α-Tetraphosphorus Trichalcogenide Diiodide Compounds containing both Sulfur and Selenium

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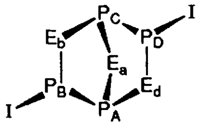
Two isomers of each of α-$P_4S_2SeI_2$ and α-$P_4SSe_2I_2$ have been identified by ^{31}P and ^{77}Se NMR spectroscopy in mixtures made by direct combination of the elements. The same compounds were formed as a result of a photochemical redistribution reaction between α-$P_4S_3I_2$ and α-$P_4Se_3I_2$ in solution in CS_2. Systematic changes in chemical shifts and in coupling constants with alterations in molecular geometry, as sulfur was replaced by selenium in the series α-$P_4S_3I_2$ **1** – α-$P_4S_2SeI_2$ **2,3** – α-$P_4SSe_2I_2$ **4,5** – α-$P_4Se_3I_2$ **6**, are reported.

Systematic changes in ^{31}P NMR endocyclic coupling constants and chemical shifts with exocyclic substitution have been reported for the bicyclic systems α-$P_4S_3X(Y)$, where X and Y are halogen, pseudohalogen, or various similar groups,[1,2] and in ^{31}P and ^{77}Se NMR parameters for P_3Se_4X (X = Cl, Br or I).[3] Interrelationships between these changes were probably connected with the strong interdependence of bond angles and lengths in the bicyclic (or *nido*-cage) structures, but, except for α-$P_4S_3I_2$,[4] α-$P_4Se_3I_2$[5] and P_3Se_4I,[6] there were no direct determinations of molecular structure to provide firm foundation for such arguments. In contrast to exocyclic substitution, endocyclic replacement of sulfur by selenium causes changes in geometry which qualitatively are clearly predictable. Analysis of ^{31}P and ^{77}Se NMR spectra of phosphorus sulfide selenides $P_4S_nSe_{3-n}$ (n = 1 or 2)[7] thus provided valuable insights into the control of NMR parameters by changes in geometry,[8] but the separation of causative factors was made difficult by the extra structural connectivity of the closed cage structure. We now report a study of the effects of endocyclic chalcogen substitution in the series of bicyclic molecules α-$P_4S_nSe_{3-n}I_2$ (n = 0–3). The NMR parameters for α-$P_4S_3I_2$ **1** and α-$P_4Se_3I_2$ **6** have been published.[1,3] Two isomers are possible for each of α-$P_4S_2SeI_2$ **2,3** and α-$P_4SSe_2I_2$ **4,5** (Table 1) with selenium or sulfur respectively in the bridging position E_a (Scheme 1). The ^{31}P and ^{77}Se NMR spectra have now been studied for all four of these new molecular species together in solutions in CS_2, made by extracting solids resulting from direct combination of the elements at high temperature. Like α-$P_4Se_3I_2$ **6**, unsymmetric α-$P_4SSe_2I_2$ **4** showed ^{77}Se and satellite ^{31}P spectra due to two sets of isotopomers containing one ^{77}Se nucleus, at positions E_a (**4a**) or E_b (**4b**) respectively.

Experimental

All operations were carried out under dry nitrogen in a glove-box or by Schlenk methods. Carbon disulfide was dried by distillation from P_4O_{10}. The NMR spectra were measured using a Bruker WM300WB spectrometer operating at 121.5 MHz for ^{31}P and 57.3 MHz for ^{77}Se. Normal capped (and wax-sealed) tubes (diameter 10 mm) were used, with a precision $(CD_3)_2CO$ capillary as external lock.

Preparation of the Mixtures.—Red phosphorus, sulfur, grey selenium and iodine in atomic ratio 4:1.5:1.5:2 were sealed together under vacuum in a Duran glass ampoule. The mixture was heated to 300 °C over 3 d, then held at 300 °C for 2 d. The homogeneous dark red melt was allowed to cool to room temperature, and the resulting solid dissolved in CS_2. The solution, after filtration to remove insoluble products and cooling to −30 °C for 7 d, yielded orange crystals. The ^{31}P NMR spectrum of a solution of these showed a mixture of the compounds α-$P_4S_nSe_{3-n}I_2$ (n = 0–3) as described below, and no other products.



Scheme 1 Labelling of ring positions

Mass Spectrum.—Electron impact mass spectra (175 °C; 70 eV, *ca.* 1.12 × 10^{-17} J) of mixed crystals obtained from a melt of composition P:S:Se:I = 4:2:1:2 showed ions due to loss of an iodine atom from each of the compositions α-$P_4S_nSe_{3-n}I_2$ (n = 0–3), but no molecular ions were observed. Only isotope patterns for the following ions derived from α-$P_4S_2SeI_2$ were sufficiently intense and clear of overlaps for useful intensity measurements [m/z for ^{80}Se peak (relative intensity of whole pattern, assignment)]: 395 (62, M − I), 364 (28, M − PI) and 268 (100, M − I_2).

Assignment of NMR Spectra

In their main ^{31}P NMR spectra (isotopomers not containing ^{77}Se) the new compounds were of two types: those (**2,5**) having symmetric spin systems AA′BB′ and those (**3,4**) having unsymmetric spin systems ABCD. The dominant features of the spectra of the mixtures were the strongly coupled spectrum of symmetric α-$P_4SSe_2I_2$ **5**, and the P_A and P_C multiplets of unsymmetric α-$P_4S_2SeI_2$ **3**. The P_A,P_C multiplet of symmetric α-$P_4S_2SeI_2$ **2** and the P_C multiplet of unsymmetric α-$P_4SSe_2I_2$ **4** were also clearly visible. Other multiplets were strongly overlapping, but most of the transitions (Table 1) were found by seeking splittings measured in the readily visible parts of the spectrum of each compound. In each case, hand analysis was followed by iterative computer fitting using NUMARIT.[9] Transitions due to isotopomers containing one ^{77}Se nucleus were then found by comparison with NUMARIT simulations using ^{31}P–^{77}Se couplings estimated by analogy with similar compounds, or by hand analysis of the ^{31}P and ^{77}Se NMR spectra in the case of the unsymmetric compounds. For symmetric α-$P_4S_2SeI_2$ **2** the multiplet due to bridgehead nuclei P_A,P_C was distinguished from that due to nuclei P_B,P_D because the former possessed a ^{77}Se satellite multiplet containing

Table 1 Occupancy of cage positions and iterative fitting of NMR spectra for α-$P_4S_nSe_{3-n}I_2$ (n = 0–3).

		Chalcogen position[a,b]			Fraction of transitions observed[a,c] for					R.m.s. deviation (Hz)
		E_a	E_b	E_d	P_A	P_C	P_B	P_D	^{77}Se	
1[d]	α-$P_4S_3I_2$	S	S	S						
2	α-$P_4S_2SeI_2$	^0Se	S	S	12/12		6/12			0.38
2a		^{77}Se	S	S	14/24		0		16/16	0.46
3	α-$P_4S_2SeI_2$	S	^0Se	S	8/8	8/8	6/8	7/8		0.05
3b		S	^{77}Se	S	0	9/16	5/16	7/16	16/16	0.22
4	α-$P_4SSe_2I_2$	^0Se	^0Se	S	7/8	8/8	5/8	6/8		0.04
4a		^{77}Se	^0Se	S	8/16	12/16	0	0	16/16	0.49
4b		^0Se	^{77}Se	S	2/16	11/16	7/16	6/16	4/16	0.39
5	α-$P_4SSe_2I_2$	S	^0Se	^0Se		23/26				0.09
5b		S	^{77}Se	^0Se		22/64			20/24	0.18
6[e]	α-$P_4Se_3I_2$	^0Se	^0Se	^0Se						
6a[e]		^{77}Se	^0Se	^0Se						
6b[e]		^0Se	^{77}Se	^0Se						

[a] Scheme 1. [b] ^0Se is any isotope of Se other than ^{77}Se. [c] Denominators exclude very weak transitions. [d] Ref. 1. [e] Ref. 3, where iterative fitting data are given.

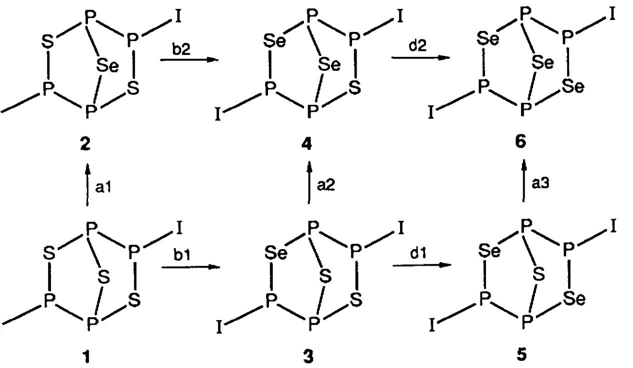
Table 2 NMR parameters for α-$P_4S_nSe_{3-n}I_2$ (n = 0–3)

Species	**1**[a] α-$P_4S_3I_2$	**2** α-$P_4S_2Se_aI_2$	**3** α-$P_4S_2Se_bI_2$	**4** α-$P_4S_dSe_2I_2$	**5** α-$P_4S_aSe_2I_2$	**6**[b] α-$P_4Se_3I_2$
(*a*) Coupling constants (Hz)[c]						
(*i*) ^{31}P–^{31}P						
$^1J(P_AP_B)$	−243.7(1)	−243.8(2)	−242.72(4)	−242.66(4)	−239.90(3)	−239.7(3)
$^1J(P_CP_D)$			−241.17(4)	−241.17(2)		
$^2J(P_AP_C)$	74.8(1)	64.5(3)	86.34(3)	75.27(3)	98.9(1)	87.2(4)
$^2J(P_AP_D)$	21.6(1)	25.8(1)	22.65(3)	27.35(2)	17.51(2)	21.4(2)
$^2J(P_BP_C)$			16.70(3)	20.46(3)		
$^3J(P_BP_D)$	9.3(1)	5.1(3)	9.52(4)	6.09(3)	9.02(8)	5.3(4)
(*ii*) ^{31}P–^{77}Se						
$^1J(P_ASe_a)$		−290.0(2)		−290.4(4)		−279.6(2)
$^1J(P_CSe_a)$				−280.4(2)		
$^2J(P_BSe_a)$		2.4		5.6(3)		6.0(2)
$^2J(P_DSe_a)$				0.0(3)		
$^1J(P_BSe_b)$			−295.9(1)	−287.6(3)	−293.4(4)	−285.41(7)
$^1J(P_CSe_b)$			−197.9(1)	−200.1(3)	−205.6(1)	−207.76(8)
$^2J(P_ASe_b)$			6.7(1)	11.4(6)	8.1(5)	13.0(1)
$^2J(P_DSe_b)$			46.1(1)	46.9(4)	47.23(9)	48.55(7)
(*b*) Chemical shifts[d]						
$\delta(P_A)$	128.72	115.28	134.27	120.21	122.06	105.25
$\delta(P_C)$			116.46	100.37		
$\delta(P_B)$	125.06	126.39	121.58	123.52	123.76	126.15
$\delta(P_D)$			128.00	129.91		
$\delta(Se_a)$		−710.52		−655.00		−598.65
$\delta(Se_b)$			−808.93	−777.48	−777.45	−744.96
(*c*) Secondary isotope shifts (ppb)[c,e]						
$^1\Delta P_A(Se_a)$		3(2)		5(2)		6(2)
$^1\Delta P_C(Se_a)$				5(1)		
$^1\Delta P_B(Se_b)$			5(1)	5(2)	7(1)	6(2)
$^1\Delta P_C(Se_b)$			5(1)	5(1)	1(1)	5(2)

[a] Ref. 1. [b] Ref. 3. [c] Standard deviations (σ) in parentheses. [d] The ^{31}P NMR shifts are relative to 85% H_3PO_4–water; ^{77}Se NMR shifts relative to saturated H_2SeO_3–water. [e] Relative to main ^{31}P NMR spectrum shifts, *i.e.* to average shifts for all selenium isotopomers, but excluding those containing any ^{77}Se.

the large splitting corresponding to the coupling $^1J(P_ASe_a)$. Similarly, for the unsymmetric compounds **3** and **4**, multiplets due to P_C possessed a widely spaced satellite multiplet due to isotopomers with ^{77}Se at position E_b (Scheme 1), distinguishing them from multiplets due to P_A. Secondary isotope shifts, $^1\Delta^{31}P(^{77}Se)$, depending on the difference in mass of ^{77}Se and the weighted average of the masses of the other selenium isotopes, typically[3] have values of 4–7 ppb. Where a value of this order was found (Table 2) this was a useful confirmation of correct assignment of a ^{77}Se satellite spectrum. Negative signs were assumed for all $^1J(^{31}P^{31}P)$ and $^1J(^{31}P^{77}Se)$ couplings.[10] Couplings $^2J(P_BP_D)$ were found to be positive for the symmetric systems, and hence were assumed to be positive in the unsymmetric ones. Further details for the individual compounds are as follows.

Spectrum of Symmetric α-$P_4S_2SeI_2$ **2**.—This was the least abundant of the new compounds in the mixtures. All ^{31}P–^{31}P couplings were obtained initially from the P_A,P_C multiplet. Trial computer fits of this multiplet, using a sequence of values of



Scheme 2 Replacements of S by Se: a1–a3 at position E_a, b1 or b2 at E_b, and d1 or d2 at E_d

$\delta(P_B)$, allowed the approximate position of the P_B,P_D multiplet to be ascertained. Six main spectrum transitions in this region could then be identified. A triplet in the ^{77}Se NMR yielded an initial value for $^1J(P_ASe_a)$, and 14 out of 24 of the corresponding satellite ^{31}P transitions in the P_A,P_C region were found for the NUMARIT fit for the ^{77}Se isotopomers **2a**. The reported value of $^2J(P_BSe_a)$ (2.4 Hz, Table 2) corresponded to failure to resolve the corresponding splitting in the ^{77}Se NMR spectrum, and was subject to greater uncertainty than were couplings corresponding to splittings which could be resolved. The difference between the zero splitting and the non-zero coupling resulted from the non-first-order nature of the spin system.

Spectrum of Unsymmetric α-$P_4S_2SeI_2$ **3**.—All 16 ^{77}Se transitions for isotopomers **3b** were well resolved, so all ^{31}P–^{77}Se couplings could be found, even though satellites in the P_A region were obscured by the main spectrum. Positive signs of $^2J(P_ASe_b)$ and $^2J(P_DSe_b)$ gave the best NUMARIT fit, in accord with results for α-$P_4Se_3I_2$ **6**.[3]

Spectrum of Unsymmetric α-$P_4SSe_2I_2$ **4**.—The P_B multiplet was located by examining the effect of changing $\delta(P_B)$ on the 'tenting' of the simulated P_A multiplet. For isotopomers **4a**, nine resolved peaks in the ^{77}Se multiplet accounted for 16 transitions; satellite peaks in the P_C region and some in the P_A region were easily visible. For isotopomers **4b**, the ^{77}Se multiplet was almost obscured by that of the more-abundant symmetric α-$P_4SSe_2I_2$ **5b**, the chemical shifts differing by only 1.5 Hz (at 57.3 MHz). However, several peaks of each satellite ^{31}P multiplet were identified, including two in the P_A region which allowed $^2J(P_ASe_b)$ to be found.

Spectrum of Symmetric α-$P_4SSe_2I_2$ **5**.—For analysis of the strongly coupled main spectrum, ^{31}P–^{31}P couplings were guessed by analogy with other compounds in the series, and trial simulations were made over a range of internal chemical shifts $\delta(P_A)$–$\delta(P_B)$. In the observed spectrum 23 out of 26 transitions could then be identified. For isotopomers **5b**, 20 transitions were fitted in the ^{77}Se NMR spectrum, allowing 22 to be assigned in the satellite ^{31}P spectrum. The quality of the fit demonstrated that assignments of the two ^{31}P chemical shifts in the main spectrum to P_A and P_B respectively were correct.

Results and Discussion

Changes in NMR Parameters with Chalcogen Substitution.—Coupling constants and chemical shifts measured here are presented in Table 2, along with those of the ternary compounds **1** and **6** for comparison. As shown in Scheme 2, replacements of sulfur by selenium are classified as replacements a1–a3 at bridging chalcogen E_a (Scheme 1), b1 or b2 for a first replacement in the six-membered ring, at E_b, and d1 or d2 for a second replacement, at E_d. Changes in each of the measured coupling constants and chemical shifts with chalcogen replacement, presented in Table 3, were remarkably constant within each of these sets, and, just as some of the NMR parameters were related to each other by exact or approximate C_2 symmetry of the molecules, *e.g.* $^1J(P_AP_B)$ was related to $^1J(P_CP_D)$, so changes in one parameter caused by replacement b1 or b2 were very similar to changes in the other parameter caused by replacement d1 or d2.

Changes in Coupling Constants.—For the boat-shaped six-membered ring P_A–P_B–E_b–P_C–P_D–E_d (Scheme 1) there will be an optimum distance $P_A \cdots P_C$, depending on the occupation of positions E_b and E_d. Replacement of the smaller sulfur by the larger selenium, as the bridge E_a between P_A and P_C (replacements a1–a3, Scheme 2), thus had a pronounced effect both on the relative stability of the compounds (see relative yield data later) and on their NMR parameters. The bond angles at Se_a in compounds **2**, **4** and **6** would have been smaller than those at S_a in compounds **1**, **3** and **5** respectively. This was reflected by changes in $^2J(P_AP_C)$ to less-positive values for replacements a1–a3 (Table 3). The dependence of $^2J(^{31}P^{31}P)$ on bond angle at a particular chalcogen transmitting the coupling has been shown previously,[3,8] but here it is necessary to distinguish between the effect of change in bond angle and that of changing the chalcogen. When the chalcogen E_a was unchanged, but the distance $P_A \cdots P_C$ and hence the angle at E_a were increased by introducing selenium in the six-membered ring positions E_b or E_d (replacements b1 or b2, or d1 or d2, respectively), changes in $^2J(P_AP_C)$ of almost equal magnitude to those for replacements a1–a3 were observed, though in the opposite sense, as expected. This supports the concept that the identity of the chalcogen is relatively unimportant.

Like $^2J(P_AP_C)$, the couplings $^2J(P_BP_C)$ and $^2J(P_AP_D)$ became less positive as the chalcogen transmitting the coupling was changed to selenium and the bond angle at it became smaller (replacements b1 or b2, and d1 or d2, respectively). The bond angles at *e.g.* chalcogen atom E_b could be increased by introduction of selenium either at E_a or at E_d. The former (replacements a1–a3) caused a much bigger increase in $^2J(P_BP_C)$ than did the latter (replacement d1 or d2), as is to be expected. Changes in $^2J(P_BP_C)$ caused by replacements b1 or b2, or a1–a3, were similar in magnitude to changes in $^2J(P_AP_C)$ caused by replacements a1–a3, or b1 or b2, relative to the sizes of the respective couplings. The effects of replacements a2 or a3, and d1 or d2, respectively, on $^2J(P_ASe_b)$, transmitted by P_B, were very similar to those on $^2J(P_BP_C)$, transmitted by Se_b, discussed above. Bond angles both at P_B and at E_b can be expected to increase with these replacements, but we have no information on how the increase in the total angle subtended by this two-atom bridge was shared between angles at the two atoms.

The effects of all replacements on $^1J(P_AP_B)$ or $^1J(P_CP_D)$ were remarkably small. Replacements b2 or d2, in the six-membered ring, had a very unequal effect on $^1J(P_ASe_a)$ and $^1J(P_CSe_a)$, only the coupling to the phosphorus adjacent to the replaced chalcogen changing greatly, when it became less negative. In contrast, $^1J(P_CSe_b)$ became more negative when the adjacent chalcogen E_a was replaced. The two ^1J couplings to Se_b changed not only unequally, but in opposite directions. Very different changes in $^1J(P_ASe_a)$ compared with $^1J(P_CSe_a)$, and in $^1J(P_BSe_b)$ compared with $^1J(P_CSe_b)$, have been reported previously,[3] for the series α-$P_4Se_3I_2$, P_3Se_4I, P_2Se_5. It is clear that simple arguments based upon bond angles will not suffice to explain changes in these ^1J couplings.

Changes in Chemical Shifts.—Increase in bond angle at either a phosphorus or a selenium atom, as sulfur was replaced by selenium at a non-adjacent position in the molecule, led to a move of its NMR chemical shift to higher frequency, *i.e.* to lower shielding, as reported previously for P_4E_3 cages.[8] Here, moves to higher frequency were observed for $\delta(Se_a)$ on replacement b2 or d2, for $\delta(Se_b)$ on replacements a1–a3, or d1 or d2, for $\delta(P_A)$ or

Table 3 Changes in NMR parameters in α-$P_4S_nSe_{3-n}I_2$ (n = 0–3) on replacing sulfur by selenium

Replacement *	a1	a2	a3	b1	b2	d1	d2
Going from:	**1**	**3**	**5**	**1**	**2**	**3**	**4**
To:	**2**	**4**	**6**	**3**	**4**	**5**	**6**
(*a*) Coupling constants (Hz)							
(*i*) ^{31}P–^{31}P							
$^1J(P_AP_B)$	−0.1	0.0	0.2	1.0	1.1	2.8	3.0
$^1J(P_CP_D)$	−0.1	0.0	0.2	2.5	2.6	1.3	1.5
$^2J(P_AP_C)$	−10.3	−11.0	−11.7	11.5	10.8	12.6	11.9
$^2J(P_AP_D)$	4.2	4.7	3.9	1.0	1.5	−5.2	−6.0
$^2J(P_BP_C)$	4.2	3.8	3.9	−4.9	−5.3	0.8	0.9
$^3J(P_BP_D)$	−4.2	−3.4	−3.7	0.2	1.0	−0.5	−0.8
(*ii*) ^{31}P–^{77}Se							
$^1J(P_ASe_a)$					−0.4		10.8
$^1J(P_CSe_a)$					9.6		0.8
$^1J(P_BSe_b)$		8.3	8.0			2.5	2.2
$^1J(P_CSe_b)$		−2.2	−2.2			−7.7	−7.7
$^2J(P_ASe_b)$		4.7	4.9			1.4	1.6
$^2J(P_DSe_b)$		0.8	1.4			1.1	1.7
(*b*) Chemical shifts							
$\delta(P_A)$	−13.4	−14.1	−16.8	5.6	4.9	−12.2	−15.0
$\delta(P_C)$	−13.4	−16.1	−16.8	−12.3	−14.9	5.6	4.9
$\delta(P_B)$	1.3	1.9	2.4	−3.5	−2.9	2.2	2.6
$\delta(P_D)$	1.3	1.9	2.4	3.0	3.5	−4.2	−3.8
$\delta(Se_a)$					55.5		56.4
$\delta(Se_b)$		31.5	32.5			31.5	32.5

* Scheme 2.

$\delta(P_C)$ on replacements b1 or b2, or d1 or d2, respectively, and for $\delta(P_B)$ or $\delta(P_D)$ on replacement a2 or a3 or on d1 or d2, or b1 or b2, respectively. Increase in bond angle had a much smaller effect on the phosphorus than on selenium chemical shifts, possibly corresponding to the shorter range of phosphorus, compared with selenium, shifts, found for these compounds. This can be seen by comparing the effects of replacements a1–a3, or d1 or d2, on $\delta(P_B)$ and on $\delta(Se_b)$. The shifts $\delta(P_A)$ and $\delta(Se_a)$ were both more sensitive to replacement at E_b than $\delta(P_B)$ and $\delta(Se_b)$ respectively were to replacement at E_a.

Chemical shifts of phosphorus atoms adjacent to replaced chalcogen atoms showed changes in which the effect of alteration in bond angles was masked by the change in shielding caused by the electronegativity difference between sulfur and selenium. Thus, bond angles P_B–P_A–E_a and E_b–P_C–E_a would be expected to increase approximately equally on replacement at E_b. In fact, the expected move to higher frequency was observed for $\delta(P_A)$ (replacement b1 or b2) but was masked for $\delta(P_C)$ by the shielding effect of Se_b. The lesser extent of this shielding effect on $\delta(P_B)$ compared with $\delta(P_C)$, for replacement b1 or b2, is remarkable.

Relative Yields of Compounds.—The very different concentrations of the compounds observed in solution by NMR probably reflected concentrations in the melts from which the solutions were obtained by cooling and extraction, though it was not possible to prove this because the concentrations in the melt were not measured directly. It was found in a separate experiment that α-$P_4S_3I_2$ **1** and α-$P_4Se_3I_2$ **6** exchanged in solution in CS_2 in daylight at room temperature, to give a very similar product distribution, although they did not exchange over the same period in the dark. This indicates that equilibrium was reached both under high temperature and under mild photolysis conditions. The exchange reaction in solution was most amenable to quantitative study, and the results are described here.

A solution in CS_2 of equimolar quantities of α-$P_4S_3I_2$ **1** and α-$P_4Se_3I_2$ **6** was sealed in an NMR tube and allowed to stand in bright daylight for 7 d. The ^{31}P NMR spectrum then showed a product distribution which did not change significantly in a further 5 weeks. Concentrations, estimated by integration over whichever peaks due to P_A or P_C were clearly visible, followed by appropriate scaling, were: 12% α-$P_4S_3I_2$ **1**, 3% symmetric α-$P_4S_2SeI_2$ **2**, 34% unsymmetric α-$P_4S_2SeI_2$ **3**, 11% unsymmetric α-$P_4SSe_2I_2$ **4**, 29% symmetric α-$P_4SSe_2I_2$ **5** and 12% α-$P_4Se_3I_2$ **6**.

If each of the different bonding combinations, P–P, P–S, P–Se and P–I, had a constant bond energy, irrespective of its position in the molecule or of the identity of the other atoms, then each of the possible chalcogen-exchange reactions, *e.g.* **1** + **6** $\longrightarrow$ **3** + **5**, would be enthalpy neutral, because the total number of each bonding combination does not change in any one of these reactions. For equimolar total sulfur and selenium contents, the expected ratio α-$P_4S_3I_2$:α-$P_4S_2SeI_2$:α-$P_4SSe_2I_2$:α-$P_4Se_3I_2$ would then be the statistical distribution 1:3:3:1. Considering the sums of the concentrations within the pairs of symmetric and unsymmetric isomers, the experimental ratio was 12:37:40:12, which is very near to this. Within the pairs there is one permutation of chalcogen atoms in symmetric compounds **2** and **5**, compared with two permutations in unsymmetric compounds **3** and **4**, so statistically the unsymmetric compounds should have been more abundant by a factor of two.

In fact, symmetric isomer **2** was much less abundant than the statistical argument suggests, while the distribution between isomers **4** and **5** was completely opposite to that predicted. This suggests that *e.g.* for replacement of sulfur in α-$P_4S_3I_2$ **1**, replacement b1 (Scheme 2) was relatively enthalpy-favoured, while replacement a1 was relatively disfavoured. This may be explained as follows. In the known structures of both ternary compounds **1** and **6**[4,5] the bond angle at chalcogen E_a (Scheme 1) is smaller than at E_b, and probably represents a strained situation. Replacement b1 then causes a relief of that strain by increasing the size of the six-membered ring, favouring formation of isomer **3**, while replacement a1 decreases the bond angle at E_a still further, as shown by the NMR evidence above, disfavouring formation of isomer **2**. The balance of enthalpy changes was such that the combined abundances of isomers **2** and **3** corresponded, perhaps coincidentally, to the enthalpy-neutral situation. A similar argument explains why, starting from α-$P_4Se_3I_2$ **6**, reverse replacement d2 was disfavoured while reverse replacement a3 was favoured, the ratio of concentrations [**5**]:[**4**] being smaller than [**3**]:[**2**] only because here the statistical distribution, favouring the unsymmetric isomer **4**, worked in the opposite direction to the enthalpy effect.

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