Phosphorus-31 Nuclear Magnetic Resonance Parameters for Compounds with the α-Tetraphosphorus Trisulphide Skeleton; Substituent Constants for an Inorganic Substrate

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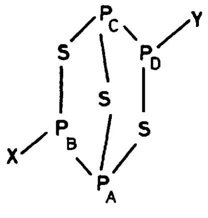
Phosphorus-31 n.m.r. spectra have been measured and assigned for symmetric compounds α-P_4S_3XY (**1**) with X = Y = Cl, Br, CN, or NCS, and for unsymmetric compounds (**1**) with X = CN, Y = Cl, Br, or I; X = N_3, Y = Cl; and X = Br, Y = I. Simple relationships between couplings in unsymmetric compounds and those in the corresponding symmetric compounds were found. Chemical shifts in the symmetric compounds were assigned by comparison with those assigned unambiguously in the unsymmetric compounds. All four coupling constants for the symmetric compounds were well fitted by two-parameter linear relationships involving substituent constants which, while based on organic reaction substituent constants, were substantially different from them.

The P_4 tetrahedron in α-P_4S_3XY (**1**) has two perpendicular edges (P_A–P_B and P_C–P_D) which are formally unbridged P–P bonds, one edge (P_B–P_D) which is not formally bonded at all, and the remaining three edges bridged by sulphur atoms. Nuclear magnetic couplings along these edges are thus widely different; some involve the phosphorus atoms P_B and P_D which carry the substituents X or Y, while others do not. In the unsymmetrically substituted case (X ≠ Y, ABCD spin system) all six P–P couplings may be obtained by solution of the ^{31}P n.m.r. spectra, while in symmetric compounds (X = Y, AA′BB′ spin system) four different couplings may be found, the two unbridged P–P bonds being equivalent, as are two of the sulphur-bridged edges. While the effects of solvent and concentration upon chemical shifts are so large as possibly to obscure small changes caused by replacement of X or Y by similar ligands,[1] these coupling constants are little affected by interactions of solvent with the molecules. Thus a study of changes of the couplings with changes in X or Y is both valid and interesting.

In earlier work with alkylthio- and arylthio-compounds (**1**; X = Y = SR),[1] I started to comment on changes in couplings with substitution. Other symmetric compounds (**1**; X = Y = Cl, Br, CN, or NCS) had been prepared previously by Fluck *et al.*,[2] by reaction of the di-iodide (**1**; X = Y = I) with the appropriate silver salt, but the ^{31}P n.m.r. spectra, though assigned as being of AA′BB′ or AA′MM′ type [except for (**1**; X = Y = NCS), see below], were not solved so as to give coupling constants. With the subsequent advance in technology, this is now possible; I have successfully repeated the described preparations, and measured and solved the spectra. Solutions containing previously unreported unsymmetric compounds (**1**; X = CN, Y = Cl, Br, or I; X = N_3, Y = Cl) have also been made, by exchange reactions between the dihalides (**1**; X = Y = Cl, Br, or I) and Me_3SiCN or Me_3SiN_3. A solution containing the bromide iodide (**1**; X = Br, Y = I) was obtained by the redistribution reaction of the corresponding dihalides.



(**1**)

Results and Discussion

Substitution Reactions of α-P_4S_3XY *Compounds: Silver Salt Reactions.*—Substitution of iodide in the di-iodide by chloride, bromide, or cyanide required heating with a stirred suspension of the silver salt in CS_2 for several days, as previously reported,[2] but the di-iodide had reacted completely with a suspension of silver thiocyanate after only 2 d at 21 °C. The dichloride solution after filtration was practically colourless (not light yellow as reported[2]), as was that of the di-isothiocyanate, while the dicyanide and dibromide gave pale yellow solutions. The compounds were thermally stable at room temperature over several days, provided they remained in solution in CS_2. On pumping off the solvent at room temperature, glasses or oils were produced, which became yellower opaque solids after standing for a few hours: these then became less soluble in CS_2 on standing, as polymerisation probably took place. For example, the di-isothiocyanate was first obtained as a mobile yellow liquid (not orange-red as reported[2]), which became canary yellow on solidification; it became almost completely insoluble in CS_2 after 3 months.

Freshly prepared solutions of the dichloride, dibromide, or di-isothiocyanate were shown by ^{31}P n.m.r. to contain only traces of other phosphorus-containing components (though the spectrum of the di-isothiocyanate was not that of a simple AA′BB′ spin system, see below). The dicyanide, however was always accompanied by substantial impurities. Typically for the product of reaction of the di-iodide with silver cyanide, *ca.* 40% of the ^{31}P n.m.r. integral was accounted for by the dicyanide, 40—50% by 'unknown **A**' and 10% by 'unknown **B**'. Unknown **A** occurred irrespective of whether the dicyanide was made by the silver salt method, or by reaction of the dichloride with excess Me_3SiCN. The ^{31}P n.m.r. of unknown **A** was clearly more complex than could be explained by a four-spin system, and so far has not been solved. The ^{31}P n.m.r. spectrum of unknown **B** could be solved exactly as a four-spin system [δ_1 171.46, δ_2 136.74, δ_3 102.92, δ_4 24.95 p.p.m.; couplings (±0.03 Hz), J_{12} 98.37, J_{13} −4.75, J_{14} −270.47, J_{23} −262.38, J_{24} 49.70, J_{34} 14.95 Hz].

Trimethylsilyl Pseudohalide Reactions.—Preparations by substitution using silver halides or pseudohalides suffer the disadvantage of a two-phase reaction mixture, starting material

Table 1. Phosphorus-31 n.m.r. parameters for α-P_4S_3XY (**1**)

(*i*) Symmetric compounds[a]

	Chemical shifts (p.p.m.)		Coupling constants[b] (Hz)				R.m.s. deviation (Hz)
X,Y	δ_A, δ_C	δ_B, δ_D	J_{AC}	J_{AB}, J_{CD}	J_{AD}, J_{BC}	J_{BD}	
Cl	133.43	161.74	65.9	−263.2	20.0	10.3	0.50
			(0.3)	(0.2)	(0.2)	(0.3)	
Br	132.05	151.15	70.1	−254.3	19.7	11.7	0.67
			(0.4)	(0.3)	(0.2)	(0.4)	
I	128.72	125.06	74.8	−243.7	21.6	9.3	0.17
			(0.1)	(0.1)	(0.1)	(0.1)	
CN	128.69	34.18	86.3	−254.7	32.1	−14.4	0.49
			(0.3)	(0.2)	(0.1)	(0.3)	
NCS	120.60	123.19	64.4	−263.8	21.6	0.4	1.13
			(2.5)	(0.5)	(0.4)	(1.2)	
SMe	105.74	126.62	57.8	−290.1	22.1	−9.0	0.87
			(0.5)	(0.4)	(0.2)	(0.5)	
SEt	103.74	122.72	58.1	−288.8	22.3	−8.4	0.99
			(0.6)	(0.4)	(0.3)	(0.6)	
SPh	109.49	127.48	60.3	−282.4	21.7	−6.0	0.34
			(0.2)	(0.1)	(0.1)	(0.2)	

(*ii*) Unsymmetric compounds

		Chemical shifts (p.p.m.)				Coupling constants[b] (Hz)						R.m.s. deviation (Hz)
X	Y	δ_A	δ_B	δ_C	δ_D	J_{AC}	J_{AB}	J_{CD}	J_{AD}	J_{BC}	J_{BD}	
CN	Cl	130.49	26.76	129.25	164.33	76.0	−253.3	−262.0	25.9	25.5	−2.0	0.60
						(0.3)	(0.4)	(0.6)	(0.5)	(0.4)	(0.4)	
CN	Br	132.14	28.37	127.43	155.13	78.2	−254.3	−253.5	25.4	26.3	−1.1	0.39
						(0.3)	(0.2)	(0.2)	(0.2)	(0.2)	(0.2)	
CN	I	133.13	31.14	124.39	131.03	80.6	−256.2	−242.1	26.0	28.6	−1.7	0.56
						(0.4)	(0.3)	(0.5)	(0.4)	(0.4)	(0.4)	
N_3	Cl	123.44	160.46	129.33	162.68	58.3	−277.8	−262.8	17.4	21.2	0.0	1.02
						(0.6)	(1.1)	(0.6)	(0.6)	(0.7)	(0.7)	
Br	I	132.04	150.39	129.05	125.12	72.4	−256.7	−242.1	20.1	21.7	9.9	0.25
						(0.2)	(0.2)	(0.2)	(0.2)	(0.2)	(0.2)	

[a] Data for X = Y = I, SMe, SEt, and SPh are from previous work (ref. 1). [b] Standard deviations (σ) in parentheses.

of low solubility being replaced by an even less soluble product. Consequently an excess of silver salt, refluxing solvent, and long reaction times are employed.[2] These conditions prevent the convenient study of partial substitution [though traces of the iodide cyanide (**1**; X = CN, Y = I) have now been observed from reaction of the di-iodide with excess silver cyanide]. A homogeneous reaction mixture, and hence complete control of reactant ratio, could however be achieved by addition of Me_3SiCN to a solution of the dihalide in CS_2. The dibromide thus yielded, after 64 h at room temperature, a mixture containing both fully, (**1**; X = Y = CN), and half, (**1**; X = CN, Y = Br), substituted products, as well as unchanged dibromide, in the ratio 15:8:1, which was not significantly different from that expected statistically (14:8:1) for this cyanide:bromide ratio (3.8:1) of groups attached to phosphorus. This indicated a labile exchange of substituents. In similar experiments with Me_3SiN_3, toluene was used instead of CS_2 to avoid the formation of azidodithioformate [$N_3C(S)S^-$] derivatives, which were likely to be violent detonators. In substitutions for chloride or bromide, equilibria could be shifted by selectively pumping off the trimethylsilyl halide by-product with the solvent; this was not possible with less volatile Me_3SiI, so the cyanide iodide (**1**; X = CN, Y = I) was obtained in only 5% conversion, and the azide iodide (**1**; X = N_3, Y = I) was not observed at all. Disubstitution could be effected by reaction of Me_3SiCN with the lighter dihalides, but no diazide (**1**; X = Y = N_3) was found when the dichloride was mixed with excess Me_3SiN_3; this compound is presumably unstable at room temperature.

The cyanide halides (**1**; X = CN, Y = Cl, Br, or I), while previously unreported, were readily identified in reaction mixtures by solution of their ^{31}P n.m.r. spectra and comparison of the resulting parameters with those for the symmetric compounds (Table 1). On partial substitution of a α-P_4S_3 dihalide, the phosphorus spin system changes from the symmetric AA′BB′ to ABCD, which, even for a similar substituent, causes a large and easily identified change in the n.m.r. spectrum. The dihalides (**1**; X = Y = Cl, Br, or I) are thus excellent model compounds for the study by n.m.r. of substitution reactions of phosphorus–halogen bonds. The di-iodide is among the most easily prepared of phosphorus–iodine compounds.

Exchange Reactions Between α-P_4S_3XY Compounds.—The dibromide reacted with the dicyanide only slowly at room temperature: 66 h after mixing, a solution containing cyanide (attached to phosphorus) and bromide in a ratio 1:8.0 was found to contain the dicyanide, the bromide cyanide, and the dibromide in the ratio 1:1.3:12.6. The statistically expected ratio was 1:16:64. This slow exchange was in contrast to that in the presence of trimethylsilyl compounds (in the reaction between the dibromide and Me_3SiCN, see above).

The dibromide reacted with the di-iodide (71 h, room temperature) more readily, to give a mixture containing a relatively high concentration of the bromide iodide, but measurement of the component ratio by ^{31}P n.m.r. was not practicable in this case, due to extreme overlapping of the spectra.

Phosphorus-31 *N.M.R. Results.*—Chemical shifts and coupling constants discussed here were obtained by iterative fitting using NUMARIT (S.E.R.C. n.m.r. Program Library, Daresbury); the various methods used to obtain initial parameters are described in the Experimental section.

Assignment of Chemical Shifts.—Because of the symmetry of the spectrum (AA′BB′ spin system), it is possible completely to assign the coupling constants of a symmetric α-P_4S_3XY compound (**1**; X = Y) without being able to decide which of the chemical shifts should be assigned to the bridgehead phosphorus atoms (P_A, P_C) and which to those carrying the substituents (P_B, P_D). For bis(alkylthio)-compounds (**1**; X = Y = SR), couplings to protons in the ligands made certain assignment possible.[1] Shifts in the dihalides and dicyanide have now been assigned *via* assignment of mixed compounds. The cyanide halides (**1**; X = CN, Y = Cl, Br, or I) all have the shift of one of their phosphorus atoms (P_B) in the range 26—32 p.p.m. (Table 1), which allows the shift of 34.18 p.p.m. for the dicyanide to be assigned to the phosphorus carrying the cyanide. Large upfield shifts for phosphorus atoms carrying cyanide substituents are well known.[3] The shift of 161.74 p.p.m. can then be assigned to phosphorus (P_D) carrying chloride in the dichloride (*cf.* 164.33 p.p.m. in the cyanide chloride) and that of 151.15 p.p.m. can similarly be assigned in the dibromide (*cf.* 155.13 p.p.m. in the cyanide bromide and 150.39 p.p.m. in the bromide iodide).

The internal shift in the di-iodide is so small (3.66 p.p.m.) that assignment by this method is more difficult: the shift of phosphorus (P_D) carrying iodide in the cyanide iodide is 131.03 p.p.m., while it is 125.12 p.p.m. in the bromide iodide. In the other cyanide halides, the shift of the phosphorus bearing the substituent is several p.p.m. higher than in the dihalide; this suggests the assignment $\delta_B = \delta_D = 125.06$ p.p.m. for the di-iodide, with 128.72 p.p.m. as the bridgehead phosphorus shift. This is supported by a similar argument for the bridgehead phosphorus atoms P_C in the cyanide halides: the shift for the cyanide halide is 4.18 p.p.m. (chloride) or 4.62 p.p.m. (bromide) lower than that for the symmetric dihalide. Assignment of 128.72 p.p.m. as the bridgehead phosphorus shift in the di-iodide leads to a similar difference of 4.33 p.p.m. in the di-iodide case. This assignment is also consistent with my observations of relative intensities in the spectra: while a pure AA′BB′ spin system, in the absence of different relaxation effects on the A and B nuclei, would give a spectrum with equal heights of the A and B parts, all of my observed spectra were in fact asymmetric in this respect, with the bridgehead-phosphorus half of the spectrum being the more intense. In the spectrum of the di-iodide, the high-frequency half is the more intense. This assignment for the di-iodide is the opposite to that previously reported. The original assignment of Baudler *et al.*[4] lacked evidence, while Blachnik *et al.*[5] gave evidence based on the sign of the change in shift on substituting selenium for sulphur. However, the shift of phosphorus bonded to iodine in α-$P_4Se_3I_2$ lies between the two shifts for α-$P_4S_3I_2$, so the change on substitution is for either assignment very small, and comparable with the large solvent shifts found for these compounds, especially as a mixed solvent was used.[5] The sign of the change in shift with selenium substitution is thus weak evidence in this case.

There was generally no ambiguity in assigning both chemical shifts and couplings in the unsymmetric compounds (**1**; X ≠ Y), so once the shift of a phosphorus atom carrying a substituent had been assigned, as above, then the assignment of shift of the bridgehead atom, coupled to it by a large (^1J) coupling, followed immediately. In the case of the bromide cyanide, however, the ^1J couplings were very similar, and two solutions of the spectrum, with opposite signs of J_{BD} and with δ_A and δ_C interchanged, gave similar root mean square (r.m.s.) deviations (0.39 and 0.52 Hz) in fitting using NUMARIT. To distinguish between these, a homonuclear COSY experiment, with additional delays to give maximum enhancement to correlation peaks due to couplings of 25 Hz, was carried out. This showed correlations due to J_{AD} and J_{BC} (Table 1) with about four times the intensity of those due to J_{AB} and J_{CD}, as predicted theoretically, thus confirming this assignment of δ_A and δ_C, which corresponded to the NUMARIT fit with the lower r.m.s. deviation.

Changes in Coupling Constant with Substitution.—Electron distributions in the molecules, and hence P–P coupling constants, are likely to be influenced more or less indirectly by the nature of the bonding (σ and π) in the phosphorus–substituent bond, and possibly by steric effects of the substituents, which may affect bond angles and hence electron distribution, both at the phosphorus carrying the substituent, and at the bridgehead phosphorus atoms where the intercyclic angle of the 'book-shaped' molecules may change. It was surprising, therefore, to find that the couplings changed in simple and predictable ways with partial substitution, and that couplings for an unsymmetric compound (**1**; X ≠ Y) may be predicted from those of the corresponding symmetric ones, as follows. The value of $^1J_{AB}$ depended almost entirely on the substituent connected to P_B, and may be predicted as being the same as in the corresponding symmetric compound. The largest deviation found was for bromide-substituted phosphorus, between the bromide iodide (−256.7 Hz) and the dibromide (−254.3 Hz). The bridge coupling, $^2J_{AC}$, depended equally on the two substituents, and may be predicted as the average of the values found for the two symmetric compounds. All of the values found deviated from this average by less than 0.1 Hz, although the couplings for the symmetric compounds had a range of >20 Hz. The coupling across the formally unbonded edge, J_{BD}, may also be predicted by averaging the values for the symmetric compounds, taking account of their signs, which could be of either value. Deviations from this average were slightly greater than for J_{AC}, but were < 1 Hz. The couplings $^2J_{AD}$ and $^2J_{BC}$ are between the phosphorus atom carrying one substituent, and the bridgehead phosphorus atom nearest to the other substituent. They might be expected to depend in an unequal way upon the two substituents. In fact they were found to depend equally upon the substituents, in the sense that while this coupling could differ between two symmetric compounds by as much as 12 Hz, the two couplings (J_{AD} and J_{BC}) within the corresponding unsymmetric compound became the same as each other, to within 3 Hz. The value for both could be predicted as the average of the J_{AD} couplings for the symmetric molecules, to within 2 Hz.

Correlations of N.M.R. Parameters.—The discovery of linear changes in each coupling constant with progressive substitution prompted a statistical analysis of the data for the symmetric compounds, to seek relationships between the dependences of the various n.m.r. parameters on the nature of the substituent. It was clear that there was a linear correlation (simple correlation coefficient = 0.985, over seven compounds) between the bridge coupling, $^2J_{AC}$, and the P–P bond coupling, $^1J_{AB}$, provided that the dicyanide case (**1**; X = Y = CN) was omitted. The necessity for this omission, and poorer correlations between other pairs of parameters, ruled out dependence on a single substituent effect. Linear dependence on two substituent constants, F_i and R_i, was therefore examined: equation (1); Y_{pi} is the observed value of

$$Y_{pi} = A_pF_i + B_pR_i + C_p \qquad (1)$$

Table 2. Analysis of multiple regression of n.m.r. parameters for symmetric α-$P_4S_3X_2$ compounds on substituent constants, using equation (1)

	Regression on organic F and R[a]				Regression on F and R values (this work)[b]					
	A	B	C	M.c.c.[c]	A	B	C	M.c.c.[c]	$A^{\beta d}$	$B^{\beta d}$
δ_A	95.0	−24.5	82.5	0.83	84.8	−13.7	86.1	0.94	1.01	−0.14
δ_B	105.5	−325.9	44.1	0.94	111.8	−345.4	40.4	0.990	0.43	−1.14
J_{AC}	34.5	37.8	59.1	0.84	33.6	49.0	59.6	0.997	0.51	0.64
J_{AB}	136.2	−34.2	−321.8	0.84	120.6	−4.4	−314.6	0.994	1.01	−0.03
J_{AD}	−11.6	35.1	31.1	0.98	−10.9	35.8	30.8	0.998	−0.40	1.15
J_{BD}	76.8	−84.3	−38.9	0.93	73.6	−77.2	−37.6	0.996	1.06	−0.96

[a] Ref. 8. [b] Table 3. [c] Multiple correlation coefficient. [d] Beta weights [equation (2)].

n.m.r. parameter p for compound i; A_p, B_p, and C_p are constants for a n.m.r. parameter, over a range of compounds, and F_i and R_i are constants for a compound over a range of n.m.r. parameters. (All variables on the right-hand side of the equation are unknown.) To facilitate fitting, the data vectors Y_p for the four n.m.r. couplings were standardised to means of zero and standard deviations of unity, so that the constant term C_p could

$$Y_{pi}^{s} = A_p^{\beta}F_i^{s} + B_p^{\beta}R_i^{s} \qquad (2)$$

be omitted: equation (2). If F_i^s and R_i^s are also standardised, then A_p^β and B_p^β are 'beta weights', which are measures of the relative importance of F and R in explaining the variation of the observed n.m.r. parameters. A least-squares fit, in which elements of the vectors A_p^β, F_i^s, B_p^β, and R_i^s were all allowed to vary, was performed.* An infinite number of equally good fits could thus be obtained: to select a single fit from these, two normalisation constraints on each product in equation (2) were required.[6] For similar fits of kinetic or thermodynamic data to obtain substitution constants for organic reactions, the reaction-dependent constants A, B, and C are arbitrarily fixed for a standard reaction, and the substituent-dependent constants are arbitrarily fixed for a particular substituent. In this case, if, for example, it is desired to separate σ- and π-bonding effects of the substituents, then there are no self-evident arbitrary values to be taken. However, dependences of the n.m.r. couplings on the organic substituent constants F and R of Swain and Lupton,[7] as revised by Hansch *et al.*,[8] were examined by multiple linear regression using a statistics package,† and moderate multiple correlation coefficients were found (Table 2), those for J_{AD} and J_{BD} being significant at the 95% level. While much better fits could be obtained assuming F_i^s and R_i^s to be unknown, as described above, it seemed sensible to select two values each of F and R from Hansch's compilation,[8] to provide the four normalisation constraints required. Fixing both substituent constants for CN and for SMe to the literature values[8] was found to give a scale for the remaining substituents which might reasonably be compared with organic substituent constants (Table 3). In practice, Hansch's values for the seven substituents studied (F and R for SPh were not reported) were standardised to mean zero and standard deviation unity (F_i^s and R_i^s) to allow compatibility with equation (2). The least-squares fit was performed with the selected values of F_i^s and R_i^s fixed, and then the resulting values of the whole F_i and R_i vectors were transformed back to their original scales, using the inverses of the standardisation transformations. The results are shown in Table 3. The coefficients A_p, B_p, and C_p relating the individual n.m.r. parameters to the obtained F_i and R_i values (Table 2) were then obtained by multiple regression analysis.

Table 3. Substituent constants

	Organic constants[a]		This work	
Substituent	F	R	F	R
Cl	0.41	−0.15	0.440	−0.180
Br	0.44	−0.17	0.507	−0.152
I	0.40	−0.19	0.572	−0.076
CN	0.51	0.19	0.510[b]	0.190[b]
NCS	0.51	−0.09	0.388	−0.138
SMe	0.20	−0.18	0.200[b]	−0.180[b]
SEt	0.23	−0.18	0.210	−0.175
SPh			0.259	−0.169

[a] Ref. 8. [b] Fixed value.

For the coupling constants, excellent agreements between experimental values and those predicted by the relationships [equation (1)] were found (Table 4), with multiple correlation coefficients >0.994 (Table 2). Surprisingly, the chemical shifts also correlated moderately with the substituent constants found; local through-space effects might have been expected to interfere in the case of δ_B. The F and R scales found (Table 3) differ markedly (except for the two arbitrarily fixed points) from organic substituent constants,[8] with values particularly for halide substituents being in different orders. The R term does not contribute significantly to $^1J_{AB}$, so the F values reported here are closely correlated with $^1J_{AB}$. Variation in the R values accounts largely for deviations of the other n.m.r. parameters from linear correlations with $^1J_{AB}$.

N.M.R. Spectra of α-$P_4S_3(NCS)_2$.—The ^{31}P n.m.r. spectrum of the di-isothiocyanate had been reported[2] as a single signal which could not be further resolved at an operating frequency of 24.29 MHz. By measurements at a higher frequency (121.50 MHz), I was able to resolve the spectrum at low temperature (200 K) as a AA′BB′ system (Table 1). At room temperature, however, the high-frequency half of the spectrum collapsed into broad peaks, while the low-frequency half changed little. Changes in frequency of the peaks could probably be explained by changes in solvent shifts with temperature, and consequent change in the internal shift δ_{AB}. It may be assumed that the transitions of the high-frequency half were mainly associated with the phosphorus atoms (P_B, P_D) carrying the thiocyanate groups, while those of the sharp half of the spectrum were mainly associated with the bridgehead phosphorus atoms (P_A, P_C). The solutions, freshly prepared by the silver salt method,[2] were substantially pure, so there was no other component present in more than trace quantity which could have taken part in an exchange reaction. Also, the appearance of the room-temperature spectrum did not change on dilution, as would have been expected if the di-isothiocyanate had been

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* A Fortran program was written to call NAG Routine E04FDF (Mark II, Numerical Algorithms Group Ltd., Oxford, 1983).

† Michigan Interactive Data Analysis System, Statistical Research Laboratory, University of Michigan, 1979, used under the MTS operating system at the University of Newcastle.

Table 4. Comparison of experimental and predicted[a] n.m.r. parameters for symmetric α-$P_4S_3X_2$

X	Origin[b]	J_{AC}	J_{AB}	J_{AD}	J_{BD}	δ_A	δ_B
Cl	E	65.9	−263.2	20.0	10.3	133.4	161.7
	P	65.6	−260.8	19.5	8.6	125.9	151.8
	O	67.5	−260.8	21.1	5.2	125.1	136.3
Br	E	70.1	−254.3	19.7	11.7	132.0	151.1
	P	69.2	−252.8	19.8	11.4	131.2	149.6
	O	67.8	−256.1	20.0	9.2	128.5	145.9
I	E	74.8	−243.7	21.6	9.3	128.7	125.1
	P	75.1	−245.4	21.8	10.3	135.6	130.5
	O	65.7	−260.8	19.8	7.8	125.2	148.2
CN	E	86.3	−254.7	32.1	−14.4	128.7	34.2
	P	86.1	−253.9	32.0	−14.8	126.7	31.8
	O	83.8	−258.8	31.8	−15.8	126.3	36.0
NCS	E	64.4	−263.8	21.6	0.4	120.6	123.2
	P	65.9	−267.2	21.6	1.5	120.9	131.4
	O	73.2	−249.3	22.0	7.8	133.2	127.3
SMe	E	57.8	−290.1	22.1	−9.0	105.7	126.6
	P	57.5	−289.7	22.2	−9.0	105.5	124.9
	O	59.2	−288.4	22.5	−8.4	105.9	123.9
SEt	E	58.1	−288.8	22.3	−8.4	103.7	122.7
	P	58.1	−288.5	22.2	−8.7	106.3	124.4
	O	60.2	−284.3	22.1	−6.1	108.8	127.0
SPh	E	60.3	−282.4	21.7	−6.0	109.5	127.5
	P	60.1	−282.6	21.9	−5.5	110.4	127.7
	O	*c*	*c*	*c*	*c*	*c*	*c*

[a] Using equation (1), with *A*, *B*, and *C* from Table 2, and *F* and *R* from Table 3. [b] E = Experimental; P = predicted using substituent constants from this work; O = predicted using organic substituent constants. [c] Substituent constants not available (see ref. 8).

exchanging with another component. Two mechanisms for the broadening remained to be considered: (a) coupling between phosphorus (P_B, P_D) and the respectively directly bonded quadrupolar ^{14}N nuclei of the thiocyanate groups, and (b) an exchange reaction which was first order in the di-isothiocyanate only. I cannot rule out (a), since I have so far been unsuccessful in experiments to decouple ^{14}N while observing ^{31}P, but (b) seems more likely.

An isomerisation equilibrium may be envisaged in which one NCS group became bonded through sulphur instead of through nitrogen to phosphorus, giving an ABCD instead of an AA′BB′ spin system. Almost all[9] thiocyanato derivatives of phosphorus so far reported have been shown or assumed to be N-bonded, but the P_4S_3 cage could be expected to provide an unusually soft bonding environment, where bonding of thiocyanate through sulphur could be possible. There is good evidence that the main component in α-$P_4S_3(NCS)_2$ is N-bonded: the i.r. spectrum showed a strong absorption at 1 975 cm^{-1}, typical of N-bonded thiocyanate; ^{15}N n.m.r. (natural abundance) showed a doublet at δ −271.3 p.p.m., with a splitting of 87.3 Hz which may be assigned as $^1J_{NP}$; and ^{13}C n.m.r. showed a broad doublet, splitting 19 Hz, at δ 148 p.p.m. [*cf.* MeNCS, with $\delta(^{13}C)$ 128.6, while MeSCN has δ 113.5 p.p.m.].[10]

One difficulty in accepting the hypothesis of a linkage isomerisation reaction on the n.m.r. time-scale was that in n.m.r. measurements (^{31}P and ^{13}C) at the lowest available temperature (200 K) there was no clear evidence for spectra of the S-bonded compound. In the ^{31}P spectrum, the expected ABCD spectrum might by coincidence have been completely overlaid by the AA′BB′ spectrum of the N-bonded compound, but by comparison with organic thiocyanates, the ^{13}C signal of the S-bonded compound could be expected to be shifted by at least 15 p.p.m. relative to the N-bonded compound. At 200 K the ^{13}C n.m.r. doublet had sharpened somewhat (δ 146.25 p.p.m., splitting 21.0 Hz) but was still broad, and there were no other peaks of comparable intensity.

Experimental

All operations were carried out under nitrogen by Schlenk methods. AnalaR CS_2 was dried over P_4O_{10} and filtered before use. N.m.r. spectra of concentrated solutions in CS_2 were measured using a Bruker WM300WB spectrometer, operating at 121.5 MHz for ^{31}P, 75.47 MHz for ^{13}C, and 30.41 MHz for ^{15}N. Capillaries containing D_3PO_4–D_2O or $(CD_3)_2CO$–$SiMe_4$ were used as lock and external standard: calculation of the chemical shift zero for ^{31}P from the observed frequency of ^2D in $(CD_3)_2CO$ was used where low-temperature or weak signals precluded the use of a D_3PO_4–D_2O capillary. Preliminary experiments showed that the error thus incurred was insignificant compared with solvent shifts due to variation of concentration or of temperature. Nitrogen-15 shifts were calculated similarly relative to 1 mol dm^{-3} $Na^{15}NO_3$–D_2O.

Trimethylsilyl cyanide and azide (Aldrich) were used as received; α-$P_4S_3I_2$ was prepared by a literature method.[11] Silver halides and pseudohalides, used for reaction[2] with α-$P_4S_3I_2$, were precipitated from slightly acidic solution to avoid formation of silver oxide or carbonate, and were dried by heating to 70 °C under vacuum for >3 h.

Procedure for Trimethylsilyl Pseudohalide Reactions: Reaction of α-$P_4S_3Br_2$ *with* Me_3SiCN.—To a stirred solution of α-$P_4S_3Br_2$[2] (0.7 mmol) in CS_2 (10 cm^3) under N_2 was added Me_3SiCN (0.1 cm^3, 0.75 mmol) directly from a pipette fused to a gas-tight syringe. After 64 h at 20 °C, solvent and volatile products were slowly pumped away (during 1 h) from the stirred solution at 18 °C to leave a yellow powder, which was further pumped upon for 1.5 h. The product redissolved slowly on being stirred with CS_2 (5 cm^3). Phosphorus-31 n.m.r. showed α-$P_4S_3(CN)_2$ (62% of total P), α-$P_4S_3Br(CN)$ (34%), and α-$P_4S_3Br_2$ (4%).

*Methods used to obtain Initial Parameters for fitting of Phosphorus-*31 *N.M.R. Spectra by NUMARIT.*—The dicyanide was almost an AA′XX′ spin system, which could be solved by hand (though the X approximation[12] failed to the extent that iterative fitting did reveal a better fit for a negative sign for J_{BD}). The dichloride and dibromide were AA′BB′ spin systems for which the X approximation gave good starting parameters. The low-temperature spectrum of the di-isothiocyanate was a close AA′BB′ system; N and δ_{AB} (where $N = J_{AB} + J_{AD}$ and $\delta_{AB} = \delta_A - \delta_B$) were approximately obtained by partial assignment, and $^1J_{AB}$ was calculated from N, assuming that the other couplings were the same as in the di-iodide. The parameters obtained by NUMARIT starting at this point were found to fit relatively poorly the relationships involving substituent constants described above, so values predicted by these relationships were used as a new starting point for NUMARIT. This led to a slightly improved fit of the spectrum, yielding n.m.r. parameters which fitted the substituent constant relationships satisfactorily. The unsymmetric compounds gave spectra from which initial parameters were obtained by first-order methods, except for the chloride cyanide, whose spectrum was solved by subspectral analysis, using an ABRX approximation, and the bromide iodide. The latter constituted a close ABCX system, the shift of the phosphorus carrying bromide being separate from the other three. However, the relationships described above, between parameters for unsymmetric compounds, and those for the corresponding symmetric ones, were by then apparent, and were used to predict the parameters for the bromide iodide with sufficient accuracy for a recognisable simulation to be obtained.

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