

Salts of Phosphonic Acid Derivatives: Illustrative Examples of Solid State NMR Spectroscopy

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High-resolution solid state ^{13}C , ^{23}Na and ^{31}P NMR data have been obtained for the acid form and for several salts of the phosphonic acids: ethane-1,2-diphosphonic acid, ethane-1-hydroxy-1,1-diphosphonic acid (HEDP), and 3-amino-1-hydroxypropane-1,1-diphosphonic acid. The data provide evidence by which sample purity and crystallinity may be examined and from which the size of the asymmetric unit may be determined. In the case of the sodium salts of ethane-1,2-diphosphonic acid, the ^{31}P and ^{23}Na spectra provide evidence of possible motion or bond fluctuonality for the phosphonic acid group.

Introduction

We have recently been involved in solid state NMR studies of organo-phosphonic and -phosphinic acids [1, 2] and of aminophosphonic acids [3]. During the course of this work we also examined a small number of the possible salts of these acids. While the scope of this examination was selective rather than exhaustive, a number of interesting and useful results were obtained. In this paper, we would like to present these results with an eye towards illustrating several practical applications of solid state NMR. It will be seen how solid state NMR may be used to address problems of sample purity and crystallinity, to provide information on the size of the asymmetric unit for crystalline compounds, and to perhaps give some clues to the presence of possible motion or bond fluctuonality.

A list of compounds examined in this study, all of which are diphosphonic acids, may be found in Table I. The phosphonic acid group has the general structure noted below. Interest in these compounds stems from their chelation properties, from questions

of hydrogen bonding, and from comparison with carboxylic acid and amino acid analogues.

Results and Discussion

The first and perhaps most obvious questions when dealing with an apparently crystalline salt are those of purity and crystal composition. That is to say, while a solution from a given titration has a certain stoichiometry, the crystals recovered from that solution may not necessarily be pure or may be of a mixed crystal composition. This point is most clearly illustrated by examining Fig. 1.

Figure 1 shows the ^{31}P cross-polarization/magic-angle spinning (CP/MAS) spectra of the acid form and the di-, tri-, and tetrasodium salts of ethane-1-hydroxy-1,1-diphosphonic acid (HEDP). (Phosphorus-31 and carbon-13 solid state chemical shift and coupling constant data for the HEDP compounds may be found in Table I.) The acid form will be discussed first. The ^{31}P spectrum (Fig. 1a) consists of two AX doublets with shifts of 25.3 and 18.7 ppm and a $|J_{\text{PP}}|$ of 52 Hz. The ^{13}C spectrum (not shown) consists of a single resonance in the methyl region and an apparent triplet at 70.1 ppm with an average $|J_{\text{PC}}|$ of 154 Hz. The ^{31}P and ^{13}C spectra of the acid compound have been discussed previously [1]. The important fact is that the indicated structure is one of a single-molecule asymmetric unit with the two phosphorus atoms within the molecule being inequivalent. The size of the asymmetric unit is most strongly suggested by the presence of only a single methyl resonance. From the indicated structure, it



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Table I. Solid state ^{31}P and ^{13}C NMR data^a for phosphonic acids^b.

Compound	$\delta_{\text{P}}/\text{ppm}$		$\delta_{\text{C}}/\text{ppm}$		$ J_{\text{PP}} /\text{Hz}$	$ J_{\text{PC}} /\text{Hz}$	Asymmetric unit ^c /molecule
(1) Ethane-1,2-diphosphonic acid $\text{P}^*-\text{CH}_2-\text{CH}_2-\text{P}^*$	32.7	—	—	—	—	—	1/2
(2) $\text{P}^*-\text{CH}_2-\text{CH}_2-\text{P}^* \text{Na}_2 \text{ salt} \cdot 4 \text{H}_2\text{O}$	29.3	—	—	—	—	—	1/2
(3) $\text{P}^*-\text{CH}_2-\text{CH}_2-\text{P}^* \text{Na}_4 \text{ salt}$	24.8	—	—	—	—	—	1/2
(4) Ethane-1-hydroxy-1,1-diphosphonic acid (HEDP) $\begin{array}{c} \text{P}^* \\ \\ \text{CH}_3-\text{C}-\text{OH} \cdot 1 \text{H}_2\text{O} \\ \\ \text{P}^* \end{array}$	25.3 ^d	18.7 ^d	70.1 ^e	17.1	51.8	154	1
(5) HEDP $\text{Na}_2 \text{ salt} \cdot 4 \text{H}_2\text{O}$	23.8	22.5	70.8 ^e	19.2	—	151	1
(6) HEDP $\text{Na}_3 \text{ salt} \cdot 6 \text{H}_2\text{O}$	27.8	18.4	71.7 ^e	21.6	—	148	1
(7) HEDP $\text{Na}_4 \text{ salt}$	27.8 20.9	22.2 18.4	28.4 ^f	24.1 21.6	—	—	?
(8) HEDP $\text{Ca}_2 \text{ salt}$	23.1	19.2	72.5	19.7	—	138	1
(9) 3-Amino-1-hydroxypropane-1,1-diphosphonic acid $\begin{array}{c} \text{P}^* \\ \\ \text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{C}-\text{OH} \\ \\ \text{P}^* \end{array}$	15.9	12.8	72.9 32.3 35.7 ^g	—	—	158	1
(10) $\begin{array}{c} \text{P}^* \\ \\ \text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{C}-\text{OH} \text{Na}_2 \text{ salt} \\ \\ \text{P}^* \end{array}$	17 to 25 ^h	h	—	—	—	—	?

^a Estimated errors: $\delta_{\text{P}} \pm 0.1 \text{ ppm}$; $|J| \pm 10 \text{ Hz}$; ^b P^* represents the PO_3H_2 group. For the aminophosphonic acid compounds **9** and **10**, the actual structure is a zwitterion; ^c from the present ^{13}C and ^{31}P solid state NMR data; ^d doublet; ^e triplet; ^f in addition there is a band at *ca.* 70 ppm which shows no fine structure; ^g these shifts may be assigned to the C-1, C-2 and C-3 carbon atoms respectively; ^h broad and unresolved.

will be noted that the carbon triplet is in principle an unresolved doublet of doublets. This assignment is confirmed by the diffraction study of Uchtman and Gloss [4].

The ^{31}P spectrum of HEDP disodium salt tetrahydrate (Fig. 1b) consists of two broad, overlapping singlets at 23.8 and 22.5 ppm. Both resonances show only moderate shifts from those for the acid form. The (P, P) scalar coupling for this compound is unresolved, as it is for all of the HEDP salts. The broadening which limits resolution most probably arises because the dipolar coupling to quadrupolar ^{23}Na is not completely removed by MAS. Such effects for sodium phosphates have been reported by several authors [5, 6]. The effects may also account

for the difference in linewidths between the ^{31}P resonances if, for example, one of the two phosphorus atoms in the molecule lies closer to the sodium atoms than the other. The crystal structure of the disodium salt is known [7], and from the atomic coordinates the non-bonding distances may be calculated. One phosphorus is clearly closer to both sodium atoms (the phosphorus to sodium distances are: P(1): 3.598 Å, 3.513 Å; P(2): 3.332 Å, 3.211 Å). While P–Na dipolar couplings for such distances are only of the order of 275 to 390 Hz, the fact that one phosphorus atom has shorter phosphorus to sodium distances may account for the discrepancy in linewidths noted in Fig. 1b. It should be noted that the general increase in linewidth observed in the ^{31}P spectrum of

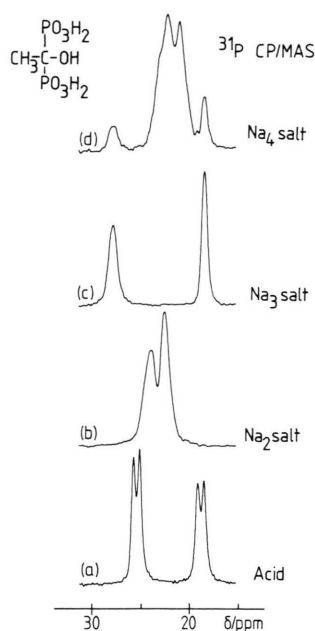


Fig. 1. ^{31}P CP/MAS centreband spectra of the derivatives of HEDP showing the effect upon successive neutralization steps. (A) HEDP acid (4). Contact time, 5 ms; recycle delay, 10 s; spinning speed, 3055 Hz; number of transients, 112. (B) HEDP disodium salt tetrahydrate (5). Contact time, 1 ms; recycle delay, 5 s; spinning speed, 3360 Hz; number of transients, 80 (C) HEDP trisodium salt hexahydrate (6). Contact time, 1 ms; recycle delay, 15 s; spinning speed, 2675 Hz; number of transients, 64. (D) HEDP tetrasodium salt (7). Contact time, 1 ms; recycle delay, 15 s; spinning speed, 2945 Hz; number of transients, 100.

the salt as compared with the acid does not, in this case, indicate a significant loss of sample crystallinity. This is shown by the fact that there is essentially no difference in the ^{13}C linewidths between the acid and salt spectra. The ^{13}C spectrum for the disodium salt, as for the acid form, consists of a singlet in the methyl region, and a triplet at *ca.* 70 ppm with an average $|J_{\text{PC}}|$ of 151 Hz. The ^{31}P and ^{13}C spectra thus indicate that there is a single molecule in the asymmetric unit. This is confirmed by the X-ray crystal structure of Barnett and Strickland [7]. Further, as no other resonances are found, the spectra indicate that the sample is essentially pure. Similar conclusions may be drawn for HEDP trisodium salt hexahydrate (Fig. 1c). In this spectrum, the phosphorus shifts of 27.8 and 18.4 ppm show only small displacements from those of the acid. The ^{13}C spectrum is again a singlet and a triplet which has an average $|J_{\text{PC}}|$ of 148 Hz.

The situation changes somewhat on examination of the ^{31}P spectrum of the tetrasodium salt of HEDP (Fig. 1d). This solid was prepared from a solution of the correct stoichiometry and has the appearance of a finely crystalline, homogeneous material. However, this sample is clearly shown by solid state NMR to be impure, of mixed crystal composition, or both. The centreband ^{31}P spectrum consists of a broad central section composed of at least three resonances and two, somewhat weaker outer resonances. The outer resonances of the centreband (27.8 and 18.4 ppm) almost certainly arise from crystals having the composition of the trisodium salt, as can be clearly seen from the stacked plot of the HEDP series in Fig. 1 and from the shift values given in Table I. Further, in the carbon spectrum, three resonances are resolved in the methyl region. One of these resonances (21.6 ppm) has the same shift as the methyl group of the trisodium salt, thus supporting the presence of crystals of this compound in the „tetrasodium salt“ sample. The remaining resonances in both the ^{13}C and ^{31}P spectra do not correspond to shifts of the three previous compounds. It is not clear, however, what particular salt species gives rise to these lines.

Before leaving the HEDP series, two additional points should be noted. Firstly, the dicalcium salt of HEDP gives spectra very similar to the two “pure” sodium salts of HEDP. The ^{31}P spectrum consists of two resonances with $|J_{\text{PP}}|$ unresolved; the ^{13}C spectrum is again composed of a singlet in the methyl region and a triplet at *ca.* 70 ppm with an average $|J_{\text{PC}}|$ of 138 Hz (see Table I for exact ^{31}P and ^{13}C shift data). Secondly, unlike the sodium salts of ethane-1,2-diphosphonic acid (*vide infra*), the ^{31}P chemical shifts for the sodium salts of HEDP do not show a simple trend as protons are subsequently replaced by sodium ions. (Indeed, from examination of the spectra in the stack plot of Fig. 1 and comparison of their linewidths, it seems likely that the two resonances cross over between **1a** and **1c**.) There are probably a number of reasons for the lack of a simple trend including: 1) the effect of the hydroxyl group; 2) a more complicated hydrogen bonding structure resulting from the closer proximity of the phosphonic acid groups; and 3) chemical shift changes due to crystallographic distortions.

Let us now turn our attention to the derivatives of ethane-1,2-diphosphonic acid. The ^{31}P and ^{23}Na spectra of the sodium salts of this acid provide inter-

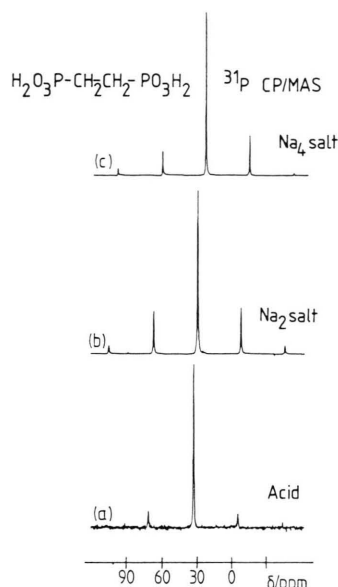


Fig. 2. ^{31}P CP/MAS spectra of the derivatives of ethane-1,2-diphosphonic acid plotted with aligned scales. (A) Acid (1). Recycle delay, 30 s; spinning speed, 3083 Hz; number of transients, 64. (B) Disodium salt tetrahydrate (2). Recycle delay, 45 s; spinning speed, 3004 Hz; number of transients, 48. (C) Tetrasodium salt (3). Recycle delay, 30 s; spinning speed, 2997 Hz; number of transients, 32. All three spectra were run with a contact time of 1 ms.

esting insights into questions of possible structure and motion in these salts. The ^{31}P spectrum of the acid form (Fig. 2a) is a single line with a chemical shift of 32.7 ppm and a half-height width of 61 Hz. The presence of a single phosphorus environment suggests an asymmetric unit consisting of half a molecule. This is confirmed by the crystal structure of Peterson *et al.* [8]. The X-ray data show the molecule to be of space group $\text{P}2_1/c$ with a centre of inversion symmetry at the midpoint of the C–C bond.

The phosphorus spectra of the di- and tetrasodium salts (Fig. 2b and 2c) are both single narrow lines with shifts of 29.3 and 24.8 ppm respectively. Now the retention of only a single type of phosphorus environment is interesting in that it implies either that the sodium ions replace the protons symmetrically in the crystal lattice, or that there is a large degree of motion in these salts. In addition, even if the sodium ions are incorporated symmetrically, it is noteworthy that the addition of these atoms does not produce distortions in the lattice which render the two phosphorus atoms in the molecule inequivalent.

As can be seen from the static and slow spinning spectra of these samples (Fig. 3), the shielding tensor patterns for the two salts are quite different (complete shielding data for these compounds may be found in Table II). The disodium salt has an essentially asymmetric pattern ($\eta = 0.86$), while that of the tetrasodium salt is nearly axially symmetric ($\eta = 0.19$). (It should be noted that this latter value is probably axially symmetric within experimental error. The difficulty of determining the asymmetry parameter near the axially symmetric limit has been discussed by several authors [9, 10].) It is felt that the pattern of the disodium salt arises because there will be at least one oxygen on each phosphorus still involved in hydrogen bonding. This would both limit motion and create inequivalences in the oxygens which would lead to an asymmetric shielding environment. Further, this must be true for essentially all of the phosphorus atoms, as the ^{31}P spectra show only a single phosphorus site. The nearly axial sym-

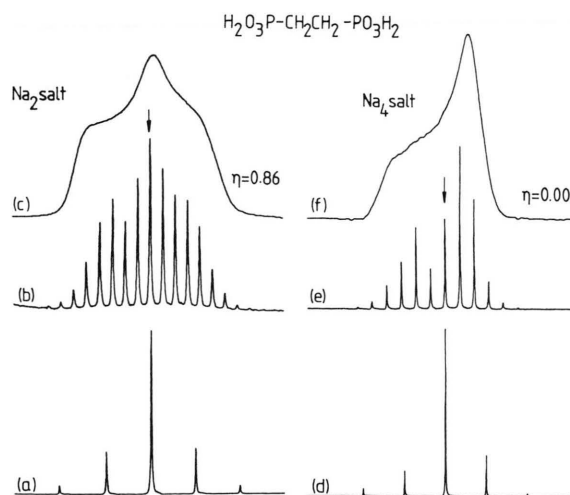


Fig. 3. Static and slow spinning ^{31}P spectra of the derivatives of ethane-1,2-diphosphonic acid. Left: disodium salt tetrahydrate (2). Right: tetrasodium salt (3). (A) CP/MAS. Spinning speed, 3004 Hz; number of transients, 48. (B) CP/MAS. Spinning speed, 840 Hz; number of transients, 80. (C) Static. Number of transients, 1038. (D) CP/MAS. Spinning speed, 3000 Hz; number of transients, 52. (E) CP/MAS. Spinning speed, 1060 Hz; number of transients, 100. (F) Static. Number of transients, 1040. For all spectra the recycle delay was 45 seconds. For the CP/MAS spectra the contact time was 1 ms. Static spectra were obtained in a high-power proton decoupled single pulse mode using a $1\ \mu\text{s}$, 18° excitation pulse.

Table II. ^{31}P Shielding tensor data^a for the phosphonic acids.

Compound	Shielding tensor components					
	$\bar{\sigma}$	$\perp$	η	σ_{11}	σ_{22}	σ_{33}
Phosphonic acids						
(1) $\text{P}^*-\text{CH}_2-\text{CH}_2-\text{P}^*$	-32.7	48.2	0.241	-62.6	-51.0	15.5
(2) $\text{P}^*-\text{CH}_2-\text{CH}_2-\text{P}^* \text{Na}_2 \text{ salt} \cdot 4 \text{H}_2\text{O}$	-29.3	-61.3	0.857	27.6	-24.9	-90.6
(3) $\text{P}^*-\text{CH}_2-\text{CH}_2-\text{P}^* \text{Na}_4 \text{ salt}$	-24.8	-59.6	0.185 ^b	10.5	-0.5	-84.4
(5) HEDP $\text{Na}_2 \text{ salt} \cdot 4 \text{H}_2\text{O}$	-23.8	-74.5	0.885	46.4	-19.5	-98.3
	-22.5	-71.7	0.858	44.1	-17.4	-94.2
(6) HEDP $\text{Na}_3 \text{ salt} \cdot 6 \text{H}_2\text{O}$	-27.8	-66.6	0.967	37.7	-26.7	-94.4
	-18.4	-73.6	0.389	32.7	4.1	-92.4

^a Given in ppm, except for η (which is dimensionless); ^b actually, axially symmetric within experimental error. Note: The shielding tensor values for compounds **2** and **3** were determined from static spectra and are thus quoted to ± 2 ppm. All other values were obtained by spinning-sideband analysis and are given to ± 5 ppm.

metry for the tetrasodium salt implies equivalence of the three oxygens. Such equivalence may arise from bond fluctuality on the NMR timescale, from electronic equivalence of the oxygens or from rapid rotation about the C_3 axis.

The sodium-23 spectra of these two compounds shed additional light onto the considerations here; however, first a short digression into the basic principles of the NMR of quadrupolar nuclei is perhaps necessary. Nuclei with spin $> 1/2$ possess a nuclear electric quadrupole moment which interacts with the electric field gradient (EFG) at the nucleus. For such nuclei, the spectrum will depend on the relative con-

tributions of the Zeeman and quadrupolar interactions and upon the symmetry of the site of the nucleus in question. The latter point is important in that for a cubic site, the electric field gradient goes to zero, and, as a result, the coupling term vanishes. For ^{23}Na in a nearly cubic environment or in an environment with sufficient motion to effectively average the EFG tensor to zero, the first order quadrupole interaction gives rise to a relatively sharp central line (corresponding to the $+1/2, -1/2$ transition) and to two relatively broad absorptions from the satellite transitions ($3/2, 1/2$ and $-1/2, -3/2$). Under such conditions, MAS will further sharpen the central transi-

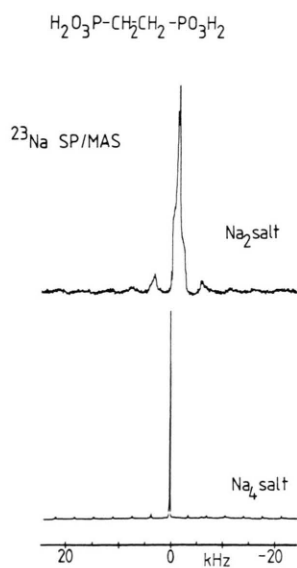


Fig. 4. ^{23}Na single pulse spectra of the sodium salts of ethane-1,2-diphosphonic acid. Top: disodium salt tetrahydrate (**2**). Recycle delay, 4 s; spinning speed, 4.6 kHz. δ_{Na} of the maxima in the centreband are -21 and -26 ppm and it is *ca.* 2800 Hz wide. Bottom: tetrasodium salt (**3**). Recycle delay, 5 s; spinning speed, 3.6 kHz; $\delta_{\text{Na}} = 2$ ppm. The number of transients in both cases was 64.

tion and break-up the satellite transitions into a number of sidebands. If the site symmetry is lower than cubic, the quadrupolar coupling will become large. The resulting NMR spectrum will still have a strong central transition; however, this will be broadened and show additional structure due to second order quadrupolar effects. These effects will not be completely averaged by MAS. Moreover, the satellite transitions may now cover such a wide frequency range that the spinning sideband signals will not be detectable above the noise level.

The sodium-23 MAS spectra of these salts show a significant contrast between the two materials. The ^{23}Na spectrum of the disodium salt, Fig. 4 (top), shows a broad centreband indicative of an asymmetric environment. For the tetrasodium salt, the ^{23}Na centreband is quite narrow with a spinning sideband manifold greater than 125 kHz wide. For this to be the case, the sodium would have to be in a relatively symmetric or a highly mobile environment. This supports the above analysis of the shielding tensor patterns. As a footnote to the preceding discussion, it should be commented that sample **3** is the only compound examined in this study which had a relatively narrow sodium-23 resonance. All of the other compounds gave broad spectra which more closely resembled Fig. 4 (top).

It should be noted from Fig. 2 and Table I that the ^{31}P shift decreases as one moves from the acid through the disodium salt to the tetrasodium salt ($\delta_{\text{P}} = 32.7, 29.3$, and 24.8 ppm respectively). This trend agrees with the results obtained by Moedritzer and Irani [11] for these compounds in the solution state ($\delta_{\text{P}} = 27.4, 23.3$, and 22.4 ppm). Possible causes for the increase in shielding in solution may include a differing charge at the phosphorus nucleus and/or a change in the P–O bond distances and angles.

The remaining example is that of the sodium salt of 3-amino-1-hydroxypropane-1,1-diphosphonic acid. Fig. 5 shows the ^{31}P spectrum of the disodium salt of this compound along with that of the acid form for reference. As has been previously reported [3], the ^{13}C , ^{15}N and ^{31}P spectra of the acid form of this compound can be fully assigned, and consist of narrow lines indicative of a highly crystalline environment. Further, the presence of a single central methylene resonance and a single nitrogen resonance strongly suggests a single-molecule asymmetric unit. However, as may be seen from Fig. 5, the ^{31}P spectrum of the salt is broad, covering a range from 17 to

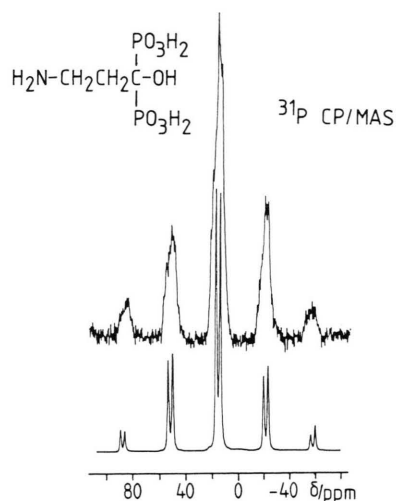


Fig. 5. ^{31}P CP/MAS of the derivatives of 3-amino-1-hydroxypropane-1,1-diphosphonic acid. Bottom: Acid form (9). Recycle delay, 5 s; number of transients, 64. Top: Disodium salt (10). Recycle delay, 15 s; number of transients, 126. In both cases the contact time was 1 ms and the spinning speed was 2.9 kHz.

25 ppm, and contains no useful fine structure. (The ^{13}C and ^{15}N spectra of the salt show similar loss of resolution as compared to the acid form.) It is felt that the appearance of the spectrum of the disodium salt results from a general decrease in short range order as compared with the acid. This loss in short range order is manifested by the loss of fine structure in the spectrum and by an increase in the range of chemical shifts observed as compared to the acid form. It should be noted that a ^{31}P spectrum of the disodium salt was also run at a higher magnetic field (7.0 Tesla as opposed to 4.7 Tesla). The half-height linewidth in ppm was the same (*ca.* 7.8 ppm) for the spectra at both fields. This being the case, it is unlikely that the broadening observed arises from unaveraged dipole coupling between the ^{31}P nuclei and the quadrupolar ^{23}Na nuclei.

Experimental

The solid-state spectra in this work were obtained using a Bruker CXP-200 spectrometer equipped with the standard 7 mm double-bearing probe system and operating at a magnetic field of 4.7 Tesla. The ^{13}C , ^{23}Na and ^{31}P frequencies for this spectrometer are 50.323, 52.938 and 81.014 MHz, respectively. Samples were contained in zirconia rotors which were fitted with Kel-F end-caps. For the ^{31}P and ^{13}C cross-polarization/magic-angle spinning experiments, typical operating parameters were: 4 μs 90° ^1H pulse;

contact time: 1–5 ms; recycle delay: 10–60 s; spinning speed: 3 kHz; and number of transients: 32–300. The sodium-23 spectra were acquired in single-pulse mode using a $2\ \mu\text{s}\ \pi/4$ excitation pulse. Specific experimental details are noted in the figure legends.

The high-frequency-positive convention has been used in the reporting of chemical shifts (δ). Carbon-13 shifts have been referenced indirectly to the ^{13}C signal of tetramethylsilane. This was done using the high frequency resonance of adamantane as a secondary reference. The shift of this adamantane line was determined to be $+38.5 \pm 0.1$ ppm by replacement with TMS. The sodium-23 spectra were referenced to Na^+ at infinite dilution [12]. This was done by replacement by the secondary reference compound solid NaCl, which has a shift of 7.1 ppm. The ^{23}Na shifts were not corrected for quadrupolar effects. The phosphorus shifts have been indirectly referenced to 85% aqueous phosphoric acid (H_3PO_4). The secondary reference used was brushite, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, the shift of which was determined to be 1.2 ± 0.1 ppm by replacement with the standard.

The convention chosen for the reporting of shielding tensor (σ) information in Table II is that of Haeberlen [13].

The isotropic shielding is:

$$\bar{\sigma} = 1/3 \text{Tr } \sigma \equiv 1/3 (\sigma_{11} + \sigma_{22} + \sigma_{33}).$$

The three tensor components, σ_{11} , σ_{22} and σ_{33} are assigned as follows:

$$|\sigma_{33} - \bar{\sigma}| \geq |\sigma_{11} - \bar{\sigma}| \geq |\sigma_{22} - \bar{\sigma}|.$$

The anisotropy Δ and asymmetry η are defined respectively as:

$$\Delta = \sigma_{33} - \bar{\sigma}$$

and

$$\eta = (\sigma_{22} - \sigma_{11})/\Delta.$$

The Hebrew symbol beth ($\beth$) is used for the anisotropy as has been suggested by Harris *et al.* [14].

Compound **1** was provided by Hoechst AG, Frankfurt, and Knapsack. Compounds **2** and **3** were prepared by the Düsseldorf group [15]. The remaining chemicals were provided by Henkel KGaA, Düsseldorf. The purity of all compounds was checked by solution-state ^{31}P NMR: the samples dissolved completely, leaving no residue, and the spectra indicated that a single phosphorus environment was present in each case.

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