

Phosphorus-31 Solid-State NMR Study of Iminophosphines: Influence of Electronic Structure and Configuration of the Double Bond on Phosphorus Shielding

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Abstract: The principal elements of the ^{31}P nuclear magnetic shielding tensors of iminophosphines of the type $\text{R}-\text{P}=\text{N}-\text{aryl}$ (aryl = $\text{C}_6\text{H}_2\text{tBu}_3$; R = tBu, $\text{Ph}_3\text{Sn}(\text{tBu})\text{N}$, aryl- $\text{N}=\text{P}-(\text{tBu})\text{N}$, aryl-NH, aryl- $\text{N}=\text{P}-(\text{adamantyl})\text{N}$, Ph_2N , carbazolyl, $\text{tBu}_2\text{C}=\text{N}$, iminofluorenyl, Cl, Br, I; 5-16) are determined from high-resolution solid-state MAS (magic angle spinning) NMR spectra. Comparison of the data with the results of IGLO calculations on shielding tensors of model compounds is used to assign the orientation of the principal axes system in the molecular frame. The observed shieldings can be correlated with structural features of the compounds. In (*E*)-configured alkyl- and amino-iminophosphines, the component at high field (δ_{33}) is approximately perpendicular to the RPN plane and the low-field component (δ_{11}) is in this plane and close to the P-R bond. Introduction of π -donor substituents ($\text{R}'_2\text{N}$) at phosphorus produces large increases in δ_{11} , which can be related to corresponding changes in the $n-\pi^*$ electronic transition energies. A similar effect is found for a change of the double-bond geometry from (*E*)- to (*Z*)-configuration. Electronegative halogen substituents (Cl, Br) give rise to a further substantial increase in the tensor component at high field, δ_{33} . Furthermore, a change of the orientation of the principal axes system in the molecular frame occurs, with δ_{33} being aligned close to the P,N bond axis and the intermediate component, δ_{22} , perpendicular to the RPN plane. A discussion of these effects is given in terms of partial triple-bond character for the P,N bond. The shape of the shielding tensor of the iodo compound (16) suggests that the electronic environment of the P,N moiety is similar to other systems containing a genuine triple bond. The unique difference between the isotropic chemical shifts in the solid state and in solution ($\Delta\delta$ 118 ppm) in this case indicates that this phenomenon is confined to the solid state and can be attributed to the substantial polarization of the P,I bond, which is a consequence of the observed intermolecular association.

Introduction

The development of a chemistry of multiple bond systems, involving heavier main group elements can be considered as one of the most exciting advances in main group chemistry during the last two decades. Among the many stable multiple bond systems which have been successfully characterized, compounds with (p-p) π -bonds to phosphorus were among the first stable examples to be synthesized¹ and still play an important role in this field.² The early success in this area may to a great part be attributed to the easy NMR observability of ^{31}P , providing synthetic chemists with a sensitive analytical probe. In contrast to the routine nature of solution ^{31}P -NMR, however, rather few solid-state NMR investigations have yet been carried out, and the first studies focused mainly on multiple bonding between phosphorus with another phosphorus (aryl-P=P-aryl)^{3,4} (1); aryl = 2,4,6-tris-*tert*-butylphenyl) or carbon (aryl-P=C(SiMe₃)₂ (2), aryl-C=P (3)⁵). The results of these studies nevertheless yielded valuable information on the nature of the multiple bonding which

complements material available from other sources (mostly X-ray diffraction methods).

Iminophosphines featuring (3p-2p) π -bonding between phosphorus and nitrogen occupy a special place among the numerous multiple bond systems because of the potential of the imino-nitrogen to vary its bonding state by means of formal electron release or acceptance.^{2,6} This results in a wide range of different structures of the multiple bond system, which in turn can be held responsible for the observed very intricate and diverse chemical reactivity.^{2,6} A particularly interesting aspect is the phenomenon of (*E/Z*)-double-bond isomerism, since it has been shown both by experiment^{2,6} and theory⁷ that inversion of the double-bond configuration is followed by considerable changes in the bonding parameters. Regarding the large chemical shift anisotropies of phosphorus nuclei in multiple bond systems³⁻⁵ as well as the sensitivity of the individual components of the shielding tensor toward changes in electron distribution and molecular geometry, solid-state NMR spectroscopy seems a promising tool to gain further understanding of the bonding situation in iminophosphines. Its potential is clearly emphasized in the recent investigation of the solid-state NMR parameters of the cation aryl-N \equiv P⁺ (4),⁸ which is currently the only phosphorus nitrogen multiple bond system having been studied with this method.

We have set out to study the phosphorus chemical shielding in a series of differently substituted iminophosphanes with both

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(1) (a) Gier, T. E. *J. Am. Chem. Soc.* 1961, 83, 1769. (b) Dimroth, K.; Hoffmann, P. *Angew. Chem., Int. Ed. Engl.* 1964, 3, 384.

(2) For a review, see: *Multiple Bonds and Low Coordination in Phosphorus Chemistry*; Regitz, M., Scherer, O., Eds.; Georg Thieme Verlag: Stuttgart, 1990.

(3) Zilm, K. W.; Webb, G. G.; Cowley, A. H.; Pakulski, M.; Orendt, A. *J. Am. Chem. Soc.* 1988, 110, 2032.

(4) Challoner, R.; McDowell, C. A. *J. Chem. Phys.* 1991, 94, 7038.

(5) Duchamp, J. C.; Pakulski, M.; Cowley, A. H.; Zilm, K. W. *J. Am. Chem. Soc.* 1990, 112, 6803.

(6) Niecke, E.; Gudat, D. *Angew. Chem., Int. Ed. Engl.* 1991, 30, 217.

(7) (a) Trinquier, G. *J. Am. Chem. Soc.* 1982, 104, 6969. (b) Nguyen, M. T.; McGinn, M. A.; Hegarty, A. F. *J. Am. Chem. Soc.* 1985, 107, 8029.

(8) Curtis, R. D.; Schriver, M. J.; Wasylshen, R. E. *J. Am. Chem. Soc.* 1991, 113, 1493.

(*E*)- and (*Z*)-configuration of the double bond by high-resolution magic angle spinning (MAS) solid-state NMR spectroscopy. Comparison of the magnitudes of the principal components of the shielding tensor as obtained from the experiments with calculated (IGLO⁹) data of model compounds yields information about the orientation of the shielding tensor in the molecular frame. The implications of variations in the electronic structure of the double bond on the chemical shielding will be discussed on the basis of both experimental and theoretical data and will be related to the NMR properties of other known phosphorus-containing multiple bond systems.

Methodology. For complete characterization of the magnetic shielding tensor of a nucleus in a molecule, knowledge of both the magnitudes and orientations of the three principal components has to be gained. Whereas the magnitudes are easily obtained from the solid-state NMR spectra of powdered samples,^{10,11} determination of the tensor orientation generally requires the investigation of single crystals;¹¹ in favorite cases, when isolated AX spin pairs with dipolar coupling are present, these data are partially accessible from polycrystalline samples by dipolar chemical shift spectroscopy.¹²

In the case of the studied iminophosphanes, the presence of additional quadrupolar nuclei gives rise to a significant complication in the solid-state ³¹P-NMR spectra since the observed line shapes depend on scalar and dipolar couplings as well as quadrupolar interactions, in addition to the effect of chemical shielding. Except in highly symmetric molecules, the number of observable discontinuities in wide-line spectra of solid samples is normally insufficient to afford complete analysis of all interactions. In order to facilitate a straightforward extraction of shielding tensor data, it seems therefore advantageous to reduce or eliminate the additional perturbations. For instance, quadrupolar interactions with abundant ¹⁴N nuclei may be removed by isotopic labeling with ¹⁵N (*I* = 1/2); however, the use of this method is limited because suitable ¹⁵N-doped precursors may be unreasonably expensive or not available at all.

Using a different approach, averaging of anisotropic dipolar interactions in solid-state NMR spectra of spin-1/2 nuclei can be afforded by MAS¹³ at adequate speed. The accessible rotation rates (1–20 kHz) generally suffice to eliminate effects of dipolar interactions unless strong coupling is present,¹⁴ but are for many inorganic compounds still in the slow-spinning regime when compared to the shielding tensor. The magnitudes of the principal tensor components may then be derived by intensity analysis of the observed spinning sideband patterns.^{15,16} Interactions with adjacent quadrupolar nuclei are scaled down by MAS, but their effects cannot be completely eliminated because their angular dependence is not averaged to 0.^{17,18} As a consequence, MAS spectra show residual dipolar coupling effects in the form of characteristic fine structure of the resonance lines. Theoretical analyses of these effects have been carried out but are rather complicated;¹⁷ when the quadrupolar interactions are weak as compared to the Zeeman energies (this is generally found for spin-1/2 nuclei coupling to ¹⁴N), the treatment can be considerably simplified by a first-order perturbation approach.¹⁸ For a concise

determination of the shielding tensor from MAS spectra, the residual dipolar interactions must be taken into account. Gobetto et al.¹⁹ have shown that for IS spin systems with axial symmetry (the shielding tensors $\sigma(I), \sigma(S)$ are coaxial with both the dipolar and scalar coupling tensors D_{IS} and J_{IS} , and all tensors have axial symmetry) each spin state m_I of the quadrupolar spin *S* gives rise to a separate spinning sideband manifold in the spectrum of *I*. These subspectra can be described by effective shielding tensors $\sigma'(I)$ with anisotropies $\sigma'_i(I) = \sigma(I) - 2D'_{IS}m_I(S)/\nu$ (D'_{IS} = effective dipolar coupling constant, ν = resonance frequency of *I*). The true shielding tensor $\sigma(I)$ is then evaluated by averaging over the subspectra. As a further advantage, MAS spectra are obtained under "high-resolution" conditions. This often allows the treatment of overlapping resonances which can occur if a sample contains several like nuclei in different chemical environments, or in the presence of impurities.

The severe limitation of solid-state NMR studies of randomly oriented samples, viz., the loss of the directional information, is frequently overcome by comparison of the experimental results with calculated shielding data. Past experience with ¹³C shielding tensors indicated that the tensor orientation is subject to much less variation than the actual magnitudes of the principal components in related compounds.^{11,20,21} It has been shown in these cases, as well as for the diphosphene **1**,³ that the orientation of the shielding tensor can be frequently derived from calculations of model compounds with much more accuracy than the actual values of the shielding themselves. In addition, it is expected that a theoretical analysis of phosphorus shielding in iminophosphines will be helpful to provide more detailed insight in certain underlying trends (e.g. substituent effects).

Experimental Section

Iminophosphines **5–16** were prepared as described elsewhere^{22–26} All NMR measurements were carried out on a Varian Unity-400 instrument operating at a field of 9.4 T and equipped with a high-speed MAS probehead. The samples were ground into a powder and transferred to 4-mm silicon nitride rotors, which were then closed with Kel-F caps. All manipulations were carried out in a glovebag under an Ar atmosphere. The samples were found to be stable in the closed rotors over a period of several days, without any necessity for further precautions.

MAS spectra were recorded at spinning rates between 7 and 10 kHz at a ³¹P resonance frequency of 161.9 MHz. No cross polarization was employed in order to prevent inhomogeneous excitation over the range of the shielding tensor.²⁷ All spectra were acquired under high-power ¹H decoupling and ³¹P $\pi/2$ pulse widths of 3–4 μ s, with relaxation delays of 60–120 s. Typical measurements required between 100 and 700 transients. Chemical shifts are referenced to external 85% H₃PO₄ and are given in the δ -scale ($\delta(\text{H}_3\text{PO}_4) = 0$). Base-line correction and deconvolution of the sidebands were performed for all spectra using both the spectrometer software and the built-in features of the MASNMR program package;²⁸ both methods gave identical results. Isotopic chemical shifts were determined via moment analysis in MASNMR; in ambiguous cases, the values were checked by comparison of MAS spectra taken at different spinning speeds. The principal components of the shielding tensor were evaluated by analysis of the spinning sideband

(9) (a) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (b) Schindler, M. S.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919. (c) Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR Basic Principles and Progress*, Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer Verlag: Berlin, 1990; Vol. 23, p 167 ff.

(10) Taylor, P. C.; Baugher, J. F.; Kriz, H. M. *Chem. Rev.* **1975**, *75*, 203.

(11) Veeman, W. S. *Prog. Nucl. Magn. Reson. Spectrosc.* **1984**, *16*, 193.

(12) Power, W. P.; Wasylishen, R. E. In *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: London, 1991; p 1 ff.

(13) (a) Andrew, E. R.; Bradbury, A.; Eades, R. G. *Nature* **1958**, *182*, 1659. (b) *Ibid.* **1959**, *183*, 1802. (c) Lowe, I. J. *Phys. Rev. Lett.* **1959**, *2*, 285.

(14) Wu, G.; Wasylishen, R. E.; Curtis, R. D. *Can. J. Chem.* **1992**, *70*, 863.

(15) Maricq, M. M.; Waugh, J. S. *J. Chem. Phys.* **1979**, *70*, 3300.

(16) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021.

(17) Zumbulyadis, N.; Henrichs, P. M.; Young, R. H. *J. Chem. Phys.* **1981**, *75*, 1603.

(18) Olivieri, A. C.; Frydman, L.; Diaz, L. E. *J. Magn. Reson.* **1987**, *75*, 50.

(19) Gobetto, R.; Harris, R. K.; Apperley, D. C. *J. Magn. Reson.* **1992**, *96*, 119.

(20) Facelli, J. C.; Orendt, A. M.; Beeler, A. J.; Solum, M. S.; Depke, G.; Malsch, K. G.; Downing, J. W.; Farvathi, S. M.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1985**, *107*, 6479.

(21) Facelli, J. C.; Orendt, A. M.; Solum, M. S.; Depke, G.; Grant, D. M.; Michl, J. *J. Am. Chem. Soc.* **1986**, *108*, 4268.

(22) (a) Niecke, E.; Lysek, M.; Symalla, E. *Chimia* **1986**, *40*, 202. (b) Romanenko, V. D.; Drapailo, A. B.; Ruban, A. V.; Markovskii, L. N. *Zh. Obshch. Khim.* **1986**, *56*, 2792.

(23) Hitchcock, P. B.; Lappert, M. F.; Rai, A. K.; Williams, H. D. *J. Chem. Soc., Chem. Commun.* **1986**, 1633.

(24) (a) Niecke, E.; Detsch, R.; Nieger, M. *Chem. Ber.* **1990**, *123*, 797. (b) Detsch, R. Ph.D. Thesis, Universität Bonn, 1992.

(25) (a) Gärtner-Winkhaus, C. Ph.D. Thesis, Universität Bonn, 1992. (b) Niecke, E.; Nieger, M.; Gärtner-Winkhaus, C.; Kramer, B. *Chem. Ber.* **1990**, *123*, 477.

(26) (a) Niecke, E.; Nieger, M.; Reichert, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1715. (b) Reichert, F. Ph.D. Thesis, Universität Bonn, 1990.

(27) Jeschke, G. Diploma Thesis, Technische Universität Dresden, 1992.

(28) Jeschke, G. *MASNMR*; Technische Universität Dresden, 1992.

intensities using MASNMR²⁸ as well as a similar computer program developed in-house;²⁹ both programs are based on iterative adaptations of the method of Herzfeld and Berger.¹⁶ The principal components were indicated according to their magnitude, with $\delta_{11} \geq \delta_{22} \geq \delta_{33}$; given shifts are typically accurate to within ± 0.5 ppm for δ_{iso} and ± 25 ppm for δ_{ii} .

IGLO⁹ calculations of the nuclear magnetic shielding tensors for the parent compounds 17–21 were performed with both "experimental"^{26,22–26} and ab-initio calculated (energy optimization using a DZP (double- ξ + polarization) basis set at the SCF level³⁰) geometries for 17–20; for 21, only the "experimental" geometry²⁴ was available. "Experimental" geometries were based on the X-ray structure data for the heteroatom skeleton; peripheral hydrogen atoms were attached at the observed bond angles, but with standard bond distances as derived from the SCF-optimized structures ($r(\text{PH})$ 1.43 Å; $r(\text{NH})$ 1.01 Å; $r(\text{CH})$ 1.10 Å³⁰). The basis set used for the IGLO calculations was of TZP quality (basis II as described in ref 9c). The calculated (absolute) shieldings were converted to chemical shifts using the reference data by Jameson et al.³¹

Results

MAS Line Shapes. With the exception of 8, the sideband manifolds in the ³¹P-MAS spectra of 6–16 display symmetric Gaussian or mixed Lorentzian/Gaussian line shapes with half-widths of 200–600 Hz; significantly sharper lines (70 Hz) are only observed for 5. No asymmetric splittings or shoulders are detected, indicating that the magnitude of residual quadrupolar splittings is smaller than the line widths. This is corroborated by comparison of the spectra of the isotopomers 14a,b, showing that replacement of ¹⁴N ($I = 1$) by ¹⁵N ($I = 1/2$) has no visible effect on the line shape. The MAS spectrum of 8 is unique, as the resonance lines appear as strongly overlapping asymmetric doublets (relative intensities approximately 2:1 for the center band) with a splitting of 440 Hz.

Chemical Shift Tensors. The failure to resolve any residual dipolar splittings prevents the identification of the subspectra associated with different spin states of the quadrupolar nuclei and thus precludes spectral analysis in terms of effective shielding tensors. On the other hand, since the contribution from each subspectrum to a particular spinning sideband will vary somewhat because of the change in σ' , a tensor analysis based on the integral sideband intensities may be susceptible to systematic errors. However, as the variation in σ' depends on the effective dipolar coupling constant D' ,¹⁹ the relative deviations will become small when the overall shielding anisotropy significantly exceeds D' and at higher magnetic fields. For the cation [$\text{P}=\text{N}-\text{aryl}$]⁺, 4 ($D' = 960$ Hz⁸), the maximum difference in effective shielding anisotropies between the ± 1 spin states of ¹⁴N is estimated according to Gobetto et al.¹⁹ as 12 ppm at a field of 9.4 T. Even if the approximate nature of this value must be conceded, owing to the nonaxiality of the shielding tensor,⁸ differences of this magnitude are small, as compared to the shielding anisotropy of 581 ppm.⁸ Regarding that the shift anisotropies in iminophosphines are of similar size, the errors introduced by complete neglect of the residual dipolar effects can be tolerated. Heuristic justification of this approach is given by the spectral data of 14a,b. Here, shielding tensor analysis based on integral sideband intensities yields identical results within experimental error for both isotopomers, thus demonstrating that the effects of residual dipolar coupling with ¹⁴N are essentially negligible.

The principal components of the shielding tensor (δ_{ii}) as well as isotropic chemical shifts (δ_{iso}) of 5–16, as obtained by analysis of the sideband intensities according to the method of Herzfeld and Berger,¹⁶ are summarized in Tables 1 and 2, respectively. With the exception of 7 and 9, where the two inequivalent ³¹P nuclei give rise to separate resonances, all spectra display a single set of sidebands, which is consistent with the crystallographic equivalency of all molecules in the unit cell. Scalar couplings (¹J_{PN}, ²J_{PP}) are not resolved, so that no corrections for J -anisotropy

Table 1. ³¹P Chemical Shift Tensor Data for R—P=N—aryl (aryl = C₆H₂tBu₃), 5–16^a

	R	double-bond conformation	δ_{11}	δ_{22}	δ_{33}	δ_{iso}
5	tBu	<i>E</i>	1035	297	130	487
6	Ph ₃ Sn(tBu)N	<i>E</i>	719	225	94	346
7	aryl—N=P(tBu)N	<i>E</i>	742	147	84	324
		<i>E</i>	685	136	133	318
8	aryl—NH	<i>E</i>	628	124	90	281
9	aryl—N=P(Ad)N	<i>E</i>	758	171	76	335
		<i>Z</i>	441	84	48	191
10	Ph ₂ N	<i>Z</i>	354	87	-9	144
11	C ₁₂ H ₈ N (carbazolyl)	<i>Z</i>	385	75	-36	141
12	tBu ₂ C=N	<i>E</i>	478	122	17	206
13	C ₁₂ H ₈ C=N (fluorenylimino)	<i>Z</i>	254	128	8	130
14a	Cl	<i>Z</i>	445	129	-140	145
14b	Cl(¹⁵ N)	<i>Z</i>	446	131	-143	145
15	Br	<i>Z</i>	400	125	-104	140
16	I	<i>Z</i>	276	192	-167	100

^a Reference: $\delta(\text{H}_3\text{PO}_4) = 0.0$; negative values indicate increased shielding.

Table 2. Isotropic ³¹P Chemical Shifts of R—P=N—aryl (aryl = C₆H₂tBu₃), 5–16, in the Solid State and in Hydrocarbon Solution^a

	R	double-bond conformation ^b	δ_{soln}	δ_{iso}	$\Delta\delta$
5	tBu	<i>E</i>	482	487	-5
6	Ph ₃ Sn(tBu)N	<i>E</i>	328	346	-18
7	aryl—N=P(tBu)N	<i>E</i>	272	324	-52
		<i>E</i>		318	-46
8	aryl—NH	<i>E</i>	272	281	-9
9	aryl—N=P(Ad)N	<i>E</i>	306	335	-29
		<i>Z</i>	233	191	42
10	Ph ₂ N	<i>Z</i>	198	144	54
11	C ₁₂ H ₈ N (carbazolyl)	<i>Z</i>	186	141	45
12	tBu ₂ C=N	<i>E</i>	178	206	-28
13	C ₁₂ H ₈ C=N (fluorenylimino)	<i>Z</i>	124	130	-6
14a	Cl	<i>Z</i>	136	145	-9
15	Br	<i>Z</i>	162	140	22
16	I	<i>Z</i>	218	100	118

^a Reference: $\delta(\text{H}_3\text{PO}_4) = 0.0$; negative values indicate increased shielding. ^b Double-bond configuration in the solid state.

need to be made; furthermore, no irregular intensity distributions associated with strong coupling effects¹⁴ are visible. The isotropic shifts in the solid state (δ_{iso}) differ in several cases considerably from the solution values (δ_{soln}) (Table 2), the most pronounced deviation (118 ppm) being observed for 16. While all tensors have the typical large anisotropies of multiple bond systems in common, characteristic trends in chemical shielding following changes in both substitution and double-bond geometry are evident. The magnitude of these effects clearly exceeds the observed variations between individual derivatives belonging to the same class (e.g. different R in R₂N).

Both the most deshielded value for δ_{iso} and the largest chemical shift anisotropy is observed for 5, which exhibits alkyl substitution at phosphorus and (*E*)-configuration of the double bond. The shielding tensor displays a marked negative axiality,¹⁶ which is a common feature for most (p-p) π -double-bond systems^{3,5,11} and is also shared by the majority of the iminophosphines included in this study. Formal replacement of the alkyl by amino substituents (6–9) or ketimino substituents (12) leads to increased shielding of all three principal components, although to a different extent. By far the largest effect is found on δ_{11} , which is upfield shifted by some 300 ppm in 6–9 as compared to 5. δ_{22} experiences much less variation ($\Delta\delta$ 100–200 ppm), while the changes in δ_{33} have to be considered insignificant ($\delta_{33} = 130$ ppm for 5, 76–133 ppm for 6–9). As a consequence, replacement of the alkyl group by an amino group significantly reduces the overall shielding anisotropy as well as the difference between δ_{22} and δ_{33} , even to

(29) Gudat, D. Unpublished results.

(30) Schoeller, W. W.; Busch, T.; Niecke, E. *Chem. Ber.* **1990**, *123*, 1653.

(31) Jameson, C. J.; De Dios, A.; Jameson, A. K. *Chem. Phys. Lett.* **1990**, *167*, 574.

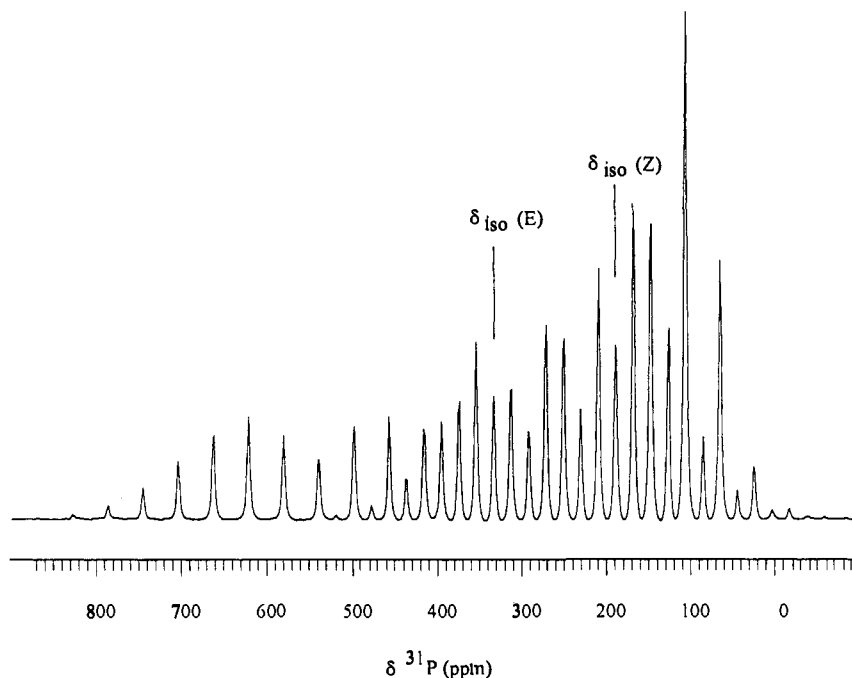


Figure 1. ^{31}P -MAS spectrum (161.9 MHz) of **9** at 6.59-kHz rotation frequency. The spectrum clearly shows the two spinning sideband manifolds with characteristically different overall shielding anisotropies. The isotropic lines are marked and assigned to the two different sites.

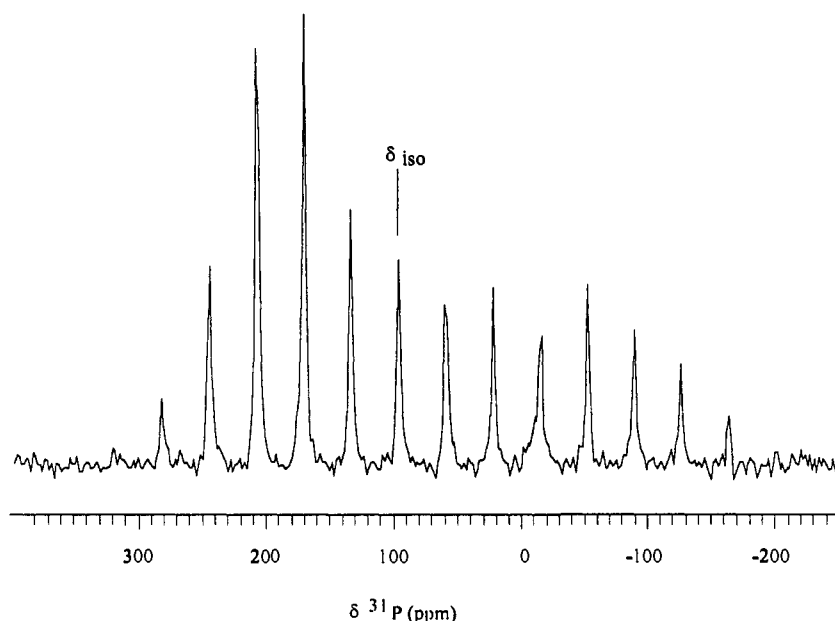


Figure 2. ^{31}P -MAS spectrum (161.9 MHz) of **16** at 6.14-kHz rotation frequency. The isotropic line is marked.

the extent that an essentially axial tensor is found for one of the phosphorus nuclei in **7**.

In addition to the substituent effect, a further increase in shielding of δ_{11} by some 200–300 ppm is associated with a change from (*E*)- (**6–9**) to the (*Z*)-configuration of the double bond (**9–11**). Systematic, albeit much smaller, changes are evident for the other components. The effect is most impressively demonstrated in the case of **9** (Figure 1). Since both phosphorus nitrogen double bonds bear identical substituents, the substantial chemical shift difference by 317 ppm for δ_{11} is in this case exclusively attributable to the different stereochemistries.

In ketimino-substituted derivatives, δ_{11} is found at considerably higher field, as in amino-iminophosphines ($\Delta\delta$ 550 ppm between **12** and **5**), while the other components are only slightly more shielded. Consequently, the overall shielding anisotropy is further significantly reduced. Comparison of the data of **12** and **13** reveals that the configuration influence on the shielding tensor is still

evident, but the magnitude of the chemical shift differences ($\Delta\delta$ 224 ppm for δ_{11}) is smaller than for amino-iminophosphines.

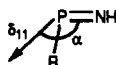
Shielding tensors very similar to each other are found for the P-halogen-substituted derivatives, **14** and **15**. The values of δ_{11} and δ_{22} are comparable to (*Z*)-amino-iminophosphines; however, δ_{33} is considerably more shielded. As a consequence, the chemical shift anisotropy is increased and the observed tensor axialities are close to 0. Still substantially higher shielding of δ_{33} is found for the P-iodo compound, **16**. Since at the same time δ_{11} is shifted to higher and δ_{22} to lower field, the tensor adopts a unique positive axiality (Figure 2). On the whole, its shape is essentially the same as for the cation **4**⁸ (see below), with the single difference of a somewhat reduced shielding anisotropy.

Model Calculations. The calculated tensor data are summarized in Table 3. The SCF-optimized conformations of **17–20** exhibit planar symmetry, requiring that two of the principal components of the shielding tensor are confined within this plane

Table 3. Principal Components and Orientation of Calculated Shielding Tensors for Iminophosphines R—P=NH, 17–21^a

	R	double-bond conformation	geometry ^b	δ_{11}	δ_{22}	δ_{33}	δ_{iso}	out-of-plane component	angle α (deg) ^c
17	H	E	scf	1546.1	188.7	40.4	591.6	δ_{33}	120.2
		Z	scf	899.7	327.1	12.1	409.6	δ_{33}	121.4
18	H ₃ C	E	scf	1429.6	309.3	33.8	590.9	δ_{33}	124.0
			exp ^d	1583.3	249.1	59.6	630.7	δ_{33}	129.9
		Z	scf	863.9	400.1	11.6	425.2	δ_{33}	127.7
			exp ^e	963.8	103.4	72.6	379.8	δ_{33}	111.2
19	H ₂ N	E	scf	1013.8	94.8	51.4	386.7	δ_{33}	105.8
			exp ^f	604.0	78.7	47.4	243.4	δ_{33}	118.3
		Z	scf	394.0	42.1	15.4	150.5	δ_{22}	123.6
			exp ^g	700.0	153.8	-110.7	247.7	δ_{22}	114.2
20	Cl	Z	scf	441.8	108.8	-231.2	106.5	δ_{22}	115.8
			exp ^h	1051.7	88.8	40.3	393.6	δ_{22}	112.4
21	HN=P—NH	E	exp ^h	466.5	48.5	12.9	176.0	δ_{22}	126.3
		Z							

^a The calculated absolute shieldings σ_{ii} were converted to chemical shifts δ_{ii} according to Jameson, de Dios, and Jameson. Reference: $\sigma(\text{H}_3\text{PO}_4) = 328.35$.³¹ ^b scf = scf-optimized geometry (ref 30); exp = experimental core geometry with attached hydrogen atoms; see text. ^c In plane angle between δ_{11} and the PN double-bond axis:



^d Based on X-ray structure of Et₃CP=N—aryl.³⁸ ^e Based on X-ray structure of 7.²⁴ ^f Based on X-ray structure of 10.²⁵ ^g Based on X-ray structure of 14a.²⁶ ^h Based on X-ray structure of 9.²⁴

(“in-plane”), while the third one is perpendicular (“out-of-plane”). In all cases but **20**, this component is the most shielded one (δ_{33}). For **20**, the out-of-plane component is δ_{22} , leaving δ_{33} as the in-plane component closest to the direction of the phosphorus–nitrogen bond. The most deshielded component (δ_{11}) is always in-plane and points close to the direction of the P—X single bond. The angle α spanned by δ_{11} and the double-bond axis is generally somewhat larger than the phosphorus valence angle. The size of α changes by less than $\pm 10^\circ$ for all calculated structures, indicating that the orientation of the principal axis system changes indeed much less than the magnitude of the shielding in each direction. For the heteronuclear substituted derivatives **18–20**, the variations in α appear to be loosely correlated to the change in the XPN angle.

Even if in the “experimental” structures the planar symmetry is broken, the measured dihedral (XPNH) angles differ from the ideal values by less than 6° .⁶ The calculated tensors remain closely aligned with respect to the corresponding best-fit planes, and in principle the same orientations of the principal axes are derived as for the case of SCF-optimized geometry. An exception is constituted by (Z)—H₂N—P=NH, **19**, where the assignment of δ_{22} (out-of-plane) and δ_{33} (in-plane) is reversed as compared to the SCF-optimized structure. The same tensor orientation, which equals that of the Cl derivative **20**, is also found for both phosphorus shielding tensors in **21**.

For a further discussion of trends in chemical shift data it is necessary to establish a correspondence between the measured and calculated shieldings for the individual compounds. The unique downfield shift of δ_{11} in **5–16** allows its unequivocal assignment as the in-plane tensor component lying closest to the P—X single bond in all cases. For alkyl-substituted (**5**) or halogen-substituted derivatives (**14–16**), the discrimination between the remaining components in the calculations is considered as satisfactory to establish δ_{33} (**5**) and δ_{22} (**14–16**), respectively, as the out-of-plane component. The calculated values of δ_{22} and δ_{33} for amino-iminophosphines are much closer, and their difference is of similar magnitude as the deviation between experimental (**8**, **10**) and calculated (**19**) data, making an assignment exceedingly difficult. As further calculations on (E)—H₂N—P=N—H (**19**) revealed that moderate alterations of bond distances or angles leave the tensor orientation unchanged, it is suggested that the alignment of the principal axes in the (E)-isomers **6–8** and **12** is presumably similar to alkyl derivatives, with δ_{33} being out-of-plane. In contrast, no unambiguous assignments can be made for **9** and the (Z)-isomers **10**, **11**, and **13**, where, according to the calculations, the out-of-plane principal axis may be either δ_{22} or δ_{33} , depending on the individual geometry.

Naturally, the numerical coincidence between experimental and calculated values of principal components is not very good as is expected given the considerable simplifications of the model compounds and the known tendency of the Hartree–Fock-based methods (such as IGLO) to overestimate strong deshielding contributions. Nonetheless, the effect of structural variations on the shielding is clearly evident. The most significant variations of shielding parameters are induced by changes of substitution or double-bond configuration. Using the indication for the experimentally determined tensor components as described above, the observed trends can be reproduced by the calculated data. The influence of the double-bond stereochemistry on the shielding tensor is not confined to amino-substituted derivatives, but seems to be a general feature of phosphorus–nitrogen double-bond systems. Variation of bond distances or angles (“experimental” vs SCF-calculated geometry) results in less pronounced, but yet significant, changes of calculated shieldings, thus giving emphasis to the sensitivity of the shielding tensor of a nucleus as a probe for changes in the three-dimensional electronic structure of its surroundings.

Discussion

Quadrupolar Splittings. Recently, Wasyllshen and co-workers³² reported quadrupolar splittings of 140 ± 20 Hz in the ³¹P-MAS spectra of monophosphazenes Ph₃P=NR' (R' = Ph, tolyl) at a magnetic field strength of 4.7 T, which can be extrapolated¹⁸ to values around 70 Hz at the higher field (9.4 T) applied here. Whereas the detection of quadrupolar interactions of this magnitude in the MAS spectra of **6–16** is precluded by the large line widths, the residual quadrupolar splitting must be much smaller in the case of **5**. Assuming similar phosphorus–nitrogen distances and comparable electric field gradients at nitrogen for both phosphazenes and iminophosphines, this effect may be attributed to a lower nuclear quadrupole coupling constant (χ) or a different geometry relation of the coupling tensors, or a combination of both, in the iminophosphine **5**. In the case of **8**, neither the crystal structure^{26a} nor solid-state ¹³C-NMR spectra^{26b} give evidence for magnetic nonequivalent molecules in the asymmetric unit, so that a quadrupolar origin of the observed line splitting seems likely. However, a simple interpretation in terms of residual dipolar coupling is questionable, since the magnitude of the splitting would require a substantially increased value of χ in this case, for which no immediate reason can be seen. Regarding that a deeper analysis of the quadrupolar

(32) Power, W. P.; Wasyllshen, R. E.; Curtiss, R. D. *Can. J. Chem.* **1989**, *67*, 1989.

interaction, even in terms of a simple perturbation treatment,¹⁸ would require knowledge of several geometric as well as energetic parameters which is presently not available, no further interpretation of the effect is attempted.

Trends in Chemical Shift Tensors. It is generally acknowledged that in the case of multiple bond systems the variations in the shielding tensor components are dominated by changes in the paramagnetic term, σ_p .³³ The magnitude of σ_p strongly depends on the availability of excited states which are connected with the ground state by magnetic-dipole-allowed transitions; large deshieldings are generally associated with low transition energies. For iminophosphines, the lowest magnetically allowed transition corresponds to the $n(\text{P})-\pi^*(\text{PN})$ electronic excitation, whose energy has been shown by previous spectroscopic studies to be sensitively affected by the electronic structure of the π -bond.^{2,6,34} Due to the nature of the angular momentum operators in the expression for σ_p , any changes in the shielding tensor related to variation of the $n-\pi^*$ excitation energy should be strongest in a direction which is perpendicular to both of the two axes through the lobes of the phosphorus lone pair and the π^* -orbital; this approximately coincides with the direction of the P—X single bond. The least effect is expected on the out-of-plane principal component which is parallel to the lobe of the π^* -orbital; within the molecular plane, the least changes of σ_p should occur parallel to the lobe of the phosphorus lone pair.

On the basis of the suggested orientation of the shielding tensor in iminophosphines, the large increase in δ_{11} upon going from P-alkyl-iminophosphines (**5**) to amino-iminophosphines (**6–11**) is considered predominantly as a direct consequence of the corresponding increase in $n-\pi^*$ excitation energy, which results from both the perturbation of the double-bond system by π -conjugation³⁴ and the higher ligand electronegativity.^{2,30} This interpretation is further corroborated by analysis of individual orbital contributions to the shielding, which shows that the largest variations of δ_{11} arise indeed from the phosphorus nonbonding orbital. In this sense, the further increased shielding of δ_{11} in ketimine-substituted derivatives suggests a higher π -donating capability of ketimino groups as compared to amino groups. The same conclusion has been derived based on the crystal structure data of **12** and **13**.²⁵ Halogen substituents lead in the case of Cl and Br to slight deshielding of δ_{11} , as compared to amino-iminophosphines of like stereochemistry, which is in accord with their lower π -donating capability.

In principle the same trends as for δ_{11} are observed for the second in-plane component in **5** and amino-iminophosphines (**6–11**). However, since the angle between the tensor axis and the lobe of the phosphorus nonbonding orbital is now much smaller than 90° , transmission of changes in the electronic structure of the double bond on the shielding is less pronounced and the degree of variation is smaller than for δ_{11} . Consequently, further contributions to the paramagnetic term σ_p , which are associated with energetically higher electronic transitions, grow in importance, thus accounting for a larger spread of the observed data. The out-of-plane component is essentially collinear with the lobes of the π -orbital, and all paramagnetic contributions associated with excitations into the π^* -orbital nearly vanish. This provides an explanation for the higher shielding of this component as well as for its insensitivity with respect to electronic effects related to the π -system. Instead, both calculations and experimental data indicate that the shielding of the out-of-plane component decreases with a higher electronegativity of the ligand X. Since larger polarity of the P—X bond lowers the energy of the antibonding $\sigma^*(\text{PX})$ -orbital, this effect can be related to an increased magnitude of the paramagnetic term owing to the lower energy

for the $n(\text{P}) \rightarrow \sigma^*(\text{PX})$ charge-transfer transition. For **14–16**, the comparatively long phosphorus–halogen distances lead to further amplification of this effect.^{6,26}

The observed large upfield shifts of δ_{33} in the halogenated compounds **14–16** need some further consideration, since an explanation based exclusively on differences in $n-\pi^*$ excitation energies seems unsatisfactory. As compared to their congeners **5–13**, the crystal structures reveal substantially larger angles at nitrogen and shortening of the phosphorus–nitrogen bond distances, while the phosphorus angles are similar.⁶ Model calculations on Cl—P=NH with systematic variations of the geometry indicate that a higher nitrogen valence angle produces a marked additional shielding contribution for both in-plane components, while the out-of-plane component is deshielded. This behavior can be interpreted in terms of increasing phosphorus–nitrogen triple-bond character. For a genuine phosphorus–nitrogen triple bond ([H—N≡P]⁺), calculations revealed an axial shielding tensor with a highly shielded parallel component along the phosphorus–nitrogen bond.³⁵ Perturbation of this system by an additional chlorine ligand is expected to lead to reorientation of this principal axis away from the phosphorus–nitrogen bond, together with a shift to lower field. The degeneracy of the perpendicular components is removed, with the now in-plane component experiencing an increasing paramagnetic contribution from the concomitant lowering of the $n-\pi^*$ transition energy. Comparison of the shielding tensors for **14–16** suggests a substantially higher degree of triple-bond character in the P-iodo derivative as compared to its lighter homologues, which is completely in accord with the observed differences in the molecular structures.⁶ For **14** and **15**, the contribution of the triple-bonded resonance structure can be held responsible for the unique reorientation of the tensor axes with respect to the other types of iminophosphines.

The influence of the (*E/Z*)-configuration of the double bond is clearly reproduced by the calculations. The shielding tensors calculated for the (*E/Z*)-isomers of HP=NH and H₃CP=NH demonstrate that the observed effect is not confined to amino-iminophosphines but is presumably a general quality of the phosphorus–nitrogen double bond. As for the substituent effect, closer analysis reveals the paramagnetic contribution to the shielding as the origin of this effect. The differences are most pronounced for δ_{11} , and the stronger deshielding in the (*E*)-isomers is related to two dominant orbital contributions which are attributable to the phosphorus lone pair and the phosphorus–nitrogen bonding orbitals; it should be noted that a different relative order is observed for the contributions originating from the P—X single bond. On the whole, the model calculations establish that the observed effect is a genuine geometry effect; however, no easy picture of its origin emerges from the data, and the calculations do not help to relate the effect to simple orbital interactions.

Isotropic Chemical Shifts. The substitution and (*E/Z*)-stereochemistry effects should be reflected in similar trends for δ_{iso} , as have been discussed above. However, as averaging over different contributions to a single value of δ_{iso} necessarily also averages over the different and possibly counteracting trends in individual principal components, the changes are less characteristic, and diagnostic information is lost to some extent. Nonetheless, as the largest changes in δ_{11} and δ_{22} can be associated with a common origin, viz., variation of $n-\pi^*$ transition energies, isotropic shifts still comprise a sensitive probe for changes in the electronic structure of the double-bond system, and comparison of δ_{iso} gives generally a very similar picture as derived from the analysis of individual principal components. This assumption is also corroborated by the observed correlation between solution shifts and $n-\pi^*$ excitation energies.^{2,6,36} In a similar way, δ_{iso}

(33) (a) Mason, J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987, p 335 ff. (b) Chesnut, D. B. In *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH Publishers: Deerfield Beach, FL, 1987; p 185 ff.

(34) Niecke, E.; Gudat, D.; Schoeller, W. W.; Rademacher, P. *J. Chem. Soc., Chem. Commun.* 1985, 1050.

(35) IGLO calculations of the shielding tensor of [HN≡P] gave values of 338 (δ_{\perp}) and -626 (δ_{\parallel}), respectively; Fleischer, U. Unpublished results.

(36) David, G.; Busch, T.; Radewacher, P.; Schoeller, W. W.; von der Göoua, V.; Niecke, E. *J. Chem. Soc., Faraday Trans. II*, in press.

Table 4. Comparison of Chemical Shielding Data of **5** and **16** with Known Phosphorus-Containing Multiple Bond Systems

	double-bond conformation	δ_{11}	δ_{22}	δ_{33}	δ_{iso}	ref
5	tBuP=N-aryl	<i>E</i>	1035	297	130	487
1	aryl-P=P-aryl	<i>E</i>	1236	249	-3	494 3
2	aryl-P=C(SiMe ₃) ₂	<i>E</i>	819	249	-31	394 5
16	IP=N-aryl		276	192	-167	118
3	aryl-C≡P		229	140	-274	31 5
4	aryl-N≡P ⁺ AlCl ₄ ⁻		308	196	-273	77 8

responds to the change between the (*E*)- and (*Z*)-geometry of the double bond; however, as the difference between corresponding stereoisomers is reduced to some 100 ppm, the effect is far less significant.

Comparison of isotropic shifts in solid state and solution further provides a valuable test for comparability of the molecular structures in both phases. The significant deviations between δ_{iso} and δ_{soln} observed in several cases (see Table 2) indicate that measurable differences exist between solid-state and solution structures. The clearest evidence in this regard is obtained in the case of **16**, where solution NMR investigations indicate the presence of separated individual molecules, while the crystal structure clearly reveals distinct intermolecular association in the solid state.⁶ The deshielding of δ_{soln} by 118 ppm may thus be taken as an indication that the triple-bond character as derived from the solid-state NMR data is substantially promoted by the intermolecular interactions in the solid, whereas the solution structure is presumably more closely related to that of amino-iminophosphines.

For the remaining compounds, the origin of the differences in isotropic shifts is less evident, but it is strongly suggested that the effect reflects distinct distortions of the molecular geometry. Experimental support for this hypothesis is gained from crystal structure studies, where it was shown in several cases that different solid modifications of the same iminophosphine may exhibit considerable variations in nitrogen bond angles as well as phosphorus–nitrogen bond distances.⁶ A similar effect could occur during the transition between solid state and solution. In addition, theoretical investigations predict generally low-energy barriers for nitrogen inversion in iminophosphines,^{2,6,7a,30} thus suggesting that dynamic (*E/Z*)-isomerization of the double bond in solution may be of importance. Direct NMR evidence for this process is provided by the observed equilibration of the two different phosphorus environments in **9**.³⁷ In general, however, the differences between δ_{iso} and δ_{soln} are smaller as those expected for a change in double-bond stereochemistry, indicating that the same double-bond configuration prevails in solution and in the solid state. An exception may be the case of **7**, where the considerably higher solution shift can be interpreted in terms of inversion of one of the two double bonds, resulting in a conformation which is similar to **9**.

Comparison with Other Phosphorus-Containing Multiple Bond Systems. The shape of the shielding tensor of **5** is closely similar to the aryl-substituted diphosphene, **1**,³ and phosphalkene, **2**,⁵ respectively (Table 4). δ_{33} and, to a somewhat lesser extent, δ_{22} are markedly deshielded in **5**, possibly reflecting the influence of the higher electronegativity of the second element in the double bond (N vs P or C), while δ_{11} is found to lie at an intermediate value. As a consequence, the shielding anisotropy in **5** is somewhat reduced with respect to its higher homologue, **1**, yet still larger, as in the phosphalkene. The orientation of the shielding tensor in **5** is in principle the same as in the diphosphene, displaying the most shielded component lying perpendicular to the nodal plane of the π -bond and the most deshielded one directed approximately along the P–X single bond.³ The increased angle between δ_{11}

and the double-bond axis for **5** is in accord with the observed larger bond angle at phosphorus. As has already been noted,^{3,5} the orientation of the shielding tensor strongly resembles known ¹³C tensors of alkenes, however, with a significant increase in anisotropy.

According to both structural⁶ and NMR data, the P-iodo-iminophosphine **16** exhibits considerable triple-bond character. This suggests that the observed shielding tensor should be comparable to that of aryl–N≡P⁺ (**4**)⁸ and aryl–C≡P (**3**),⁵ featuring genuine phosphorus–carbon or phosphorus–nitrogen triple bonds, which is indeed the case. The reduced shielding anisotropy in **16** as compared to the cation **4**⁸ results mainly from the less pronounced shielding of δ_{33} , indicating⁵ that perturbation of the phosphorus–nitrogen π -system by interaction with iodide (**16**) leads to a more pronounced decrease in bond order, as compared to AlCl₄⁻ (**4**). The close correspondence between the magnitude of the principal components can be considered as a further strong argument that, similar to that in **4**, the most shielded principal component of **16** is in-plane and close to the phosphorus–nitrogen bond axis.

Conclusions

³¹P nuclear magnetic shielding tensors of the iminophosphines **5**–**16** may be determined from high-resolution MAS NMR measurements. In combination with ab-initio chemical shift calculations, which allow by comparison the approximate determination of the tensor orientation in the molecular frame, this provides a detailed understanding of the correspondence between electronic structure of the π -bond and chemical shielding. Two major interactions are identified which mediate the influence of substituents at the double bond on the shielding tensor and whose magnitude clearly exceeds that of further contributions to the total shielding. (i) Attachment of π -donor type ligands at phosphorus strongly reduces the paramagnetic shielding contribution, which can be related to a higher energy of the magnetically allowed $n-\pi^*$ electronic transition; this effect is strongest for the most deshielded principal component which is oriented closest to the P–X single bond. The shielding in this direction is further subtly dependent on the stereochemistry of the double bond, allowing a discrimination between (*E*)- and (*Z*)-configuration solely on the basis of the NMR data. (ii) The presence of strongly electronegative halogen ligands, which has been shown to result in increased nitrogen valence angles,³⁰ gives rise to a large additional shielding contribution for the principal component closest to the phosphorus–nitrogen bond. This effect can be explained as a consequence of partial triple-bond character of the phosphorus–nitrogen bond and may lead to an unprecedented change in the orientation of the shielding tensor. Whereas for the majority of known double-bond systems the most shielded principal component is perpendicular to the nodal plane of the π -orbital, it is close to the direction of the phosphorus–nitrogen multiple bond in halogenated iminophosphines; amino-iminophosphines are a borderline case where either alternative may prevail. In the case of the P-iodo derivative **16**, intermolecular association in the solid state produces perturbation of the π -system to an extent that the shielding tensor shows the characteristic features of a genuine triple-bond system. Comparison of isotropic chemical shifts gives evidence that this special situation is not preserved in solution.

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(37) Niecke, E.; Detsch, R.; Nieger, M.; Reichert, F.; Schoeller, W. W. *Bull. Soc. Chim. Fr.* **1993**, 130, 25.

(38) Barion, D.; Gärtner-Winkhaus, C.; Link, M.; Nieger, M.; Niecke, E. *Chem. Ber.* **1993**, 126, 2187.