Phosphorus-31, Nitrogen-15, and Nitrogen-14 Nuclear Magnetic Resonance Spectra of α-Tetraphosphorus Trisulphide Isothiocyanates

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Phosphorus-31 n.m.r. spectra of α-$P_4S_3(NCS)_2$ (**1**), α-P_4S_3(NCS)Cl (**2**), and α-P_4S_3(NCS)I (**3**) have been measured both for natural-abundance ^{14}N isotopomers [(**1a**), (**2a**), and (**3a**)] and completely ^{15}N-containing isotopomers [(**1b**), (**2b**), and (**3b**)] over a range of temperatures. Assignment and computer fitting of spectra of the ^{15}N compounds has yielded accurate values of ^{31}P–^{31}P and ^{31}P–^{15}N coupling constants, and has allowed their variation with temperature to be studied. Measurement of ^{15}N n.m.r. spectra [compounds (**1b**) and (**3b**)] has allowed the signs of the ^{31}P–^{15}N couplings to be confirmed. A ^{14}N T_1 relaxation study of α-$P_4S_3(^{14}NCS)_2$ (**1a**) showed a normal relaxation rate, and abnormal broadening in the ^{31}P n.m.r. spectra of the ^{14}N compounds was ascribed instead to the influence of abnormally large $^1J_{PN}$ coupling constants in the scalar coupling relaxation mechanism. Large ^{31}P–^{15}N coupling constants are reported for phosphorus(III) isothiocyanates, and for α-P_4S_3 derivatives. Similarly, large values of $^1J(^{31}P–^{13}C)$ for α-$P_4S_3(^{13}CN)(^{12}CN)$, and of the secondary isotope shifts $^1\Delta[^{31}P(^{37/35}Cl)]$ for α-$P_4S_3(^{15}NCS)$Cl (**2b**) and α-$P_4S_3Cl_2$, are reported.

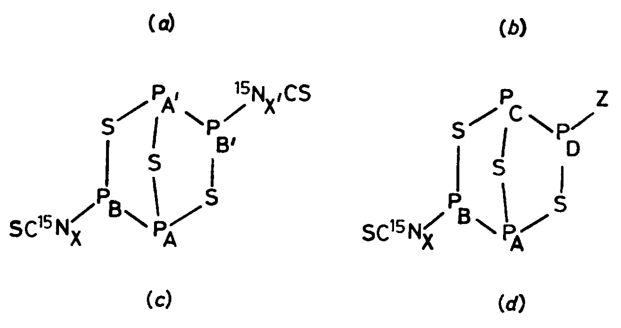
The phosphorus-31 n.m.r. spectrum of α-$P_4S_3(^{14}NCS)_2$ (**1a**) [Scheme (*a*)] corresponded to the expected AA′BB′ spin system at 200 K, while at room temperature the high-frequency half of the spectrum collapsed into broad peaks (Figure 1). Parameters for the low-temperature spectrum have already been reported,[1] but it was not possible to distinguish between ^{31}P–^{14}N scalar coupling relaxation and chemical exchange, as causes for the extreme broadening of parts of the ^{31}P n.m.r. spectrum at higher temperatures.

The unsymmetric compounds α-$P_4S_3(^{14}NCS)$Cl (**2a**) and α-$P_4S_3(^{14}NCS)$I (**3a**) have now been made,[2] and their ^{31}P n.m.r. spectra, described below, have been found to show similar changes with temperature to those of the di-isothiocyanate (**1a**): peaks primarily due to the phosphorus nuclei carrying the NCS group, P_B [Scheme (*b*)], were sufficiently visible at 200 K for crude computer fits as static ABCD spin systems to succeed, but were broadened so as to be invisible at 300 K. However, not all α-P_4S_3 cage compounds containing phosphorus–nitrogen bonds show this extreme behaviour: some members (R = Ph; R′ = Me, Et, or Ph) of a series of amino derivatives α-$P_4S_3(NRR')_2$, currently under investigation,[3] show normal phosphorus spectra, with only slight broadening of the P_B parts, at 300 K.

Rationalisation of the anomalous behaviour of the isothiocyanate compounds [(**1a**), (**2a**), and (**3a**)] in terms of relaxation of ^{31}P nuclei by scalar coupling to ^{14}N requires exceptionally slow quadrupolar relaxation of ^{14}N, or exceptionally large $^1J_{PN}$ coupling constants, by comparison with pyramidal amino compounds. While ^{14}N relaxation could be studied directly (see below), a knowledge of the phosphorus–nitrogen couplings was necessary for a full interpretation. These coupling constants, also of interest in themselves, could be obtained accurately only by studying the completely ^{15}N-substituted isotopomers [(**1b**), (**2b**), and (**3b**)]. The possibility of chemical exchange could be investigated in these strongly coupled systems also only if information were not lost as a result of broadening of the ^{31}P n.m.r. spectrum by ^{14}N. Consequently the ^{15}N isotopomers [(**1b**), (**2b**), and (**3b**)] have now been made,[2] and their n.m.r. spectra measured at several temperatures and analysed.

Preparative Routes

The original general method of preparation of pseudohalide derivatives of the α-P_4S_3 cage,[4] by stirring a suspension of excess of silver pseudohalide with a solution of α-$P_4S_3I_2$ in CS_2, is useful for complete substitution by a given ligand, and was used to make both ^{14}N (natural abundance) and ^{15}N (99%) isotopomers of α-$P_4S_3(NCS)_2$ (**1**). For the particular substitution of thiocyanate for iodide, the reaction proceeded practically quantitatively at room temperature, the yellow colour of the iodide disappearing as it was added slowly to the AgNCS. Solutions of α-$P_4S_3(NCS)_2$ in CS_2 with concentrations of 0.1—0.2 mol dm^{-3} were sufficiently stable for extended n.m.r. measurements, but further concentration led to the precipitation of insoluble products.[1]



(*a*) (*b*) (*c*) (*d*)

Scheme. N.m.r. spin system labelling for: (*a*) symmetric molecules without ^{15}N [Y = ^{14}NCS (**1a**) or ^{35}Cl (**4a**)]; (*b*) asymmetric molecules without ^{15}N [(**2a**; Y = ^{14}NCS, Z = Cl), (**3a**; Y = ^{14}NCS, Z = I), or (**4b**; Y = ^{37}Cl, Z = ^{35}Cl)]; (*c*) α-$P_4S_3(^{15}NCS)_2$ (**1b**); (*d*) α-$P_4S_3(^{15}NCS)$ halides [Z = ^{35}Cl (**2b**) or I (**3b**)]

Compounds of the general formula α-P_4S_3Y(Z) [Scheme (*b*)] readily undergo ligand-exchange reactions in solution, often at room temperature, so asymmetric compounds (Y ≠ Z) have not yet been isolated, but have been studied in equilibrium with the corresponding symmetric compounds. These mixtures may be obtained conveniently, for pseudohalide compounds, by reaction of a solution of the dihalide α-$P_4S_3Z_2$ with

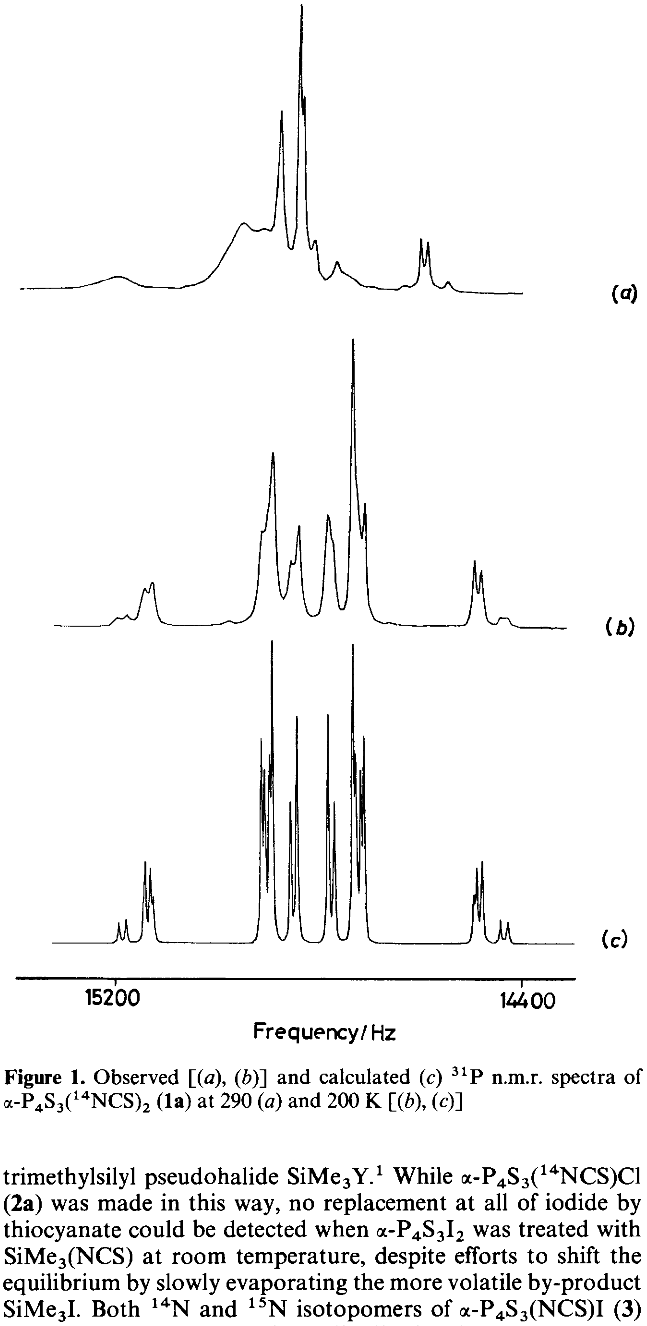


Figure 1. Observed [(*a*), (*b*)] and calculated (*c*) ^{31}P n.m.r. spectra of α-$P_4S_3(^{14}NCS)_2$ (**1a**) at 290 (*a*) and 200 K [(*b*), (*c*)]

trimethylsilyl pseudohalide $SiMe_3Y$.[1] While α-$P_4S_3(^{14}NCS)Cl$ (**2a**) was made in this way, no replacement at all of iodide by thiocyanate could be detected when α-$P_4S_3I_2$ was treated with $SiMe_3(NCS)$ at room temperature, despite efforts to shift the equilibrium by slowly evaporating the more volatile by-product $SiMe_3I$. Both ^{14}N and ^{15}N isotopomers of α-$P_4S_3(NCS)I$ (**3**) consequently were made by redistribution between α-$P_4S_3I_2$ and α-$P_4S_3(NCS)_2$ (**1**), in solution in CS_2. Surprisingly, no reaction could be detected by n.m.r. spectroscopy after 17 h at 24 °C, but a useful concentration of α-$P_4S_3(NCS)I$ was observed after 86 h at 46 °C. (N.m.r. integration to measure conversion was impracticable because of overlapping spectra.) Reaction between α-$P_4S_3I_2$ and α-$P_4S_3(NCS)_2$ was thus much slower than reaction between α-$P_4S_3I_2$ and α-$P_4S_3Br_2$;[1] this observation made intermolecular exchange reactions of the isothiocyanate compounds on the n.m.r. time-scale seem unlikely. Identification of the isothiocyanate halides [(**2**) and (**3**)] in the equilibrium mixtures depended on the similarity of their observed ^{31}P–^{31}P coupling constants to those predicted from those of α-$P_4S_3(NCS)_2$ (**1**) and the corresponding dihalide α-$P_4S_3Z_2$, and of their observed ^{31}P–^{15}N coupling constants to those of α-$P_4S_3(^{15}NCS)_2$ (**1b**) (see below).

For reasons of economy in the ^{15}N case, a method was required to convert the α-$P_4S_3I_2/\alpha$-$P_4S_3(^{15}NCS)I/\alpha$-$P_4S_3(^{15}NCS)_2$ mixture into one containing α-$P_4S_3Cl_2$ and α-$P_4S_3(^{15}NCS)Cl$ (**2b**) respectively. Complete removal of phosphorus–iodine compounds was necessary to avoid further confusion in the already very complex n.m.r. spectra. This was achieved by stirring the solution with excess of AgCl. Reaction was much slower than that of α-$P_4S_3I_2$ with AgNCS, but was complete after 116 h at 50 °C. Thiocyanate attached to phosphorus was not noticeably replaced by chloride in this method, although sufficient AgCl to do so was taken.

Some bright yellow precipitate was formed from the α-$P_4S_3Cl_2/\alpha$-$P_4S_3(^{15}NCS)Cl/\alpha$-$P_4S_3(^{15}NCS)_2$ mixture in 15 weeks at 20 °C, but ^{31}P n.m.r. spectroscopy showed that the components remaining in solution had changed little. Some α-P_4S_4 and traces of α-P_4S_5 and of P_4S_3 had appeared, so it was of interest to discover the fate of thiocyanate during this slight decomposition. First-order multiplets due to ^{31}P–^{15}N coupling in simple phosphorus isothiocyanates were sought in the ^{31}P n.m.r. spectra of the solution, and small concentrations of $P(^{15}NCS)_3$, $P(^{15}NCS)_2Cl$, and possibly $P(^{15}NCS)Cl_2S$ (see below) were identified by the published chemical shifts of the corresponding ^{14}N isotopomers.[5]

Assignments of N.M.R. Spectra

Spectra of α-$P_4S_3(^{14}NCS)Cl$ (**2a**).—^{31}P N.m.r. spectra were obtained at 296 K, at 20-K intervals in the range 280—200 K, and at 190 K. Phosphorus–phosphorus coupling constants could be predicted[1] from those of α-$P_4S_3(^{14}NCS)_2$ and α-$P_4S_3Cl_2$, and chemical shifts were expected in the order $\nu_D \gg \nu_C > \nu_A \approx \nu_B$ [Scheme (*b*)]. At 296 K, the P_D and P_C multiplets were recognised, though of the eight peaks of the P_C multiplet, peaks 2, 3, 6, and 7 were broadened (Figure 2). On cooling, peaks 1, 4, 5, and 8 of this muliplet were invariant with respect to each other, while the broadened peaks merged so that at 190 K the whole multiplet was a doublet of triplets. Dilution of the solution served to sharpen the peaks only slightly, so any exchange must have been intramolecular. While at first sight the changes in the P_C multiplet suggested a skeletal rearrangement exchanging P_A with P_B, similar to that reported for P_3Se_4I by Blachnik *et al.*,[6] the changes in the spectrum occurred as the temperature was changed in the wrong sense, so an alternative explanation was sought.

In the expected region of the P_A and P_B absorptions only a pattern of four peaks, changing with temperature, was clearly visible. These were assumed to be the strong inner peaks of the P_A halves of the expected four AB subspectra. The location of the transitions mainly associated with P_B was not obvious at any temperature, so a series of computer simulations was carried out using NUMARIT (S.E.R.C. n.m.r. Program Library, Daresbury), varying ν_B in 50-Hz intervals. Allowing for selective broadening of some peaks by scalar coupling relaxation by ^{14}N, the changes in the P_C multiplet could then be explained as resulting from the onset of 'deceptive simplicity' as differential shifts with temperature of ν_A and ν_B caused δ_{AB} ($=\nu_A - \nu_B$) to decrease with decreasing temperature. The spectrum at 200 K could roughly be fitted by computer, ignoring ^{31}P–^{14}N couplings, because one broad peak, corresponding to the strongest of the predicted 'P_B transitions,' could be identified (Figure 2). At 220 K and above, all 'P_B peaks' were too broad for their positions to be measured, while at 190 K the loss of information due to deceptive simplicity made fitting impossible.

The order of shifts found was $\nu_A > \nu_B$. The values of the shifts and couplings obtained, while acceptable, are not listed here for the ^{14}N isotopomers [(**2a**) and (**3a**)] because their errors were larger than the expected differences between these parameters and those obtained much more accurately for the ^{15}N

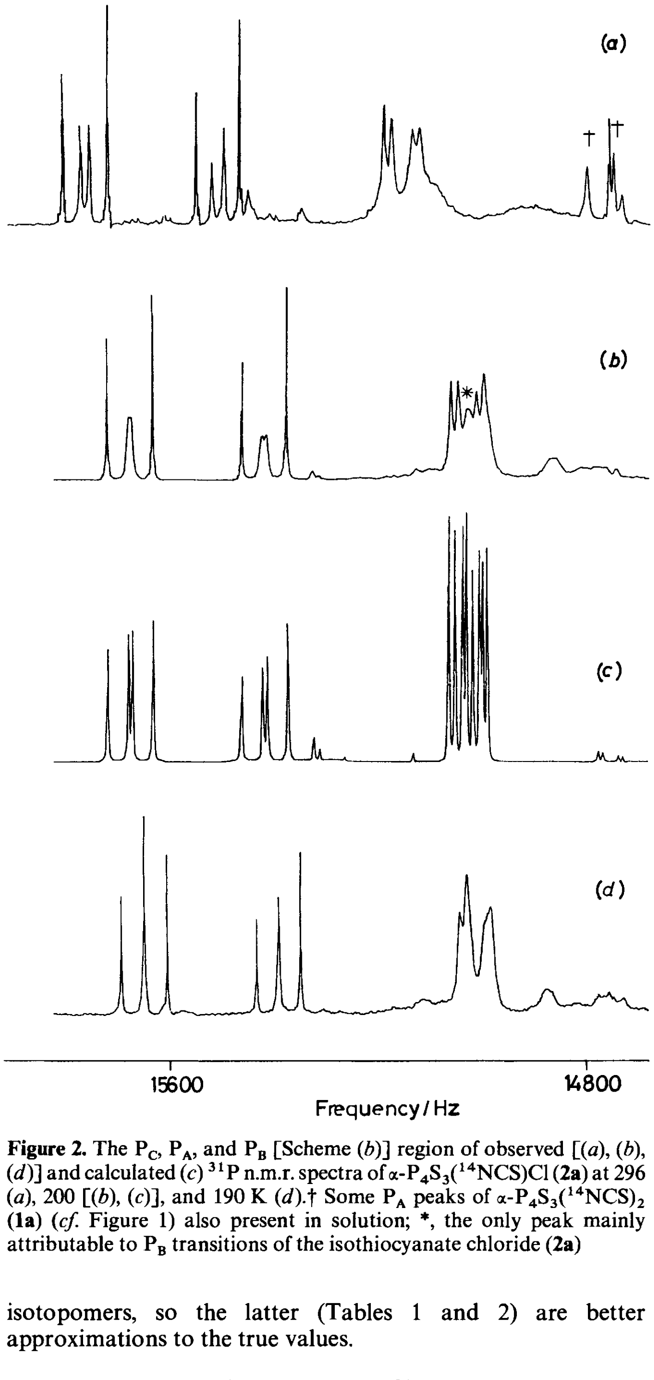


Figure 2. The P_C, P_A, and P_B [Scheme (*b*)] region of observed [(*a*), (*b*), (*d*)] and calculated (*c*) ^{31}P n.m.r. spectra of α-$P_4S_3(^{14}NCS)Cl$ (**2a**) at 296 (*a*), 200 [(*b*), (*c*)], and 190 K (*d*). † Some P_A peaks of α-$P_4S_3(^{14}NCS)_2$ (**1a**) (*cf.* Figure 1) also present in solution; *, the only peak mainly attributable to P_B transitions of the isothiocyanate chloride (**2a**)

isotopomers, so the latter (Tables 1 and 2) are better approximations to the true values.

Spectra of α-$P_4S_3(^{14}NCS)I$ (**3a**).—^{31}P N.m.r. spectra were obtained at 10-K intervals in the range 300—190 K. Ignoring ^{31}P–^{14}N coupling, the molecule constituted a strongly coupled ABCD spin system, all four chemical shifts being within a 3.8 p.p.m. range (460 Hz at 121.5 MHz), and while coupling constants could be predicted [1] the ordering of the chemical shifts was unknown. The spectra overlapped those both of α-$P_4S_3I_2$ and of α-$P_4S_3(^{14}NCS)_2$, but because of differential changes in chemical shifts with temperature, different peaks were obscured at most of the temperatures studied. Eight peaks on the low-frequency side of the spectrum could be traced throughout the temperature range, though their separations changed markedly; this multiplet could be assigned to P_A or P_C [Scheme (*b*)]. The spectrum at 220 K was analysed first: the highest- and lowest-frequency chemical shifts could be estimated and the middle ones interpolated. Spectra were simulated using different permutations of assignments of these shifts, until a simulation was recognised and used as a basis for a fit. As for the isothiocyanate chloride (**2a**), only one broad peak of those mainly associated with P_B [Scheme (*b*)] could be found for inclusion.

The order of shifts found was $\nu_D > \nu_A > \nu_B > \nu_C$. The order $\nu_A > \nu_B$ was as found for the isothiocyanate chloride (**2a**), and the opposite of that found for the di-isothiocyanate (**1a**), the bridgehead shift ν_A moving further to high frequency than did the shift ν_B, on replacing one isothiocyanate group by halide. Similarly, on the side of the molecule carrying the iodine atom, greater sensitivity of the bridgehead shift ν_C than of ν_D to substitution at P_B resulted in the order $\nu_D > \nu_C$ for the isothiocyanate iodide (**3a**), in contrast to that for the di-iodide.[1]

Sufficient peaks could be traced through the spectra at 210 and 200 K for computer fitting also to succeed, but attempts to fit the spectrum at 230 K were unsuccessful, and at above this temperature no peaks mainly due to P_B could be seen. Difficulties in tracing the rest of the spectrum could be ascribed to δ_{AD} becoming very small with increasing temperature [see shifts for the ^{15}N isotopomer (**3b**) at 300 K (Table 2)].

Spectra of α-$P_4S_3(^{15}NCS)_2$ (**1b**).—^{31}P N.m.r. spectra for this AA′BB′XX′ spin system [Scheme (*c*)] were obtained at 300, 270, and 250 K, and at 10-K intervals in the range 230—190 K. ^{15}N N.m.r. spectra were obtained at 300 and 210 K. At 300 K the ^{31}P spectrum contained only sharp peaks and there was no evidence of exchange on the n.m.r. time-scale.

In some of the low-temperature spectra, peaks in the bridgehead, P_A, part of the spectrum were broadened, so that only the most prominent peaks were visible above an envelope, while peaks in the P_B part remained sharp. Both parts of the spectrum became sharp if the sample was left in the spectrometer for 1—2 h at low temperature before accumulation. By this method, sharp ^{31}P n.m.r. spectra were obtained eventually at all temperatures listed above, except for 250 and 270 K, where some broadening of the P_A part was accepted. It was found that, because of the many closely spaced transitions in the P_A part of the spectra, line broadening of only about 2.5 Hz, *i.e.* 0.02 p.p.m., was sufficient to simulate the observed envelope. The effect could then be explained as being due to temperature fluctuation during accumulation: because of the extreme sensitivity of ν_A to temperature (ν_A changed by 1.4 p.p.m. over 100 K) (Figure 3), a temperature instability of ± 1 K could produce the observed broadening. In contrast, the lower sensitivity of ν_B to temperature meant that peaks in the P_B part would have been broadened by only about 0.5 Hz by this temperature fluctuation.

The internal chemical shift, δ_{AB}, was found to decrease with increasing temperature, so the low-temperature spectra were assigned with least difficulty. Of the ^{31}P–^{15}N couplings, $^1J_{BX}$ was much larger than the others, and $^3J_{BB'}$ and $^5J_{XX'}$ were both small, so at 210 K the ^{31}P n.m.r. spectrum resembled roughly an AA′BB′ spectrum in which only the high-frequency, B half was split into two similar subspectra by $^1J_{BX}$, and from this splitting a quite good estimate of J_{BX} could be obtained. A computer simulation, using ^{31}P–^{31}P couplings from the ^{14}N isotopomer,[1] and setting the smaller ^{31}P–^{15}N couplings to zero, was followed by a series of constrained partial fits, allowing first the chemical shifts, $^1J_{BX}$, and $^4J_{BX'}$ to vary, and then freeing $^2J_{AX}$ and $^3J_{AX'}$ as well. This led to an excellent final fit over 97 observed ^{31}P transitions. At several points in the spectrum adjacent peaks were predicted to have similar intensities, but the observed peaks were different in height by a factor of up to about two. The shorter observed peak corresponded in each case to two transitions predicted to be degenerate if the ^{15}N–^{15}N coupling $^5J_{XX'}$ was zero. Clearly this coupling was significantly non-zero, but because no splitting of the degenerate transitions could be

Table 1. Coupling constants* for α-P_4S_3 isothiocyanates

	^{31}P–^{31}P Couplings						^{31}P–^{15}N Couplings			
Temperature (K)	$^2J_{AA'}$ or $^2J_{AC}$	$^1J_{AB}$ $^1J_{AB}$	$^1J_{CD}$	$^2J_{AB'}$ $^2J_{AD}$	$^2J_{BC}$	$^3J_{BB'}$ $^3J_{BD}$	$^2J_{AX}$ $^2J_{AX}$	$^3J_{AX'}$ $^3J_{CX}$	$^1J_{BX}$ $^1J_{BX}$	$^4J_{BX'}$ $^4J_{DX}$
(*i*) For α-$P_4S_3(^{15}NCS)_2$ (**1b**)										
300	65.18	−261.73		23.31		−0.51	−4.05	1.43	103.64	−3.08
	(0.03)	(0.01)		(0.01)		(0.03)	(0.02)	(0.02)	(0.03)	(0.02)
250	65.13	−262.41		23.38		−0.45	−4.45	1.29	102.51	−3.11
	(0.04)	(0.02)		(0.01)		(0.05)	(0.02)	(0.02)	(0.03)	(0.02)
230	65.00	−262.79		23.27		−0.21	−4.30	1.37	101.76	−3.10
	(0.03)	(0.02)		(0.01)		(0.03)	(0.02)	(0.01)	(0.02)	(0.02)
220	64.91	−262.98		23.30		−0.24	−4.27	1.39	101.51	−3.14
	(0.03)	(0.03)		(0.01)		(0.01)	(0.02)	(0.02)	(0.02)	(0.02)
210	64.88	−263.17		23.28		−0.25	−4.34	1.44	101.11	−3.11
	(0.03)	(0.02)		(0.02)		(0.03)	(0.02)	(0.02)	(0.03)	(0.02)
200	64.86	−263.43		23.23		−0.29	−4.56	1.40	100.67	−3.10
	(0.03)	(0.01)		(0.01)		(0.03)	(0.02)	(0.01)	(0.02)	(0.02)
190	64.74	−263.57		23.20		−0.27	−4.54	1.50	100.26	−3.08
	(0.03)	(0.01)		(0.01)		(0.03)	(0.02)	(0.01)	(0.02)	(0.02)
(*ii*) For α-$P_4S_3(^{15}NCS)Cl$ (**2b**)										
300	65.9	−263.3	−260.8	19.7	23.1	4.4	−4.2	0.8	103.9	−3.6
	(0.2)	(0.2)	(0.1)	(0.1)	(0.1)	(0.2)	(0.2)	(0.1)	(0.3)	(0.1)
260	65.6	−264.0	−261.2	19.8	23.1	4.5	−4.3	0.7	103.2	−3.6
	(0.2)	(0.1)	(0.1)	(0.1)	(0.1)	(0.2)	(0.2)	(0.1)	(0.4)	(0.2)
240	65.51	−264.15	−261.58	19.65	23.18	4.77	−4.39	1.37	102.2	−3.61
	(0.05)	(0.03)	(0.03)	(0.03)	(0.03)	(0.07)	(0.05)	(0.04)	(0.1)	(0.04)
220	65.31	−264.62	−261.95	19.69	23.26	4.84	−4.49	1.40	101.55	−3.57
	(0.02)	(0.01)	(0.01)	(0.03)	(0.01)	(0.01)	(0.02)	(0.01)	(0.05)	(0.02)
200	65.11	−265.08	−262.33	19.59	23.29	4.99	−4.65	1.25	100.8	−3.64
	(0.05)	(0.02)	(0.02)	(0.02)	(0.02)	(0.02)	(0.04)	(0.03)	(0.1)	(0.04)
(*iii*) For α-$P_4S_3(^{15}NCS)I$ (**3b**)										
300	69.81	−266.41	−239.77	19.22	25.45	3.69	−4.37	1.33	104.52	−3.93
	(0.04)	(0.01)	(0.01)	(0.03)	(0.02)	(0.03)	(0.02)	(0.03)	(0.05)	(0.02)
220	69.31	−267.53	−241.33	19.3	25.67	4.13	−4.78	1.30	102.6	−3.35
	(0.04)	(0.04)	(0.07)	(0.1)	(0.09)	(0.05)	(0.07)	(0.06)	(0.1)	(0.08)

* Coupling constants are in Hz; standard deviations (σ) are shown in parentheses. For spin system labelling see Scheme (*c*) or (*d*).

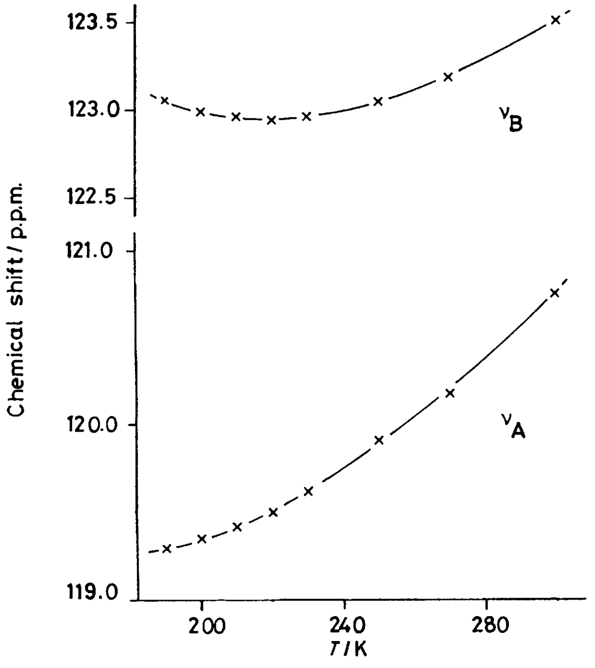


Figure 3. Variation of chemical shifts with temperature for α-$P_4S_3(^{15}NCS)_2$ (**1b**) [Scheme (*c*)]

observed, even though the data were processed with resolution enhancement, the value of the coupling found by NUMARIT was necessarily zero to within its own standard deviation.

Spectra for adjacent temperatures in the series, and for 300 K, were then successively fitted: in each case, the chemical shifts were fitted to a few observed peaks first, because even for 10-K intervals many transitions could not be traced between spectra with certainty.

Computer fitting of the ^{31}P n.m.r. spectrum of α-$P_4S_3(^{15}NCS)_2$ (**1b**) gave relative signs of coupling constants within the ^{31}P–^{31}P and ^{31}P–^{15}N sets respectively. Absolute signs within the ^{31}P–^{31}P set followed from the usual assumption of negative $^1J_{PP}$ couplings for three-co-ordinate phosphorus, but the ^{31}P spectrum was invariant to changing the signs of all the couplings in the ^{31}P–^{15}N set, so it did not allow determination of their absolute signs. For an AA′MM′XX′ spin system, where ν_A and ν_M are widely separated, the X spectrum is symmetrical; however, in an AA′BB′XX′ system the strong coupling between A and B leads to asymmetry of the X multiplet. The sense of this asymmetry does depend on the relationship between the signs of the coupling constants to X, and the signs of the couplings in the AB set. Observation of the ^{15}N spectrum of the di-isothiocyanate (**1b**) at 300 K (Figure 4), which possessed the asymmetry predicted by computer simulation, thus gave the absolute signs of all the couplings (Table 1). Positive $^1J_{BX}$ corresponded to the expected negative $^1K_{BX}$. It should be noted that, in using programs such as NUMARIT, simulations of the ^{15}N spectrum appear reversed unless the opposite signs for the

Table 2. Chemical shifts[a] and iterative fitting data for α-P_4S_3 isothiocyanates

Temperature (K)	^{31}P Shifts[b] ν_A	ν_B	ν_C	ν_D	^{15}N shift ν_X	No. of ^{31}P transitions assigned	Root mean square deviation (Hz)
(*i*) For α-$P_4S_3(^{15}NCS)_2$ (**1b**)							
300	120.75	123.50			−274.05	97	0.08
270	120.18	123.18				30	0.09
250	119.91	123.05				41	0.06
230	119.61	122.96				81	0.07
220	119.50	122.94				90	0.08
210	119.41	122.96				97	0.10
200	119.35	122.99				93	0.08
190	119.30	123.06				95	0.08
(*ii*) For α-$P_4S_3(^{15}NCS)^{35}Cl$ (**2b**)							
300	125.43	123.94	128.89	162.26		53	0.2
260	124.82	123.49	128.44	162.03		53	0.2
240	124.54	123.32	128.27	161.97		53	0.07
220	124.32	123.22	128.17	161.99		56	0.03
200	124.22	123.23	128.19	162.11		51	0.05
(*iii*) For α-$P_4S_3(^{15}NCS)I$ (**3b**)							
300	126.85	124.78	123.99	126.95	−273.69	67	0.05
220	125.76	123.95	123.33	127.05		56	0.10

[a] Chemical shifts are in p.p.m. [b] For labelling of shifts, see Scheme (*d*).

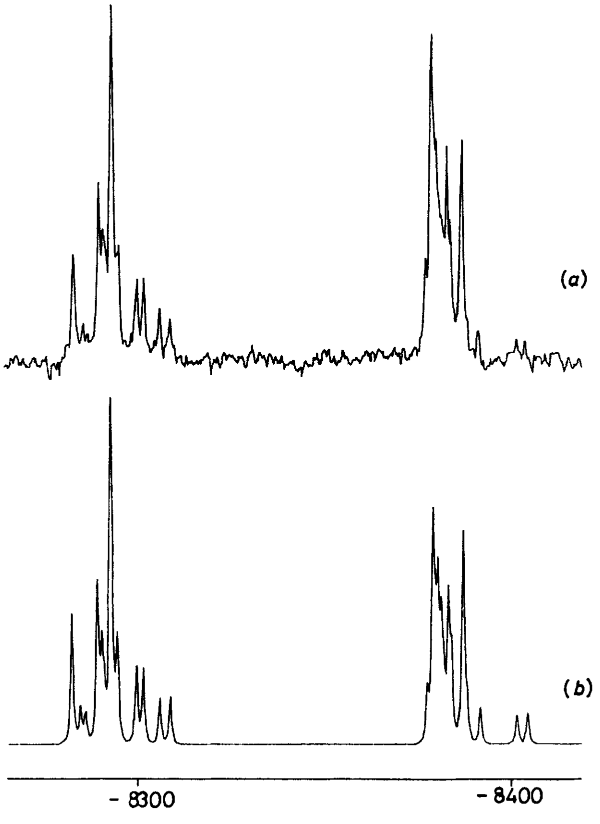


Figure 4. Observed (*a*) and calculated (*b*) ^{15}N n.m.r. spectra of α-$P_4S_3(^{15}NCS)_2$ (**1b**) at 300 K

^{31}P–^{15}N couplings are used. This is because ^{15}N nuclei, with negative gyromagnetic ratio, may be thought of as precessing with negative Larmor frequency; spectrometers do not sense the direction of precession, so ^{15}N spectra are produced with the 'wrong' sign of their frequency scale. This is ignored in reporting chemical shifts, so that increasing shift may remain associated with decreasing shielding, but it cannot be ignored when the sense of asymmetry due to coupling to other nuclear species is considered.

Spectra of α-$P_4S_3(^{15}NCS)Cl$ (**2b**).—^{31}P N.m.r. spectra for this ABCDX spin system [Scheme (*d*)] were obtained at 300 K and 20-K intervals in the range 260—200 K. A computer simulation of the spectrum at 200 K, using ^{31}P–^{31}P couplings found for the ^{14}N isotopomer (**2a**), and J_{BX} found for the di-isothiocyanate (**1b**), could be recognised, and allowed fitting of the ^{31}P chemical shifts and of J_{BX}. A splitting in the P_D multiplet could be associated with J_{DX}. Values of J_{AX} and J_{CX} emerged from a fuller computer fit: corresponding pairs of transitions were predicted to be non-degenerate even if these couplings had been zero, so there was no problem of insufficient resolution in this case. From an excellent final fit over 51 observed ^{31}P transitions, values of $^1J_{AB}$ and $^1J_{CD}$ were found which compared well with those for the ^{14}N isotopomer (**2a**), while $^2J_{AC}$, as well as the smaller couplings $^2J_{AD}$, $^2J_{BC}$, and $^3J_{BD}$, were significantly different. This confirmed that loss of information due to broadening by coupling to ^{14}N had made unreliable even some of the apparently better determined couplings for the ^{14}N isotopomer.

Spectra of the ^{15}N isotopomer (**2b**) at the remaining temperatures were fitted successively as for the di-isothiocyanate (**1b**), but without special difficulty. There was no evidence for chemical exchange on the n.m.r. time-scale at any temperature studied.

In the P_D multiplet at 200 K, five peaks due to the isotopomer α-$P_4S_3(^{15}NCS)^{37}Cl$ could partly be resolved. The results (Table 2) of the computer fits discussed above thus apply to the ^{35}Cl isotopomer (**2b**), but the secondary isotope shift $^1\Delta[^{31}P(^{37/35}Cl)]$ could be measured as −0.0294 (σ = 0.0003) p.p.m.

Chlorine Isotopomers of α-$P_4S_3Cl_2$ (**4**).—The ^{31}P n.m.r. spectrum of α-$P_4S_3Cl_2$ at 200 K, obtained along with that of the isothiocyanate chloride (**2b**) discussed above, in contrast to the spectrum at room temperature reported previously,[1] was sufficiently well resolved to show peaks due to α-$P_4S_3{}^{35}Cl^{37}Cl$

(**4b**) as well as to α-$P_4S_3{}^{35}Cl_2$ (**4a**). The $^{35}Cl^{37}Cl$ isotopomer constituted an ABCD spin system [Scheme (*b*)], in which $\nu_D \gtrsim \nu_B \gg \nu_A \approx \nu_C$. The small chemical shift difference δ_{BD}, corresponding to the secondary chlorine isotope shift $^1\Delta$, resulted in five peaks in each (P_D, P_B and P_A, P_C) part of the spectrum which were well enough resolved from those of the $^{35}Cl_2$ isotopomer (**4a**) for a computer fit of chemical shifts to be carried out. Only $^4\Delta[^{31}P_D(^{37/35}Cl)]$ was not significantly different from zero. Results were: $^1\Delta(P_B)$ −0.0283; $^2\Delta(P_A)$ −0.0011; and $^3\Delta(P_C)$ −0.0047 p.p.m. (σ 0.0007 p.p.m. in each case).

Spectra of α-$P_4S_3(^{15}NCS)I$ (**3b**).—^{31}P N.m.r. spectra at 300 and 220 K, and a ^{15}N n.m.r. spectrum at 300 K, were obtained. Computer simulation of the ^{31}P spectrum at 220 K, using parameters for the ^{14}N isotopomer (**3a**), as described above for the isothiocyanate chloride (**2b**), was unsuccessful: the spectrum was too sensitive to the exact values of the parameters, and only a few transitions could be recognised. The ^{31}P–^{31}P couplings predicted from those for the ^{15}N isotopomer of the di-isothiocyanate (**1b**) and α-$P_4S_3I_2$, and ^{31}P–^{15}N couplings for the isothiocyanate chloride (**2b**), were found to be a better starting point. Successive refinements led to a final fit over 56 observed ^{31}P transitions.

Knowledge gained of changes in coupling constants with temperature for the other two ^{15}N compounds [(**1b**) and (**2b**)] (see Discussion) was used to predict couplings for the isothiocyanate iodide (**3b**) at 300 K from those found at 220 K. Progressive fitting then led to a final fit over 67 observed ^{31}P transitions. While visually the multiplets mainly due to P_A and P_D appeared to have crossed over between the two temperatures, the chemical shifts obtained had not quite done so (Table 2). The predicted ^{15}N n.m.r. spectrum could now be recognised, though the experimental spectrum overlapped considerably with that of the di-isothiocyanate (**1b**). A computer fit yielded the nitrogen chemical shift, though the ^{31}P–^{15}N coupling constants (Table 1) were obtained from fitting the better-quality ^{31}P spectrum only.

*Nitrogen-*14 *N.M.R. Spectrum of* α-$P_4S_3(^{14}NCS)_2$ (**1a**).—This spectrum was measured at 297 K and at 20-K intervals in the range 280—200 K. At each temperature a single unresolved peak, varying in width at half-height between 178 Hz at 297 K and 530 Hz at 200 K, was observed. The relaxation time T_1 was measured by the inversion-recovery method at 297, 280, 260, and 240 K, some points being confirmed by repeated measurement. The empirical equation (1), where T_1 is in milliseconds, was found by regression analysis to represent the results in this range.

$$\ln T_1 = 5.14 - 1\,228/T \qquad (1)$$

*Phosphorus-*31 *N.M.R. Spectra of Monophosphorus* $[^{15}N]$*Isothiocyanates.*—A clear quartet at δ 86.5 p.p.m. was assigned to $P(^{15}NCS)_3$; Fluck[5] reported chemical shifts of 85.6, 86.3, and 86.6 p.p.m. for $P(^{14}NCS)_3$ in various solutions. The observed ^{31}P–^{15}N coupling constant was 78.8 Hz.

An approximate triplet at δ 113.3 p.p.m. was assigned to $P(^{15}NCS)_2Cl$ [literature[5] (^{14}N isotopomer) 114.0 p.p.m.]; a difference of 2.4 Hz between the two splittings was probably due to unresolved overlap of the spectra of the ^{35}Cl and ^{37}Cl isotopomers. The average splitting corresponded to $J(^{31}P$–$^{15}N)$ 95 Hz. A doublet at δ 17.6 p.p.m. may have been due to $P(^{15}NCS)Cl_2S$ (literature[5] 16.0 p.p.m.). This assignment was supported by the smaller splitting, 21.2 Hz, which probably corresponded to a positive ^{31}P–^{15}N coupling constant in the expected range for a phosphorus(V)–nitrogen(III) compound.[7]

Discussion

There was no counterpart to the broadening of the P_B parts of the ^{31}P n.m.r. spectra of the ^{14}N isotopomers [(**1a**), (**2a**), and (**3a**)] in the spectra observed for the ^{15}N isotopomers [(**1b**), (**2b**), and (**3b**)]. Therefore chemical exchange on the n.m.r. time-scale was not responsible for this broadening, which instead could be attributed to scalar coupling relaxation of ^{31}P by ^{14}N, which was itself undergoing quadrupolar relaxation. When ^{14}N relaxation is too fast, compared with a ^{31}P–^{14}N coupling constant, for splittings due to this coupling to be resolved, the broadening, due to this mechanism, of the phosphorus peak of an isolated P–N bond in a molecule is given approximately by equation (2).

$$w_{\frac{1}{2}}{}^{P} = (8/3)\pi J^2 T_1{}^{N} \qquad (2)$$

The measured ^{14}N relaxation time for the di-isothiocyanate (**1a**), 2.73 ms at 297 K, was in the expected range,[8] but the exceptional broadening of the phosphorus peaks could be attributed to an abnormally large ^{31}P–^{14}N coupling constant, −73.9 Hz, appearing as a square term in equation (2).

Accurate phosphorus–nitrogen coupling constants, now measured for the ^{15}N isotopomers, were much larger than for phosphorus(III) amino compounds. Monophosphorus isothiocyanates showed larger coupling constants than corresponding dimethylamino compounds: 78.8 Hz for $P(^{15}NCS)_3$ and 95 Hz for $P(^{15}NCS)_2Cl$, compared with 60.1 Hz for $P(^{15}NMe_2)(^{14}NMe_2)_2$ and 77.6 Hz for $P(^{15}NMe_2)(^{14}NMe_2)Cl$.[9] Large phosphorus(III)–nitrogen coupling constants tend to be associated with the presence of electronegative ligands on the phosphorus, such as chlorine. Despite the absence of very electronegative groups in the cases of the α-P_4S_3 cage compounds, these showed even larger $^1J(^{31}P$–$^{15}N)$ couplings of +103.64 Hz for α-$P_4S_3(^{15}NCS)_2$ (**1b**), +103.9 Hz for α-$P_4S_3(^{15}NCS)Cl$ (**2b**), and +104.52 Hz for α-$P_4S_3(^{15}NCS)I$ (**3b**). Clearly the nature of the bonding in, and bond angles of, the α-P_4S_3 skeleton must have been peculiarly contributing to the corresponding large negative values of ^1K. Negative ^1K is usually attributed to *s* character of the non-bonding pair of electrons on phosphorus.

A similarly large $^1J(^{31}P$–$^{13}C)$ coupling constant of −114 Hz has been found for α-$P_4S_3(^{13}CN)(^{12}CN)$, compared with −60.2 Hz for $P(^{13}CN)(^{12}CN)_2$ (the negative sign being assumed in each case).[3] Just as ^1J coupling constants are often supposed to depend on, *inter alia*, strengths and multiplicities of bonds, so are $^1\Delta$ secondary isotope shifts.[10] The values of $^1\Delta[^{31}P(^{37/35}Cl)]$ now reported for the P–Cl bonds in α-P_4S_3 chlorides are also numerically larger than for monophosphorus(III) compounds: values of −0.0294 p.p.m. for α-$P_4S_3(^{15}NCS)Cl$ (**2b**) and −0.0283 p.p.m. for α-$P_4S_3{}^{35}ClCl$ (**4**) were about 1.5 times the value of −0.019 p.p.m. reported for PCl_3.[11]

The sharpening of the ^{31}P n.m.r. spectra of the ^{14}N isothiocyanate compounds [(**1a**), (**2a**), and (**3a**)] at low temperature was consistent with the scalar coupling relaxation mechanism proposed above. According to equation (2), narrower phosphorus peaks are expected when the ^{14}N relaxation rate increases (and ^{14}N peaks become broader). Measurements of T_1 for ^{14}N in α-$P_4S_3(^{14}NCS)_2$ (**1a**) showed the expected increase in ^{14}N relaxation rate on lowering the temperature, corresponding to increasing solvent viscosity and increasing rotational correlation time of the molecules. Assuming an exponential dependence of viscosity on $1/T$, and that $T_1{}^N$ is directly proportional to temperature, but inversely proportional to viscosity,[8] then $\ln(T_1{}^N/T)$ should be linearly dependent on $1/T$. By their nature, T_1 measurements do not yield very accurate results, and those obtained were fitted by this relationship almost as well as the linear dependence of $\ln(T_1{}^N)$ on $1/T$, reported above.

Values of all four ^{31}P–^{15}N coupling constants were very

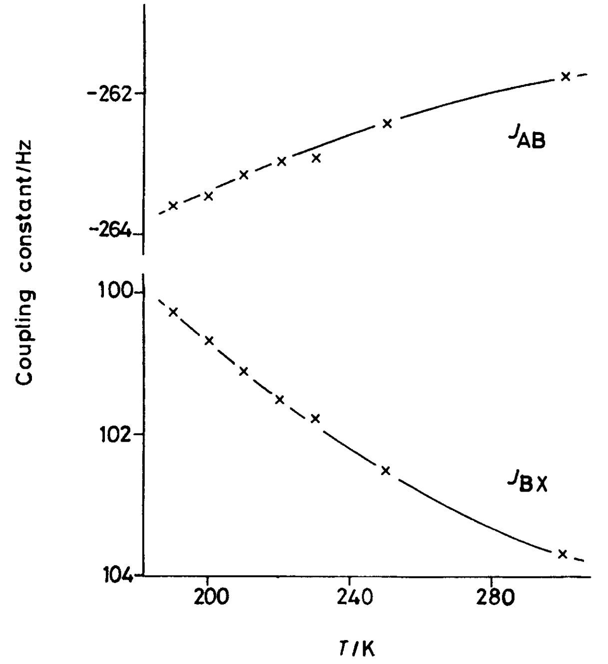


Figure 5. Variation of endocyclic (J_{AB}) and exocyclic (J_{BX}) ^{1}J coupling constants with temperature for α-$P_4S_3(^{15}NCS)_2$ (**1b**); the relative reversal of ordinate scales reflects the negative gyromagnetic ratio of ^{15}N

similar between the three α-P_4S_3 isothiocyanate compounds [(**1b**), (**2b**), and (**3b**)] (Table 1). Like the ^{31}P–^{31}P coupling constant $^{1}J_{AB}$, they were little influenced by the distant substituent, in contrast to $^{2}J_{AC}$ which depended equally on the two substituents, as found previously.[1] An interesting distinction was in the change of coupling constants with temperature (Figure 5): for both α-$P_4S_3(^{15}NCS)_2$ (**1b**) and α-$P_4S_3(^{15}NCS)Cl$ (**2b**), for which considerable variable-temperature studies were carried out, the endocyclic ^{31}P–^{31}P couplings $^{1}J_{AB}$ [(**1b**) and (**2b**)] and $^{1}J_{CD}$ (**2b**) became numerically smaller (less negative ^{1}K) with increasing temperature (changes of 1.5—1.8 Hz over 100 K), while the exocyclic ^{31}P–^{15}N couplings $^{1}J_{BX}$ became numerically larger (more negative ^{1}K) (changes of 3.0—3.1 Hz over 100 K). The two-temperature study of α-P_4S_3-$(^{15}NCS)I$ (**3b**) was consistent with these trends.

The ^{31}P chemical shifts of the α-P_4S_3 isothiocyanates [(**1b**), (**2b**), and (**3b**)] generally increased, corresponding to decreasing shielding, with increasing temperature (Figure 3) as expected, but with the bridgehead phosphorus shifts (ν_A, ν_C) increasing most rapidly. The greater sensitivity of the bridgehead phosphorus atoms of P_4S_3 cage compounds to the environment of the molecules has been commented upon previously,[12] but here the effect was unusually noticeable: *e.g.* for the isothiocyanate chloride (**2b**), ν_A changed by 1.20 p.p.m. in 100 K, while for the bridgehead nearest to the chlorine substituent ν_C changed by only 0.70 p.p.m. The experimental difficulties resulting from this temperature sensitivity, in obtaining good spectra, are mentioned above. For the di-isothiocyanate (**1b**), decreasing temperature caused ν_A and ν_B to diverge, making the ^{31}P n.m.r. spectrum easier to analyse, while for the isothiocyanate halides [(**2b**) and (**3b**)] ν_A and ν_B were in the opposite order and hence converged with decreasing temperature, causing problems of deceptive simplicity in the case of α-$P_4S_3(NCS)Cl$.

Experimental

All operations were carried out under nitrogen by Schlenk methods. AnalaR CS_2 was distilled from P_4O_{10} before use. Silver salts were dried by heating to 65 °C under vacuum for > 3 h. N.m.r. spectra of solutions in CS_2 in 5-mm diameter tubes were measured using a Bruker WM300WB spectrometer, operating at 121.5 MHz for ^{31}P and 30.43 MHz for ^{15}N. 10-mm Tubes were used for ^{14}N, and an operating frequency of 21.69 MHz. Capillaries containing $(CD_3)_2CO$ were used in all cases for locking, and chemical shifts, obtained by substitution experiments using the same capillaries and frequency offsets, are reported relative to H_3PO_4–H_2O for ^{31}P or neat CH_3NO_2 for ^{15}N.

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