

## Magic-angle Spinning Phosphorus-31 Nuclear Magnetic Resonance of Polycrystalline Sodium Phosphates

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The magic-angle spinning  $^{31}\text{P}$  n.m.r. spectra of a range of solid sodium ortho-, pyro-, poly-, and metaphosphates have been obtained. Counter ion, hydration state, crystalline form and inequivalence within a molecule all affect the solid-state chemical shift, which therefore deviates from the solution chemical shift. The multiplicity of  $^{31}\text{P}$  resonances indicates a level of structural inequivalence at least as large as that revealed by X-ray diffraction. Shielding anisotropies have also been obtained, which agree with previous studies but additionally show deviation from isotropic symmetry for some orthophosphates and deviation from axial symmetry for some terminal polyphosphate groups.

Phosphates can exist as anions containing one or more phosphorus atoms. The former are called orthophosphates while the latter can exist as chains or rings and are known as polyphosphates and metaphosphates respectively.<sup>1-4</sup> The one exception to this nomenclature is in polyphosphates which contain two phosphorus atoms, which are known as pyrophosphates. It should be noted that an element of confusion arises in older work in which longer chain polyphosphates are called metaphosphates since no suitable analytical procedure was available to differentiate between them.

$^{31}\text{P}$  N.m.r. of solutions is able to differentiate end and chain phosphorus units, thus determining the chain length, and also the level of protonation.<sup>5,6</sup> In principle solid-state n.m.r. can provide this and crystallographic information, *viz.* hydration state, crystalline form, inequivalence within the unit cell, and even inequivalence within an ostensibly symmetrical molecule. Examples of all these effects have been noted. Spectra can often be obtained after only four pulses, with or without resort to cross polarisation and with a minimum of sample preparation. This compares very favourably with powder X-ray diffraction. Moreover, crystallographic inequivalence can often be obtained by a simple inspection of the multiplicity of n.m.r. spectral lines otherwise requiring a single-crystal structural determination. The latter, however, would yield a complete structural determination which is obviously not available from n.m.r.

Although  $^{31}\text{P}$  n.m.r. of alkali-metal phosphate solutions is well documented,<sup>5,6</sup> little has been published on solids, and that is split between potassium and sodium phosphates.<sup>7,8</sup> Sodium phosphates in their solid form are of particular interest to industry as a major constituent of washing powders and as a coating for colour pigments. For this reason we have studied solid sodium ortho-, pyro-, tripoly-, trimeta-, tetrameta-, hexameta-, and octameta-phosphates in various levels of protonation and hydration states (see Table) with magic-angle spinning n.m.r.<sup>9</sup>

### Experimental

The samples were as supplied by Albright and Wilson Ltd. and were loaded as powders into rotors of the Andrew-Beams type<sup>10</sup> and spun at 2.5–3.0 kHz. A small amount of KBr was added to each sample and, with the probe tuned to the  $^{79}\text{Br}$

frequency, the magic angle was set by optimising the linewidth of the spinning sidebands.<sup>11</sup> The probe was then retuned for  $^{31}\text{P}$  observation.

Spectra were obtained at a frequency of 81.01 MHz on a Bruker CXP 200 spectrometer by pulsing the  $^{31}\text{P}$  frequency channel and collecting a free induction decay (denoted single pulse or s.p.) or *via* cross polarisation from the proton spin reservoir (denoted c.p.). In both instances these pulse sequences were followed by high-power proton decoupling during acquisition unless specified otherwise.

Most spectra contain extensive manifolds of spinning sidebands since accessible spinning speeds are usually less than the relevant shielding anisotropies expressed in Hz. In cases where any doubt existed, the positions of the centrebands were located by varying the spinning speed.

Chemical shifts,  $\delta_p$ , were obtained, by replacement, relative to a static sample of 85%  $\text{H}_3\text{PO}_4$  in water. Chemical shifts are quoted according to the modern convention, *i.e.* high frequency positive. Unfortunately an anomalous convention still persists for  $^{31}\text{P}$ .

The principal components of the shielding anisotropy were obtained by graphical analysis of the spinning sidebands.<sup>12</sup>

### Results and Discussion

*Isotropic Shifts.—(a) General discussion.* As explained above the chemical shifts are referenced to a static sample of phosphoric acid. Such a sample gives rise to somewhat variable chemical shifts for two reasons. First the sample distorts the local field to produce a broad non-Lorentzian lineshape and secondly the water content of a nominally 85% solution is variable. The former is avoidable by either shimming specifically on this sample or restricting its size. The latter is more difficult to control, especially from laboratory to laboratory. The chemical shifts quoted are self-consistent but there are greater errors in the values relative to  $\text{H}_3\text{PO}_4$ .

Isotropic shifts of the solid phosphates were obtained by magic-angle spinning (m.a.s.). Polyphosphate linewidths are

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**Table.** Polycrystalline sodium phosphate chemical shifts and shielding tensors

Compound	Isotropic shifts <sup>a</sup>		Shielding tensor data <sup>a</sup>					
	Solution $\delta_p$	Solid $\delta_p$	$\sigma_{11}$	$\sigma_{22}$	$\sigma_{33}$	$\bar{\sigma}^b$	$\Delta\sigma^c$	$\eta^c$
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	—	6.9	—	—	—	—	—	—
$\text{Na}_2\text{HPO}_4$	—	-0.2	35	35	-69	0.3	-104	0
$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$	—	0.4	61	10	-72	-0.3	-108	0.71
$\text{Na}_4\text{P}_2\text{O}_7$	-5.2	2.9	51	30	-88	-2.3	-129	0.25
		1.3	49	29	-80	-0.7	-119	0.25
$\text{Na}_3\text{HP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ (A)	-6.8	-2.3	77	13	-84	2.0	-129	0.74
		-5.0	-79	5	89	5.0	$\pm 126$	1.0
$\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$	—	-8.2	82	11	-69	8.0	-116	0.92
$\text{Na}_5\text{P}_3\text{O}_{10}$ (I)	-4.8	1.2	60	38	-101	-1.0	-150	0.22
	-19.6	-7.4	-83	-23	127	7.0	180	0.5
$\text{Na}_5\text{P}_3\text{O}_{10}$ (II)	-4.8	4.7	72	30	-91	3.7	-142	0.44
	-19.6	-6.1	-66	-21	107	6.7	151	0.45
		2.7	72	18	-98	-2.7	-143	0.57
$\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$	-4.8	0.6	55	38	-96	-1.0	-143	0.18
	-19.6	-6.9	-78	-16	114	6.7	161	0.58
		-15.5	-99	-24	173	16.7	235	0.48
$\text{Na}_3\text{P}_3\text{O}_9$	-20.8	-18.6	-85	-33	176	19.3	235	0.33
		-20.9	-87	-3	155	21.7	200	0.63
$\text{Na}_4\text{P}_4\text{O}_{12} \cdot 4\text{H}_2\text{O}$	-23.7	-19.7	-79	-28	163	18.7	217	0.35
		-22.4	-80	-18	166	22.7	215	0.43
$\text{Na}_6\text{P}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$	-22.1	-18.1	-88	-5	148	18.3	195	0.64
		-22.9	-86	-19	173	22.7	225	0.45
		-15.2	-83	-31	160	15.3	217	0.36
$\text{Na}_8\text{P}_8\text{O}_{24} \cdot 6\text{H}_2\text{O}$	-21.2	-16.8	-79	-31	161	17.0	216	0.33
		-21.7						
		-22.9	-92	-13	171	22.0	224	0.53

<sup>a</sup> All data (except for  $\eta$ ) are in p.p.m. and referenced to 85%  $\text{H}_3\text{PO}_4$ . <sup>b</sup> From the spinning-sideband analysis. <sup>c</sup> For definitions, see text.

quite strongly dependent on the spinning angle. For example the non-spin linewidth of sodium tripolyphosphate is ca. 100 p.p.m.<sup>7</sup> which results in a linewidth dependence of  $100 \times 0.025 = 2.5$  p.p.m. per degree of offset from the magic angle.<sup>13</sup> Accordingly considerable effort was made to optimise the angle. Despite this, linewidths were still comparatively large, e.g. 1.3 p.p.m. at 80 MHz for anhydrous sodium tripolyphosphate. We tentatively interpret this as being due, at least in part, to the second-order effect of dipolar coupling with the quadrupolar sodium cation. This assertion is supported by the fact that the linewidth of anhydrous sodium pyrophosphate does not follow the ratio of the two frequencies at which it has been observed, i.e. 81.01 and 36.4 MHz. It should be noted that the scalar coupling (measured in solution) between the end and chain phosphorus nuclei in this compound is 18 Hz, which is only a small fraction of the observed solid linewidth.

It can be seen from the Table that large chemical shift differences to higher frequency commonly occur from solution to the solid state. This was noted before for potassium phosphates<sup>8</sup> but the interpretation is disputed.<sup>14</sup> In some instances the shifts are similar in solution and solid states, in particular for the metaphosphates, but sufficient differences occur to render the use of solution shifts in the interpretation of solid-state spectra extremely questionable.

Certain trends in isotropic chemical shifts can be discerned. As in solution, sodium orthophosphates and end groups of polyphosphates resonate at higher frequency than chain phosphates.

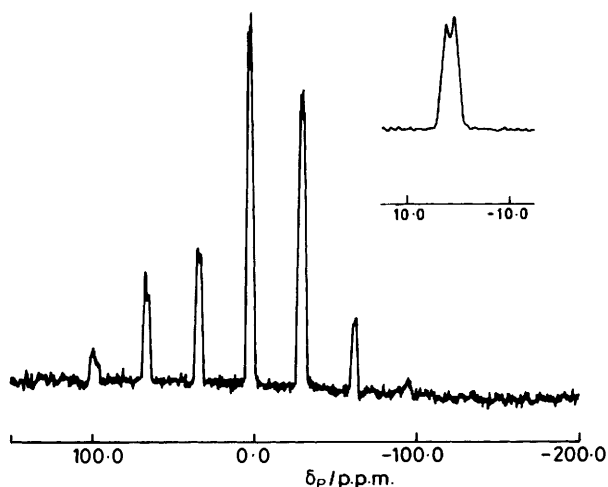
The level of protonation exerts a considerable influence. Anhydrous sodium pyrophosphate resonates at ca. 2.1 p.p.m. while the dihydrogen salt signal is at -8.2 p.p.m. As expected, the monohydrogen salt has an intermediate chemical shift, ca. -3.7 p.p.m., but this is not strictly comparable because a change in hydration state is additionally involved. The same trend is exhibited in sodium pyrophosphate solution spectra where

the tetrasodium salt resonates at -5.2 p.p.m. while the monohydrogen salt signal is at -6.8 p.p.m. Although the spectra of solid sodium orthophosphates show the same overall trend of lower frequency at higher hydrogen levels, also noted previously for analogous calcium<sup>15,16</sup> and potassium salts,<sup>8</sup> the monohydrogen and dihydrogen orthophosphates appear to give signals in the opposite sense. This could be due to the change in hydration state.

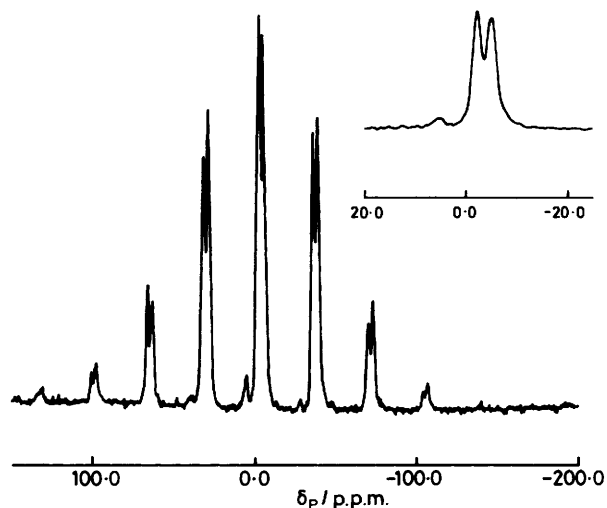
With the sodium phosphate chemical shift data presented here it is difficult to make a direct comparison to establish the effect of hydration state. Chemical shift differences occur, for instance for anhydrous and hexahydrated sodium tripolyphosphate, but the shifts are of the same order as the differences between different crystalline forms of the anhydrous salt.

Perhaps of more interest than the effects of the level of protonation and hydration state is the information contained in the multiplicity of the m.a.s. spectra. In most instances more than one resonance is observed for the end or chain groups and this contains information on subtle crystallographic features.

Sodium pyrophosphate has two end-phosphorus atoms which are ostensibly identical. The anhydrous (most commonly occurring) dihydrogen salt exhibits one resonance at -8.2 p.p.m. but both the anhydrous tetrasodium, Figure 1, and trisodium monohydrate (form A), Figure 2, salts exhibit splittings, of 1.6 (Duncan and Douglass,<sup>7</sup> 1.2 p.p.m.) and 2.7 p.p.m. respectively. The single-crystal X-ray structure of anhydrous tetrasodium pyrophosphate<sup>17</sup> shows a space group of  $P2_12_12_1$  with four molecules per unit cell. The asymmetric unit is a complete phosphate ion, with differences (0.1 Å) in the chain P-O distances. A single-crystal X-ray structure of the trisodium monohydrate salt has not been determined, although the powder diffraction pattern is known.<sup>18</sup> Since the splitting of the n.m.r. peaks is considerably larger than for the anhydrous tetrasodium salt, one might assume that the asymmetry is also larger.

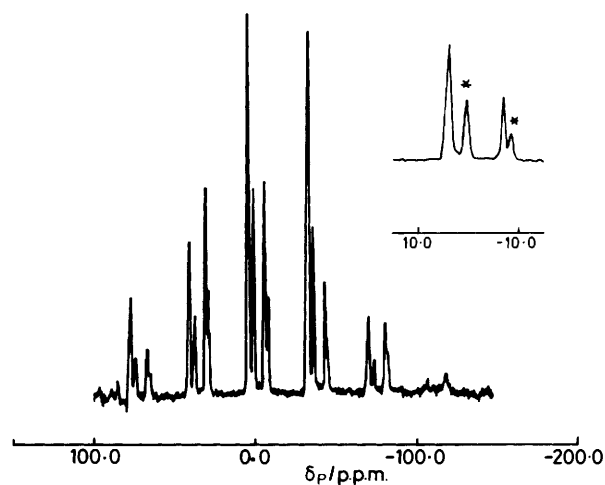


**Figure 1.** Phosphorus-31 s.p.-m.a.s. n.m.r. spectrum of solid anhydrous tetrasodium pyrophosphate,  $\text{Na}_4\text{P}_2\text{O}_7$ . Clearly there are many spinning sidebands and the inset shows an expansion of the centreband. Spectrometer conditions: number of transients = 8, recycle delay = 3 s, no proton irradiation

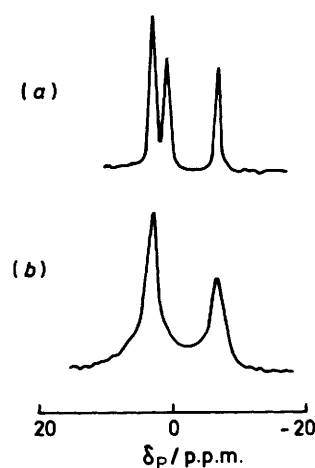


**Figure 2.** Phosphorus-31 c.p.-m.a.s. n.m.r. spectrum of solid trisodium hydrogenpyrophosphate monohydrate,  $\text{Na}_3\text{HP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ . The inset shows an expansion of the centreband. Spectrometer conditions: number of transients = 16, contact time = 2 ms, recycle delay = 5 s, proton decoupling

(b) *Polyphosphates.* Pentasodium tripolyphosphate exists in many different states of hydration but only the anhydrous and hexahydrate states have been studied here. The anhydrous salt occurs in two different forms: (I) and (II). A mixed salt of (I) and (II) and a pure form (I) have been studied. It is worth noting in passing that forms (I) and (II) have indistinguishable phosphorus  $T_1$ 's in the mixed salt (95% confidence limits 60–74 s) suggesting that the two forms are co-crystallised. We are conducting a spin-diffusion experiment<sup>19</sup> to attempt confirmation of this. In both forms (I) and (II) both end and chain groups resonate at higher frequency in the solid, Figure 3, than in solution [1.2 and 4.7 p.p.m. end (I) and (II), –7.4 and –6.1 chain (I) and (II) as opposed to –4.8 and –19.6 p.p.m.]. The splitting for forms (I) and (II) is larger for the end groups (3.5 p.p.m.) than for the chain groups (1.3 p.p.m.). This is confirmed in the X-ray crystal structures, where end phosphorus–oxygen



**Figure 3.** Phosphorus-31 s.p.-m.a.s. n.m.r. spectrum from a mixture of forms (I) and (II) for anhydrous pentasodium tripolyphosphate,  $\text{Na}_5\text{P}_3\text{O}_{10}$ . The inset shows an expansion of the centreband. The peaks marked with an asterisk are assigned to form (I). Spectrometer conditions: number of transients = 8, recycle delay = 500 s, no proton irradiation



**Figure 4.** Phosphorus-31 m.a.s. n.m.r. spectra of pentasodium tripolyphosphate hexahydrate,  $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$ . (a) C.p. with proton decoupling, number of transients = 16, contact time = 2 ms, recycle delay = 5 s; and (b) s.p. with no proton irradiation, number of transients = 8, recycle delay = 800 s. In both cases only an expansion of the centreband is shown

distances are more perturbed in going from form (I)<sup>20</sup> to (II)<sup>21</sup> than the chain phosphorus–oxygen distances. X-Ray studies further show that in both instances the space group is  $C2/c$ , with four molecules per unit cell, and the molecule is symmetrical. This in turn is supported by the n.m.r. evidence, which does not detect any further multiplicity beyond end and chain and forms (I) and (II).

The hexahydrate form of pentasodium tripolyphosphate gives three resonances, Figure 4(a), two end phosphates at 2.7 and 0.6 p.p.m. and the chain phosphate at –6.9 p.p.m. Once again, a change in hydration results in different chemical shifts. The X-ray crystal structure<sup>22</sup> reveals a space group  $P1$  with two molecules per unit cell. Although both molecules are identical, the end phosphates are inequivalent, as is also shown by n.m.r. Furthermore, if high-power proton decoupling is not employed in the n.m.r. experiment, all resonances broaden but the end

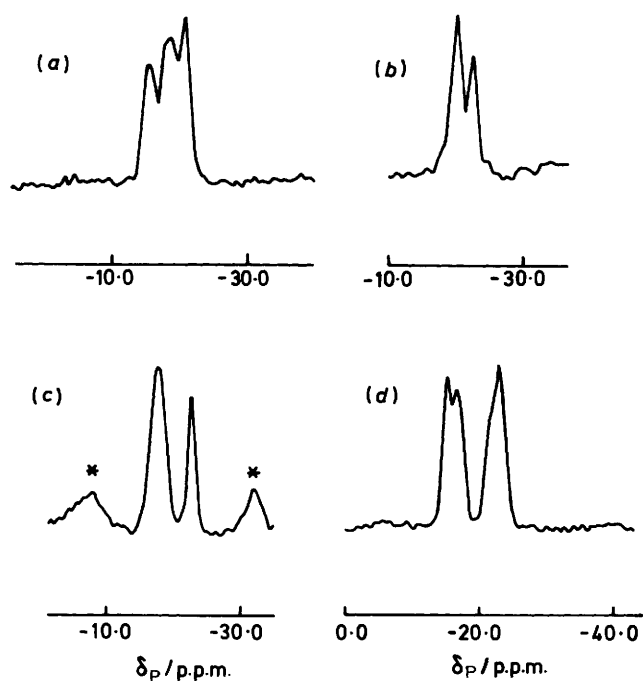


Figure 5. Phosphorus-31 m.a.s. n.m.r. spectra centrebands of (a)  $\text{Na}_3\text{P}_3\text{O}_9$ : s.p., number of transients = 8, recycle delay = 800 s, no proton irradiation; (b)  $\text{Na}_4\text{P}_4\text{O}_{12}\cdot 4\text{H}_2\text{O}$ : c.p., number of transients = 12, contact time = 1 ms, recycle delay = 60 s, proton decoupling; (c)  $\text{Na}_6\text{P}_6\text{O}_{18}\cdot 6\text{H}_2\text{O}$ : c.p., number of transients = 24, contact time = 2 ms, recycle delay = 5 s, proton decoupling (the asterisks indicate bands due to impurities); and (d)  $\text{Na}_8\text{P}_8\text{O}_{24}\cdot 6\text{H}_2\text{O}$ : c.p., number of transients = 32, contact time = 2 ms, recycle delay = 5 s, proton decoupling

phosphate at 0.6 p.p.m. broadens beyond detection, Figure 4(b). The *X*-ray crystal structure reveals that one end phosphate is involved in hydrogen bonding to five molecules of water while the other is only associated with one. We, therefore, assign the peak at 0.6 p.p.m. to the highly hydrogen-bonded end phosphate.

Polyphosphates with more than three phosphorus atoms are available but tend to form glasses with a distribution of chain length. The n.m.r. resonances broaden considerably, reflecting a distribution of chemical shift, with sodium polyphosphate end groups resonating at *ca.* 1 p.p.m. and chain groups moving to lower frequency for longer chains, *e.g.* we find resonances at -16.6 p.p.m. for pentapolyphosphate and -20.1 p.p.m. for pentadecapolyphosphate.

(c) *Metaphosphates*. Metaphosphates are more easily purified than long-chain polyphosphates, resulting in markedly simpler liquid-state n.m.r. spectra and crystals which give narrower spectra for the solid state.

Trisodium trimetaphosphate has been studied in its most common, the anhydrous, form. The n.m.r. spectrum of the solid consists of three lines of roughly equal intensity at -15.5, -18.6, and -20.9 p.p.m. [Figure 5(a)] (*cf.* liquid-state resonance at -20.8 p.p.m.). The *X*-ray crystal structure,<sup>23</sup> however, indicates a *Pm $\bar{c}$ n* space group with four molecules per unit cell and a phosphate ring of chair conformation with a mirror plane. The published result of the *X*-ray analysis is, therefore, not consistent with the n.m.r. data since it predicts two identical phosphorus nuclei and a third unique one. One possibility is that our sample contains more than one crystalline form, but powder *X*-ray data of our sample do not indicate that this is the case. The potassium analogue reveals similar multiplicity in the n.m.r. spectrum.<sup>8</sup>

Tetrasodium tetrametaphosphate exists in the anhydrous or tetrahydrate state. We have examined the latter in its  $\alpha$  form. The spectrum of the solid consists of two lines at -19.7 and -22.4 p.p.m. (plus trisodium hydrogenpyrophosphate monohydrate impurity peaks), *cf.* liquid-state resonance at -23.7 p.p.m., Figure 5(b). The *X*-ray crystal structure<sup>24</sup> of this monoclinic form is entirely consistent with the n.m.r. spectrum, revealing a *P2<sub>1</sub>/a* space group, two molecules per unit cell and each molecule containing two pairs of inequivalent phosphorus atoms.

Hexasodium hexametaphosphate hexahydrate yields two resolved resonances of roughly equal intensity at -18.1 and -22.9 p.p.m. (disregarding orthophosphate and pyrophosphate impurity peaks at 1.7 and -8.0 p.p.m. respectively), Figure 5(c), *cf.* solution-state peak at -22.1 p.p.m. The resonance at -18.1 is particularly broad, indicating incomplete resolution of two overlapping resonances. N.m.r. therefore suggests there are three types of phosphorus, two types being similar. The *X*-ray structure<sup>25</sup> reveals a *Cma* space group and three sets of two inequivalent phosphorus atoms per molecule. On the basis of this and preceding data in this work, it appears that n.m.r. readily reveals structural inequivalences in these systems where further refinement of the structural model using *X*-ray diffraction data is questionable.

Octasodium octametaphosphate hexahydrate yields four lines, -15.2, -16.8, -22.9 and a shoulder at *ca.* -21.7 p.p.m., Figure 5(d), *cf.* a solution-state resonance at -21.2 p.p.m. (Once again this sample contains impurities, orthophosphate at 0.9 and pyrophosphate at *ca.* -8 p.p.m.) N.m.r. of the solid therefore suggests that there are two sets of four inequivalent phosphorus atoms per molecule. Dispensing with high-power proton decoupling broadens all resonances equally so that there are no gross differences in water co-ordination. The *X*-ray structure has not been determined.

*Shielding Anisotropy and Asymmetry*.—The shielding anisotropy  $\Delta\sigma$  and the asymmetry factor  $\eta$  yield information primarily on the symmetry of bonding about the phosphorus atom.  $\Delta\sigma$  and  $\eta$  are determined from the break points in the powder pattern of a static polycrystalline sample ( $\sigma_{11}$ ,  $\sigma_{22}$ ,  $\sigma_{33}$ ), or by treatment of the spinning sidebands of a slow-spinning sample.<sup>12,26</sup> In this study the graphical analysis proposed by Herzfeld and Berger<sup>12</sup> has been employed. The convention proposed by Haeberlen<sup>27</sup> is used for the assignment of  $\sigma_{11}$  and  $\sigma_{33}$  such that  $|\sigma_{33} - \bar{\sigma}| > |\sigma_{11} - \bar{\sigma}| \geq |\sigma_{22} - \bar{\sigma}|$  and for axial symmetry  $\sigma_{11} = \sigma_{22}$  and  $\eta = 0$ .  $\bar{\sigma}$  is the isotropic shielding and is one third of the trace of the shielding tensor:  $\bar{\sigma} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3$ . The shielding anisotropy  $\Delta\sigma$  is given by  $\Delta\sigma = \sigma_{33} - (\sigma_{11} + \sigma_{22})/2$  and the asymmetry by  $\eta = (\sigma_{22} - \sigma_{11})/(\sigma_{33} - \bar{\sigma})$ . Rather than calculate  $\eta$  some authors prefer to use  $\sigma_{11} - \sigma_{22}$  as a measure of asymmetry. Duncan and Douglass<sup>7</sup> have used such an approach in their treatment of various phosphates but an element of confusion arises since, having defined  $\sigma_{11}$  and  $\sigma_{33}$  as above, they then proceed to use the convention proposed by Mehring<sup>28</sup> and reverse the assignment by referring to  $\sigma_{33} - \sigma_{22}$ .

The shielding tensors derived in the present work are given in the Table and are quoted with the convention that positive indicates more shielding (lower frequency resonance). The isotropic shielding is, of course, equivalent to the chemical shift obtained from the m.a.s. experiment, but opposite in sign. The isotropic shifts resulting from analysis of all the spinning sidebands ( $-\bar{\sigma}$ ) reproduce the single isotropic resonance positions quite accurately. This can be seen as a measure of the accuracy associated with the full sideband analysis.

Since chemical shielding is determined by the orbital angular momenta of the electrons and this is related to electron density<sup>29</sup> then it follows that the <sup>31</sup>P shielding anisotropy will

reflect the asymmetry of electron density about the P atom. The main factors affecting this will be substituent electronegativity and distance. It should be noted that as  $\eta \rightarrow 1$  the assignment of sign to the shielding anisotropy becomes subject to increasing error. For a totally isotropic system  $\Delta\sigma = 0$  and  $\eta = 0$ . For axial symmetry  $\Delta\sigma$  is finite while  $\eta = 0$ . For non-axial symmetry  $\Delta\sigma$  is finite and  $0 < \eta \leq 1$ .

Orthophosphates might be expected to be isotropic, and this is indeed found for  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ , and previously<sup>8</sup> for  $\text{K}_3\text{PO}_4$ . However, a change in the level of protonation to  $\text{Na}_2\text{HPO}_4$  produces a significant anisotropy ( $-104$  p.p.m.) but retains axial symmetry.  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  exhibits a significant anisotropy and a large asymmetry. Clearly counter ions and hydration have an effect.

Terminal groups in polyphosphates may be expected to have an approximate three-fold axis of local symmetry and hence show axial symmetry of the shielding tensor. This was in fact previously found for sodium and potassium polyphosphates<sup>7,8</sup> but not for  $\alpha\text{-Ca}_2\text{P}_2\text{O}_7$  where  $\eta = 0.55$  and  $0.32$ .<sup>7</sup> In contrast to Duncan and Douglass,<sup>7</sup> we observe deviations from axial symmetry for  $\text{Na}_4\text{P}_2\text{O}_7$ , where  $\eta = 0.25$ . In  $\text{Na}_5\text{P}_3\text{O}_{10}$  (I) the asymmetry of the end group is also finite but low at 0.22, whereas form (II) has a larger asymmetry at 0.44. Again basicity (and hydration) changes disrupt symmetry greatly, with  $\text{Na}_3\text{HP}_2\text{O}_7 \cdot \text{H}_2\text{O}$  (A),  $\eta = 0.74$ ,  $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$ ,  $\eta = 0.92$ , and  $\text{Na}_5\text{P}_3\text{O}_{10} \cdot 6\text{H}_2\text{O}$  somewhat less at  $\eta = 0.57$ . On the other hand, shielding anisotropies vary little and are always negative, within the range  $-119$  to  $-150$  p.p.m.

Chain phosphorus atoms are expected to have at most a two-fold axis of local symmetry and therefore finite  $\eta$ . Finite values of  $\eta$  were observed with no obvious trends emerging. One point, however, is that  $\eta$  is never very large (maximum  $\eta = 0.64$  in  $\text{Na}_6\text{P}_6\text{O}_{18} \cdot 6\text{H}_2\text{O}$ , smaller than some of the asymmetries achieved by end phosphorus atoms). The shielding anisotropy is always positive for chain phosphorus nuclei, as found previously,<sup>8</sup> in clear contrast to the situation for end phosphate groups. The shorter polyphosphate chains (*i.e.* with two or three phosphorus atoms) exhibit  $\Delta\sigma$  in the range 151–180 p.p.m. while metaphosphates have  $\Delta\sigma$  in the range 195–235 p.p.m.

### Conclusions

Phosphorus co-ordination (end or chain), chain length, hydration state, crystalline form, and solid-state molecular distortions all contribute to the isotropic  $^{31}\text{P}$  shifts of solid sodium phosphates.\* For short-chain polyphosphates these effects are of similar magnitude but for longer-chain polyphosphates or metaphosphates, phosphorus co-ordination differences give rise to the largest shifts. Although the information content of spectra is potentially high, the comparatively small range of shifts (6.9 to  $-22.9$  p.p.m.), compared with the large shifts caused by any one of the above effects, means that analysis is almost restricted to the recognition of materials previously calibrated by X-ray diffraction. However, the sign of the shielding anisotropy provides a

definitive assignment of the nature of phosphorus co-ordination (*i.e.* of differentiating end and middle units), thus enabling the measurement of chain length from peak areas. Furthermore, the shielding anisotropy parameters provide additional structural information which is readily interpreted for terminal phosphorus atoms in terms of deviations from axial symmetry.

### Acknowledgements

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\* Note added in proof. Two papers concerning m.a.s. n.m.r. of polycrystalline phosphates have been published recently.<sup>30,31</sup> Haubenreisser *et al.*<sup>31</sup> studied the pentasodium tripolyphosphate and their results are in close agreement with ours. In the case of the hexahydrate however, the third resonance (at 0.6 p.p.m.) was observed as a low-intensity shoulder. Whether the variability in intensity is due to variability in decoupling levels (as suggested in our work) or to the variability in concentration of an impurity remains to be established.