Phosphorus-31 Chemical Shift Anisotropies in Organophosphorus Compounds

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Summary ^{31}P magnetic shielding anisotropies, $\sigma_{||} - \sigma\perp$, of ± 6, $+210$, and $+127$ p.p.m. are reported for Me_3P, Me_3PO, and Me_3PS, respectively.

ALTHOUGH it is well known that the magnetic shielding of a nucleus is a tensor of the second rank, normally only the trace of this quantity is measured in high resolution n.m.r. spectroscopy.[1] Remarkably little information is available about the individual components of these tensors for the heavier nuclei, although a knowledge of them should illumine the nature of chemical bonding, and should also be useful for structural purposes. In the case of ^{31}P, chemical shift anisotropies have been measured for a few compounds,[2] but no work has been reported on organo-phosphorus molecules.

We now report measurements of the ^{31}P shielding anisotropy, $\sigma_{\parallel} - \sigma_{\perp}$, in the representative molecules Me_3P, Me_3PO, and Me_3PS, all of which have C_{3v} symmetry so that a single parameter $S(C_{3v})$ suffices to describe the mean orientation of the molecule in a liquid crystal solvent. The three compounds were examined as ca. 20 mole % solutions in the liquid crystal solvents EBBA (N-p-ethoxybenzyli-dene-p-butylaniline) and DHOAB (pp'-dihexyloxyazoxy-benzene) at a number of different temperatures, and $^1H-\{^{31}P\}$ double resonance experiments were used to obtain the P resonance frequencies [$\nu(^{31}P)$] in both the nematic and the isotropic solutions. With free rotation of the methyl groups the partially oriented molecules give $[A_3]_3X$ spin systems, but for Me_3PO and Me_3PS the ^1H n.m.r. spectra were too poorly resolved to permit full analysis. However, comparison of ordinary and ^{31}P-decoupled ^1H n.m.r. spectra made it possible to determine the P–H splitting [$2D_{PH} + J_{PH}$], and it was also easy to determine this parameter from the well resolved spectrum of Me_3P. Plots of [$2D_{PH} + J_{PH}$] against $\nu(^{31}P)$ showed that the direct and indirect couplings had the same sign (negative)[3] in all the samples of Me_3PO and Me_3PS examined, and equations (1) and (2) were then used to determine $S(C_{3v})$, the mean degree of orientation of the molecular 3-fold symmetry axis, where r_{PH} is the length

$$D_{PH} = - \frac{h\gamma(H)\gamma(P)}{8\pi^2 r_{PH}^3} . \langle 3\cos^2\phi - 1 \rangle . S(C_{3v}) \quad (1)$$

$$\langle \cos^2\phi \rangle = \cos^2\alpha \cos^2\beta + \tfrac{1}{2}\sin^2\alpha \sin^2\beta \quad (2)$$

of the P–H vector, ϕ is the instantaneous angle it makes with the C_{3v} symmetry axis, α is the angle between this axis and a PC bond, and β is the angle between the P–H vector and its associated PC bond. The methyl groups are assumed to rotate freely and have a negligible angle of tilt, and anisotropy of the indirect couplings is ignored. In Me_3P the small value of J_{PH} leads to an ambiguity in the sign of D_{PH} and hence of $S(C_{3v})$.

The results (Table) have been corrected for the ^1H chemical shift anisotropy and isotropic temperature dependence. Any differences between the molecular geometry in solution and in the gaseous phase will have only small effects upon the derived shielding anisotropies. The uncertainty in the sign of $\sigma_{\parallel} - \sigma_{\perp}$ for Me_3P is unimportant as this parameter is close to zero, and most significantly is much smaller than in the four-co-ordinate P species. In Me_3PO and Me_3PS π-bonding involving P $3d$ orbitals and the

TABLE. Selected data on organophosphorus compounds partially oriented in liquid crystal solvents

	Me_3P[a,d]	Me_3PO[b,e]	Me_3PS[c,f]
$^2J(^{31}P-H)/Hz$[h]	$+2\cdot5\pm0\cdot2$	-12 ± 1	$-13\pm0\cdot5$
$[J_{PH} + 2D_{PH}]/Hz$	$\pm58\pm0\cdot5$	-162 ± 6	-101 ± 5
D_{PH}/Hz	$\pm29\pm1$	-75 ± 3	-44 ± 3
$\cos^2\alpha\cos^2\beta + \tfrac{1}{2}\sin^2\alpha$ $\sin^2\beta$	$0\cdot258$	$0\cdot199$	$0\cdot199$
r_{PH}/nm	$0\cdot241$	$0\cdot240$	$0\cdot240$
$S(C_{3v})$	$\pm0\cdot074$	$-0\cdot106$	$-0\cdot062$
	$\pm0\cdot003$	$\pm0\cdot004$	$\pm0\cdot004$
$\Delta\nu(^{31}P)/Hz$[g]	$-7\cdot5\pm1\cdot5$	$+360\pm10$	$+127\pm8$
$[\sigma_{\parallel} - \sigma_{\perp}]/p.p.m.$	$\pm6\pm2$	$+210\pm15$	$+127\pm15$

[a] In EBBA at 28 °C. Other measurements were taken from 22 to 70 °C. [b] In DHOAB at 76 °C. Other measurements were taken from 72 to 130 °C. [c] In EBBA at 22 °C; other measurements were performed in DHOAB from 74 to 141 °C. [d] Geometry from L. S. Bartell, J. Chem. Phys., 1960, 32, 832. [e] Geometry from H.K. Wang, Acta Chem. Scand., 1965, 19, 879. [f] Geometry assumed to be same as in Me_3PO. [g] $\Delta\nu(^{31}P) = \nu(^{31}P)$nematic $- \nu(^{31}P)$isotropic. [h] Measured above the nematic–isotropic transition temperature.

p_x and p_y orbitals of the chalcogen will provide a mobile electron cloud with cylindrical symmetry whose circulation will be unhindered when the C_{3v} symmetry axis is parallel to B_0 and hindered when it is perpendicular. Thus $\sigma_{\parallel} - \sigma_{\perp}$ should be positive as is observed in these two molecules, and the smaller value in Me_3PS may reflect reduced π-bonding. In Me_3P the electron lone-pair is thought to occupy an orbital which has substantial s-character, and hence the induced circulation associated with it should be predominantly isotropic and $\sigma_{\parallel} - \sigma_{\perp}$ should be small, again in agreement with the observed result. This explanation ignores the electronic circulation associated with the σ-bonds of the molecules, but this is likely to make smaller contributions to the P shielding anisotropy.

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[2] N. Zumbulyadis and B. P. Dailey, Mol. Phys., 1974, 27, 633; P. K. Bhattacharyya and B. P. Dailey, ibid., 1974, 28, 209; N. Zumbulyadis and B. P. Dailey, J. Magnetic Resonance, 1974, 13, 189.
[3] W. McFarlane, Proc. Roy. Soc., 1968, A, 306, 185.