

## Correlation of $^{31}\text{P}$ chemical shift parameters to molecular structures of hexacoordinate organophosphorus compounds in the solid state

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$^{31}\text{P}$  principal elements of chemical shift tensors  $\delta_{ii}$  for a series of hexacoordinate organophosphorus compounds have been obtained from spinning sideband intensities employing the MASNMR program based on a graphical method of Berger and Herzfeld. It was found that anisotropy parameters  $\Delta\delta$  and span  $\Omega$  reflect the distortion of the molecular structure from the ideal octahedral geometry. The asymmetry parameter  $\eta$  and skew  $\kappa$  suggest that the phosphorus shielding depends not only on the local bonding, but also on the octahedral structure as a whole. Comparison of isotropic chemical shifts in solution and in solids revealed that in both phases the molecular structures are not changed. Moreover, this work shows that for  $\text{P}^{\text{VI}}$  moieties with unknown X-ray structure, crucial information regarding the geometry can be obtained from solid-state NMR data and a molecular modelling approach.

In recent years solid-state NMR spectroscopy has become a powerful technique to study the properties of powder patterns.<sup>1,2</sup> In particular, the  $^{31}\text{P}$  nucleus, because of the 100% natural abundance and high sensitivity, can provide unique information about the structure and dynamics of investigated material in easy experiments and in a reasonable time period.

Several relationships between  $^{31}\text{P}$  shielding parameters and molecular structures of tetra-coordinate compounds have been reported. The linear relationship between the asymmetry parameters and the intracyclic O–P–O bond angle for a series of thiooxyphosphates was found by Dutasta *et al.*<sup>3</sup> Turner *et al.* have shown that  $^{31}\text{P}$  chemical shift anisotropy (CSA) increases linearly with deviation of the O–P–O angle from the tetrahedral value.<sup>4</sup> Similar conclusions regarding the CSA and the degree of departure from cubic symmetry was obtained by Herzfeld *et al.*<sup>5</sup> Grimmer observed a linear relationship between the chemical shift anisotropy and the P–O bond length for various axially symmetric halogenophosphates.<sup>6</sup> Correlation of the  $^{31}\text{P}$  chemical shift tensor and the shielding parameters to the molecular structure of bis(organothiophosphoryl) disulfides was reported by Potrzebowski.<sup>7</sup> Moreover, Maciel and co-workers have analysed the series of pentacoordinate phosphorus compounds to see the differences in  $\delta_{\text{iso}}$  values in the solid and liquid phase.<sup>8</sup>

Because of high instability, the studies of hexacoordinated organophosphorus compounds by  $^{31}\text{P}$  solid-state NMR spectroscopy are limited to very few examples. Holmes and co-workers, searching for models of pentaoxyphosphoranes with a ring system in the diequatorial as well as axial–equatorial position have compared the  $^{31}\text{P}$  isotropic chemical shift in the solid state and liquid phase to distinguish between the pentacoordinate system and the pseudo-hexacoordinate member.<sup>9</sup>

### Results and discussion

#### $^{31}\text{P}$ CP MASNMR studies

This paper describes  $^{31}\text{P}$  cross polarization magic angle spinning (CP MAS) studies of six hexacoordinated compounds **I**, **II**, **IIIa**, **b**, **c** and **IV**. The geometrical parameters, bond lengths, bond angles and numbering system around the central phosphorus atom are shown in Table 1. All structures are octahedral. In cases **II** and **III**, deviation from an ideal geometry is seen.

Although replacement of the oxygen by nitrogen (compound **II**) causes changes in bond lengths and bond angles due to the presence of a five-membered ring formed by bipyridyl, the overall geometry is only slightly distorted. A substituted six-membered ring attached to phosphorus has a more significant influence on octahedral geometry. For **III**, the O(5)–P–O(6) angles are considerably larger than the appropriate bond angles in five-membered rings. In molecules **IIIa–c** dioxaphosphorinane rings are in (a) chair, (b) chair and boat and (c) boat conformations. The different conformations of six-membered rings do not affect the local environment of phosphorus centres.

In an ideal geometry octahedral atoms found at opposite sides of phosphorus should be in a line giving bond angles  $180^\circ$ . Assuming that the degree of distortion from octahedral ( $\Delta^\circ$ ) can be expressed by the difference between  $180^\circ$  and the average value of opposite atom angles the following values of  $\Delta^\circ$  were established: (i) for compound **I**, which is ideally symmetrical, all angles [O(1)–P–O(5), O(2)–P–O(4), O(3)–P–O(6)] are equal to  $178.7^\circ$  and  $\Delta^\circ$  is  $1.3^\circ$ , (ii) for compound **II**,  $\Delta^\circ$  is  $7.4^\circ$ , (iii) for compounds **IIIa**, **b** and **c** the values  $\Delta^\circ$  are  $6.1^\circ$ ,  $5.4^\circ$  and  $6.5^\circ$ , respectively.

The calculated values of  $\Delta^\circ$  are very small, however, owing to great sensitivity of phosphorus nuclei to changes in the local environment even such subtle effects can be easily recognized by high-resolution NMR techniques in the solids. Fig. 1 displays  $^{31}\text{P}$  CP MAS spectra for selected compounds.

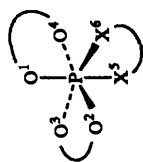
In compounds **II** and **IV** the phosphorus is directly bonded to the quadrupole nucleus  $^{14}\text{N}$  ( $I = 1$ ). As reported by several authors the MAS line shape for the isotropic signal of a spin  $I = 1/2$  nucleus bonded to an  $I = 1$  nucleus with a large electric field gradient (efg) is usually observed as an asymmetric doublet.<sup>10–13</sup> The line shape strongly depends on the orientation of the efg with respect to the molecular frame. The line-width for **II** observed at half-height of the  $^{31}\text{P}$  CP MASNMR spectrum is 220 Hz. The corresponding results for **I** and **III** are found to be 80 and 120 Hz, respectively. Thus it can be speculated that in this case the nuclear quadrupolar coupling causes only broadening of the  $^{31}\text{P}$  resonances and splitting is in the range 100–150 Hz. Similar values were reported by Curtis *et al.* for other P–N systems.<sup>14</sup>

Moreover, for dipolar coupled spectra, the relationship between sample speed rotation as well as dipolar coupling and

Table 1 Selected geometrical parameters in a series of hexacoordinated phosphorus compounds

Compound	Bond lengths/Å						Bond angles (°)						Ref.
	P-O(1)	P-O(2)	P-O(3)	P-O(4)	P-X(5) <sup>a</sup>	P-X(6) <sup>a</sup>	O(1)-P-O(2)	O(3)-P-O(4)	X(5)-P-X(6)	O(1)-P-O(3)	O(1)-P-X(5)	O(2)-P-O(4)	
I	1.723	1.706	1.706	1.724	1.707	1.724	91.4	91.3	91.3	92.7	178.7	178.7	178.7
II	1.671	1.668	1.668	1.672	1.899	1.896	92.8	93.1	81.7	95.7	172.5	172.7	171.5
IIIa	1.757	1.735	1.796	1.719	1.662	1.630	89.4	88.7	98.0	86.7	172.7	173.6	175.4
IIIb	1.753	1.708	1.797	1.710	1.666	1.633	89.8	89.2	97.6	86.3	172.5	175.5	175.7
IIIc	1.763	1.702	1.762	1.731	1.658	1.670	91.5	89.2	97.9	87.2	170.0	173.1	177.5

<sup>a</sup> For I and III, X(5) = O; for II, X(5) = X(6) = N.

Table 2 <sup>31</sup>P chemical shift parameters for a series of hexacoordinated phosphorus compounds<sup>a</sup>

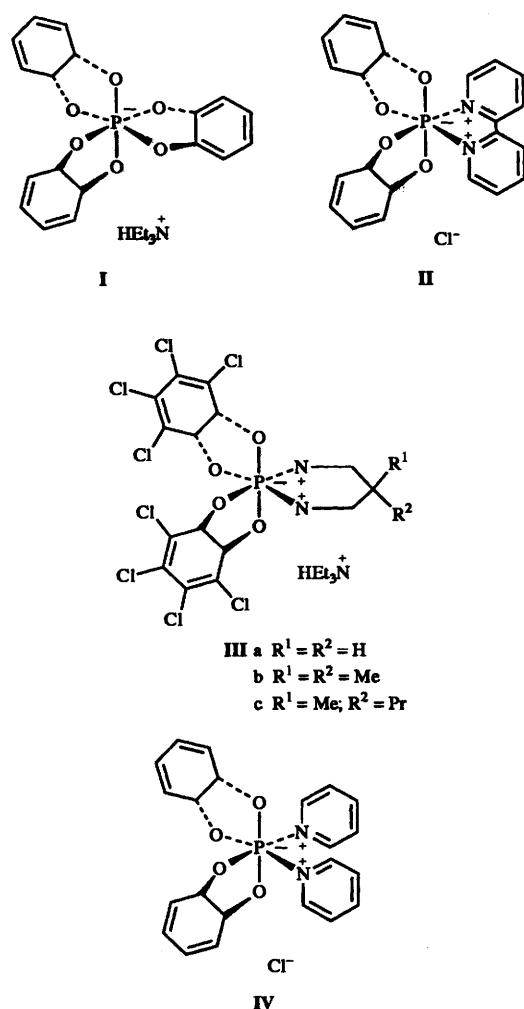
Compound	$\delta_{\text{iso}}$ liquid	$\delta_{\text{iso}}$ solid	$\delta_{11}$	$\delta_{22}$	$\delta_{33}$	$\Delta\delta$ (ppm)	$\Omega$ (ppm)	$\eta$	$\kappa$
I	-82.9	-81.3	-76	-82	-86	8	10	0.57	0.21
II	-95.0	-95.6	-77	-99	-111	28	34	0.63	0.10
IIIa	-99.8	-100.1	-76	-93	-131	46.4	55	0.56	0.13
IIIb	-100.1	-97.8	-76	-89	-127	44.6	51	0.43	0.17
IIIc	-98.7	-93.7	-69	-85	-127	49.3	58	0.44	0.15
IV	-100.1	-101.5	-48	-118	-138	79.4	90	0.39	-0.18

<sup>a</sup> Errors in the experimental principal components of the chemical shift tensor are  $\pm 5$  ppm. The principal components  $\delta_{ii}$  were used for calculation of the shielding parameters. Anisotropy  $\Delta\delta$ , symmetry  $\eta$ , span  $\Omega$  and skew  $\kappa$  are defined as: If  $|\delta_{11} - \delta_{\text{iso}}| > |\delta_{33} - \delta_{\text{iso}}|$  then  $\Delta\delta = \delta_{11} - (\delta_{22} + \delta_{33})/2$ ,  $\eta = (\delta_{22} - \delta_{33})/(\delta_{11} - \delta_{\text{iso}})$ . If  $|\delta_{11} - \delta_{\text{iso}}| < |\delta_{33} - \delta_{\text{iso}}|$  and  $\delta_{11} > \delta_{22} > \delta_{33}$  then  $\Delta\delta = \delta_{33} - (\delta_{11} + \delta_{22})/2$ ,  $\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{\text{iso}})$ . Moreover  $\Omega = \delta_{11} - \delta_{33}$ ,  $\kappa = (\delta_{22} - \delta_{\text{iso}})/\Omega$ .

Table 3 Selected geometrical parameters in a series of hexacoordinated phosphorus compounds taken from MM + calculation

Compound	Bond lengths/Å						Bond angles (°)						
	P-O(1)	P-O(2)	P-O(3)	P-O(4)	P-X(5) <sup>a</sup>	P-X(6) <sup>a</sup>	O(1)-P-O(2)	O(3)-P-O(4)	X(5)-P-X(6)	O(1)-P-O(3)	O(1)-P-X(5)	O(2)-P-O(4)	O(3)-P-X(6)
I	1.722	1.722	1.722	1.722	1.722	1.722	88.0	88.0	88.0	92.0	177.1	177.1	177.3
II	1.728	1.724	1.729	1.729	1.787	1.787	87.4	87.4	83.7	82.2	174.9	178.6	174.9
IV	1.719	1.680	1.719	1.688	1.844	1.775	88.4	84.6	81.3	76.5	155.4	146.5	152.1

<sup>a</sup> For I, X(5) = X(6) = O; for II and IV, X(5) = X(6) = N.



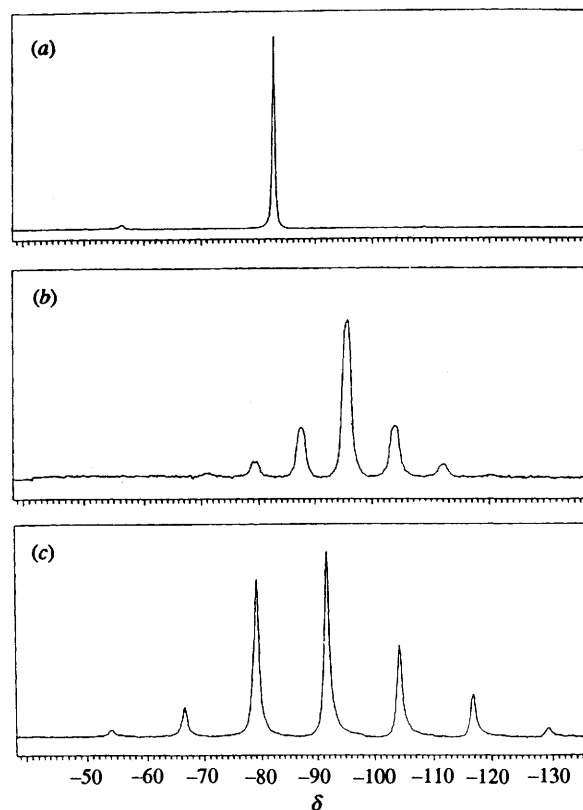
chemical shift anisotropy is crucial for analysis of the MAS line shape. The dipolar interactions constant  $D_{AB}$  expressed by eqn. (1) is dependent only on the inverse cube of the separation of

$$D_{AB} = [(\gamma_A \gamma_B \hbar) / 2\pi] \langle r_{AB}^{-3} \rangle (\mu_0 / 4\pi) \quad (1)$$

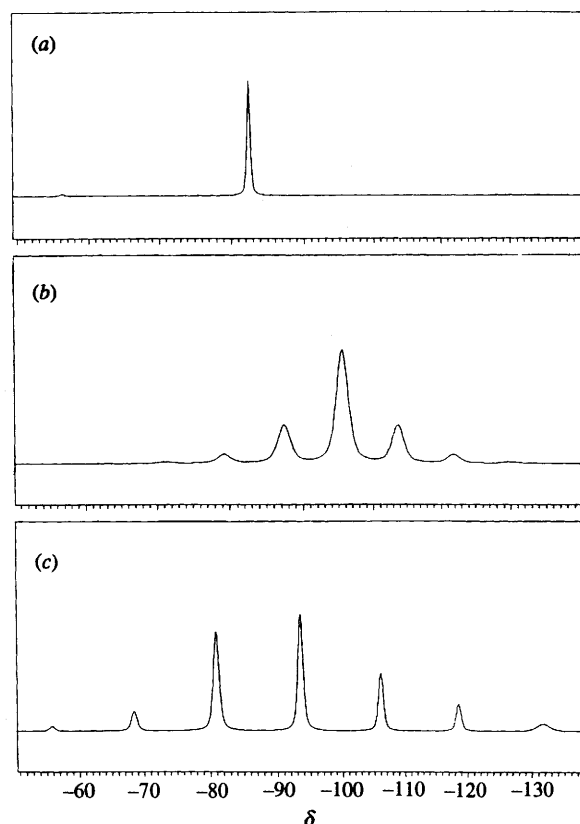
two nuclei A and B. For compound **II**,  $D_{AB}$  calculated using the P–N distance taken from X-ray crystallographic data (1.899 Å) was found to be *ca.* 514 Hz. Thus, it can be concluded that in this case, even under slow rotation of samples the line shape and spinning sidebands pattern of MAS spectra are affected by chemical shielding.

With the above mentioned precautions, employing the MASNMR program based on the Berger and Herzfeld algorithm, the values of principal components of the  $^{31}\text{P}$  chemical shift tensors were obtained.<sup>18–19</sup> The calculated principal elements  $\delta_{ii}$ , anisotropy  $\Delta\delta$ , asymmetry  $\eta$ , span  $\Omega$  and skew  $\kappa$  are given in Table 2. The accuracy of calculations was confirmed by comparison with theoretical spectra shown in Fig. 2.

The  $^{31}\text{P}$  spectral parameters, compared with results published elsewhere, reveal that  $^{31}\text{P}$  anisotropy for  $\text{P}^{\text{VI}}$  moieties is much lower than appropriate data for tetra- and penta-coordinated organophosphorus compounds.<sup>2–8</sup> Moreover, it is apparent that there is a straightforward relationship between the molecular structure of hexacoordinated compounds and  $^{31}\text{P}$  shielding, in particular anisotropy  $\Delta\delta$  and span  $\Omega$ . For a very symmetrical structure (compound **I**) the span  $\Omega$  is found to be 10 ppm (from static measurements) while for compounds



**Fig. 1** 121.49 MHz  $^{31}\text{P}$  CP MAS spectra of selected hexacoordinated organophosphorus compounds. (a) **I**,  $\gamma_{\text{rot}} = 3.18$  kHz, (b) **II**,  $\gamma_{\text{rot}} = 1.0$  kHz, (c) **IIIc**,  $\gamma_{\text{rot}} = 1.5$  kHz. All spectra have 8 K data points, a contact time of 5 ms and 16–100 scans.



**Fig. 2** Theoretical  $^{31}\text{P}$  CP MAS spectra of selected hexacoordinated organophosphorus compounds. (a) **I**,  $\gamma_{\text{rot}} = 3.18$  kHz, (b) **II**,  $\gamma_{\text{rot}} = 1.0$  kHz and (c) **IIIc**,  $\gamma_{\text{rot}} = 1.5$  kHz. The spectra were obtained employing the MASNMR program commercially available from Bruker.

III the values are in the range 50–60 ppm. Furthermore, the small differences in  $\Omega$  for IIIa, IIIb and IIIc indicate that they correspond to minute geometry distortions around the phosphorus atom. The results in Table 2 show little effect of changes of geometry on the asymmetry parameters of hexacoordinated compounds, suggesting that the phosphorus shielding depends not only on the local bonding, but on the octahedral structure as a whole. Another valuable conclusion is obtained from comparison of isotropic chemical shifts in solution and in the solid state. Very similar values of  $\delta_{\text{iso}}$  provide unambiguous evidence that in both phases the geometries are not changed.

#### Molecular mechanics studies

In order to check the usefulness of the  $^{31}\text{P}$  NMR technique in the structural analysis of  $\text{P}^{\text{VI}}$  moieties with an unknown X-ray structure further results were obtained from an approach involving correlation of NMR data with  $\text{P}^{\text{VI}}$  geometry calculated by employing molecular mechanics (MM). Calculations were performed with the HyperChem program<sup>20</sup> and MM + force field<sup>21</sup> until the root square of the gradient vector was less than  $0.001 \text{ kcal } \text{\AA}^{-1}$ . Energy minimizations were carried out with the HyperChem default values. The computational method was justified by carrying out calculations on compounds I and II, and assessing the level of agreement between the calculated and experimental results. MM + geometrical parameters are given in Table 3.

From comparison of data shown in Table 1 and Table 3 it is clear that calculated bond distances and bond angles for I and II roughly correspond to those taken from X-ray diffraction (XRD). The theoretical  $\Delta^\circ$  parameters are  $2.8^\circ$  and  $3.9^\circ$  for I and II, respectively. These values are slightly different compared with experimental  $\Delta^\circ$ . The limitations of the accuracy of computational calculations must be stressed. The calculations were performed for systems in the gas phase neglecting the crystallographic effects. The overall geometry for both compounds is found to be octahedral.

The X-ray structure for IV is not known. In contrast to compound II two pyridyl substituents and two five-membered rings are attached to phosphorus. Table 3 shows the geometrical parameters of IV taken from molecular modelling results. Fig. 3 displays the computer-generated structure of IV. The calculated  $\Delta^\circ$  value is found to be  $25.4^\circ$ . Thus, for this compound the significant geometrical distortion, and in consequence, large  $^{31}\text{P}$  shielding anisotropy is predicted. In fact, as seen from Table 2, the shielding parameters  $\Delta\delta$  and  $\Omega$  for IV are considerably larger compared with other hexacoordinated entities under investigation. Comparing shielding anisotropy  $\Delta\delta$  and span  $\Omega$  with  $\Delta^\circ$  for all compounds it seems that  $\Delta^\circ$  for compound IV taken from the MM approach is somewhat too large (as in the case of compound I). Thus from comparison of molecular modelling and solid-state NMR data, semi-quantitative results can be obtained.

#### Conclusions

Hexacoordinated phosphorus compounds are postulated as intermediates in chemical and biochemical processes.<sup>22,23</sup> Various mechanisms, including a hexacoordinated transition-state, are suggested in the hydrolysis of c-AMP catalysed by c-AMP phosphodiesterase. A number of synthetic and structural works employing different experimental techniques with  $\text{P}^{\text{VI}}$  model species have been carried out in order to establish the relationship between the structure and stability.<sup>24–26</sup> From an experimental point of view,  $\text{P}^{\text{VI}}$  species, because of extremely high instability, are a very demanding class of compounds. Each technique which provides new information about the  $\text{P}^{\text{VI}}$  structure is valuable.

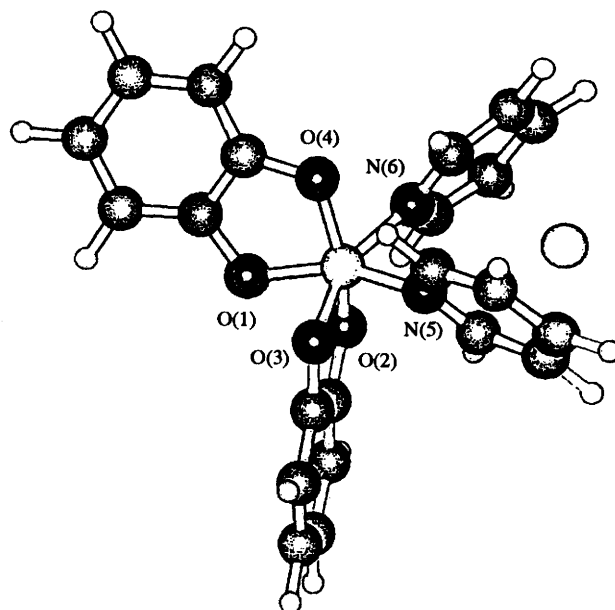


Fig. 3 Computer generated structure of compound IV

This paper clearly shows that  $^{31}\text{P}$  solid-state NMR spectroscopy can be considered as a complementary tool in the structural analysis of hexacoordinated compounds. In particular this technique is useful for structural elucidation of  $\text{P}^{\text{VI}}$  species when single crystals are not suitable for XRD studies. From analysis of  $^{31}\text{P}$  chemical shift parameters, anisotropy  $\Delta\delta$  and span  $\Omega$ , semi-quantitative information regarding the geometry around the central phosphorus atom can be obtained. Comparison of isotropic chemical shifts in solution and in solid carries information on the changes of molecular structures in both phases. Finally, the results from molecular mechanics calculations are consistent with data taken from XRD studies. Thus, this multi-technique approach involving MM, XRD and solid-state NMR spectroscopy can provide detailed information about the  $\text{P}^{\text{VI}}$  geometry.

#### Experimental

Hexacoordinated phosphorus compounds III were synthesized according to the procedure published elsewhere.<sup>17</sup> Because of high instability and sensitivity to the moisture of the compounds under investigation, rotors were packed in a dry-box and kept at a low temperature.

#### NMR measurements

CP MAS solid-state  $^{31}\text{P}$  NMR spectra were recorded on a Bruker 300 MSL instrument with high-power proton decoupling at 121.496 MHz. Powder samples of hexacoordinated phosphorus compounds were placed in a cylindrical rotor and spun at 1.0–4.5 kHz or measured without rotation. For the  $^{31}\text{P}$  experiments, the field strength for  $^1\text{H}$  decoupling was 1.05 mT, a contact time of 5 ms, a repetition of 6 s and spectral width of 50 kHz were used and 8 K data points represented the FID. Spectra were accumulated 100 times which gave a reasonable signal-to-noise ratio.  $^{31}\text{P}$  chemical shifts were calibrated indirectly through bis(dineopentoxothiophosphoryl) disulfide set at 84.0 ppm.

The principal elements of the  $^{31}\text{P}$  chemical shift tensor and shielding parameters were calculated employing the MASNMR program. The details describing the method and accuracy of calculations are exhaustively discussed elsewhere.<sup>18,19</sup>

The principal components  $\delta_{ii}$  were used for calculation of the shielding parameters; anisotropy  $\Delta\delta$ , asymmetry  $\eta$ , span  $\Omega$  and skew  $\kappa$ .<sup>27</sup>

If  $|\delta_{11} - \delta_{\text{iso}}| > |\delta_{33} - \delta_{\text{iso}}|$  then

$$\Delta\delta = \delta_{11} - (\delta_{22} + \delta_{33})/2 \quad (2)$$

$$\eta = (\delta_{22} - \delta_{33})/(\delta_{11} - \delta_{\text{iso}}) \quad (3)$$

If  $|\delta_{11} - \delta_{\text{iso}}| < |\delta_{33} - \delta_{\text{iso}}|$  and  $\delta_{11} > \delta_{22} > \delta_{33}$  then

$$\Delta\delta = \delta_{33} - (\delta_{11} + \delta_{22})/2 \quad (4)$$

$$\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{\text{iso}}) \quad (5)$$

Moreover

$$\Omega = \delta_{11} - \delta_{33} \quad (6)$$

$$\kappa = 3(\delta_{22} - \delta_{\text{iso}})/\Omega \quad (7)$$

### Computer calculations

Calculations were performed with the HyperChem program executed on an IBM compatible 486 (66 MHz), computer. Energy minimizations were carried out with the HyperChem default values. All molecular mechanical studies were performed with the MM+ force field until the root square of the gradient vector was less than 0.001 kcal Å<sup>-1</sup>. The calculations were performed for systems in the gas phase neglecting the crystallographic effects.

### References

- 1 C. A. Fyfe, *Solid State NMR for Chemists*, C.F.C. Press, Guelph, Ontario, 1983.
- 2 M. Mehring, *Principles of High Resolution NMR in Solids*, Springer, Berlin, 1983, 2nd edn.
- 3 J. P. Dutasta, J. B. Robert and L. Wiesenfeld, *Chem. Phys. Lett.*, 1981, **77**, 336.
- 4 G. L. Turner, K. L. Smith, R. J. Kirkpatrick and E. Oldfield, *J. Magn. Reson.*, 1986, **70**, 408.
- 5 J. Herzfeld, R. G. Griffin and R. A. Haberkorn, *Biochemistry*, 1978, **17**, 2711.
- 6 A. R. Grimmer, *Spectrochim. Acta, Part A*, 1978, **34**, 941.
- 7 M. J. Potrzebowski, *J. Chem. Soc., Perkin Trans. 2*, 1993, 63.
- 8 L. W. Dennis, V. J. Bartuska and G. E. Maciel, *J. Am. Chem. Soc.*, 1982, **104**, 230.
- 9 T. K. Prakasha, R. O. Day and R. R. Holmes, *Inorg. Chem.*, 1992, **31**, 191.
- 10 J. G. Hexem, M. H. Frey and S. J. Opella, *J. Chem. Phys.*, 1982, **77**, 3847.
- 11 A. Naito, S. Ganapathy, K. Akasaka and C. A. McDowell, *J. Chem. Phys.*, 1981, **74**, 3190.
- 12 C. J. Groombridge, R. K. Harris, K. J. Packer, B. J. Say and S. F. Tanner, *J. Chem. Soc., Chem. Commun.*, 1980, 174.
- 13 N. Zumbulyadis, P. M. Heinrichs and R. H. Young, *J. Chem. Phys.*, 1981, **75**, 1603.
- 14 R. D. Curtis, B. W. Royan, R. E. Wasylishen, M. D. Lumsden and N. Burford, *Inorg. Chem.*, 1992, **31**, 3386.
- 15 H. R. Allcock and E. C. Bissell, *J. Chem. Soc., Chem. Commun.*, 1972, 679.
- 16 W. S. Sheldrick, A. Schmidpeter and T. von Griesge, *Z. Naturforsch., Teil B*, 1978, **33**, 583.
- 17 J. Kowara, A. Skowrońska, M. W. Wiczorek and G. Bujacz, manuscript in preparation.
- 18 G. Jeschke and G. Grossman, *J. Magn. Reson.*, 1993, **A103**, 323.
- 19 J. Herzfeld and A. Berger, *J. Chem. Phys.*, 1980, **73**, 6021.
- 20 HyperChem, Autodesk Inc., 2320 Marinship Way, San Ramon, CA 94965, USA.
- 21 MM+ for HyperChem is derived from public domain code developed by N. L. Allinger, referred to as MM2 (1977) and distributed by the Quantum Chemistry Program Exchange (QCPE).
- 22 F. Ramirez and J. F. Marecek, *Pure Appl. Chem.*, 1980, **52**, 1021.
- 23 R. Kluger and G. R. J. Thatcher, *J. Am. Chem. Soc.*, 1985, **107**, 6006.
- 24 A. Skowrońska, J. Stanek-Gwara and M. Nowakowski, *Phosphorus Chemistry, Proceedings in 1981*, eds. J. G. Verkade and L. D. Quin, ACS Symposium, Series 171, Am. Chem. Soc., Washington DC, 1981; A. Skowrońska, J. Burski, J. Stanek-Gwara, R. Kamiński and J. Kowara, *Phosphorus and Sulfur*, 1987, **30**, 283.
- 25 F. H. Westheimer and Ch. L. Leman, *J. Am. Chem. Soc.*, 1976, **98**, 179.
- 26 R. R. Holmes, R. O. Day, J. A. Deiters, K. C. Kumara-Swamy, J. M. Holmes, S. D. Burton and T. K. Prakasha, *Phosphorus Chemistry, Developments in American Science*, eds. E. N. Walsh, E. J. Griffiths, R. W. Parry and L. D. Quin, ACS Symposium, Series 486, Am. Chem. Soc., Washington DC, 1992.
- 27 J. Mason, *Solid State Nuclear Magn. Reson.*, 1993, **2**, 285.

Paper 4/06640E

Received 31st October 1994

Accepted 5th January 1995