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A Phosphorus-31 Solid-State Nuclear Magnetic Resonance Study of Thiaphospholium Cations

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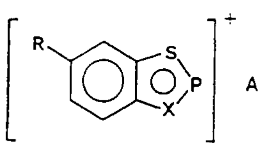
Three different benzophospholium salts (benzo-1,3,2-dithiaphospholium (**1a**), 5-methylbenzo-1,3,2-diathiaphospholium (**1b**), and benzo-1,3,2-azathiaphospholium (**1c**)) have been investigated in the solid state using ^{31}P NMR spectroscopy. The magnitude of the phosphorus chemical shift anisotropy ($\Delta\delta$) determined for all three derivatives is in excess of 500 ppm. Dipolar-chemical shift ^{31}P NMR experiments on the thiazaphospholium salt **1c** allowed the ^{31}P chemical shift tensor to be oriented in the molecular frame of reference. The most shielded principal component, δ_{33}, is oriented perpendicular to the P,N dipolar vector with the intermediate principal component, δ_{22}, oriented in the molecular plane and approximately along the bisector of the NPS bond angle. These orientations agree well with ab initio chemical shielding calculations. Comparison of the three principal components of the phosphorus chemical shift tensors of **1a–c** provides strong evidence that the orientation of the ^{31}P chemical shift tensors of **1a** and **1b** are similar to that of **1c**. Finally, the solid-state ^{31}P NMR results are consistent with previous data that indicate incorporation of the phosphorus center into the 10π-electron manifold.

Introduction

With recent developments in solid-state nuclear magnetic resonance (NMR) spectroscopy, it has become possible to obtain information on anisotropic nuclear spin interactions by studying static solid samples.[1-3] Indeed, several authors have reported chemical shift anisotropies ($\Delta\delta$) for a variety of carbon centers in numerous organic solids and have been successful in correlating these parameters with the nature of the local electronic environment.[3-8] For example, three-coordinate (unsaturated) carbon nuclei that participate in typical double-bond formation, such as in olefins, generally have significantly larger chemical shift anisotropies than four-coordinate carbon nuclei that are part of a fully saturated bonding environment.[3-8] In addition, the most shielded direction about the carbon center involved in double-bond formation is invariably in the direction perpendicular to the molecular plane containing that carbon.[3,6-8] Similar features are apparent for the ^{31}P nucleus, although examples are limited.[5,9-11] For instance, Zilm et al. have demonstrated that the phosphorus chemical shift anisotropies for the dicoordinate P(III) centers in $(t\text{-Bu})_3C_6H_2P{=}PC_6H_2(t\text{-Bu})_3$ and $(t\text{-Bu})_3C_6H_2P{=}C[Si(CH_3)_3]_2$ are substantially larger than those observed for the single-bonded P(III) sites in the diphosphine analogues.[10,11]

We have recently described the preparation of several novel benzothiaphospholium salts, **1**.[12-16] X-ray diffraction experiments show them to consist of discrete ions. The thiaphospholium cations are planar (maximum deviation at the P atom of 0.027 Å from the molecular plane), and the P–S bond lengths are shorter than those for systems containing single P(III)–S bonds. These structural features are consistent with spectroscopic data[12-15,17] that are interpreted in terms of a delocalized 9-atom 10π-electron framework involving the first examples of stable 3pπ–3pπ bonding between phosphorus and sulfur.



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Compound	X	R
1a	S	H
1b	S	CH_3
1c	N-H	H

Given the inherent sensitivity of the chemical shift anisotropy of a nucleus to the type of bonding environment,[3-11] we decided to investigate derivatives of **1** by solid-state ^{31}P NMR spectroscopy. The thiazaphospholium derivative **1c** provides a unique opportunity to determine the orientation of the three principal components of the phosphorus chemical shift tensor in the molecular frame of reference. More specifically, the P(III) nucleus in **1c** is directly dipolar coupled to a ^{14}N nucleus ($I = 1$); therefore, the orientation of the ^{31}P chemical shift tensor can be referenced with respect to the ^{14}N,^{31}P bond vector, r_{PN}. The phosphorus chemical shift parameters determined for **1** will be compared to the following: (i) results from ab initio chemical shielding calculations on **1c**, (ii) those of related systems containing P(III) involved in single and double bonds, and (iii) other molecular

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systems containing P(V) participating in multiple bonding with nitrogen and sulfur.

Theory

In the solid state, the ^{31}P NMR line shape is dominated by three interactions: (i) the chemical shift anisotropy, $\Delta\delta$, (ii) homonuclear (^{31}P,^{31}P) dipolar couplings, and (iii) heteronuclear (^{31}P,X) dipolar couplings. If no NMR-active nuclei are bonded to the phosphorus center being investigated, then, in general, the ^{31}P NMR line shape observed for a powder sample is a broad resonance with three distinct features representing the chemical shift tensor, δ_{11}, δ_{22}, and δ_{33}. The principal components, δ_{ii}, can be used to define two parameters as indicated in eq 1, $\Delta\delta$ and η, which are useful when comparing shielding environments for phosphorus nuclei in different molecules.[5,6,18,19] If $|\delta_{11} - \delta_{iso}| \geq |\delta_{33} - \delta_{iso}|$, then

$$\Delta\delta = \delta_{11} - (\delta_{22} + \delta_{33})/2 \qquad (1a)$$

$$\eta = (\delta_{22} - \delta_{33})/(\delta_{11} - \delta_{iso}) \qquad (1b)$$

If $|\delta_{11} - \delta_{iso}| \leq |\delta_{33} - \delta_{iso}|$ and $\delta_{11} \geq \delta_{22} \geq \delta_{33}$, then

$$\Delta\delta = \delta_{33} - (\delta_{11} + \delta_{22})/2 \qquad (1c)$$

$$\eta = (\delta_{22} - \delta_{11})/(\delta_{33} - \delta_{iso}) \qquad (1d)$$

If the phosphorus nucleus is bonded to a NMR-active nucleus such as ^{14}N ($I = 1$), then the ^{31}P chemical shift powder pattern is split at each δ_{ii} by dipolar coupling with the ^{14}N nucleus. The magnitudes of the "dipolar splittings", $\Delta\nu_{ii}$, are related to the mutual orientation of the dipolar and chemical shift tensors as described elsewhere.[20-25] However, the expressions in eq 2 are

$$\Delta\nu_{11} = |R_{eff}|[1 - 3(\sin\beta\cos\alpha)^2] \qquad (2a)$$

$$\Delta\nu_{22} = |R_{eff}|[1 - 3(\sin\beta\sin\alpha)^2] \qquad (2b)$$

$$\Delta\nu_{33} = |R_{eff}|[1 - 3\cos^2\beta] \qquad (2c)$$

useful for interpreting "dipolar-chemical shift NMR spectra" of "isolated" A–X spin pairs, where $R_{eff} = R_{AX} - \Delta J/3$, $R_{AX} = (\mu_0/4\pi)(h/4\pi^2)\gamma_A\gamma_X\langle r_{AX}^{-3}\rangle$ is the dipolar coupling constant, and ΔJ is the anisotropy in the indirect spin–spin coupling constant. The angles α and β (Figure 1) describe the orientations of δ_{ii} with respect to the bond vector, r_{AX}, and are physical characteristics of each particular molecular fragment. The dipolar coupling constant, R_{AX}, is related to the average inverse cube of the A–X bond distance.

The detailed NMR powder line shape for an A–X spin-pair is very sensitive to the values of α, β, and the magnitude of R. For example, if $\beta = 0°$, the splitting at δ_{33} in the A spin NMR spectrum is $2|R_{eff}|$. On the other hand, if $\beta = 90°$, then the most shielded direction around the A nucleus is perpendicular to the dipolar vector and the splitting $\Delta\nu_{33}$ is $|R_{eff}|$. Thus, by measuring the dipolar-chemical shift NMR spectrum for such an isolated spin-pair, one can obtain accurate values for δ_{11}, δ_{22}, and δ_{33} as well as information regarding the orientation of the shift tensor from the parameters α and β.

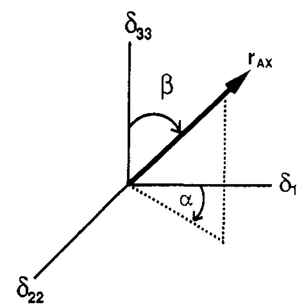

Figure 1. Angles α and β defining the orientation of the three principal components of the chemical shift tensor relative to the dipolar vector, r_{AX}.

Experimental Section

Tetrachloroaluminate salts **1a–c** (~500 mg) were ground into a fine powder and packed into cylindrical zirconium oxide rotors (7-mm o.d.) in a glovebox (N_2). All rotors were topped with solid caps which had been coated with a medium-tipped felt marker to form an air tight seal. Samples prepared in this manner were found to be stable on the lab bench for approximately 2 weeks (vide infra).

Phosphorus-31 solid-state NMR spectra were recorded at 81.03 MHz on a Bruker MSL-200 NMR spectrometer. Proton/phosphorus cross polarization (CP) under the Hartmann–Hahn match was used to enhance the signal to noise ratio of all ^{31}P NMR spectra. Contact times were optimized and were typically 6–10 ms. All ^{31}P CP NMR spectra were acquired with high-power proton decoupling with $\pi/2$ pulse widths of 2.5–3.0 μs. For the magic angle spinning (MAS) NMR experiments, typical rotor frequencies were from 2 to 4.5 kHz. Recycle times between acquisition of successive transients were 100 s for **1a** and **1c** and 15 s for **1b**. Typically, several hundred scans were accumulated for the MAS NMR experiments whereas static NMR spectra were signal-averaged for approximately 4000 transients. The sweep width for all NMR spectra was 125 kHz with acquisition file sizes of 4096 points and 1024 points for MAS and static CP NMR spectra, respectively. To improve the quality of the ^{31}P CP NMR spectra of static samples, a spin-echo sequence was applied to the ^{31}P nuclei.[26] The delay time between the ^{31}P $\pi/2$ and π pulses was typically 30 μs. The audio frequency filter was opened to its widest value, 2 MHz, to help alleviate problems associated with acoustic ringing. Prior to Fourier transformation, sensitivity enhancements of 30 and 250 Hz were applied to the MAS and static free induction decays, respectively. All ^{31}P NMR spectra were referenced with respect to liquid H_3PO_4 (85%) at 0 ppm by setting the observed phosphorus signal of $NH_4H_2PO_4$ at +0.81 ppm.

Calculations of theoretical dipolar-chemical shift NMR spectra were performed on an IBM personal computer equipped with an INTEL 80386 processor and a 80287 math coprocessor using an algorithm employing the interpolation scheme of Alderman et al.[27] The theoretical NMR spectra were then convoluted with a Gaussian line-broadening function. The ^{14}N electric field gradient of **1c** was calculated using the GAMESS ab initio calculation package with a 6-31G basis set.[28] Self-consistent field (SCF) and shielding calculations on **1c** were performed on a Stellar GS2500 vector processing computer. The necessary SCF results were obtained with the Gaussian 90 ab initio program[29] using STO-3G and

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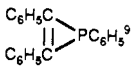
Table I. Phosphorus-31 Chemical Shift Parameters for **1a–c** and Compounds Containing a P(III) or P(V) Center[a,b]

compd	δ_{11}	δ_{22}	δ_{33}	δ_{iso}	$\Delta\delta$	η
1a	766	520	−13	424.3 408[c]	−656	0.56
1b	755	520	−25	416.7 414[c]	−663	0.53
1c-expt	684	252	34	323.3 306[c] 317[d]	541	0.60
1c-STO-3G	1487	469	320	759	1092	0.20
1c-6-31G	1173	401	−145	476	900	0.78
$(C_6H_5)HPPH(C_6H_5)$[10]	−27	−27	−117	−57	−90	0.00
	58	−28	−636	−202	−651	0.20
$R_1P{=}PR_1$[10,e]	1236	249	−3	494	1113	0.34
$R_1P{=}C[Si(CH_3)_3]_2$[11]	819	249	−31	394	637	0.66
$(C_6H_5)_3P{=}S$[31]	107	86	−64	43	−160	0.20
$(C_6H_5)_3P{=}N(C_6H_5)$[32]	50	31	−85	−1.3	−126	0.23

[a] Errors in the experimental principal components of the chemical shift tensor are ±2 ppm. [b] Principal components of the absolute shielding tensor can be calculated from the following expression:[33] $\sigma_{ii} = 328.35 - \delta_{ii}$. [c] Isotropic chemical shifts values are from previous ^{31}P NMR experiments in $CDCl_3$ solution. [d] This value was taken from ref 52. [e] $R_1 = C_6H_2(t\text{-Bu})_3$.

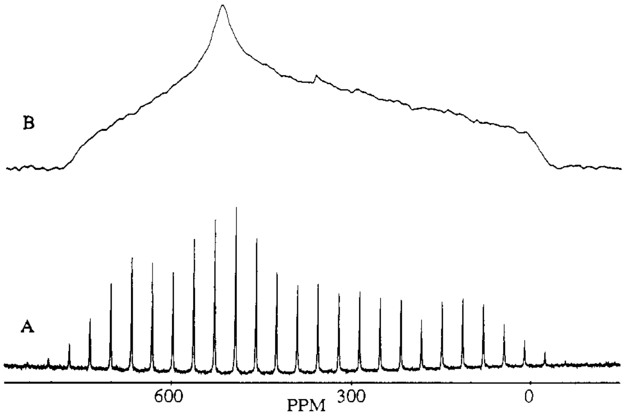


Figure 2. Phosphorus-31 CP NMR spectra for a powder sample of **1a**. Spectrum A was obtained with magic angle sample spinning at 2.79 kHz; (B) is a spin-echo CP NMR spectrum of a static powder sample.

6-31G basis sets. The molecular coordinates used were previously determined by X-ray crystallography.[15] The ^{31}P shielding tensor of **1c** was calculated using the RPAC program of Bouman and Hansen,[30] which utilizes the LORG (localized orbital-local origin) method.

Results and Discussion

(a) Principal Components of the ^{31}P Chemical Shift Tensor. The ^{31}P NMR results for **1** are summarized in Table I. Magic angle spinning and static ^{31}P CP NMR spectra for the dithiaphospholium salt **1a** are shown in Figure 2. Long proton spin–lattice relaxation times and efficient ^{31}P transverse relaxation—caused by close contacts between the phosphorus nuclei and the quadrupolar chlorine nuclei of the tetrachloroaluminate counterions[14,15]—made it extremely difficult to acquire useful static NMR spectra. These problems were overcome by combining the cross polarization technique with a spin-echo pulse sequence outlined by Rance and Byrd.[26] In addition, the air- and moisture-sensitive nature of the thiaphospholium salts led to the contamination of some samples. From the isotropic chemical shift data, it appears that the impurities are phosphorus(V) species. These impurities did not manifest themselves in the ^{31}P CP NMR spectra of freshly packed samples and only became apparent in the NMR spectra of samples which were left in the rotors for a period in excess of 2 weeks.

The principal components of the phosphorus chemical shift tensor of **1a** were obtained directly from the static CP NMR spectrum in Figure 2B and are presented in Table I with the corresponding values for **1b** and **1c**. Although the ^{31}P NMR spectrum in Figure 2B is distorted, the principal values of the chemical shift tensor are accurate to ±2 ppm. The distorted line shape is a result of (i) incomplete radio-frequency excitation due to a finite pulse width and/or (ii) lack of data sampling exactly on the echo maximum. Also included in Table I are the values of δ_{ii} (i = 1–3) calculated by the RPAC program for **1c** as well as previously reported chemical shift parameters for the phosphorus(III) centers of a diphosphine,[10] a phosphirene,[9] a diphosphene,[10] a phosphaalkene,[11] and the phosphorus(V) centers of a phosphine sulfide[31] and a monophosphazene.[32]

Agreement between the isotropic chemical shifts of **1** determined from the magic angle spinning NMR experiments in the solid state with values observed previously for these compounds in $CDCl_3$ is good (see Table I) and indicates that the structural integrity of the solid thiaphospholium salts is maintained in chloroform solution. To our knowledge, there are no isotropic chemical shifts reported for dicoordinate phosphorus compounds similar to **1**. It is interesting however, to point out that δ_{iso} of **1c**, 323.3 ppm, compares reasonably well with values reported for numerous acyclic and cyclic systems which have a formal phosphorus(III) to nitrogen double bond.[34–37]

The breadths of the ^{31}P CP NMR spectra in Figure 2 are in excess of 700 ppm indicating that the chemical shift anisotropy of **1a** is quite large. In fact, the phosphorus chemical shift anisotropy of all three derivatives investigated was observed to be in excess of 500 ppm. As can be seen from the data in Table I, the chemical shift anisotropies of the P(III) centers of the thiaphospholium cations are significantly larger than the corresponding values for the phosphorus nuclei of typical single-bonded P(III) species and multiply-bonded P(V) species. Indeed, the magnitudes of $\Delta\delta$ for **1** are more reminiscent of those reported for the P(III) centers of the phosphirene and, particularly, the phosphaalkene. Interestingly, the two low-frequency ^{31}P principal components of **1c** (i.e., δ_{22} and δ_{33}) compare well with the corresponding values recently reported for bis(2,4,6-tri-*tert*-butylphenyl)diphosphene[10] and $(t\text{-Bu})_3C_6H_2P{=}C[Si(CH_3)_3]_2$.[11] The major discrepancy with a comparison of the shift tensors of **1c** and the two phosphene compounds is associated with the δ_{11} principal component. A possible reason for this discrepancy will be discussed later in the manuscript.

The theoretical LORG calculations on the cation of **1c** failed to accurately predict the magnitudes of the principal components of the chemical shift tensor using both a minimal and a double-ζ basis set (see Table I). The largest discrepancy between experimental and both theoretical ^{31}P chemical shift tensors is related to δ_{11}. We anticipate that the addition of polarized functions to the heavy atoms in **1c** as well as consideration of the anion would bring the calculations in closer agreement with experiment. Unfortunately, the size of the molecule and available computer resources did not permit such a calculation. As well, it is possible that the neglect of electron correlation effects is a

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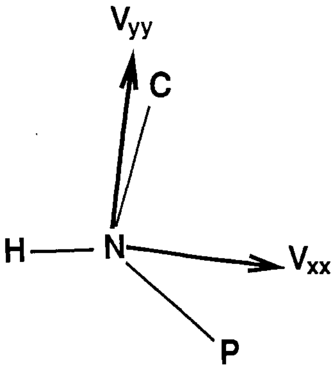

Figure 3. Orientation of the ^{14}N electric field gradient tensor as determined from ab initio molecular orbital calculations. V_{xx} makes an angle of 41° with respect to the N–P bond.

problem. This conclusion is based on the fact that electron correlation becomes increasingly important for phosphorus as the atom becomes more deshielded. The result is that, invariably, the calculated anisotropy of the chemical shift tensor is overestimated.[38]

(b) Orientation of the ^{31}P Chemical Shift Tensor. As alluded to in the Introduction, the presence of the ^{14}N,^{31}P spin-pair in **1c** provides one with an opportunity to determine the orientation of the phosphorus chemical shift tensor in the molecular frame of reference. Before invoking eq 2, however, one must consider the possible influence of the quadrupolar ^{14}N nucleus ($I = 1$) on the ^{31}P NMR line shape. More specifically, it has been demonstrated that eq 2 is only strictly valid if the magnitude of the ^{14}N quadrupolar coupling constant, $\chi = e^2q_{zz}Q/h$, is much smaller than the ^{14}N Larmor frequency, ν_L.[25,39,40] To date, there have been no measurements of $\chi(^{14}\mathrm{N})$ for compound **1c** so we performed a molecular orbital calculation of this parameter using the GAMESS ab initio routine.[28] These computations predict that the largest principal component of the nitrogen electric field gradient (efg), V_{zz} ($V_{ii} = eq_{ii}$), is oriented perpendicular to the molecular plane having a value corresponding to $\chi = -2.1$ MHz.[41] The intermediate component and the smallest principal component have values corresponding to +1.1 and +1.0 MHz, respectively, and are oriented in the molecular plane as depicted in Figure 3. The orientation of the ^{14}N electric field gradient determined here for **1c** is similar to experimental results for the tricoordinate amino nitrogen (i.e., N–H) of imidazole.[42] Since molecular orbital calculations tend to overestimate the magnitude of $\chi(^{14}\mathrm{N})$,[43] we expect that $\chi = -2.1$ MHz represents an *upper* limit for the nitrogen of compound **1c**. At 4.7 T, $\nu_L(^{14}\mathrm{N}) = 14.46$ MHz and therefore the ratio of $\nu_L(^{14}\mathrm{N})/\chi(^{14}\mathrm{N})$ is a *minimum* of 6.8. On this basis, we assume that eq 2 represents an analytical expression that is suitable for calculating the dipolar splittings observed in the static ^{31}P NMR spectrum of **1c**. This conclusion is supported by the results obtained from the CP/MAS NMR spectra of **1**. It has been demonstrated by several authors[44-48] that the MAS line shape observed for the isotropic signal of a spin $I = {}^1/_2$ nucleus which is bonded to a $I = 1$ nucleus with a large electric field gradient (efg) is usually an asymmetric doublet (note that the line shape has a strong dependence on the orientation of the efg as well). For **1a** and **1b**, the ^{31}P line widths observed at half-height in their respective CP/MAS NMR spectra were 100 and 80 Hz. The corresponding result for **1c** was 161 Hz; simulation of this NMR spectrum using the routine of Hexem[44] and the theoretically determined values for the nuclear quadrupolar coupling constant predict a splitting of 52 Hz for the isotropic ^{31}P resonance of **1c**.

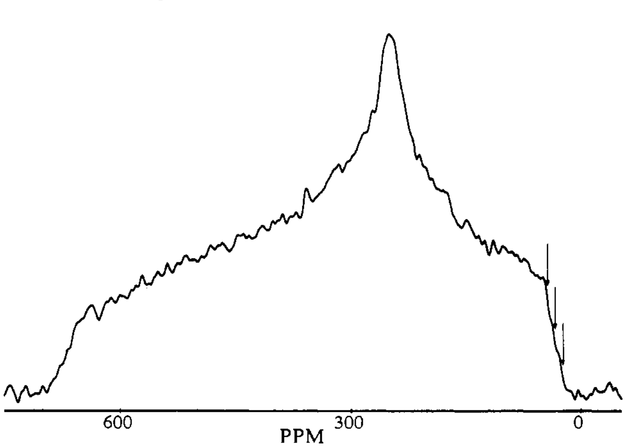

Figure 4. ^{31}P CP NMR spectrum for a static powder sample of **1c**. The three shoulders at δ_{33} with splitting $\Delta\nu_{33}$ are labeled.

The static ^{31}P CP NMR spectrum of compound **1c** is shown in Figure 4. The low-frequency end of this NMR spectrum (i.e., δ_{33}) is split into three distinct shoulders due to direct dipolar coupling of the ^{31}P nucleus with the ^{14}N nucleus. Substituting the value of this dipolar splitting into eq 2 indicates that the angle β is 90 ± 2° and the value for the dipolar interaction constant, R, is 794 ± 35 Hz. This value of β places the most shielded element of the ^{31}P chemical shift tensor of **1c** perpendicular to the molecular plane, consistent with previous results reported for the diphosphene and the phosphaalkene for which the P(III) center is involved in pπ–pπ double-bond formation.[10,11] This orientation of δ_{33} is also consistent with the theoretical results with both the STO-3G and 6-31G basis sets. The value of β determined here for **1c** is markedly different from the value of $\beta = 0°$ determined for the P(V) center of several monophosphazenes.[32] Clearly, this indicates a dramatic difference in the P,N bonding environments between **1c** and the corresponding bond in the monophosphazenes. The magnitude determined for R, 794 ± 35 Hz, compares well with that calculated from the X-ray diffraction determined PN bond length, $r_{PN} = 1.643$ Å ($R_{calc} = 793$ Hz).[15] The fact that there is such a close agreement between the NMR-derived bond length and the X-ray diffraction value suggests that (i) there is very limited librational motion about the P(III) center of **1c**[49-51] and (ii) the contributions of the indirect couplings (i.e., J and ΔJ) to the ^{31}P NMR line shape are negligible.

There is no discernible "dipolar splitting" at the δ_{22} ^{31}P resonance position in the static NMR spectrum of **1c** (Figure 4). When this is combined with the observed splitting at δ_{11} ($\Delta\nu_{11} = 730 \pm 60$ Hz), the angle of α compatible with these two conditions was determined to be 38 ± 5°. This can, in principle, correspond to two different orientations of δ_{11} and δ_{22}, as depicted in Figure 5. The results reported by Zilm et al. for the P(III) center of a diphosphene[10] indicate that δ_{22} in this system is oriented approximately along the direction bisecting the PPC angle (i.e., where a phosphorus "lone pair" would reside). For **1c**, only the

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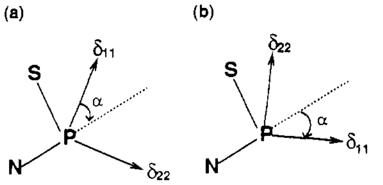

Figure 5. Possible orientations of δ_{11} and δ_{22} for the phosphorus chemical shift tensor of **1c**. Note that δ_{33} is oriented perpendicular to the plane of the molecule.

orientation depicted in Figure 5a is consistent with the results of Zilm et al., and therefore, we conclude that the orientation shown in Figure 5a is a reasonable representation of the ^{31}P chemical shift tensor of **1c**. This assignment places the intermediate principal component, δ_{22}, of the ^{31}P center of **1c** approximately along the direction of the angle bisecting the SPN fragment.

The experimentally determined orientation shown in Figure 5a is very similar to the results obtained using the LORG routine with either a STO-3G or 6-31G basis set. The two calculations suggest that δ_{11} is oriented slightly off the PN axis with a value of α = 16 and 31° determined from the 6-31G and STO-3G calculations, respectively. Note that the experimentally determined value, $\alpha = 38 \pm 5°$, is somewhat larger than that expected on the basis of the LORG results.

The fact that the most shielded principal component of the ^{31}P chemical shift tensor, δ_{33}, shows little variation in compounds **1a–c** implies that this component has the same orientation in all three compounds, i.e., δ_{33} is perpendicular to the molecular plane. Also, note that the values of δ_{33} in compounds **1** are comparable to the values reported for the substituted diphosphene and phosphaalkene systems, which contain P═P and P═C double bonds, respectively (see Table I). Again, the orientation of δ_{33} is perpendicular to the molecular plane. On going from the system containing the SPN fragment (**1c**) to systems containing the SPS fragment (**1a**,**b**), δ_{22} shows the largest variation, 268 ppm. The least shielded component, δ_{11}, changes by approximately 80 ppm. These observations are consistent with the orientation of δ_{22} and δ_{11} being approximately the same in all three compounds (**1a–c**).

One can also rationalize the difference in the δ_{11} ^{31}P principal components determined for **1** as compared to the corresponding results reported by Zilm et al. (see Table I).[10,11] Because δ_{11} is oriented perpendicular to the phosphorus lone pair and the π electron manifold, qualitative arguments similar to those discussed by Sardashti et al.[52] would predict that δ_{11} of **1** correlates with the n → π^* transition energies, $\Delta E_{n \rightarrow \pi^*}$. The ultraviolet spectroscopic results[17] for **1** are consistent with this interpretation.

Conclusions

Solid-state ^{31}P NMR spectroscopy has been used to investigate the shielding properties of several novel thiaphospholium salts. A comparison of isotropic ^{31}P chemical shifts observed for the three derivatives of **1** with magic angle spinning and previous solution NMR experiments in $CDCl_3$ confirms that the structural integrity of the thiaphospholium salts is maintained in this solvent. Dipolar-chemical shift ^{31}P NMR experiments on the ^{31}P,^{14}N spin-pair of **1c** allowed the ^{31}P chemical shift tensor to be oriented in the molecular frame of reference. The important feature here is that the most shielded principal component, δ_{33}, of the ^{31}P shift tensor is oriented perpendicular to the molecular plane in analogy to other systems containing a P(III) double-bonded center. This result is supported by theoretical calculations of the ^{31}P chemical shift tensor of **1c**, although the computations do not predict the magnitude of the three principal components accurately. Finally, a comparison of the three principal components of **1c** with **1a** and **1b** suggests that the orientations of the ^{31}P chemical shift tensors in **1a** and **1b** are similar to that determined for **1c**.

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