Measurements of ^{31}P Chemical Shielding Anisotropies and Signs of Spin–Spin Coupling Constants of Oriented $PX(CH_3)_3$ Systems in Smectic A Solution

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Abstract: The phosphorus-31 magnetic shielding anisotropes in $P(CH_3)_3$, $PO(CH_3)_3$, and $PS(CH_3)_3$ have been obtained from studies in a smectic A liquid crystal solution using a pulsed FT NMR spectrometer. The results were obtained from measurements in the smectic phase alone and at a single temperature, and were also found to be independent of the particular smectic liquid crystal medium chosen to produce the orientation. The signs of J_{PCH} were also measured for these systems, as well as $J_{P\text{-}Se}$ for $PSe(CH_3)_3$. A change in sign is observed as one goes from $P(CH_3)_3$ to $PX(CH_3)_3$, which indicates that the dipolar form of the P–X bond predominates. In addition, the parallel component of the shielding tensor was found to be essentially constant for all the molecules studied.

The chemical shielding anisotropy $\Delta\sigma$, defined as $\Delta\sigma = [\sigma_{zz} - \frac{1}{2}(\sigma_{xx} + \sigma_{yy})]$, is one of the principal quantities obtainable from liquid crystal studies. This parameter gives a much more detailed insight into the electronic structure of the molecule than the more commonly observed isotropic chemical shift. For molecules with C_3 or higher symmetry, the shielding anisotropy may be combined with the isotropic chemical shift and absolute shielding scales to yield the complete chemical shielding tensor, which provides much more information about bonding and structure than ordinary isotropic shift data.

We have previously shown in a number of publications[1-6] that the use of smectic liquid crystals as orienting solvents provides both a simple and accurate technique for the study of chemical shielding anisotropies. Smectic liquid crystals exhibit the attractive property of retaining their alignment, once formed in a high magnetic field, even on rotation about an axis perpendicular to the field direction. Hence, it is possible to obtain NMR spectra of solutes ordered in a smectic liquid crystal phase and the degree of orientation with respect to the direction of the field can be varied in an arbitrary fashion. The sample is oriented by first aligning it in the isotropic phase and then cooling it into the smectic phase. The effective orientation parameter then becomes S_α.

$$S_\alpha = \frac{(3\cos^2\theta - 1)}{2} S_{zz} \tag{1}$$

where S_α described the orientation of the molecular symmetry axis with respect to the magnetic field direction, θ being the angle between the magnetic field direction and the optic axis of the smectic liquid crystal, and S_{zz} is a measure of the ordering of the solute by the ordered smectic solvent. Simple rotation of the NMR sample tube causes S_α to vary. Rotating the sample tube by 90° causes S to change from S_{zz} to $-S_{zz/2}$. Hence one can vary S_α over the range of S_{zz} to $-S_{zz/2}$ and obtain the chemical shielding anisotropy from the slope of the plot of the resulting data.

In this study, we have measured ^{31}P shielding anisotropies and signs of the J_{PCH} spin-spin coupling constants for trimethylphosphine ($P(CH_3)_3$), trimethylphosphine oxide ($PO(CH_3)_3$), and trimethylphosphine sulfide ($PS(CH_3)_3$), using various smectic liquid crystal solvents. The magnitudes and signs of the J_{PCH} and $J_{P\text{-}Se}$ coupling constants in $PSe(CH_3)_3$ are also reported. All parameters have been obtained without changing the temperature, concentration, or phase of the medium and without referring to the isotropic value of the chemical shift. From the results obtained in this study, it is observed that as one grafts an O, S, or Se atom onto the $P(CH_3)_3$ system, the sign of the J_{PCH} coupling constant changes from positive to negative. It is also evident that the parallel component of the ^{31}P shielding tensor in $P(CH_3)_3$, $PO(CH_3)_3$, and $PS(CH_3)_3$ is essentially constant. A discussion of these findings will be presented.

Experimental Section

The following smectic liquid crystal solvents have been utilized in this study: (I) 4-*n*-octyloxybenzylidene-4′-*p*-aminoacetophenone (OBAA); (II) 4-*n*-pentyloxybenzylidene-4′-*p*-aminoacetophenone (PBAA); (III) a mixture of 50 mol % 4-*n*-hexyloxybenzylidene-4′-*p*-aminoacetophenone (HBAA) and 50 mol % PBAA.

The liquid crystals were all synthesized in this laboratory, and their properties have been discussed in detail previously.[1,2,4]

Both trimethylphosphine and trimethylphosphine oxide were obtained commercially and used without further purification. Trimethylphosphine sulfide and trimethylphosphine selenide were obtained by the direct combination of the particular element with trimethylphosphine, in vacuo, keeping the temperature of the mixture below the boiling point of trimethylphosphine. The resulting solid was then recrystallized several times from ethanol. The trimethylphosphine sulfide obtained has a melting point of 155 °C, which is in agreement with an earlier synthesis by Hooge and Christen,[7] but is in contrast with Malatesta[8] and Cahours and Hofmann,[9] who obtained a mp of 105 °C, on crystallizing the product from H_2O. The trimethylphosphine selenide was observed to have a mp of 140 °C, in accord with that obtained earlier by Renshaw and Bell[10] using a similar synthetic route, whereas the product obtained over a century ago by Hofmann[9] was reported to melt at 84 °C.

Samples were prepared by adding approximately 8 mol % of the solute to 0.25 g of the liquid crystal solvent which, prior to the addition of solute, was degassed over many freeze-pump-thaw cycles. Samples were then sealed and thoroughly mixed in an oil bath before their insertion into the NMR sample probe; 5-mm sample tubes (Wilmad, 506-pp) were utilized. $PS(CH_3)_3$ and $PSe(CH_3)_3$ were investigated in OBAA only, while $P(CH_3)_3$ and $PO(CH_3)_3$ were studied in all three liquid crystal solvents to determine whether the results were indeed independent of the particular liquid crystal medium chosen.

All spectra were observed on a JEOL JNM-PFT-100 pulsed NMR spectrometer, interfaced with a Nicolet 290 computer and 1080 signal averager, and a variable temperature controller. ^2D field/frequency lock was utilized for ^{31}P measurements, with DMSO-d_6 serving as the lock sample. Chemical shifts were measured relative to the pulse frequency (first address of the computer readout), with an external capillary of 85% H_3PO_4 also employed, for checking purposes.

Theory

The ^{31}P NMR spectra of $PX(CH_3)_3$ systems consist of a symmetric ten-line multiplet in both the isotropic and liquid crystal phases, with intensities in the ratio of the binomial coefficients of order ten. The successive splitting between adjacent lines is given by:

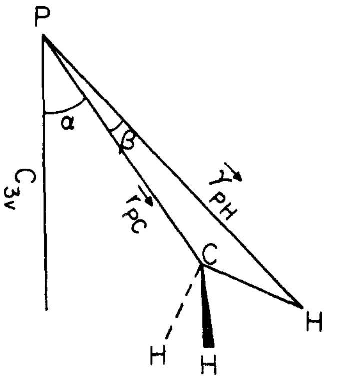

Figure 1. Analysis of the dipolar coupling in a nonrigid pyramidal $YP(CH_3)_3$ molecule. $\vec{\gamma}_{PC}$ and $\vec{\gamma}_{PH}$ refer to internuclear distance vectors.

$$\Delta\nu_{PCH} = J_{PCH} + 2D_{PCH} \qquad (2)$$

J_{PCH} is the indirect coupling constant and D_{PCH} is the direct dipolar coupling constant which is given by:

$$D_{PCH} = \frac{\hbar}{2\pi}\gamma_P\gamma_H P_2(\cos\theta)S_{zz}/r_{P-H}{}^3 \qquad (3)$$

where S_{zz} is the diagonal z component of the ordering matrix, r_{P-H} is the internuclear distance, and θ is the angle between the threefold axis of symmetry and r_{P-H}.

Because of internal rotation an average value for $\cos^2\theta$ has to be calculated.

From standard trigonometric relationships (cf. Figure 1) one easily obtains:

$$\cos\theta = \cos\alpha\cos\beta + \sin\alpha\sin\beta\cos\phi \qquad (4)$$

where α is the angle between the C_{3v} axis and r_{P-C}, β is the angle between r_{P-C} and r_{P-H} and ϕ is the dihedral angle between the plane determined by the C_{3v} axis and r_{P-C} and the plane determined by r_{P-C} and r_{P-H}.

Squaring and taking the appropriate averages yields:

$$\langle\cos^2\theta\rangle = \cos^2\alpha\cos^2\beta + \sin^2\alpha\sin^2\beta \qquad (5)$$

It has been demonstrated previously[1] that the chemical shielding anisotropy, $\Delta\sigma$, is easily obtained from measurements in the smectic phase at a single temperature and without reference to the isotropic chemical shift from the following:

$$\Delta\sigma = \frac{\sigma_{0°} - \sigma_{90°}}{S_{zz}} \qquad (6)$$

where $\sigma_{0°}$ is the observed chemical shift of the solute when the optical axis of the liquid crystal is aligned with the external magnetic field H_0 and $\sigma_{90°}$ is the chemical shift observed when the optical axis is perpendicular to H_0.

Results

The theoretically predicted spectral pattern was observed for all molecules, as well as the dependence of the spectral splitting on rotation of the sample tube. A spectrum of $PO(CH_3)_3$, obtained after an accumulation of 16 000 scans, is illustrated in Figure 2. From an independent knowledge of both the magnitude of the isotropic indirect J_{PCH} coupling constant and the sign of the ordering parameter S_{zz}, one can simply obtain the absolute sign of J_{PCH} from measuring the change in spectral splitting which occurs on rotating the sample 90°. Hence, the sign of this parameter has been assigned for all systems investigated in this analysis.

$P(CH_3)_3$. Trimethylphosphine was investigated in all three smectic liquid crystal solvents, and the spectral parameters obtained are illustrated in Table I. The results reported are indeed independent of the particular smectic liquid crystal medium chosen to produce the orientation. From the measured dipolar splittings and the knowledge of the molecular geometry,[11] it is possible to calculate the magnitude of S_{zz}. As electrical polarizability data are currently not available for $PX(CH_3)_3$ systems, the sign of S_{zz} can only be inferred from a consideration of the shape of the molecule. Since $P(CH_3)_3$ structurally bears a similarity to PF_3, the sign of this parameter is assumed to be negative.[12] In addition, a negative S_{zz} may be arrived at by referring to a previous study by McFarlane,[15] who by using spin-tickling techniques found the sign of J_{PCH} in $P(CH_3)_3$ to be positive. This information thereby establishes the sign of the shielding anisotropy as being positive for the system. Both the magnitudes of J_{PCH} and the isotropic chemical shift measured for $P(CH_3)_3$ in this study are found to be in agreement with previously reported values, as illustrated in Table IV.

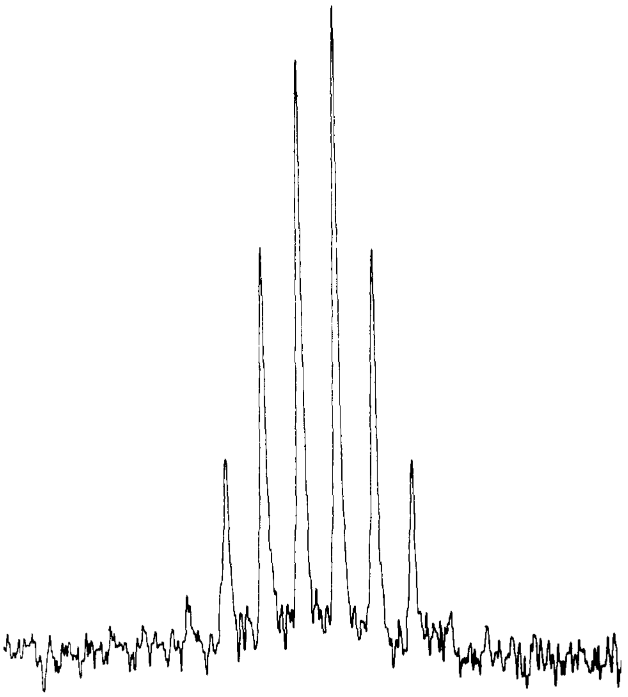

Figure 2. ^{31}P Fourier transform NMR spectra of $PO(CH_3)_3$ in OBAA at 90 °C; 16 000 scans; dwell time 200 μs; pulse with 10.2 μs; repetition rate 3 s.

$PO(CH_3)_3$. Trimethylphosphine oxide was also studied in all three smectic liquid crystal solvents and the results obtained are summarized in Table II. The molecular geometry of Wilkins et al.[13] obtained from electron diffraction data, was used. Since, in $PO(CH_3)_3$, the long axis of the molecule is not the molecular symmetry axis, it is reasonable to assume that the molecule will order in a manner similar to CHF_3[1] and assign a negative S_{zz} to this system. From this assumption, the sign of J_{PCH} is then negative, and that of $\Delta\sigma$ is positive. Again on changing the liquid crystal medium, no discernible change in $\Delta\sigma$ or J_{PCH} was observed.

$PS(CH_3)_3$ and $PSe(CH_3)_3$. The pertinent spectral parameters illustrated in Table III for these systems were measured in the smectic liquid crystal solvent OBAA. Since no accurate structural data are currently available for $PSe(CH_3)_3$, the shielding anisotropy of this molecule could not be calculated. A negative ordering parameter is assigned to trimethylphosphine sulfide. This then defines $\Delta\sigma$ to be positive in $PS(CH_3)_3$ and J_{PCH} as being negative in both trimethylphosphine sulfide and trimethylphosphine selenide. The phosphorus–selenium indirect coupling constant in $PSe(CH_3)_3$ was measured as

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Table I. Phosphorus NMR Data for $P(CH_3)_3$ in Smectic Liquid Crystals

Sample[a]	Temp, °C	$\|\Delta\nu_{PCH}\|$, Hz	$2D_{PCH}$	J_{PCH}	S_{zz}	$\Delta\sigma$, ppm	Av $\Delta\sigma$, ppm
1	74	46.4	−49.20	+2.80	−0.067 53	+6.97	
			−49.17	+2.77	−0.067 49	+6.98	
	86	49.4	−52.00	+2.60	−0.071 38	+8.07	+7.63 ± 0.5
			−52.17	+2.77	−0.071 61	+8.04	
	94	51.9	−54.80	+2.90	−0.075 22	+7.84	
			−54.67	+2.77	−0.075 04	+7.86	
2	90	50.9	−53.60	+2.70	−0.073 57	+7.82	
			−53.64	+2.74	−0.073 63	+7.81	+7.86 ± 0.05
	103	53.1	−55.87	+2.77	−0.076 69	+7.90	
			−55.84	+2.74	−0.076 65	+7.91	
3	90	46.4	−48.93	+2.53	−0.067 16	+8.40	
			−49.00	+2.60	−0.067 26	+8.10	+8.15 ± 0.1
	100	49.4	−52.07	+2.67	−0.071 47	+8.05	
			−52.00	+2.60	−0.071 38	+8.06	

[a] Sample 1 employs a liquid crystal No. III, sample 2 uses No. I, and sample 3 uses No. II.

Table II. Phosphorus NMR Data for $PO(CH_3)_3$

Sample[a]	Temp, °C	$\|\Delta\sigma_{PCH}\|$ Hz	$2D_{PCH}$	J_{PCH}	S_{zz}	$\Delta\sigma$, ppm	Av $\Delta\sigma$, ppm
1	69	148.5	−135.00	−13.50	−0.110 02	+174.4	
			−135.00	−13.50	−0.110 02	+174.4	
	79	146.5	−132.80	−13.70	−0.108 22	+173.5	
			−133.00	−13.50	−0.108 38	+173.3	+173.9 ± 0.5
	90	144.3	−131.00	−13.30	−0.106 75	+173.8	
			−130.80	−13.50	−0.106 59	+173.8	
2	59	134.5	−121.33	−13.17	−0.098 87	+172.4	
			−121.28	−13.22	−0.098 83	+172.4	+173.1 ± 0.7
	69	132.0	−118.73	−13.27	−0.096 76	+173.8	
			−118.78	−13.22	−0.096 80	+173.7	
3	57	129.4	−116.07	−13.33	−0.094 59	+173.5	
			−116.10	−13.30	−0.094 61	+173.4	+173.9 ± 0.6
	69	125.7	−112.40	−13.30	−0.091 60	+174.3	
			−112.40	−13.30	−0.091 60	+174.3	

[a] Sample 1 employs liquid crystal No. I, sample 2 uses No. II, and sample 3 uses No. III.

Table III. Phosphorus NMR Data for $SP(CH_3)_3$ in OBAA

Temp, °C	$\Delta\nu_{PCH}$, Hz	$2D_{PCH}$	J_{PCH}	S_{zz}	$\Delta\sigma$, ppm	Av $\Delta\sigma$, ppm
62	59.1	−43.5	−15.6	−0.034 89	+110.2	
72	52.1	−36.5	−15.6	−0.029 28	+111.9	+111.6 ± 1.0
80	48.8	−33.2	−15.6	−0.026 63	+112.7	

Table IV. Comparison of Magnitudes and Signs of Isotropic Chemical Shifts and Indirect Coupling Constants of $PX(CH_3)_3$ Systems between the Results Obtained from his Analysis and those Reported Previously

Molecule	σ, ppm[a]	J_{PCH}, Hz	Ref
$P(CH_3)_3$	+64.00 ± 0.03	+2.7 ± 0.1	This work[b]
	+63.3	+2.7 ± 0.1	15
	+61	±2.66	16
$PO(CH_3)_3$	−31.44 ± 0.03	−13.3 ± 0.2	This work
	−36.2		17
$PS(CH_3)_3$	−28.6 ± 0.1	−15.6 ± 0.1	This work
	−28.9	−13.0 ± 0.1	15
	−59.1		18
$PSe(CH_3)_3$	−10.2 ± 0.1	−14.1 ± 0.1	This work
	−8.7	−13.2 ± 0.1	15

[a] σ is the isotropic chemical shift measured with respect to an 85% H_3PO_4 external reference. [b] All values reported from this study were measured in the isotropic phase of OBAA.

being −704 Hz in OBAA which agrees with an earlier result reported by McFarlane,[14] who measured −684 Hz for the same quantity from a heteronuclear magnetic triple resonance experiment.

Discussion

The components of the ^{31}P nuclear magnetic shielding tensor for various X_3PY systems are listed in Table V. Although calculated values for these quantities are not available for direct comparisons, some qualitative trends are discernible. Wagner[19] has reported LCAO-MO calculations for a series of phosphoryl compounds X_3PO taking into account the varying polarity of the X-P bonds. The calculations predict appreciable participation of the P atom d orbitals in the π bonding and an increase in the P-O bond order with increasing X group electronegativity. Thus the total bond order varies from a nearly single bond in $(CH_3)_3PO$ to a nearly triple bond in F_3PO. The corresponding force constants (8.2 and 11.4

Table V. The ^{31}P Magnetic Shielding Tensor for Some Phosphines and Phosphoryl Compounds

Molecule	$\Delta\sigma$, ppm[a]	σ_{11}, ppm[b]	$\sigma_{\perp}$, ppm[b]	Ref
PF_3	$+181 \pm 5$	357 ± 5	175 ± 5	4
OPF_3	$+284 \pm 15$	594 ± 15	260 ± 15	4
$P(CH_3)_3$	$+7.63 \pm 0.5$	409 ± 5	401 ± 5	This work
$PO(CH_3)_3$	$+173.6 \pm 0.5$	424 ± 5	250 ± 5	This work
$PS(CH_3)_3$	$+111.6 \pm 0.5$	386 ± 5	274 ± 5	This work

[a] Experimentally measured parameter. [b] Absolute shielding scale is based on the PH_3 shielding tensor.[21,22] (See also N. Zumbulyadis, Dissertation, Columbia University, 1974.)

mdyn/Å, respectively) tend to support these findings. The increased bond order in F_3PO is associated with an increase in the cylindrically symmetric charge density around the P–O bond direction. One thus expects σ_{11} in F_3PO to be larger than σ_{11} in $(CH_3)_3PO$, as observed.

The observed difference in σ_{11} between F_3PO and $(CH_3)_3PO$ and the previously reported difference[4] between PF_3 and F_3PO suggest that trends in the individual screening tensor components of nuclei in similar environments bear a more direct correlation to the molecular electronic structure than the more commonly studied trends in the averaged isotropic part of the shielding tensor.

While this manuscript was in preparation Kennedy and McFarlane[20] published similar observations.

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Mass Spectrometer Study of Evaporation of α-Amino Acids

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Abstract: The NH_4^+ proton transfer mass spectra of 19 α-amino acids have been obtained by evaporation of 5–8-nmol samples from a rapidly heated Teflon surface. The protonated amino acid parents are observed in all samples and serve as the base peaks in all spectra but two. Time evolutions of fragment ions are coincident with those of the protonated parent in nearly all cases, indicating that deamination, dehydration, and loss of formic acid occur predominantly in the gas phase. Analyses of the rates of sublimation yield activation energies for sublimation ranging from 12 to 34 kcal/mol. Vapor pressures for the amino acids at the experimentally observed threshold temperatures for sublimation were estimated from the time evolutions of protonated parent ions. Enthalpies of sublimation derived from activation energies for rates of sublimation are used with literature values of heats of solution to calculate heats of aqueous solvation of the α-amino acids.

Mass spectrometric studies of the α-amino acids have been stimulated by a basic interest in their gaseous ion chemistry and the desire to develop a rapid sensitive analytical technique for determination of these biologically important compounds. Electron impact studies were originally carried out by Junk and Svec,[1] chemical ionization mass spectrometry by Milne et al.,[2] Leclerq and Desiderio,[3] Meot-Ner and Field,[4,5] and more recently by Tsang and Harrison.[6] Our interest in these compounds is more in consideration of them as a class of biologically important fragile molecules that present problems in nondestructive evaporation. Both analytical applications of mass spectrometry and basic research on gaseous ion chemistry of amino acids are limited by volatility problems.

We have investigated the evaporation of 19 underivatized α-amino acids from Teflon foil covered probes in a collision chamber of a tandem mass spectrometer. These data have been used to determine parameters of a Langmuir type kinetic vapor