Solid-state Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy of Phosphorus Sulphides

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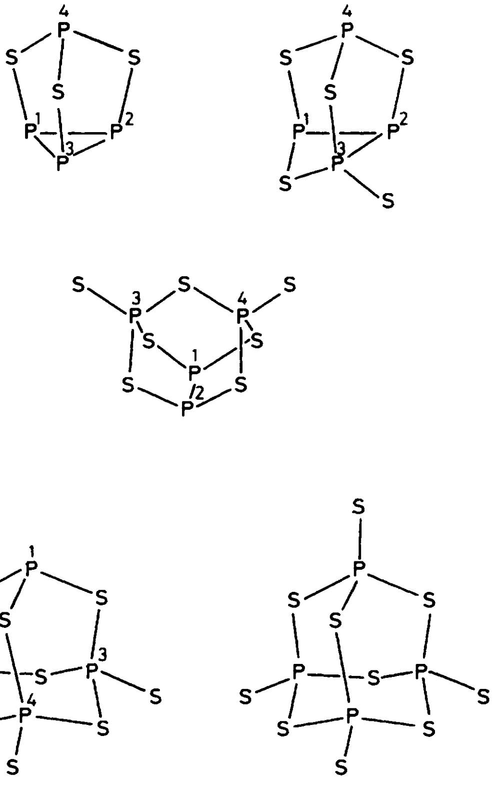
Magic-angle spinning ^{31}P n.m.r. spectra of solid binary phosphorus sulphides P_4S_n (n = 3, 5, 7, 9, or 10) have been obtained. The multiplicity of ^{31}P resonances are correlated with the structural inequivalences revealed by *X*-ray diffraction. In the case of P_4S_5 there are considerable solution-to-solid changes in the chemical shifts. Spinning side band analysis of the solid-state spectra has yielded data on effective shielding tensor components.

The binary phosphorus sulphides P_4S_n (n = 3, 4, 5, 7, 9, or 10) are an interesting group of compounds, all being structurally based upon the P_4 tetrahedron.[1] The compound P_4S_3 is used in the manufacture of 'strike anywhere' matches and P_4S_{10} is used both in organic synthesis and as a precursor in the preparation of lubricant additives. Their solution-state ^{31}P n.m.r. spectra have been reported[2–6] and a number of solid phases structurally characterised by *X*-ray crystallography.[7–14] The scheme shows the observed molecular structures for the systems we have studied. However, there have only been scattered reports[15–18] (at relatively poor resolution) of solid-state ^{31}P n.m.r. spectra. Additionally, some compounds exist in two or more polymorphic forms in the solid state (*e.g.* P_4S_9). We have measured high-resolution solid-state spectra of a number of P_4S_n species, enabling more detailed information than previously to be obtained.



Scheme 1. The phosphorus sulphides studied for the work presented here, with the atomic numbering for the phosphorus nuclei as used in the Table

Experimental

The compounds P_4S_3 and P_4S_{10} were obtained from Fluka: P_4S_3 was freed of higher phosphorus sulphides by suspension in boiling water for 1 h, followed by filtration, drying, *in vacuo*, and recrystallisation from toluene; P_4S_{10} was recrystallised six times from toluene. The compound P_4S_5 was prepared as described in the literature,[19] P_4S_7 was prepared by the published method using decalin as the solvent,[20] P_4S_9 was obtained from the reaction of sulphur with P_4S_3, using α-bromonaphthalene as solvent,[20] and recrystallised from toluene to remove traces of P_4S_7 and P_4S_{10}. Sample purity was assessed by Raman spectroscopy, mass spectrometry, and, where possible, by solution-state ^{31}P n.m.r. spectroscopy. The moisture-sensitive compounds were packed into KEL-F rotors in a nitrogen glove-box; the rotors were fitted with tight end-caps together with poly(tetrafluoroethylene) tape to ensure an airtight seal.

Solid-state spectra were obtained at a frequency of 81.01 MHz using a Bruker CXP 200 spectrometer. Spinning speeds were in the range of 2—4 kHz. Most spectra contain extensive manifolds of spinning sidebands. In cases where any doubt existed, the positions of the centrebands were located by varying the spinning speed. Shielding tensor components were derived by spinning sideband analysis using an iterative computer program based on the equations given by Maricq and Waugh.[21] We use the convention $|\sigma_{33} - \sigma_{iso}| \geqslant |\sigma_{11} - \sigma_{iso}| \geqslant |\sigma_{22} - \sigma_{iso}|$, together with definitions of anisotropy, $\zeta = \sigma_{33} - \sigma_{iso}$ and asymmetry, $\eta = (\sigma_{22} - \sigma_{11})/\zeta$. Solution-state results were obtained at 36.2 MHz using a JEOL FX90Q spectrometer, the solvent being carbon disulphide or toluene.

Chemical shifts, δ_P, were obtained, by replacement, relative to a static sample of 85% H_3PO_4 in water. Chemical shifts are quoted according to modern convention, *i.e.* high-frequency positive.

Results and Discussion

The isotropic ^{31}P chemical shifts, shielding tensor components, and literature solution-state ^{31}P n.m.r. data are shown in the Table.

Phosphorus sesquisulphide, P_4S_3, is probably the best known phosphorus sulphide. Unlike the other phosphorus sulphides, it is not moisture-sensitive. There is a first-order solid–solid phase transition for P_4S_3 at 314 K, with the high-temperature phase (phase I) undergoing rapid molecular reorientation and diffusion, whereas the low-temperature phase (II) is a relatively

Table. Solution and solid-state chemical shifts and shielding tensors for phosphorus sulphides

Compound		Isotropic shifts, δ/p.p.m.		Linewidth/ Hz	Shielding tensor data/p.p.m.[a]			
		Solution	Solid		σ_{11}	σ_{22}	σ_{33}	$\lvert ב \rvert$
P_4S_3[b]	P(4)	64.6	91.0	250	10	−35	−247	156
			84.5	200	19	−24	−249	164
			(89 ± 8)		(−3)	(−25)	(−238)	
	P(1)—P(3)	−126.4	−87.5	1 200	≈ −110	≈ 7	≈ 365	≈ 277
			(−87 ± 16)		(−101)	(−44)	(406)	
P_4S_5[c]	P(4)	231.7	232.7	190	−302	−302	−94	139
	P(3)	89.6[d]	120.2[d]	140	≈ −17	≈ −113	≈ −235	≈ 115
					≈ −40	≈ −67	≈ −250	≈ 130
	P(1)	122.7[d]	139.8[d]	—	≈ −300	≈ −203	≈ 82	≈ 222
	P(2)	125.9	111.4	—	—	—	—	
P_4S_7[e]	P(4)	110.3	113.0		−271	−124	55	168
	P(3)		111.6		−275	−131	72	184
	P(2)	89.3	96.0		−20	−85	−187	91
					−36	−78	−170	74
	P(1)		82.0		−172	−84	6	88
					−10[f]	−69	−163[f]	81
P_4S_9[g]	P(1)	57.9	67.5					
	P(2)—P(4)	63.6	57.8					
P_4S_{10}[g]		56.8	50.2 56.0 60.1					

[a] In the cases of P(3) for P_4S_5 and of both P(1) and P(2) for P_4S_7, data are given separately for the two components of *J*-split doublets (values for the high-frequency component being given first). The results are not strictly shielding tensor components but involve the direct and indirect coupling tensors also. For other resonances, where splittings arising from coupling are not resolved, the tensor components given here clearly represent some sort of average. [b] Data from ref. 18 shown in parentheses. The values are averages for the apical sites, as also for basal sites. [c] Solution-state data are taken from ref. 4. Reported solution-state coupling constants are P(3)–P(4) 54, P(1)–P(4) 19, P(2)–P(4) 28, P(1)–P(3) −184, P(2)–P(3) −284, and P(1)–P(2) 120 Hz; solid-state splittings are P(3) 250 and P(1) 195 Hz, in each case ±*ca.* 10 Hz. [d] Assignments of P(1) and P(3) may be reversed. [e] The solution spectrum consists of two singlets; solid state splittings are P(2) 218 and P(1) 226 Hz. [f] The conventional numbering of the components causes the apparent anomaly with respect to the other peak for P(1). The situation arises because σ_{22} is approximately midway between σ_{33} and σ_{11}, so small variations or errors change the numbering. [g] Solution data from ref. 6, which also gives $|^2J_{PP}|$ = 96.6 Hz.

rigid solid for which the *X*-ray crystal structure is known.[7] The samples studied here belong to phase II and none of the spectra showed any evidence of phase I. For phase II there are two molecules involved in the asymmetric unit, each with mirror-plane symmetry passing through the apical phosphorus and one of the basal phosphorus atoms.

Early low-field magic angle spinning (m.a.s.) n.m.r. work[15] on powdered phase II material yielded approximate chemical shifts δ_P of 72 and −103 p.p.m. (±10 p.p.m.) for apical and basal sites respectively. Single-crystal n.m.r. data have also been obtained by Gibby *et al.*[18,*] (phase not specified, but implicitly phase II) giving shielding tensor data for both types of site. Phosphorus-31 relaxation studies[16] showed that there was little dependence of T_1 on the applied field B_0 for phase II. Typical values of T_1 were found to be in the region of 100 s. Phase I has been studied by ^{31}P n.m.r. spectroscopy without any artificial line-narrowing techniques,[17] and chemical shifts δ_P of 72 (apical) and −113 (basal) p.p.m. found (±5 p.p.m.), together with $|^2J_{PP}|$ = 70 ± 3 Hz. Gibby *et al.*[18] concluded that for their material also there was rapid molecular motion, but only about the approximate C_3 molecular axis.

Our ^{31}P m.a.s. spectrum of phase-II P_4S_3 (Figure 1) shows a pair of closely spaced relatively sharp lines (δ_P = 91.0 and 84.5 p.p.m.), together with a broader line at substantially lower frequency (δ_P = −87.5 p.p.m.). The shifts are in good agreement with those of Gibby *et al.*,[18] but there is *ca.* 16 p.p.m. discrepancy from those of Andrew and Wynn.[15] Both sets of lines have a substantial number of spinning sidebands, these being more widespread for the signal at −87.5 p.p.m. than for the others. Because of the differences in linewidths and the occurrence of spinning sidebands, it is not easy to estimate

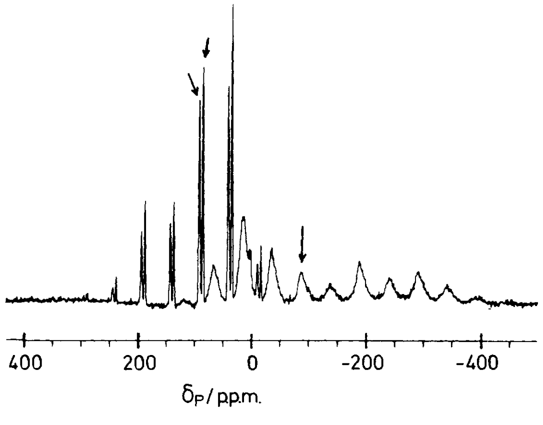


Figure 1. 81.01-MHz ^{31}P m.a.s. n.m.r. spectrum of solid P_4S_3 (phase II). Operating conditions: number of transients 196; relaxation delay 300 s; spinning speed 4.1 kHz. The centrebands are indicated by arrows

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* Curiously, these authors state the asymmetric unit is one molecule. For phase II it is, strictly speaking, two different half-molecules, as mentioned above.

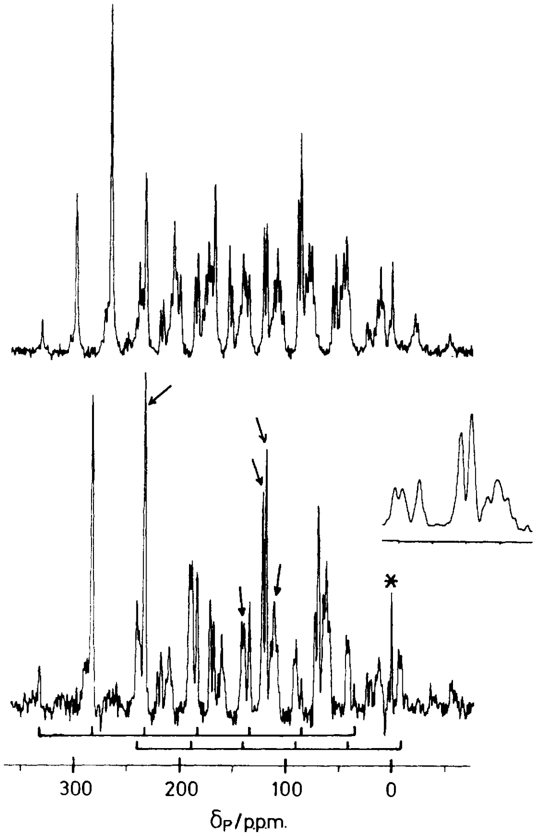

Figure 2. 81.01-MHz ^{31}P m.a.s. n.m.r. spectra of solid α-P_4S_5. Operating conditions: relaxation delay 300 s; spinning speed 2.6 (above) and 4.0 kHz (below); 90° pulses with duration 4 μs. The inset is an expansion of the centrebands, which are indicated in the main spectrum at the bottom by arrows. The linkages show the spinning sideband manifolds for P(4) and P(2). The asterisk indicates an impurity peak (possibly H_3PO_4)

relative intensities, but integration suggests a ratio of 1:2.6 for the pair of lines (together) compared to the broader line. It is evident that the two lines may be assigned to apical phosphorus nuclei and the broader system to basal atoms. Such an assignment is fully in accord with the chemical shifts. Moreover, it is consistent with the crystal structure if it is assumed that crystallographic inequivalences among basal nuclei and all effects of indirect (scalar) couplings are obscured by the large linewidths (and indeed form the principal causes of it). The existence of *two* sharper peaks (not resolved in the earlier work) appears to arise from intermolecular crystallographic inequivalence of apical phosphorus atoms, the linewidths being sufficient to obscure splittings caused by P–S–P coupling (typically *ca.* 70 Hz in magnitude compared to the *ca.* 200 Hz expected for intra-basal |$^1J_{PP}$|). The peak heights for the two sharper lines are slightly different because of differing linewidths.

The calculated shielding tensor components are in reasonable agreement with the single-crystal data of Gibby *et al.*[18] (assuming the same phase was examined). The values for the two sharper lines are probably equal within experimental error, with the possible exception of σ_{22}.

To obtain suitable spectra of P_4S_3, we found it to be essential to use long recycle delays (*ca.* 300 s), which is consistent with the relaxation measurements of Andrew *et al.*[16]

Tetraphosphorus pentasulphide, P_4S_5, exists as α and β isomers.[9,11] We have studied the α form. Figure 2 shows the value of data collected at different spinning speeds. The choice of spinning rate is critical in order to observe all of the resonances without any being obscured by spinning sidebands. Four bands can be identified: a singlet, two doublets, and a triplet. The results are not in good agreement with those of Andrew and Wynn,[15] but these authors were unable to achieve m.a.s. for their P_4S_5 sample. The *X*-ray structure of α-P_4S_5 reveals[11] that the asymmetric unit consists of a single molecule. The spectrum is assigned as follows: the singlet arises from P(4), the doublets are due to P(1) and P(3), both coupled to P(2), and the triplet is due to P(2), coupled to P(1) and P(3). Comparison of the solution and solid-state data shows dramatic changes in chemical shifts for P(1), P(2), and P(3). Moreover, the change for P(2) appears to be in the opposite direction to those for P(1) and P(3). Large solution-to-solid changes are also observed for P_4S_3, and it may be noted that in this case solution-state shifts vary with solvent.[22] We have no detailed explanation for these effects at present, though the magnitudes indicate substantial changes in geometry rather than mere intermolecular packing considerations. The importance of geometry for n.m.r. parameters in phosphorus–sulphur cage compounds has been emphasised by Tattershall.[23] It is noteworthy that the shift of P(4) remains sensibly constant from solution to solid. The data given in the Table suggest the shielding tensor for P(4) is axial, but this is likely to be an artefact, since spinning sideband analysis is not sensitive to low values of asymmetry. The spectra of Figure 2 illustrate the ability of solid-state n.m.r. to distinguish different isomers in these systems. The β form of P_4S_5 has a structure[9] with no P=S double bonds, and the molecular site symmetry indicates that two of the phosphorus atoms are equivalent, which is inconsistent with our spectra.

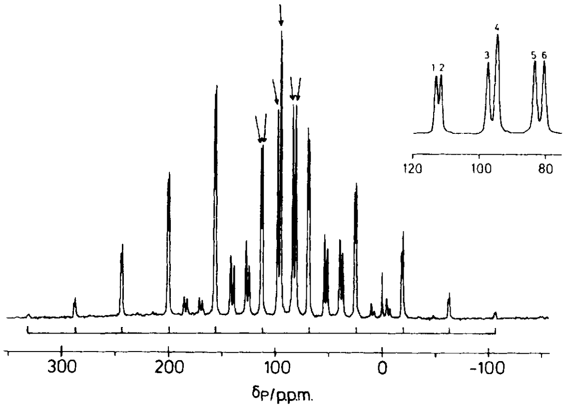

Figure 3. 81.01-MHz ^{31}P m.a.s. n.m.r. spectrum of solid α-P_4S_7. Operating conditions: relaxation delay 800 s; number of transients 16; spinning speed 3 550 Hz. The linkages below the spectrum show the spinning sideband manifolds for P(3) and P(4). The inset is an expansion of the centrebands, which are indicated in the main spectrum by arrows. The peak numbers on the inset are as mentioned in the text

Tetraphosphorus heptasulphide, P_4S_7, exists as α and β isomers, although in the solid state the latter is believed to contain P_4S_6 and P_4S_5. We have studied the α form, for which the asymmetric unit consists of a complete molecule.[11] In CS_2 solution we observed two singlets at 110.3 and 89.3 p.p.m. respectively. We would have expected two triplets since all of the other phosphorus sulphides show ^{31}P–^{31}P couplings in solution. It may be that on going from P_4S_9 thrrugh to P_4S_3 the sign of the coupling constant changes and thus for P_4S_7 it is accidentally zero (or very small). The solid-state spectrum is shown in Figure 3. If it is assumed that, as for P_4S_3, splittings arising from two-bond scalar coupling are obscured, the spectrum can be assigned as follows. There are two groups of signals which are centred at approximately the same chemical

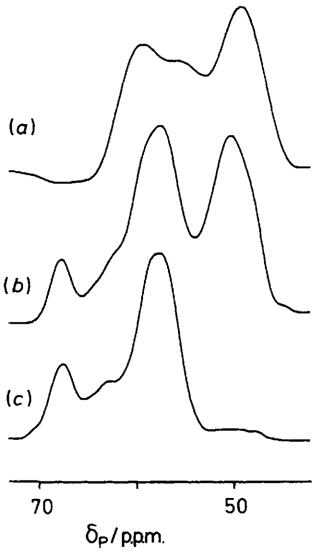

Figure 4. Expansion of the centrebands for the 81.01-MHz ^{31}P m.a.s. n.m.r. spectra for three samples of solid P_4S_9 and P_4S_{10}: (*a*) relatively pure P_4S_{10}; (*b*) P_4S_9 in admixture with P_4S_{10}, and (*c*) relatively pure P_4S_9. Operating conditions: pulse duration (90°) 4 μs for (*a*) and (*b*), 5 μs for (*c*); relaxation delay 300 s for (*a*), 800 s for (*b*) and (*c*); number of transients 32 (*a*), 56 (*b*), 48 (*c*)

shifts as the two signals in the solution spectrum (in contrast to the situation for P_4S_3 and P_4S_5). In the solid state resonances 1 and 2 (see Figure 3) are due to P(4) and P(3), which have become inequivalent due to crystal-packing effects. The pattern of resonances 2—6 results from a large splitting (14.0 p.p.m., arising from the manner in which the molecular symmetry is lowered in the solid), combined with a coupling *J* of 236 Hz between P(1) and P(2), which are directly bonded together. This interpretation was confirmed by additional measurements at higher field (7.04 T). The signal intensities for the four phosphorus nuclei are equal within experimental error when account is taken of the spinning sidebands. There are rather different shielding anisotropies for the two groups of signals P(1), P(2) and P(3), P(4), the magnitude for the phosphorus(v) nuclei being (surprisingly) greater than those for P^{III}. Average values from two different spinning speeds are $\beth$ = 168 and 184 p.p.m. for P(4) and P(3) respectively, corresponding values of the asymmetry being η = 0.88 and 0.79. Similar data for P(1) and P(2), but further averaged over the *J*-split components, are $\beth$ = −85 and −83 p.p.m., with η = 0.87 and 0.65 respectively. The complexity of the spectra for this compound shows that it is the α form and underlines the sensitivity of solid-state n.m.r. spectroscopy to weak interactions which are not obvious from *X*-ray crystallography. While our paper was in preparation an article appeared reporting[24] both solid (m.a.s.) and solution-state n.m.r. data for P_4S_7. The m.a.s. results are in good agreement with our own.

Tetraphosphorus nonasulphide, P_4S_9, is an impurity in commercial P_4S_{10} and is itself very difficult to free from P_4S_{10}. Figure 4 shows, at expanded scale, the centrebands for three samples with differing proportions of P_4S_9 and P_4S_{10}. By measurements on these samples which were also studied by Raman spectroscopy and powder diffraction we have tentatively identified the bands as being due to P_4S_9 and P_4S_{10} as follows. The decasulphide gives a major peak at δ_P = 50.2 p.p.m., with a significant resonance at 56.0 p.p.m. and a possible weak signal at 60.1 p.p.m., whereas the nonasulphide has its most prominent band at 57.8 p.p.m., a somewhat weaker signal at 67.5 p.p.m., and a further possible peak at 63.3 p.p.m. Some spectra suggest further splittings may be present. Thamm *et al.*[6] report that a solution of P_4S_{10} gives a single ^{31}P signal at δ_P = 56.8 p.p.m., so there is little change in going to the solid state. Andrew and Wynn[15] studied solid P_4S_{10} by m.a.s. n.m.r. and obtained a signal at 45 p.p.m. The discrepancy with our results is similar to those for P_4S_3 and is probably attributable to referencing procedures. *X*-Ray work[11,13] shows that the asymmetric unit is one entire molecule, so in principle four signals should be observed. Relative intensities of the centrebands may, of course, be distorted by differences in spinning sideband patterns. Such differences appear to exist but are difficult to quantify. The sidebands extend over the range δ −50 to +130 p.p.m. for both P_4S_{10} and P_4S_9.

The nonasulphide exists in at least two solid phases,[12] phase I being disordered and phase II ordered. The crystal structure of the latter is known[12] and the asymmetric unit has been shown to be one-third of a molecule, the C_3 axis being retained in the solid. Therefore our relatively pure P_4S_9 sample cannot be of phase II only. Our spectra are in agreement with the crystal structure since the bands at 67.5 and 57.8 p.p.m. are in the approximate intensity ratio 1:3. However, this implies a reversal of chemical shifts from the solution state[6] (without appreciable shift change otherwise).

Other studies suggest that Raman spectroscopy is a rather better tool for identification of these two species. It was not feasible to obtain shielding tensor components for either P_4S_9 or P_4S_{10}.

It is of interest from the Table that shielding tensor components for the separate lines arising from coupling in the case of P(3) for P_4S_5 and of both P(1) and P(2) for P_4S_7 appear to differ. We believe this to be a real effect arising from the tensor properties of both direct (dipolar) and indirect coupling. Strictly, therefore, the data in the Table are merely apparent shielding tensor components. In principle, more detailed analysis should yield separate information about shielding and coupling, but in practice this would be very difficult to achieve. Averages of the results for *J*-split resonances are likely to be a reasonable approximation to true shielding tensor components. Indeed, this is an implicit assumption in presenting the values for cases where *J* splitting cannot be resolved. As might be expected from the considerable differences in chemical environment, the tensor data in the Table show substantial variations, except for the consistencies in the case of P_4S_7 mentioned above.

Conclusions

The usefulness of m.a.s. ^{31}P n.m.r. for the characterisation of binary phosphorus sulphides has been demonstrated. This technique allows identification of the phase and gives information about molecular structure, which is particularly valuable for the study of materials which are not available in suitable form for single-crystal *X*-ray studies.

Acknowledgements

We are grateful to the S.E.R.C. for the award of C.A.S.E. studentships (to P. J. W. and P. T. W.), involving the Food Research Institute (Norwich) and Exxon Chemicals respectively. We thank Dr. D. C. Apperley for carrying out the spinning sideband analyses.

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Received 13*th July* 1988; *Paper* 8/02825G