B, carrying the *endo*-oriented group, shows a ^{31}P chemical shift about 57 ppm higher than that of P_D.[2] The difference increases in *endo,exo*-α-$P_4S_3(CN)_2$ to 78 ppm,[3] while now for *endo,exo*-α-$P_4Se_3(CN)_2$ it is 87 ppm. This means that $\delta(P_B)$ does not have a low value characteristic of phosphorus carrying a cyano group. In principle, the *endo*-oriented substituent might have been iodide rather than cyanide. The neighbouring atom, Se_b, is 328 ppm to low frequency of Se_d, which is in a similar environment to it, except for inversion of configuration at the adjacent phosphorus. This is a very large diastereomeric shift. We confirmed the identity of the compound, and our assignments of chemical shifts, by *ab initio* calculation of ^{31}P and ^{77}Se relative NMR shieldings (see below).

Balancing rules for ^{31}P–^{77}Se NMR couplings

Application of balancing rules for both ^{31}P–^{31}P and ^{31}P–^{77}Se couplings, for the three sets of compounds, *exo,exo*-α-$P_4Se_3X_2$, *exo,exo*-α-P_4Se_3XI and *exo,exo*-α-$P_4Se_3I_2$ (X = NPr^i_2, NMePh or CN), in solution in CS_2 at room temperature are shown in Table 2 in a format similar to that used previously for ^{31}P–^{31}P couplings.[11] The rules are given in the form of the definitions set out in the footnotes to the Table. Pairs of couplings, related by the C_2 axis in the symmetric compounds **2** (X = Y), are found to balance. Table 2 lists the errors in couplings for *exo,exo*-α-$P_4Se_3X_2$, predicted using the rules. While all couplings are predicted usefully well for the dicyanide **2** (X = Y = CN), couplings $^2J(P_AP_C)$ and $^2J(P_BP_D)$ balance progressively more poorly in the series X = CN, NMePh, NPr^i_2. All other couplings are predicted usefully, even for X = NPr^i_2.

For cases where J_1 and J_2 are not the same in the unsymmetric molecules, it must be decided, at least for presentation purposes, which of the pair of couplings is J_1 and which is J_2. This amounts to deciding, for Table 1, with which row of couplings of the unsymmetric compounds to associate the couplings of the respective symmetric compounds. In some cases the association may seem obvious, *e.g.* that the value of $^2J(P_BSe_a)$ should depend primarily on the substituent attached to P_B rather than to P_D, but even that cannot be proved. Reversing the association changes the values of *diff1* and *diff2*, but not the value of *error*. The predicted couplings are invariant to reversing the association. The associations given here are mostly such that values of *diff1* and *diff2* for X = CN are of opposite signs to those for X = amide. For the pair $^1J(P_ASe_d)$, $^1J(P_CSe_b)$, very large differences are found to balance well, irrespectively of which association is taken. Inability to be sure of the better associations precludes meaningful discussion of substituent effects on couplings in the unsymmetric compounds.

Ab initio MO calculations

Calculations were done using GAUSSIAN 98.[14] Geometries were calculated for *exo,exo*-α-$P_4Se_3X(CN)I$ **2** and for *endo,exo*-α-$P_4Se_3(CN)_2$ **4** at the RHF/3-21G* level, as had been done previously for the *exo,exo*-dicyanide **2** (X = Y = CN).[8] For

Table 2 Relationships[a] between NMR coupling constants for *exo,exo-a*-$P_4Se_3X_2$, *exo,exo-a*-P_4Se_3XI,[b] and *exo,exo-a*-$P_4Se_3I_2$

		X = NPr^i_2			X = NMePh			X = CN		
J_1	J_2	*diff1*	*diff2*	error	*diff1*	*diff2*	error	*diff1*	*diff2*	error
Couplings through or to Se_a										
$^2J(P_AP_C)$	$^2J(P_AP_C)$	17.3	−25.4	−8.1	10.4	−17.5	−7.1	−3.8	4.8	1.0
$^1J(P_ASe_a)$	$^1J(P_CSe_a)$	−23.1	19.1	−4.0	−19.2	16.8	−2.4	6.7	−6.2	0.5
$^2J(P_BSe_a)$	$^2J(P_DSe_a)$	12.1	−5.9	6.2	8.1	−5.7	2.4	2.8	−5.7	−2.9
Couplings in ring segment P_A–P_B–Se_b–P_C or P_C–P_D–Se_d–P_A										
$^2J(P_ASe_b)$	$^2J(P_CSe_d)$	2.9	−7.0	−4.1	2.7	−1.9	0.8	−1.6	1.6	0.0
$^1J(P_AP_B)$	$^1J(P_CP_D)$	8.5	−10.9	−2.4	6.6	−7.8	−1.2	−3.8	4.6	0.8
$^1J(P_BSe_b)$	$^1J(P_DSe_d)$				6.3	−8.6	−2.3	−5.9	7.3	1.4
$^1J(P_ASe_d)$	$^1J(P_CSe_b)$	56.7	−52.8	3.9	41.9	−39.3	2.6	−17.9	16.0	−1.9
$^2J(P_AP_D)$	$^2J(P_BP_C)$	−2.8	3.0	0.2	−0.6	2.0	1.4	−7.4	6.9	−0.5
Couplings in ring segment P_B–P_A–Se_d–P_D or P_D–P_C–Se_b–P_B										
$^3J(P_BP_D)$	$^3J(P_BP_D)$	15.7	−5.3	10.4	11.6	−5.3	6.3	10.0	−14.6	−4.6
$^2J(P_BSe_d)$	$^2J(P_DSe_b)$	−2.8	4.6	1.8	−0.3	3.6	3.3	−2.3	1.5	−0.8

[a] For each substituent X and pair of related coupling constants J_1 and J_2 for compounds *exo,exo-a*-P_4Se_3XI (**XI**), *exo,exo-a*-$P_4Se_3X_2$ (**X_2**) and *exo,exo-a*-$P_4Se_3I_2$ (**I_2**): *diff1* = J_1(**XI**) − J_1(**X_2**); *diff2* = J_2(**XI**) − J_2(**I_2**) and *error* = *diff1* + *diff2*. The entry *error* is the observed error in predicting J_1(**X_2**), using the rule: J_1(**X_2**, predicted) = J_1(**XI**) + J_2(**XI**) − J_2(**I_2**). All differences between coupling constants are given in Hz. [b] Atom labelling for *exo,exo-a*-P_4Se_3XI **2** is with substituent X bonded to P_B and iodine bonded to P_D.

density functional calculations, we chose the MPW1PW91 method,[15] rather than B3LYP, because this may give better geometries for compounds of the heavier main-group elements,[16] and carried out geometry optimisations for the *exo,exo*- and *endo,exo*-dicyanides **2** and **4**, using Ahlrichs' SVP or pTZV basis sets.[17] Single d polarisation functions were used for pTZV. Energy minima were confirmed by vibrational analysis in each case. Bond lengths, bond angles, and enough torsion angles to define the geometries are given in Table 1 of the Electronic Supplementary Information (ESI), and energies are given in Supplementary Table 2. Files are provided in ESI for online viewing of the structures. The MPW1PW91/pTZV geometry for *exo,exo*-α-$P_4Se_3(CN)_2$ was quite similar to the RHF/LanL2DZ(d) geometry reported previously.[8] The geometric parameters differing most clearly between MPW1PW91/SVP and MPW1PW91/pTZV geometries were the torsion angles P_A–P_B–Se_b–P_C and P_A–Se_d–P_D–P_C, which represent twisting of the five-membered rings, probably because of non-bonded interactions. The twist P_A–P_B–Se_b–P_C is particularly large in *endo,exo*-α-$P_4Se_3(CN)_2$ **4** (20.5° at the RHF/3-21G* level, compared with 9.9° in *endo,exo*-α-$P_4S_3(NH_2)_2$),[11] corresponding to an increased book angle P_B–P_A–Se_d. Although the cyanide group has a low steric requirement, the *endo*-CN is placed so that one of its π-bonding orbitals overlaps with the p-type lone pair orbital of Se_d, as shown in the NBO plot in Fig. 1. With overlap integral $S = 0.0943$, compared with 0.0585 for the *exo*-CN π overlap with the Se_a lone pair, or 0.0690 and 0.0608 for the lone pair–lone pair overlaps P_D–Se_b and P_B–Se_a respectively, this forces the book angle at P_A apart. From the DF calculations, *endo,exo*-α-$P_4Se_3(CN)_2$ **4** was about 19 kJ mol^{-1} less stable than its isomer *exo,exo*-α-$P_4Se_3(CN)_2$ **2**. This is consistent with its being a kinetic product which isomerised as observed.

Gauge including atomic orbitals (GIAO) calculations of ^{31}P and ^{77}Se NMR shieldings were made at the RHF/3-21G* and RHF/pTZV levels using RHF/3-21G* geometries, at the MPW1PW91/SVP and MPW1PW91/pTZV levels using MPW1PW91/SVP geometries, and at the MPW1PW91/pTZV level using MPW1PW91/pTZV geometries. Shieldings are reported in Tables 3 and 4, along with calculated chemical shifts obtained for ^{31}P or ^{77}Se by fitting observed shifts by calculated shieldings over all environments for this nucleus in two compounds (Table 3) or three compounds (Table 4). It has been demonstrated previously that there are different, systematic errors in calculating shieldings of phosphorus nuclei in different kinds of molecular environment.[18] These are sufficiently large, at the levels of calculation used in the present work, to make unhelpful the calculation of chemical shifts by comparison of shieldings between phosphorus–chalcogen polycyclic compounds and an NMR standard such as H_3PO_4–water, in which phosphorus is in a very different electronic situation. Even for molecular standards such as PCl_3, or Me_2Se for selenium, the errors are likely to have little relationship to those for the present molecules, so these calculations have not been done. Instead, comparison of differences in calculated shieldings with differences in observed chemical shifts, between similar environments within a molecule, or between similar molecules, has been found to be an effective way of using relatively low-level *ab initio* calculations to assist in assigning NMR spectra. Linear fitting of observed shifts by calculated shieldings, holding the coefficients at −1, is a way of comparing these differences in shifts in a readily assimilable way.[18] Rms deviations, of observed chemical shifts from shifts calculated in this way, are included in Table 3.

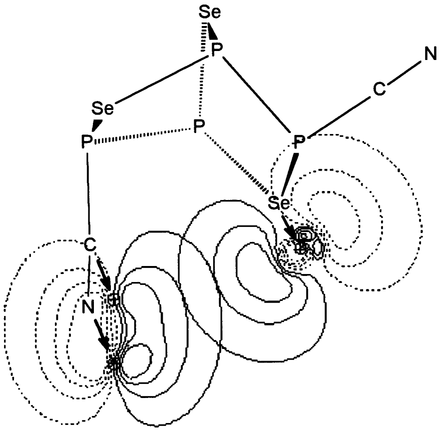

Fig. 1 Non-bonding overlap of a C_bN_b π-bonding orbital with a Se_d lone pair in *endo,exo*-α-$P_4S_3(CN)_2$ **4**. The orbitals are pre-orthogonal NBOs calculated at the MPW1PW91/SVP level. An approximate perspective view of the geometry is shown offset above.

It may be seen that the lowest level, RHF/3-21G*, calculations were adequate for assigning either ^{31}P or ^{77}Se chemical shifts. At this level, calculated shifts for atoms near to a single iodine, in *exo,exo*-α-$P_4Se_3(CN)I$, do not appear to suffer from exceptionally high errors caused by ignoring relativistic effects.

Table 3 Calculated *ab initio* NMR shieldings[a] and chemical shifts[b] for *exo*,*exo*- or *endo*,*exo*-*a*-$P_4Se_3(CN)_2$ (**2** or **4**)

		2		**4**					**2**		**4**			
GIAO calc.[c]	Geometry	P_A	P_B	P_A	P_B	P_C	P_D	Rms dev. P[d]	Se_a	Se_b	Se_a	Se_b	Se_d	Rms dev. Se[d]
Calculated shieldings:														
HF/321	HF/321	393.42	471.88	395.80	430.36	367.18	477.62		1766.97	2026.80	1836.48	2180.04	1920.43	
HF/TZV	HF/321	318.83	382.58	320.96	338.89	288.55	390.95		1549.16	1801.61	1618.17	1954.33	1697.82	
DF/SVP	DF/SVP	226.50	333.44	222.52	264.26	187.33	347.94		1011.05	1347.49	1083.18	1533.14	1204.72	
DF/TZV	DF/SVP	163.81	276.92	160.06	201.13	121.07	293.72		1005.72	1316.28	1070.45	1490.10	1169.40	
DF/TZV	DF/TZV	158.82	277.36	153.31	204.47	115.39	293.17		998.03	1306.21	1058.56	1471.82	1164.05	
Calculated relative chemical shifts:[e]														
HF/321	HF/321	113.55	35.09	111.17	76.61	139.79	29.35	12.90	−591.65	−851.48	−661.16	−1004.72	−745.11	34.41
HF/TZV	HF/321	105.55	41.80	103.42	85.49	135.83	33.43	12.75	−595.76	−848.21	−664.77	−1000.93	−744.42	37.42
DF/SVP	DF/SVP	121.42	14.48	125.40	83.66	160.59	−0.02	14.94	−545.95	−882.39	−618.08	−1068.04	−739.62	12.95
DF/TZV	DF/SVP	123.23	10.12	126.98	85.91	165.97	−6.68	17.82	−566.15	−876.71	−630.88	−1050.53	−729.83	11.07
DF/TZV	DF/TZV	125.86	7.32	131.37	80.21	169.29	−8.50	21.20	−569.12	−877.30	−629.65	−1042.91	−735.14	13.99
Experimental chemical shifts:[f]														
		106.16	29.17	107.42	99.94	149.50	13.34		−547.81	−870.78	−642.45	−1060.54	−732.52	

[a] GIAO isotropic shieldings for gas phase molecules, as reported by GAUSSIAN 98. [b] All shieldings and shifts are in ppm. [c] HF = RHF; DF = MPW1PW91; SVP = Ahlrichs SVP; TZV = Ahlrichs TZV with single d polarisation functions added. [d] Root mean square deviation of observed from calculated chemical shifts. [e] Obtained by subtracting calculated shieldings from constants found empirically for P or Se for each row. [f] For solutions in CS_2.

Table 4 Calculated *ab initio* NMR shieldings and chemical shifts[a] for *exo*,*exo*-α-$P_4Se_3(CN)I$ **2** (X = CN, Y = I)

Atom	Calculated shielding[b]	Calculated chemical shift[c]	Experimental chemical shift[d]
P_A	390.71	112.21	108.87
P_B	473.89	29.03	26.56
P_C	386.01	116.91	102.65
P_D	366.42	136.50	132.33
Se_a	1782.39	−605.09	−571.19
Se_b	1998.34	−821.04	−845.07
Se_d	1941.48	−764.18	−764.19

[a] All shieldings and shifts are in ppm. [b] GIAO isotropic shieldings for gas phase molecules, calculated at the RHF/3-21G* level on a RHF/3-21G* optimised geometry. [c] Obtained by subtracting calculated shieldings from constants found empirically for P or Se for this compound together with *exo*,*exo*- and *endo*,*exo*-α-$P_4Se_3(CN)_2$. [d] For solutions in CS_2.

The order of the closely separated shifts $\delta(P_A)$ and $\delta(P_C)$ in this compound was incorrectly predicted (Table 4), but, in practice, these multiplets could be distinguished readily because of their different $^1J(PP)$ coupling constants, linking them with nuclei P_B and P_D respectively, which were identified clearly by the present calculations. Using geometries found for the dicyanides by the DF method did not in this case improve the fit of ^{31}P shieldings, but did lead to significantly improved differences in ^{77}Se shieldings. The large diastereomeric shift between Se_b and Se_d in **4**, commented upon above, was reproduced to an accuracy of 0.4 ppm at the GIAO/MPW1PW91/SVP level. Geometry optimisation at the MPW1PW91/pTZV level led to marginally poorer fits of both ^{31}P and ^{77}Se shifts. We conclude that calculating MPW1PW91/SVP geometries (where this basis set is available for the elements concerned), and performing GIAO calculations at the same level, is a useful method for assigning ^{77}Se as well as ^{31}P NMR chemical shifts. Our identification of the three cyano compounds from their NMR spectra was confirmed. By comparison, our previous identification of the sulfur analogue *endo*,*exo*-α-$P_4S_3(CN)_2$, which had been only by comparison of its NMR parameters with those of more distant compounds,[3] was supported. The finding that lower-level methods (RHF instead of DF, or using smaller basis sets) give better fits of GIAO shieldings to experimental chemical shifts measured in solutions, appears commonplace in our current work on bicyclic or cage polyphosphorus molecules. While the underlying cancellation of systematic errors may appear fortuitous, the better fit of several differences in NMR shift shows that it is taking place, making positive results useful.

Experimental

All operations were carried out under nitrogen by Schlenk methods. Toluene was dried over sodium, CS_2 by distillation from P_4O_{10}, and amines over NaOH. α-$P_4Se_3I_2$ was made by heating a stoichiometric mixture of red phosphorus, grey selenium and iodine in a sealed glass tube slowly to 240 °C, holding it at 240–300 °C for three days, then extracting the crushed product with CS_2. The procedure to make *exo*,*exo*-α-$P_4Se_3(CN)_2$ has been described previously.[8] NMR spectra were measured in 10 mm diameter tubes using a Bruker WM300WB spectrometer operating at 121.5 MHz for ^{31}P or 57.3 MHz for ^{77}Se. For proton-containing compounds, ^{31}P spectra were obtained with inverse-gated ^1H decoupling and a pulse interval of 4 seconds, to suppress proton coupling while avoiding the Nuclear Overhauser Effect. The number of scans accumulated is included in Table 1. 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 or H_2SeO_3–water. The minimum peak width obtainable using this method was 3.5–4 Hz at half height.

Preparation of solutions of *exo*,*exo*-α-$P_4Se_3X_2$ and *exo*,*exo*-α-P_4Se_3XI (X = NMePh or NPr^i_2)

α-$P_4Se_3I_2$ (0.5 g, 0.814 mmol) was suspended in C_6H_5Me (10 cm^3) by stirring at 60 °C, followed by rapid cooling to 15 °C. To this stirred suspension a solution of the amine HX (3.254 mmol) in C_6H_5Me (10 cm^3) was added dropwise over 1 hour. Further stirring at room temperature for 46 h gave a pale lemon solution and a yellow precipitate. For X = NPr^i_2 the solution contained α-$P_4Se_3X_2$ as the only solute detected by ^{31}P NMR, while for X = NMePh a low concentration of α-P_4Se_3XI was also present. Solvent was evaporated from the unseparated mixtures by pumping, and the dry residues were stirred with CS_2 (15 cm^3). The yellow solutions were shown by ^{31}P NMR to contain α-$P_4Se_3X_2$, α-P_4Se_3XI and α-$P_4Se_3I_2$ in the ratio 31 : 61 : 8 for X = NMePh or 84 : 3.4 : 12 for X = NPr^i_2.

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