Chemical Shift Tensors of Directly Bonded Phosphorus Nuclei in Unsaturated Four-Membered Rings. Solid-State $^{31}$P NMR and Theoretical Study of Trans- and Cis-Substituted Diphosphetes

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Received: October 21, 1998; In Final Form: December 18, 1998

The chemical shift (CS) tensors of two four-membered heterocyclic diphosphetes, trans- and cis-1,2-dihydro-1-methyl-2-phenyl-3,4-bis(tert-butyl)-1,2-diphosphate, have been investigated by solid-state $^{31}$P NMR spectroscopy. The dipolar chemical shift method has been employed to determine the magnitudes of the principal components of the $^{31}$P CS tensors in these compounds, as well as their orientations relative to the $^{31}$P−$^{31}$P dipolar vector. The spans of the phenyl- and methyl-substituted phosphorus CS tensors of the trans isomer are 248 and 280 ppm, respectively, significantly larger than the corresponding values for the cis isomer, 139 and 173 ppm. The orientations of the CS tensors in the molecular framework are proposed on the basis of ab initio calculations using the gauge-independent atomic orbitals method. The combined experimental−theoretical results suggest that, for both the trans and cis isomers, the least shielded principal components, $\delta_{11}$, are oriented in the plane defined by the four-membered ring. For the trans isomer, the most shielded principal components, $\delta_{33}$, are approximately perpendicular to this plane; however, for the cis isomer, it is the $\delta_{22}$ components that are perpendicular to the plane of the four-membered ring. The spectra of magic-angle spinning samples of the trans isomer exhibit asymmetric, spinning-frequency dependent line shapes, while those of the cis isomer are invariant to spinning frequency. These observations are consistent with the CS tensors derived from the $^{31}$P NMR spectra of stationary samples.

Introduction

Isotropic phosphorus chemical shielding has been studied extensively in solutions.1–3 Nevertheless, the origins of the observed shielding are not well understood.4,5 In general, second-rank tensors are required to describe chemical shielding interactions. The symmetric portion of these tensors may be described by three principal components and three angles describing the orientation of the principal axis system (PAS). Any serious effort to understand chemical shielding requires the investigation of these tensors as opposed to their isotropic averages. Solid-state NMR is ideally suited for the characterization of the symmetric portion of chemical shielding tensors and can also provide some information on the orientation of the principal components.5–8

The sensitivity of nuclear shielding to variations in molecular structure is dramatic, particularly for phosphorus in strained environments such as those found in cyclic systems. The chemical shielding range of most cyclic phosphines in solution is approximately 350 ppm, much greater than the approximately 120 ppm range observed for the corresponding acyclic compounds.2 Extreme examples of shielding and deshielding have been found in cyclic systems. For example, $\delta_{11} = -488$ ppm for the P$_4$ tetrahedron, which consists of strained three-membered rings.9 In contrast, some of the least shielded values for tertiary phosphines have been reported for bridging $^{31}$P nuclei in five-membered bicyclic systems.10 For $^{31}$P NMR in general, the nuclear shielding of phosphorus in cyclic systems is not fully understood, although the effects of a localized electron lone pair on the observed chemical shifts are thought to be important.11 A recent study suggests that the lone-pair electrons are delocalized significantly in heterocyclic systems.12 To investigate the effect of the lone-pair electrons on the observed shielding, Chesnut and Quin undertook a theoretical study of cyclic phosphines.13 One conclusion of this study is that the deshielded phosphorus in the phospholide ion 1, 126 ppm relative to that of the phosphole,14 2 (Chart 1), is due to the fact that the lone-pair electrons of the ion lie in the ring plane. In this orientation, the energy of the molecular orbitals containing the lone-pair electrons is closer to that of the lowest unoccupied molecular orbital. On the basis of traditional nuclear shielding theory,15–18 a small orbital energy difference between occupied and unoccupied orbitals may lead to deshielding. Hence, the deshielding of phosphorus in the phospholide ion is explained without resorting to arguments about delocalization of lone-pair electrons.13

The chemical shielding tensor describes the shielding relative to a bare nucleus. Experimentally, one measures a chemical shift (CS) tensor relative to a given reference, 85% H$_3$PO$_4$ for phosphorus. Although $^{31}$P CS tensors have been reported for phosphorus nuclei in a variety of environments,19 only a few of these involve $^{31}$P nuclei in strained-ring systems. Barra and Robert have investigated the $^{31}$P CS tensors of 1,2,3-triphenylphosphirene,20 3, and 1,2,2-triphenyl-3,3-bis(trimethylsilyl)-

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10.1021/jp984116h CCC: $18.00 © 1999 American Chemical Society
Published on Web 02/09/1999
Observation led to the suggestion that the phosphorus lone-pair within the range observed for related acyclic compounds. This opportunity to investigate the orientation of the CS tensor relative to the dipolar vector. Finally, ab initio chemical shielding calculations are performed on model compounds of the trans and cis isomers, allowing the proposal of an orientation, in the molecular framework, of the principal components of the CS tensors for each phosphorus.

**Background Theory**

**Powder Line Shapes of AB Spin Systems in Stationary Samples.** In general, when considering two coupled spins that are not magnetically equivalent, four transitions occur for a given crystallite orientation. The frequencies ($\nu$) and intensities ($I$) of these transitions are described by eqs 1–4.

\[
\begin{align*}
\nu_1 &= \frac{1}{2}(\nu_A + \nu_B + D + A) & I_1 &= 1 - \frac{B}{D} \\
\nu_2 &= \frac{1}{2}(\nu_A + \nu_B + D - A) & I_2 &= 1 + \frac{B}{D} \\
\nu_3 &= \frac{1}{2}(\nu_A + \nu_B - D + A) & I_3 &= 1 - \frac{B}{D} \\
\nu_4 &= \frac{1}{2}(\nu_A + \nu_B - D - A) & I_4 &= 1 + \frac{B}{D}
\end{align*}
\]

In these equations, $\nu_A$ and $\nu_B$ are the resonance frequencies of spins $A$ and $B$ in the absence of spin–spin interactions. For example, $\nu_A$ is defined by

\[
\nu_A = \frac{\gamma B_0}{2\pi} [1 - (\sigma_{11}^A \sin^2 \theta \cos^2 \phi + \sigma_{22}^A \sin^2 \theta \sin^2 \phi + \sigma_{33}^A \cos^2 \theta)]
\]

where $\gamma$ is the magnetogyric ratio and the angles $\theta$ and $\phi$ orient the applied field, $B_0$, in the principal axis system of the CS tensor (Figure 1). The principal components of the CS tensor are described by $\sigma_{ij}^A$ such that $\sigma_{11}^A \geq \sigma_{22}^A \geq \sigma_{33}^A$. The resonance frequency of $\nu_B$ is related to $\sigma_{ij}^B$ in an analogous manner. The terms $A$ and $B$ depend on the isotropic value of the indirect spin–spin coupling, $J_{iso}$, as well as on the effective dipolar coupling, $R_{eff}$:

\[
A = J_{iso} - R_{eff}(3 \cos^2 \phi - 1) \\
B = J_{iso} + R_{eff}(3 \cos^2 \phi - 1)/2 \\
D = [(\nu_A - \nu_B)^2 + B^2]^{1/2}
\]

The angle $\phi$ describes the orientation of the applied magnetic field relative to the dipolar vector, $r_{AB}$ (the $31P-31P$ bond axis for the diphosphetes). Experimentally, one measures an effective...
dipolar coupling that contains contributions from the direct dipolar coupling, $R_{DD}$, as well as from the anisotropy$^\text{31}$ in the $J$ tensor, $\Delta J$:

$$R_{\text{eff}} = R_{DD} - \frac{\Delta J}{3} \tag{9}$$

The former is inversely related to the cube of the internuclear separation, $r_{AB}$:

$$R_{DD} = \left(\frac{\mu_0}{4\pi}\right)\left(\frac{\hbar}{2\pi}\right)\gamma^2(r_{AB}^{-3}) \tag{10}$$

where the angular brackets indicate that the observed dipolar coupling is subject to motional averaging.$^\text{33}$

Crystallography in powder samples are arranged randomly, giving rise to the so-called powder NMR pattern. This pattern may be described by the spin, $\Omega$, and the skew, $\kappa$.$^\text{34}$ The skew indicates the range of the CS tensor principal components such that $\Omega = \delta_{11} - \delta_{33}$, whereas the skew describes the appearance of the powder line shape in terms of the relative values of the principal components, $\kappa = 3(\delta_{22} - \delta_{11})/\Omega$ with $-1 \leq \kappa \leq 1$. Since there are four NMR transitions arising from an isolated spin pair (eqs 1–4), the observed NMR spectrum of a powder sample is a superposition of four subspectra. The frequencies and intensities of these transitions depend on the orientations of the crystallites in the applied magnetic field, and in the case of an AB spin pair, may be complicated by second-order effects, resulting in complex powder patterns.$^\text{26, 35}$

With high-power proton decoupling, the $^{31}$P NMR spectra of stationary samples of the trans and cis isomers are dominated by the orientation-dependent nuclear shielding interactions at the phosphorus nuclei. To a lesser extent, the orientation dependence of the direct dipolar coupling between the directly bonded $^{31}$P nuclei will also affect the NMR line shapes. The dipolar splitting observed in a particular direction depends on the orientation of $r_{PP}$ relative to the applied magnetic field.$^\text{36}$ Hence, the dipolar splitting observed when the applied magnetic field is parallel to a particular principal component of the CS tensor offers information about the orientation of that component relative to $r_{PP}$. The orientation of the principal components of the CS tensor, relative to the dipolar vector, may be discussed in terms of a set of Euler angles that describe the transformation from the PAS of the dipolar tensor to that of the CS tensor.$^\text{37}$

However, it is more convenient to discuss the CS tensor orientation in terms of the angles, $\theta_0$, formed by the CS tensor components, $\delta_i$, with $r_{PP}$, and the Euler angle $\alpha$, which describes the relative orientation of the two CS tensors. Since in the absence of motion the dipolar tensor is axially symmetric, the calculated powder spectrum is invariant to simultaneous rotation of the two CS tensors about $r_{PP}$. Also, eq 5 shows that two values, an angle $\theta_0$ and its supplement, will yield the same calculated frequency. A calculated powder spectrum based on the dipolar chemical shift method thus yields an infinite set of solutions, with a given tensor component oriented along one of two cones, as illustrated in Figure 2. In the absence of local site symmetry, no further information about the orientation of the CS tensor may be gained from this experiment. However, there is growing evidence that modern ab initio calculations can provide valuable insight into the orientation in the molecular frame of reference of CS tensors.$^\text{32, 38–40}$

**Line Shapes of AB Spin Systems under Conditions of Magic-Angle Spinning (MAS).** With high-power decoupling of the abundant spins under rapid MAS conditions, the NMR spectrum of an isolated spin will consist of an isotropic peak.

![Figure 2](image-url)
Both laboratory, which incorporates the POWDER routine of Alder-atomic orbitals (GIAO) method within the Gaussian 94 suite an IBM RISC/6000 workstation using the gauge-independent orientations were used in our calculations. Crystal orientations using the Monte Carlo method; 10,000

Calculations

| TABLE 1: Summary of Basis Sets Used for ab Initio Calculations |
|---|---|---|---|
| basis | P | adjacent | other nuclei |
| I | 3-21G | 3-21G | 3-21G |
| II | 6-31G(d) | 6-31G(d) | 6-31G(d) |
| III | 6-31+G(d) | 6-31+G(d) | 6-31G(d) |
| IV | TZ ANO | 3-21G | 3-21G |

a Nuclei directly bonded to the phosphorus. b Carbons of the phenyl group, excluding the ipso carbon.

Bruker MSL-200 (B₀ = 4.7 T) or AMX-400 (B₀ = 9.4 T) NMR spectrometers operating at 81 and 162 MHz, respectively. Fine crystalline samples were packed into 7 and 4 mm o.d. zirconium oxide rotors for the 4.7 and 9.4 T spectrometers, respectively. Cross polarization (CP) under the Hartmann–Hahn match condition was used, with contact times of 2–5 ms. All spectra were acquired with high-power proton decoupling; typical 1H 90° pulse widths were 4.0–5.5 μs. Recycle times ranged from 10 to 60 s. Sample spinning frequencies ranged from 1 to 5 kHz at the lower field and from 2 to 12 kHz at the higher field. All 31P chemical shifts were referenced to 85% H₃PO₄(aq) by setting the isotropic peak of solid NH₄H₂PO₄ to +0.81 ppm. Fully proton-coupled and partially proton-decoupled solution 31P NMR spectra of the trans and cis isomers were acquired on a Bruker AC 250 (B₀ = 5.9 T) spectrometer operating at 101 MHz.

Simulations of the spectra of stationary samples, based on eqs 1–4, were performed with a program written in this laboratory, which incorporates the POWDER routine of Alderman et al.⁵⁹ Both R₀₀ and Iₜₜ were considered in the calculation of the line shapes, which were convoluted with a Gaussian line-broadening function. Spectra of MAS samples were simulated, with the parameters obtained from an analysis of the corresponding stationary spectra, using the program NMRLAB.⁵⁰ This program performs powder averaging by sampling numerous crystal orientations using the Monte Carlo method; 10,000 orientations were used in our calculations.

Ab initio nuclear shielding calculations were performed on an IBM RISC/6000 workstation using the gauge-independent atomic orbitals (GIAO) method⁶¹⁄₂ within the Gaussian 94 suite of programs.⁵³ To keep computational time within practical limits, calculations were performed on model compounds of the trans and cis isomers in which the tert-butyl groups were replaced with hydrogen atoms (Chart 2). Restricted Hartree–Fock (RHF) calculations used locally dense basis sets⁶⁴ that included the 3-21G, 6-31G(d), 6-31+G(d) basis sets and the Roos triple-ζ atomic natural orbital (TZ ANO)⁶⁵⁶⁶ on the phosphorus atoms. The latter is a contracted (17s,12p,5d,4f)/[6s,5p,3d,2f] basis set. These basis sets, labeled I–IV, respectively, are summarized in Table 1. The molecular structure, excluding the hydrogen atoms, is from an X-ray crystallographic investigation of the trans and cis isomers. The relative positions of the hydrogen atoms were determined by ab initio geometry optimizations at the RHF/6-31G(d) level. 31P chemical shifts were calculated by taking the absolute shielding of 85% H₃PO₄(aq) to be 328.35 ppm (i.e., δ(calc) = 328.35 − σ(calc)).

Results and Discussion

31P CS Tensors of the Trans Isomer. The 31P NMR spectra of a stationary sample of the trans isomer are shown in Figure 3 along with spectra calculated using best-fit experimental parameters. Because the 31P nuclei of this compound do not possess any local symmetry, assumptions cannot be made about the orientations of their CS tensors. Hence, a complete line shape analysis was performed by refining the parameters describing the CS tensors, in a trial-and-error manner, and comparing the calculated and experimental spectra obtained at both 4.7 and 9.4 T. Analysis of these spectra yielded the principal components of the 31P CS tensors, summarized in Table 2. The spans of the CS tensors for the two nuclei are comparable, but the corresponding skewes are significantly different.

To discuss the accuracy of the calculated CS tensors, it is useful to consider calculated values for both the trans and cis isomers, summarized in Table 2. A statistical analysis of the experimental and calculated values is listed in Table 3. The correlation coefficients (r) show that the correlation between experimental and calculated data is reasonable for all basis sets. However, the slope, a, and intercept, b, of the best-fit lines show that only basis sets III and IV correlate well with experiment (perfect agreement between experiment and theory would yield values of 1 and 0 for a and b, respectively). Plots of the magnitudes of the experimental CS tensor components versus those calculated with basis sets III and IV are shown in Figures 4 and 5. The negative intercepts for the best-fit lines of these two basis sets show that the calculated values are converging to values that are shielded by approximately 30 ppm relative to the experimental values. It is also instructive to consider the last column in Table 3, the deviations of the calculated data from the corresponding experimental values. These also show that agreement with experiment improves with the larger basis sets. Figures 3 and 4, as well as Table 3, imply that agreement with experimental results is actually better with the smaller basis set III. However, one must recall that we are comparing experimental data acquired in the solid state with calculated values for isolated molecules. Gas-phase NMR studies show that the 31P nucleus is usually shielded significantly compared to values obtained for the same molecule in the liquid phase. In addition, ab initio calculations at the SCF level on PH₃ show that the calculated phosphorus shielding converges to values that are shielded compared to their experimental values.

Studies suggest that the effects of electron correlations, which have not been considered in these calculations, may be important, particularly for nuclei with localized lone-pair electrons. Unfortunately, it is not practical at this time to carry out such calculations on the molecules considered here.

We must also consider the effect of substituting hydrogen atoms for tert-butyl groups on the unsaturated ring carbons. Recent
TABLE 2: Experimental and Calculated Phosphorus Chemical Shift Tensors in the 1,2-Dihydro-1,2-diphosphate Derivatives

<table>
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<tr>
<th></th>
<th>δ_{11} (ppm)</th>
<th>δ_{22} (ppm)</th>
<th>δ_{33} (ppm)</th>
<th>δ_{iso} (ppm)</th>
<th>Ω</th>
<th>κ</th>
<th>θ_{11}</th>
<th>θ_{22}</th>
<th>θ_{33}</th>
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<td>41</td>
<td>57</td>
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<td>172</td>
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a All chemical shifts are in ppm. Estimated errors in the principal components are less than 5 ppm; those of the isotropic peaks are less than 0.5 ppm. b See Table 1 for a summary of the basis sets (I–IV) used for the ab initio calculations.

TABLE 3: Statistical Comparison of the Calculated and Experimental CS Tensor Components

<table>
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<tr>
<th>basis set</th>
<th>r</th>
<th>a</th>
<th>b/ppm</th>
<th>deviation/ppm</th>
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<td>40</td>
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</table>

a Correlation coefficients for the plot of calculated vs experimental data (Table 2). b The components of the best-fit line for the correlation between calculated and experimental data (i.e., δ_{calc} = aδ_{exp} + b). The deviation of the calculated CS tensor components from the corresponding experimental data (\(\sum(n(δ_{calc} − δ_{exp}))^2\)) where n is the number of data points.

Figure 4. Chemical shift tensor components, calculated using basis set III, plotted vs the experimental values. The filled and open squares are the tensor components of 31P—Ph and 31P—Me, respectively, for the trans isomer. The filled and open circles are the corresponding values for the cis isomer. The solid line indicates points of agreement between experiment and theory—points below this line are calculated tensor components that are shielded compared to experimental values.

Figure 5. Chemical shift tensor components calculated using basis set IV plotted vs the experimental values. See the caption of Figure 4 for a description of the points.

Theoretical calculations on diphosphates suggest that such substituents do not have a significant effect on the molecular structure about the phosphorus atoms. Nevertheless, the necessary simplicity of our model makes a rigorous comparison of experimental and calculated results difficult. Hence, the slightly better agreement between basis set III and experiment may be fortuitous. With the above factors, we consider agreement to be good with either basis set III or IV. Finally, we note that cancellation of errors results in calculated isotropic chemical shifts that are much closer to experimental values than are the individual tensor components, particularly for basis set III, illustrating the importance of considering the individual tensor components when assessing the accuracy of a computational technique.

Analysis of the experimental spectra of the trans isomer indicates that the orientations of the two CS tensors are similar, with both δ_{11} components perpendicular to the P−P bond (i.e., δ_{11} = 90°). The corresponding values for 31P—Ph and 44° for 31P—Me. The corresponding values for θ_{33} are 50 and 46°. The calculated orientations of the 31P CS tensors of the model compound for the trans isomer are in good agreement with the experimental results (Table 2). With the exception of the lowest level calculation, the calculated orientation is virtually invariant to the basis set. Calculations on small molecules (PH3 and P2H4) show that inclusion of electron correlation has a large effect on the calculated magnitudes of the CS tensor components but does not significantly alter the calculated orientations. Hence, we turn to the calculated results to propose orientations for the 31P CS tensor in the molecular framework. These calculations...
The observed powder spectrum of an isolated spin pair is usually sensitive to $R_{eff}$. Given that $\Delta J/3$ has been found to be relatively small in other systems containing P–P bonds, it is reasonable to assume that $R_{eff} \approx R_{DP}$ (eq 9). Hence, $\delta_{pp}$ may be calculated from eq 10. The dipolar coupling constant used in the spectral simulations is 1.8 kHz, a value that is estimated to be accurate to within ±0.2 kHz. Hence, the P–P bond length is calculated to be 2.22 ± 0.07 Å, comparable to the value obtained from an X-ray diffraction study, $2.20 \pm 0.10 \text{ Å}$. 25

The C$_2$P$_2$ ring of the trans isomer is distorted slightly, with a C–P–P–C torsion angle of 9.9°. The corresponding value for the cis isomer is 1.6°. However, the angles formed by the substituents with the approximate plane defined by the four-membered ring are approximately interchanged. Hence, the shielding at $31^P$–Ph in the direction perpendicular to the C$_2$P$_2$ ring is 160 ppm greater for the trans isomer than for the cis isomer (i.e., $\delta_{33}(\text{trans}) - \delta_{33}(\text{cis}) = -160$ ppm). Likewise, the shielding at $31^P$–Me in this direction is 92 ppm greater for the trans isomer. The increased shielding observed in this direction is partially offset by the decreased shielding of the $\delta_{32}$ components of the trans isomer compared to the $\delta_{33}$ components of the cis isomer. It is interesting to note that the least shielded components, $\delta_{11}$, apparently are the least sensitive to the relative orientation of the substituents, since their orientations and magnitudes in the two molecules are comparable.

Barra and Robert report a linear relationship between the span of the $31^P$ CS tensor and the bond angle defining the strain at the phosphorus atom of interest.21 Our results are in qualitative agreement with this observation, since the spans of the $31^P$ CS tensors of both isomers investigated here are significantly smaller than those found in three-membered heterocyclic compounds but comparable to that of a fused 1,2,3-benzothiadiphosphe, which contains two five-membered rings. However, we note that ring strain cannot explain the smaller spans of the CS tensors of the cis isomer compared to that of the trans isomer, since the endocyclic bond angles at each of the phosphorus atoms are similar (trans, 75.9° and 76.4°; cis, 76.2° and 76.9°). 25

The C$_2$P$_2$ ring of the trans isomer is distorted slightly, with a C–P–P–C torsion angle of 9.9°. The corresponding value for the cis isomer is 1.6°. However, the angles formed by the substituents with the approximate plane defined by the four-membered ring are comparable. Hence, the major structural difference between the two compounds is the relative orientation of the two substituents about the P–P bond.

**AB Features in NMR Spectra of a Stationary Sample of the Trans Isomer.** Spectra of a dipolar-coupled spin pair that have comparable chemical shifts at certain crystallite orientations may contain unusual (AB) features.29,30 Such characteristics are observed in the spectra of stationary samples of the trans isomer (Figure 3). They are most evident in the spectrum acquired at 4.7 T, a consequence of the smaller chemical shift difference (in Hz) between the two nuclei at this magnetic field strength. Such features were predicted in early studies and have since been observed experimentally.29,30

The low-frequency regions of stationary spectra of the trans isomer (Figure 3) arise from crystallites oriented such that $\delta_{33}$...
is parallel to \( B_0 \). This region of the spectrum acquired at 4.7 T is characterized by three shoulders of about equal intensity. The corresponding region of the spectrum acquired at 9.4 T contains four shoulders, with the outer shoulders of significantly greater intensity than the inner ones. To understand the factors giving rise to the observed line shape, the spectra of a hypothetical single crystal oriented such that the \( \delta_{33} \) components are parallel to \( B_0 \) (Figure 8) were calculated using eqs 1–4. These spectra accurately reproduce the shoulder positions and relative intensities observed in the NMR spectra of the powder sample and illustrate that the central shoulder of the 4.7 T spectrum is actually a superposition of the two inner peaks. Contrary to the “AB quartet” observed in NMR studies of solutions, where the inner peaks are always more intense than the outer ones, the outer peaks are of greater intensity here. This can be understood by considering the orientation of the CS tensors. Since the orientations of the \( \delta_{33} \) components of the two \( ^{31} \text{P} \) CS tensors of the trans isomer are coincident, the difference in the chemical shifts when \( B_0 \) is along this direction corresponds to the difference between the two \( \delta_{33} \) components; approximately 20 ppm or 1.6 and 3.2 kHz at 4.7 and 9.4 T, respectively. Since \( \theta_{33} = 90^\circ \), the effective dipolar coupling in this direction is 1.8 kHz (i.e., \( \pm R_{\text{eff}} (3 \cos^2 \theta_{33} - 1) = \mp R_{\text{eff}} \)). Clearly, the chemical shift difference between the two \( ^{31} \text{P} \) nuclei is not significantly greater than \( R_{\text{eff}} \) at either field strength. Therefore, second-order effects must be considered when discussing the spectral features in this direction. These effects can be understood in terms of eqs 1–4; since \( \theta_{33} = 90^\circ \) and \( J_1 R_{\text{eff}} \gg J_{00} \), \( B \) is negative (eq 7). Hence, \( I_1 = I_0 > 1 \) (eqs 1 and 4) and \( I_2 = I_1 < 1 \) (eqs 2 and 3). Dipolar-coupled AB spectra of this type were previously observed in \(^{13} \text{C} \) NMR spectra of a single crystal of diammonium oxalate\(^{-13} \text{C} \).\(^{27} \) Here, we see that similar effects may also be observed in spectra of a powder sample.

\(^{31} \text{P} \) NMR Spectra of MAS Samples. \(^ {31} \text{P} \) NMR spectra of MAS samples of the trans and cis isomers, with the corresponding calculated spectra, are shown in Figures 9 and 10, respectively. The isotropic peaks of the trans isomer are at \(-56.4 \) and \(-59.4 \) ppm, while those of the cis isomer are at \(-42.3 \) and \(-56.3 \) ppm. Uncertainties are estimated to be less than 0.5 ppm. Selective decoupling of the phenyl ring \(^1 \text{H} \) in solution \(^{31} \text{P} \) NMR spectra indicates that \(^{31} \text{P} \)-Ph of the trans isomer is more shielded than \(^{31} \text{P} \)-Me and that the assignment is reversed for the cis isomer. The latter observation is consistent with previous studies of phenyl- and methyl-substituted phosphorus nuclei, which found that \(^{31} \text{P} \)-Me is shielded by approximately 18 ppm relative to \(^{31} \text{P} \)-Ph.\(^{23} \) The calculated chemical shifts of the \(^{31} \text{P} \) nuclei in these compounds (Table 2) are in qualitative agreement with the assignment of the isotropic peaks as discussed above. Splittings due to \( J( \text{\(^{31} \text{P} \)-\(^{31} \text{P} \)}) \) are not detected in either spectrum, indicating that these values must be significantly less than the line width of 100 Hz. This is consistent with the solution \(^{31} \text{P} \) NMR studies, which indicate that \( J( \text{\(^{31} \text{P} \)-\(^{31} \text{P} \)}) \) is 44 and 63 Hz for the trans and cis isomers, respectively. The presence of intense spinning sidebands observed in these spectra at moderate MAS frequencies (Figures 9 and 10) confirms that the spans of the \( ^{31} \text{P} \) CS tensors are relatively large.

The individual peaks in the \(^{31} \text{P} \) MAS NMR spectra of the trans isomer are broader than those of the cis isomer and exhibit asymmetric line shapes at low MAS frequencies (Figure 9). This is more apparent in Figure 11, which shows the MAS line shapes of the trans and cis isomers with all spinning sidebands summed into the isotropic peaks. The asymmetric peaks of the trans isomer arise from the fact that at certain crystallite orientations, the chemical shift difference between the two phosphorus nuclei is comparable to the dipolar coupling between them. The case discussed above, in which the crystallites are oriented such that the four-membered ring is perpendicular to \( B_0 \), is an example of this. The symmetric line shapes of the MAS peaks of the cis

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**Figure 8.** \( \delta_{33} \) region of spectra of a stationary sample of the trans isomer (upper trace) compared with the hypothetical spectra of a single crystal oriented such that \( \delta_{33} \) is along \( B_0 \).

**Figure 9.** Calculated (A) and experimental (B) spectra of a MAS sample of trans-1,2-dihydro-1-methyl-2-phenyl-3,4-bis(tert-butyl)-1,2-diphosphate at \( v_{\text{rot}} = 2.5 \) kHz and \( B_0 = 4.7 \) T.

**Figure 10.** Calculated (A) and experimental (B) spectra of a MAS sample of cis-1,2-dihydro-1-methyl-2-phenyl-3,4-bis(tert-butyl)-1,2-diphosphate at \( v_{\text{rot}} = 4 \) kHz and \( B_0 = 9.4 \) T.
order correction coefficients are inversely dependent on $\gamma$.

The line widths of the total MAS peaks in the spectra of the trans isomer, those of the cis isomer appear to be simulated correctly.

The line widths at half-height in the spectra shown in Figure 11 are 190 and 110 Hz for the trans and cis isomers, respectively. The line widths of the total MAS peaks in the spectra of the trans isomer show a strong dependence on $\nu_{\text{rot}}$. For example, for spectra obtained at 4.7 T, the line widths of the isotropic peaks of both phosphorus nuclei reach a maximum of approximately 210 Hz at $\nu_{\text{rot}} = 3.0$ kHz and decrease at faster or slower MAS frequencies. A similar pattern is observed for spectra of the trans isomer.

Contrary to what one may expect, the maximum line width does not occur at the slowest MAS frequency, reflecting the different dependence on $\Delta \nu$ of the correction terms. In contrast to the line widths of MAS spectra of the trans isomer, those of the cis isomer are nearly independent of $\nu_{\text{rot}}$ probably because of the larger $\nu_{\text{A}}$, which partially quenches the effect of the MAS frequency-dependent terms in eq 12. Although the NMR line widths of MAS samples often increase with $B_0$, the opposite effect is observed here. This may be understood by considering eqs 11 and 12; since $\nu_{\text{A}}$ increases with the field strength, the line broadening due to the $G$, $F$, and $K$ terms is partially quenched. This phenomenon has been observed previously in the MAS spectra of dipolar-coupled spin pairs.

**Conclusions**

The dipolar chemical shift method has been used to determine the magnitudes of the principal components of the $^{31}$P CS tensors of trans- and cis-substituted diphosphetes, as well as their orientations relative to the dipolar vector. The relative orientations of the phenyl and methyl substituents have a large effect on the orientations and magnitudes of the CS tensors. When the substituents are trans to one another, the spans of the CS tensors are over 100 ppm larger than when they are cis to one another. Spectral features, observed in the NMR spectra of MAS and stationary samples, have been interpreted in terms of the detailed theory governing homonuclear dipolar-coupled spin pairs.

There are significant discrepancies between the magnitudes of the calculated and experimental CS tensor components, perhaps because the effects of electron correlation have not been considered in the ab initio calculations. Clearly, higher-order calculations are required. Nevertheless, the calculated orientations of the principal components of the CS tensors relative to the dipolar vector are in reasonable agreement with experimental findings and are essentially invariant to basis set size. Hence, an orientation in the molecular framework, based on the combined experimental— theoretical results, has been proposed.

In general, we have observed that $^{31}$P CS tensors in diphosphetes are very sensitive to isomerism. It is hoped that this work will initiate further studies, both experimental and theoretical, of phosphorus nuclei in strained environments.

**Acknowledgment.** We are grateful to members of the solid-state NMR group and to Dr. Klaus Eichele for helpful suggestions. R.E.W. thanks the Natural Sciences and Engineering Research Council (NSERC) of Canada for operating and equipment grants and the Canada Council for a Killam Research Fellowship. G.M.B. thanks NSERC, the Izaak Walton Killam Trust, and the Walter C. Sumner Foundation for postgraduate scholarships. All NMR spectra were obtained at the Atlantic Region Magnetic Resonance Centre (ARMRC), which is also supported by NSERC.

**References and Notes**


