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β-TETRAPHOSPHORUS TRICHALCOGENIDE COMPOUNDS CONTAINING TWO DIFFERENT EXOCYCLIC LIGANDS AS WELL AS BOTH SULFUR AND SELENIUM

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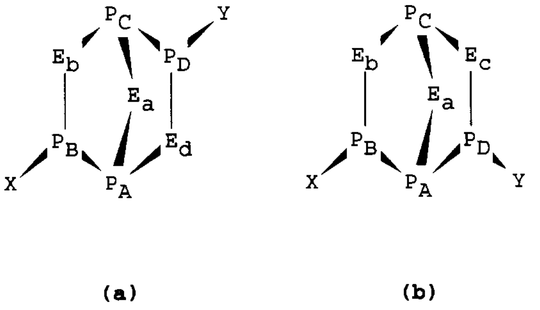
Abstract—All eight possible bicyclic molecules β-$P_4S_nSe_{3-n}(I)CHI_2$ (n = 0–3) were formed on reaction of mixtures of the tricyclic compounds $P_4S_nSe_{3-n}$ with CHI_3 in solution in CS_2, and identified in the reaction mixture by analysis of their ^{31}P NMR spectra. Differences in coupling constants caused by the presence of sulfur rather than selenium in the products were interpreted in terms of concerted twisting of the fused five-membered rings, caused by a combination of the unsymmetric exocyclic ligand and endocyclic chalcogen substitution.

The bicyclic structures of α- or β-$P_4E_3(X)Y$ molecules (Scheme 1) where E is sulfur or selenium and X and Y are halogen, pseudohalogen or various similar groups, provide interesting ^{31}P NMR spin systems yielding as parameters six ^{31}P–^{31}P coupling constants and four chemical shifts. In unsymmetric compounds α-$P_4S_3(X)Y$ these NMR parameters are controlled by both ligands X and Y in a complex manner, for which a set of empirical rules of predictive value has been developed,[1,2] and subsequently used.[3,4] The rules applied also to compounds α-$P_4Se_3(X)Y$, and, more interestingly, a similar set of rules could be developed for molecules β-$P_4E_3(X)Y$ (X, Y = halogen) (Scheme 1b).[5] In each case, the constraints of the cage structure, causing interdependency of changes in its various bond angles and hence of changes in its NMR parameters, appeared to be responsible for the working of these rules.



Scheme 1. Labelling of ring positions for α-$P_4E_3(X)Y$ (a) and β-$P_4E_3(X)Y$ (b) molecules (E = S or Se).

To test the influence of such changes in cage geometry on coupling constants and chemical shifts, the effect of endocyclic replacement of sulfur by selenium in the series of molecules α-$P_4S_nSe_{3-n}I_2$ (n = 0–3) was examined.[6] While crystallographic structural data are generally not available in this field, the nature of changes in bond angles due to this chalcogen replacement was fairly predictable. Increased bond angle at chalcogen resulted in a more positive ^2J(P–P) coupling transmitted by it, while increased bond angle at phosphorus or at selenium resulted in higher frequency ^{31}P or ^{77}Se chemical shifts, respectively, although change in δ_P due to geometric variation could be masked by the

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electronegativity effect of replacement of a directly neighbouring chalcogen. Chalcogen replacement in a particular cage position (a *versus* b or d, Scheme 1a) caused remarkably consistent changes in NMR parameters, almost independently of the extent of chalcogen substitution elsewhere in the molecule. A similar study for molecules β-$P_4S_nSe_{3-n}I_2$ showed changes in NMR parameters which were often in the same sense and of similar numerical values, for chalcogen substitution at comparable positions in the two cage skeletons.[7]

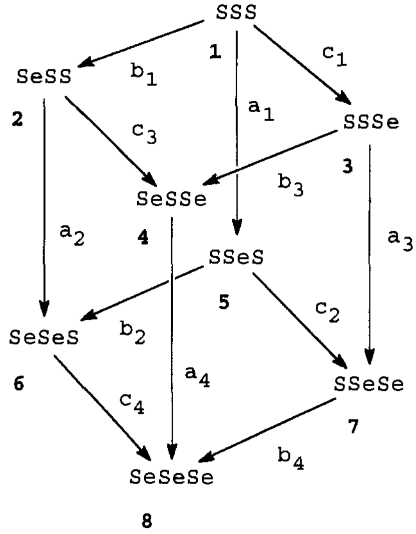
We succeeded recently in observing the first α- and β-$P_4E_3(I)Y$ compounds in which an organic ligand Y was directly bonded to a phosphorus atom of the cage skeleton.[8] This allowed the study of the influence of two ligands of widely differing steric and to some extent electronic requirements on the NMR parameters of the β-P_4S_3 or β-P_4Se_3 skeletons.

We now report that by reaction of CHI_3 with mixtures of the tricyclic compounds $P_4S_nSe_{3-n}$ ($n = 0$–3) we have observed in solution all six molecules β-$P_4SSe_2(I)CHI_2$ or β-$P_4S_2Se(I)CHI_2$, in which the odd chalcogen atom occupies any of the three positions E_b, E_a or E_c (Scheme 1b, $X = I$, $Y = CHI_2$). For the first time, this enables study of the effect of a combination of both exocyclic ligand and endocyclic chalcogen substitution on NMR parameters of a β-skeleton. In particular, changes due to skeletal distortion in the large 'through-space' coupling $^2J(P_BP_D)$ can be examined.

RESULTS AND DISCUSSION

Representation of products and relationships

Compounds β-$P_4S_nSe_{3-n}(I)CHI_2$ ($n = 1$–3) can be thought of as being derived from β-$P_4S_3(I)CHI_2$ by replacements of sulfur by selenium in positions E_a, E_b or E_c (Scheme 1b; $X = I$, $Y = CHI_2$). The whole set can be represented as corners of a cube (Scheme 2), such that replacements at position E_a, referred to as a_i where i is a serial number, are vertical edges of the cube, replacements b_i are one set of parallel horizonal edges and replacements c_i are the other. Replacements b involve an increase of 1 in compound number, c of 2, and a of 4. Compound numbers, overall formulae and occupancy of cage positions are given, along with iterative fitting data for the NMR spectra, in Table 1.



Scheme 2. Replacements of S by Se in β-$P_4S_nSe_{3-n}(I)CHI_2$: a_1–a_4 at position E_a (see Scheme 1b; $X = I$, $Y = CHI_2$), b_1–b_4 at E_b, c_1–c_4 at E_c. The sequence of symbols for each compound is $E_bE_aE_c$.

Assignment of NMR spectra

The ^{31}P NMR spectra of the trisulfide **1** and the triselenide **8** have been reported.[8] The twelve multiplets due to isomers of β-$P_4S_2Se(I)CHI_2$ **2**, **3**, **5** could be distinguished from those due to β-$P_4SSe_2(I)CHI_2$ **4**, **6**, **7** because of their greater relative intensities in spectra of sulfur-rich rather than selenium-rich mixtures. Multiplets could be assigned further according to which of the four skeletal positions P_A, P_B, P_C or P_D they corresponded to: those due to P_A possessed two large ^1J splittings (270–300 Hz), those due to P_B or P_D had one ^1J and one through-space-^2J splitting (150–170 Hz), while multiplets due to P_C contained no large splittings. Assignment of P_B *versus* P_D was on the basis of the different range of their chemical shifts, as observed for the trisulfide **1** or the triselenide **8**. Next, in each resulting set of three multiplets due to P_A, P_B or P_D, one multiplet could be assigned to a particular isomer on grounds of extreme chemical shift. Phosphorus chemical shifts for these skeletal positions are similar for the trisulfide **1** to those for the triselenide **8** because the shielding effect of replacing an adjacent sulfur by selenium was compensated by the geometric effect of two such replacements in the non-adjacent positions.[6,7] The largest variations in shift were produced by chalcogen replacement adjacent to a phosphorus atom, without replacements in either of the other two positions. Thus, for example, in the P_A set for β-$P_4SSe_2(I)CHI_2$, the highest value of $\delta(P_A)$ could be assigned to the isomer **4** in which only position E_a was occupied by sulfur rather than selenium, while in the P_A set for β-$P_4S_2Se(I)CHI_2$ the lowest chemical shift belonged to the isomer **5** in which only E_a was selenium rather than sulfur. After this stage, one multiplet had been assigned

Table 1. Occupancy of cage positions and iterative fitting of NMR spectra of β-$P_4S_nSe_{3-n}$(I)CHI_2 (n = 0–3)

	Formula	Chalcogen position[a] E_b	E_c	E_a	Number of transitions observed[a,b] for P_A	P_B	P_C	P_D	R.m.s. deviation (Hz)
1	β-P_4S_3(I)CHI_2	S	S	S	8	8	8	8	0.019
2	β-P_4S_2Se(I)CHI_2	Se	S	S	8	8	6	7	0.045
3		S	Se	S	4	7	8	7	0.033
5		S	S	Se	7	6	6	8	0.037
4	β-P_4SSe_2(I)CHI_2	Se	Se	S	8	8	8	8	0.080
6		Se	S	Se	8	8	8	8	0.089
7		S	Se	Se	4	8	8	8	0.087
8	β-P_4Se_3(I)CHI_2	Se	Se	Se	8	8	8	8	0.037

[a] Scheme 1b (X = I, Y = CHI_2).
[b] From a maximum of eight.

with certainty to each new compound **2**–**7**. The remaining three multiplets for each could then be selected unambiguously as yielding a self-consistent set of coupling constants including those observed in the assigned multiplet. For each compound, initial analysis of the spectrum as a first-order spin system was followed by iterative fitting using the program NUMARIT.[9] Resulting coupling constants and chemical shifts are given in Table 2.

Relative yields of products

Relative concentrations of solutes in CS_2 were estimated throughout by integration of NMR spectra. A mixture containing P_4S_3, P_4S_2Se and P_4SSe_2 in molar ratio 67 : 28 : 5.6 reacted with CHI_3 in solution in CS_2 in diffuse light over 1 h, to give a solution containing β-P_4S_3(I)CHI_2 **1**, β-P_4S_2Se(I)CHI_2 (**2**, **3**, **5**), P_4S_3, P_4S_2Se and P_4SSe_2 in molar ratio 8.1 : 4.8 : 57 : 26 : 4.2. the isomers of β-p_4S_2Se(I)CHI_2 were distributed in the ratio Se_b**2** : Se_c**3** : Se_a**5** = 41 : 34 : 25. In a parallel experiment, a mixture of P_4SSe_2 and P_4Se_3 in molar ratio 1 : 1, obtained by fractional crystallization, yielded a solution containing β-P_4SSe_2(I)CHI_2 (**4**, **6**, **7**), β-P_4Se_3(I)CHI_2 **8**, P_4S_2Se, P_4SSe_2 and P_4Se_3 in the molar ratio 8.3 : 10 : 5.9 : 28 : 47, with the isomers of β-P_4SSe_2(I)CHI_2 in the ratio S_a**4** : S_c**6** : S_b**7** = 37 : 33 : 30.

It can be seen that P_4Se_3 was consumed less readily in the reaction with CHI_3 than was P_4SSe_2, and that P_4S_3 was of greater reactivity than P_4S_2Se. In

Table 2. NMR parameters for β-$P_4S_nSe_{3-n}$(I)CHI_2 (n = 0–3)

Species	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Chalcogens[a]	$S_bS_aS_c$	$Se_bS_aS_c$	$S_bS_aSe_c$	$Se_bS_aSe_c$	$S_bSe_aS_c$	$Se_bSe_aS_c$	$S_bSe_aSe_c$	$Se_bSe_aSe_c$
Chemical shifts								
$\delta(P_A)$	148.49	153.98	155.17	160.74	136.09	141.06	142.07	147.01
$\delta(P_B)$	108.11	99.13	115.86	106.95	109.81	102.13	117.06	109.47
$\delta(P_C)$	195.99	192.97	192.39	189.70	183.76	178.53	176.75	171.29
$\delta(P_D)$	83.01	93.61	79.45	88.49	82.83	93.29	79.72	88.60
Coupling constants[b]								
$^1J(P_AP_B)$	−279.51 (1)	−276.67 (3)	−288.91 (3)	−289.18 (5)	−276.74 (3)	−274.12 (5)	−286.23 (8)	−286.53 (2)
$^1J(P_AP_D)$	−284.95 (1)	−289.35 (3)	−286.21 (2)	−292.87 (5)	−284.17 (2)	−289.62 (5)	−284.23 (5)	−291.83 (2)
$^2J(P_AP_C)$	75.50 (1)	85.10 (3)	83.21 (2)	94.36 (5)	65.49 (2)	74.80 (5)	72.81 (6)	83.54 (2)
$^2J(P_BP_C)$	53.33 (1)	49.01 (3)	48.56 (2)	45.06 (5)	58.36 (3)	53.88 (5)	53.55 (5)	50.27 (2)
$^2J(P_CP_D)$	43.59 (1)	38.81 (3)	41.93 (2)	38.31 (5)	48.90 (2)	44.26 (5)	46.97 (5)	43.46 (2)
$^2J(P_BP_D)$	157.97 (1)	169.78 (4)	153.11 (2)	161.82 (5)	156.31 (3)	168.26 (5)	152.05 (5)	160.65 (2)

[a] For labelling, see Scheme 1b (X = I, Y = CHI_2).
[b] Coupling constants are in Hz with standard deviations (σ) in parentheses.

the second experiment, the greater reactivity of P_4SSe_2 was not reflected in a higher yield of sulfur-containing β-compounds. Because of the mixture of isomers of β-compounds containing both sulfur and selenium, the concentration of each was low relative to those of the products containing only selenium. This resulted in a relative underestimation of the concentrations of the mixed compounds because of the effect of noise on the NMR integrals. The apparent deficiency of sulfur-rich compounds β-$P_4SSe_2(I)CHI_2$ may therefore not be a real effect. No other sulfur-containing products in significant concentrations were observed to provide an alternative explanation.

Within the isomer sets (**2**, **3**, **5**) and (**4**, **6**, **7**), compounds with the larger selenium atom in the bridging position E_a were less abundant than with the smaller sulfur atom in this position (isomer **5** *versus* isomers **2** or **3** and isomers **6** or **7** *versus* isomer **4**), as previously reported for the series α-$P_4S_nSe_{3-n}I_2$,[6] although now the preference was much less marked. Position E_c, near the bulky ligand CHI_2, was less readily occupied by the larger selenium atom, and position E_b, near to the smaller iodide ligand, was less readily occupied by the smaller sulfur atom, than vice versa, in both series (isomer **3** *versus* **2** or isomer **7** *versus* **6**).

Rearrangement to products with the α-skeleton

The product solutions were allowed to stand at room temperature in the dark. As found previously,[8] β-compounds **1** or **8**, containing only sulfur or only selenium, rearranged to the corresponding α-compounds (Scheme 1a; $X = I$, $Y = CHI_2$), which were now found as major components in the mixtures after 5 days. Besides these organoiodides, diiodides in the series α-$P_4S_nSe_{3-n}I_2$ resulted from ligand redistribution reactions. Some further NMR multiplets due to minor components with non-symmetric spin systems were seen, but none of these matched predicted multiplets for the expected mixed sulfide selenides α-$P_4S_nSe_{3-n}(I)CHI_2$ ($n = 1$–2). Not enough multiplets with matching splittings were unobscured by other components for the whole spectrum of any other new compound to be analysed.

Changes in NMR parameters with chalcogen substitution

The effect on chemical shifts and coupling constants of replacing sulfur atoms by selenium atoms in the set β-$P_4S_nSe_{3-n}(I)CHI_2$ ($n = 0$–3) (Scheme 2) is shown in Table 3. Most of the changes are remarkably similar to those for the β-diiodides.[7] Until now,[6,7] changes in coupling constants on chalcogen substitution have been ascribed to changes in bond angles, but the present work shows the need to consider twisting of the rings as an additional factor. The α-P_4E_3 skeleton can retain its C_2 symmetry while exhibiting concerted twisting of its two five-membered rings, so that the distance E_b—E_d (Scheme 1a) decreases while the distance P_B—P_D increases, or vice versa. This could happen without changes in bond angles in going from the structure of one symmetrically substituted compound α-$P_4S_3X_2$ to another, and be responsible for some of the observed changes in NMR parameters.[3] Such an effect is not possible between symmetrically substituted compounds β-$P_4S_3X_2$, where twisting would make the two five-membered rings non-identical,

Table 3. Changes in NMR parameters[a] in β-$P_4S_nSe_{3-n}(I)CHI_2$ ($n = 0$–3) on replacing sulfur by selenium

Replacement[b]	a_1	a_2	a_3	a_4	b_1	b_2	b_3	b_4	c_1	c_2	c_3	c_4
Going from	**1**	**2**	**3**	**4**	**1**	**5**	**3**	**7**	**1**	**5**	**2**	**6**
To	**5**	**6**	**7**	**8**	**2**	**6**	**4**	**8**	**3**	**7**	**4**	**8**
$\delta(P_A)$	−12.4	−12.9	−13.1	−13.7	5.5	5.0	5.6	4.9	6.7	6.0	6.8	6.0
$\delta(P_B)$	1.7	3.0	1.2	2.5	−9.0	−7.7	−8.9	−7.6	7.8	7.2	7.8	7.3
$\delta(P_C)$	−12.2	−14.4	−15.6	−18.4	−3.0	−5.2	−2.7	−5.5	−3.6	−7.0	−3.3	−7.2
$\delta(P_D)$	−0.2	−0.3	0.3	0.1	10.6	10.5	9.0	8.9	−3.6	−3.1	−5.1	−4.7
$^1J(P_AP_B)$	2.8	2.6	2.7	2.6	2.8	2.6	−0.3	−0.3	−9.4	−9.5	−12.5	−12.4
$^1J(P_AP_D)$	0.8	−0.3	2.0	1.0	−4.4	−5.5	−6.7	−7.6	−1.3	−0.1	−3.5	−2.2
$^2J(P_AP_C)$	−10.0	−10.3	−10.4	−10.8	9.6	9.3	11.1	10.7	7.7	7.3	9.3	8.7
$^2J(P_BP_C)$	5.0	4.9	5.0	5.2	−4.3	−4.5	−3.5	−3.3	−4.8	−4.8	−4.0	−3.6
$^2J(P_CP_D)$	5.3	5.5	5.0	5.1	−4.8	−4.6	−3.6	−3.5	−1.7	−1.9	−0.5	−0.8
$^2J(P_BP_D)$	−1.7	−1.5	−1.1	−1.2	11.8	11.9	8.7	8.6	−4.9	−4.3	−8.0	−7.6

[a] Chemical shift differences are in p.p.m. and coupling constant differences in Hz.

[b] Scheme 2.

with consequent loss of the C_s symmetry of the molecule. However, when the presence of two different ligands prevents any symmetry, such twisting could take place, as well as changes in bond angles. The point is illustrated by ^2J(P—S—P) couplings in compounds containing the ligand NMePh. Here $^2J(P_BP_C)$ is unusually small in both α-$P_4S_3(NMePh)_2$ and its derivatives α-P_4S_3(X)NMePh, probably due to ring twisting.[2,3] In β-$P_4S_3(NMePh)_2$, however, the corresponding $^2J(P_CP_D)$ has a similar value to that for β-$P_4S_3I_2$, and only in β-P_4S_3(I)NMePh, where ring twisting is possible, do both $^2J(P_CP_D)$ and $^2J(P_BP_C)$ move to a lower value.[10] A similar removal of symmetry and consequent twisting may also be caused by chalcogen substitution.

On a simple model involving through-space interaction of lone pairs of electrons on P_B and P_D, it might be assumed that the coupling $^2J(P_BP_D)$ would have a maximum value in the absence of ring twisting in a symmetric compound β-$P_4S_3X_2$, and that unsymmetric chalcogen substitution (at positions E_b or E_c, Scheme 1b) would reduce it. In fact (Table 3) replacements b_1–b_4 strongly increase $^2J(P_BP_D)$ in the organoiodides **1**–**8**, while replacements c_1–c_4 decrease it, irrespective of whether these replacements make the molecule more or less symmetrical in respect of chalcogen position occupancy. An explanation is that the cage distortion caused by unsymmetric ligand substitution persists in all compounds in the series, but is counteracted by replacements b (introducing selenium in the five-membered ring carrying the iodine ligand) and supplemented by replacements c.

Twisting of the rings is probably responsible also for the variations of $^1J(P_AP_B)$ in the series β-$P_4S_nSe_{3-n}(I)CHI_2$. All values of $^1J(P_AP_B)$ are more negative than in the symmetric β-$P_4S_3I_2$ or β-$P_4Se_3I_2$, but the most negative values are found for compounds **3**, **4**, **7**, **8** where selenium in position E_c augments the twisting caused by the different ligands, as proposed above. This is shown in Table 3 as large negative changes in $^1J(P_AP_B)$ for replacements c_1–c_4.

The third concurring piece of evidence for ring twisting effects concerned the changes on chalcogen substitution in ^2J(P—P) couplings transmitted by chalcogen. While $^2J(P_AP_C)$ is bigger in α- or β-$P_4Se_3I_2$ than in α- or β-$P_4S_3I_2$, respectively, replacement of any one sulfur by selenium in the diiodide series or in the present organoiodides leads to a decrease in the value of the ^2J coupling transmitted by it. This general effect is due probably to the imposition of a smaller bond angle at the introduced larger selenium, because the distance between the bridged phosphorus atoms is held relatively constant by the rest of the structure.[6] However, replacements a_1–a_4 (Table 3) more strongly decrease the value of $^2J(P_AP_C)$ than replacements b_1–b_4 decrease $^2J(P_BP_C)$, or replacements c_1–c_4 decrease $^2J(P_CP_D)$. The parallel sensitivity of the relative yield data (see above) to the occupancy of position E_a points to a stronger control by the rest of the structure over the distance P_A—P_C than over P_B—P_C. An alternative explanation is that replacements a_i, even in an unsymmetric β-structure, cause little tendency to concerted ring twisting, whereas twisting is caused by replacements b_i so as to allow the bond angle at E_b to remain more constant. The effect of replacements c_1–c_4 on $^2J(P_CP_D)$ was particularly small for the organoiodides, again supporting the hypothesis that twisting caused by the introduction of Se_c was increased by the unsymmetric ligand substitution. If the augmented twisting were caused by repulsion of the chalcogen E_c by the CHI_2 group, this would fit in with lower preference of selenium for the E_c rather than the E_b site (see above), which otherwise conflicts with smaller change in the coupling constant.

While ring twisting resulting from replacements c_i has the same effect as increasing the bond angle at E_c, the atom E_b in a β-molecule consequently moves in the same direction (due to the repulsion E_c—E_b) and hence is affected in the same way as by a decreased bond angle at it. Thus replacements c_i cause negative changes in $^2J(P_BP_C)$, in general for β-molecules. The case for α-molecules is necessarily the opposite: the corresponding twist due to introduction of selenium at E_d would cause repulsion not of E_b but of P_B (Scheme 1a) and the effect on E_b would be equivalent to an increased bond angle at it. The changes $^2J(P_BP_C)$ for replacements d_i in the α-diiodides were therefore positive, though at one atom further removed from the cause of the effect, the changes were small.[6]

EXPERIMENTAL

All operations were carried out under nitrogen by Schlenk methods. CS_2 was dried by distillation from P_4O_{10}. NMR spectra were measured in 10 mm diameter tubes using a Bruker WM300WB spectrometer operating at 121.5 MHz for ^{31}P. 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.

Typical procedure. A sample of mixed tetraphosphorus trichalcogenides,[11] estimated by ^{31}P NMR integration to consist of equimolar quantities of P_4SSe_2 and P_4Se_3 (0.337 g, $\bar{M} = 337.3$ g mol^{-1}, 1.00 mmol), was mixed with CHI_3 (0.394 g, 1.00

mmol) and the mixture further dried by pumping at room temperature before being stirred with CS_2 (20 cm^3). Almost all of the combined solids dissolved to give a clear yellow solution. After 70 min in diffuse light from fluorescent striplamps, the solution was concentrated to about half its volume by pumping at 15°C. ^{31}P NMR then showed the mixture of β-compounds **4**, **6**, **7** and **8** and phosphorus chalcogenides described above. Insufficient concentrations of the new β-compounds **4**, **6** or **7** were obtained for practicable ^{77}Se NMR spectroscopy. The remaining solution was sampled again after 5 days in the dark at 20°C, when the β-compounds were found to be almost entirely absent, but α-$P_4Se_3(I)CHI_2$,[8] α-$P_4Se_3I_2$, and minor concentrations of the other members of the series α-$P_4S_nSe_{3-n}I_2$ had appeared.[6] Exposure of the original NMR sample to glass-filtered sunlight for 10 min, instead of standing in the dark for the longer period, caused similar decomposition.

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