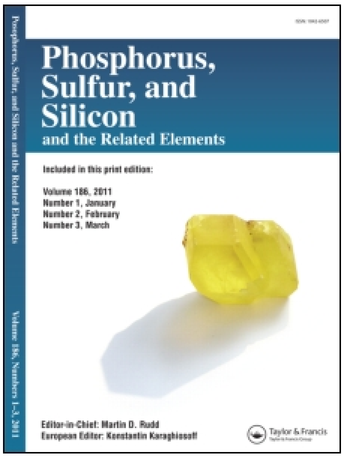

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

DETERMINATION OF THE ^{31}P NMR CHEMICAL SHIELDING TENSOR ANISOTROPY OF SOME MOLECULES IN SOLUTION

P. Rubini[a]; H. El Alaoui[a]; El Abdallaoui[a]
[a] Laboratoire d'Etudes des Systèmes Organiques et Colloïdaux, (L.E.S.O.C., UA CNRS n° 406), Université Henri Poincaré-Nancy I, Faculté des Sciences, Vandoeuvre-lès-Nancy, Cédex, France

To cite this Article Rubini, P. , Alaoui, H. El and Abdallaoui, El(1994) 'DETERMINATION OF THE ^{31}P NMR CHEMICAL SHIELDING TENSOR ANISOTROPY OF SOME MOLECULES IN SOLUTION', Phosphorus, Sulfur, and Silicon and the Related Elements, 97: 1, 57 — 61

To link to this Article: DOI: 10.1080/10426509408020727

URL: http://dx.doi.org/10.1080/10426509408020727

Phosphorus, Sulfur, and Silicon, 1994, Vol. 97, pp. 57–61
Reprints available directly from the publisher
Photocopying permitted by license only

DETERMINATION OF THE ^{31}P NMR CHEMICAL SHIELDING TENSOR ANISOTROPY OF SOME MOLECULES IN SOLUTION

P. RUBINI* and H. EL ALAOUI EL ABDALLAOUI
Laboratoire d'Etudes des Systèmes Organiques et Colloïdaux, (L.E.S.O.C., UA CNRS n° 406), Université Henri Poincaré-Nancy I, Faculté des Sciences, B.P. 239, 54506 Vandoeuvre-lès-Nancy Cédex, France

(Received June 28, 1994; in final form September 6, 1994)

The chemical shielding tensor anisotropy of the ^{31}P nucleus in tris(piperidino)phosphine oxide and triphenylphosphine sulfide molecules was determined in solution from ^{31}P and ^{13}C spin-lattice relaxation time measurements. The quadrupolar coupling constant χ of the ^{17}O nucleus of tris(piperidino)phosphine oxide was also deduced from these experiments and ^{17}O NMR spectra. The $\Delta\sigma$ value for triphenylphosphine sulfide is compared to those reported in the literature. The $\Delta\sigma$ and χ parameters for tris(piperidino)phosphine oxide are discussed in terms of the influence of the piperidino substituent on the electronic distribution in the PO bond.

Key words: Chemical shielding anisotropy tensor, quadrupolar coupling constant, tris(piperidino)phosphine oxide, triphenylphosphine sulfide, ^{31}P, ^{13}C and ^{17}O NMR relaxation.

INTRODUCTION

The knowledge of the ^{31}P NMR chemical shift tensor components allows a better understanding of the electronic effects surrounding the phosphorus nucleus and of the influence of structural parameters (bond length, angles, . . .) on the shielding. For phosphorylated molecules—all containing the P = O linkage—the value of the shieding tensor is sensitive to different factors such as P—O bond length, O—P—O bond angles or $d_p - p_0$ π-bond order[1] and, consequently, their determination may bring information on the structure of these compounds.

Generally the principal values of the chemical shielding tensor are obtained from NMR experiments in the solid state either on single crystals or on polycrystalline samples. In some cases these parameters are difficult to reach, particularly when the P atom is connected to nitrogen atoms because the interaction of the ^{31}P nuclei with the ^{14}N quadrupolar nuclei (scalar and dipolar couplings) can strongly affect the spectra which are considerably more complicated to interpret. The question arises also to know whether the tensor values deduced from solid samples are correct when the molecules are in solution.

It is possible to obtain the information in the liquid state in some particular cases when the chemical shift tensor is axial because there are only two principal values ($\sigma_{//}$ and $\sigma_{\perp}$, the shielding components along and perpendicular to the principal axis) to determine. Indeed $\Delta\sigma = \sigma_{//} - \sigma_{\perp}$ can be obtained from relaxation measurements at different frequencies when the chemical shift anisotropy mechanism is efficient.[2–5] As $\sigma_{iso} = 1/3(\sigma_{//} + 2\sigma_{\perp})$ is easily measured from the chemical shift of the NMR signal, the two values $\sigma_{//}$ and $\sigma_{\perp}$ can be readily deduced.

Phosphorylated and thio-phosphorylated molecules present an axial or near-axial ^{31}P chemical shift tensor[6] and the ^{31}P relaxation is essentially governed by the chemical shift anisotropy mechanism in high magnetic fields.[4] Some time ago we studied a series of molecules containing the P = O linkage[4] but, for some compounds such HMPA (hexamethylphosphoramide), it was not possible to obtain $\Delta\sigma$ neither in the solid state (the compound is a liquid at room temperature) nor in solution because its determination needs the knowledge of the reorientational correlation time of the molecule obtained from the relaxation study of a rigid part of the compound (in HMPA the methyl groups are rapidly rotating; see explanations below). As it is interesting to compare the $\Delta\sigma$ values for phosphorylated molecules with different substituents (in particular NR_2) in order to quantify their influence on the electronic structure of the P = O moiety, we studied the tris(piperidino)phosphine oxide molecule which allowed us to compare the influence of a N-substituent to that of alkyl or O-alkyl groups. The $\Delta\sigma$ determination was completed by the determination of the quadrupolar coupling constant χ of the ^{17}O nucleus from ^{17}O NMR experiments.

The χ value is sensitive to the electric field gradients around the considered nucleus and its variation may bring information on the changes in the electronic distribution of the PO bond due to different substituents on P atom.

This work was completed by experiments performed on triphenylphosphine sulfide molecule. The $\Delta\sigma$ value obtained in solution was compared to that obtained in the literature from different methods.

RESULTS

^{31}P longitudinal relaxation times of tris(piperidino)phosphine oxide and triphenylphosphine sulfide obtained at three different frequencies are summarized in Table I. T_1 values strongly depend on the intensity of the magnetic field B_0 indicating the efficiency of the chemical shift anisotropy (CSA) mechanism, the only one which gives rise to a field dependence of T_1 in the extreme narrowing limit conditions:

$$T^{-1}_{1,CSA} = \frac{2}{15}\gamma_P^2 \cdot B_0^2 \cdot \Delta\sigma^2 \cdot \tau_r$$

where γ_P is the ^{31}P gyromagnetic ratio, τ_r the correlation time corresponding to the reorientation of the principal component of the chemical shift tensor and $\Delta\sigma = \sigma_{//} - \sigma_\perp$ the chemical shift anisotropy ($\sigma_{//}$ and $\sigma_\perp$ being the parallel and perpendicular components to the symmetry axis of the chemical shift tensor which is considered to be axial).

The study of the linear variation of $T_1^{-1} = f(B_0^2)$ allows the determination of the CSA contribution, the slope of the linear plot providing the quantity $\Delta\sigma^2 \cdot \tau_r$ (4.42 10^{-19} and 6.50 10^{-19} s for tris(piperidino)phosphine oxide and triphenylphosphine sulfide respectively). This mechanism contributes for 39% and 68% to the total relaxation rate for tris(piperidino)phosphine oxide and triphenylphosphine sulfide respectively at 161.2 MHz, the other mechanisms being probably due to dipole-dipole ^{31}P-^{1}H and spin-rotation interactions.

TABLE I

^{31}P longitudinal relaxation time T_1 for 0.5 M solutions of tris(piperidino)phosphine oxide and triphenylphosphine sulfide in deuterated chloroform at three frequencies: 32.4 MHz (first line), 121.4 MHz (second line) and 161.9 MHz (third line), correlation time τ_r for the reorientation of the molecules in solution, anisotropy of the chemical shielding tensor and quadrupolar coupling constant of the ^{17}O nucleus in tris(piperidino)phosphine oxide

	tris(piperidino) phosphine oxide	triphenyl-phosphine sulfide
T_1 (s)	10.35 7.65 6.45	21.3 10.7 7.5
$10^{11} \times \tau_r$ (s)	1.6	2.7
$\Delta\sigma$ (ppm)	166	156
χ (^{17}O) (MHz)	6.3	-

$\Delta\sigma$ can be found if τ_r is known. τ_r can be determined from T_1 and NOE measurements of the ^{13}C nuclei of the CH_2 groups for tris(piperidino)phosphine oxide and the para-carbon of the phenyl substituents of triphenylphosphine sulfide. T_1 of the para-carbon of the triphenylphosphine sulfide phenyl groups is not affected by the rotation of the phenyl groups because it is situated on the rotation axis (T_1 = 1.52 s and NOE factor = 1.79).

The T_1 values of the three different CH_2 groups of the piperidino substituent are: 1.43, 1.46 and 1.42 s giving rise to a mean value of 1.44 s. The corresponding average NOE value is 1.975 allowing us to deduce the dipole-dipole ^{13}C-^{1}H contribution and the τ_r value:

$$T_{1,DD}^{-1} = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{\gamma_C^2 \gamma_H^2 \hbar^2}{r^6} \tau_r \times N_H$$

where γ_H and γ_C are the gyromagnetic ratios of the ^{13}C and ^{1}H nuclei, r the C—H bond length ($r = 1.09 \times 10^{-10}$ m) and $N_H = 2$.

Finally we found: $\tau_r = 1.6 \times 10^{-11}$ s and $\Delta\sigma = 166$ ppm for tris(piperidino)phosphine oxide.

A similar calculation using $r = 1.084 \times 10^{-10}$ m and $N_H = 1$ leads to $\tau_r = 2.7 \times 10^{-11}$ s and $\Delta\sigma = 156$ ppm for triphenylphosphine sulfide.

The quadrupolar coupling constant (QCC) χ of the ^{17}O nucleus in tris(piperidino)phosphine oxide was also determined from the line-width $\Delta\nu$ of the ^{17}O NMR signal. For this nucleus, quadrupolar relaxation (Q) is the predominant relaxation mechanism. Thus,

$$\pi\Delta\nu = T_{2,Q}^{-1} = T_{1,Q}^{-1} = \frac{3\pi^2}{10}\frac{2I + 3}{I^2(2I - 1)}\left(1 + \frac{\xi^2}{3}\right)\cdot\chi^2\cdot\tau_r$$

where $I = 5/2$ for ^{17}O and ξ is the asymmetry parameter assumed to be negligible here.

The ^{17}O NMR signal is a doublet due to the coupling of the ^{17}O nucleus with phosphorus. The linewidth was determined by simulation of the spectrum assuming lorentzian lines: $\Delta\nu = 184$ Hz and $J(^{31}P - {}^{17}O) = 140$ Hz. The corresponding χ value is equal to 6.3 MHz.

We were unsuccessful in obtaining a ^{33}S NMR signal for triphenylphosphine sulfide (the linewidth of the signal is probably higher than 2 kHz) and, consequently, in determining the QCC of this nucleus.

DISCUSSION

The validity of our method to determine $\Delta\sigma$ values for phosphorus molecules in solution can be tested from the value obtained for triphenylphosphine sulfide. Indeed Robert *et al.* have reported two studies on this compound: one is relative to the determination of $\Delta\sigma$ in a liquid crystal solvent[10] ($\Delta\sigma = 112$ ppm) and the other corresponds to the determination of the principal values of the chemical shielding tensor from NMR powder patterns in the solid state ($\Delta\sigma' = \sigma_{11} - \sigma_{33} = 171$ ppm or $\Delta\sigma = \sigma_{11} + \sigma_{22}/2 - \sigma_{33} = 160.5$ ppm). According to the own assertion of these authors the former method suffers from several limitations and the discrepancy observed for the two methods might be also due to conformational problems in solution comparatively to the solid state.[6] Nevertheless our result is in good agreement with that obtained from NMR solid state experiments (156 ppm against 160 ppm). This good agreement between results obtained from our methodology and those from NMR solid state experiments was already reported for the triphenylphosphine oxide molecule.[3] The triphenylphosphine sulfide value agrees well with the value obtained for P_4S_{10}.[11]

The $\Delta\sigma$ value for tris(piperidino)phosphine oxide, which is in fact a phosphoramide molecule, (the first reported to our knowledge) is slightly lower than that observed for trialkylphosphine oxides[4,6] ($\Delta\sigma = 198$ and 189 ppm for the methyl and phenyl compounds respectively) or for triphenylphosphate[4] ($\Delta\sigma = 214$ ppm) and comparable to the estimated values obtained for trimethyl or triethylphosphate[4] (177 and 159 ppm respectively). These differences may be due to several factors: (i) the eventual participation of the different substituents on the phosphorus atom to the π-bonding of the $P = O$ moiety (due to the π-overlap of p orbitals of the oxygen atom with empty orbitals 3d and 3p of the P atom) according to their ability to donate (F, Cl, Br, OH, OR, NR_2, etc.) or not to donate (H, CH_3, C_2H_5, C_6H_5, etc.) π-electrons in the phosphorus d orbitals[12,13] and (ii) variations in the bond lengths and/or bond angles.[1]

The difference in the electronic structure of this phosphoramide and phosphates or phosphine oxides is more reflected by the QCC of the ^{17}O nucleus. The value obtained for tris(piperidino)phosphine oxide ($\chi = 6.3$ MHz) is significantly higher than that observed for triphenylphosphine oxide ($\chi = 4.8$ MHz) or triphenylphosphate (χ = 4.1 MHz). This is in agreement with a lower π-electron transfer from oxygen to phosphorus in tris(piperidino)phosphine oxide than that observed for the other molecules since χ depends on the field gradients at the oxygen nucleus, field gradients which are the result of an imbalance in the populations of valence-level p-orbitals on the oxygen atom.[14–15] This can be explained by a good π-donor character of the piperidino substituents leading, in turn, to an effect on the distribution of the electronic density between the O and P atoms. The lower π-electron transfer from oxygen to phosphorus is in agreement with the well-known basic character of phosphoramides.

EXPERIMENTAL

Trispiperidinophosphine oxide (Aldrich) and triphenylphosphine sulfide (Aldrich) were used as received. NMR samples were prepared in $CDCl_3$ (Euriso-Top) as 0.5 mol.l^{-1} solutions and degassed by the freeze and pump method; the NMR tubes were sealed under vacuum.

^{31}P relaxation measurements were performed at 34°C on WP80 (B_0 = 1.88 T), CXP 300 (B_0 = 7.05 T) and AM 400 (B_0 = 9.4 T) Bruker spectrometers at 32.4, 121.4 and 161.9 MHz respectively using the inversion-recovery method with fast acquisition[7] or the so-called superfast method needing only the acquisition of two experiments.[8] ^{17}O and ^{13}C{^{1}H}NMR spectra and T_1 measurements were made at 54.24 and 100.6 MHz respectively on a AM 400 Bruker apparatus. NOE factors for ^{13}C were determined at 32.4 MHz using the gated decoupling technique with frequency shift.[9]

CONCLUSION

It has been demonstrated in this paper that the chemical shift anisotropy of the ^{31}P nucleus in phosphorylated or thio-phosphorylated molecules can be determined *in solution* from T_1 measurements at different frequencies. This method can represent an alternative to the determinative of $\Delta\sigma$ in the solid state in some cases and also a means to verify (or to determine) whether $\Delta\sigma$ is the same for the liquid and the solid states. It is not restricted to phosphorus molecules and can be extended, as already made in very few cases,[2] to compounds containing the carbonyl group for which the ^{13}C relaxation is also governed, at least in part, by CSA mechanism.

REFERENCES AND NOTES

1. Sun Un and M. P. Klein, *J. Am. Chem. Soc.*, **111**, 5119 (1989).
2. G. F. Hawkes, E. W. Randall, S. Aime and R. J. Gobetto, *J. Magn. Reson.*, **68**, 597 (1986).
3. P. Rubini and H. El Alaoui El Abdallaoui, *J. Chim. Phys.*, **87**, 345 (1990).
4. H. El Alaoui El Abdallaoui and P. Rubini, *Spectrochimica Acta*, **Part A 49A**, 329 (1993).
5. J.-C. Hargé, H. El Alaoui El Abdallaoui and P. Rubini, *J. Magn. Reson.*, **31**, 752 (1993).
6. J.-B. Robert and L. Wiesenfeld, *Mol. Phys.*, **44**, 319 (1981).
7. D. Canet, G. C. Levy and I. R. Peat, *J. Magn. Reson.*, **18**, 199 (1975).
8. D. Canet, J. Brondeau and K. Elbayed, *J. Magn. Reson.*, **77**, 483 (1988).
9. M. L. Martin, J. J. Delpuech and G. J. Martin, "Practical NMR Spectroscopy," (Wiley-Heyden, London 1980).
10. J. B. Robert and L. Wiesenfeld, *J. Magn. Reson.*, **38**, 357 (1980).
11. H. Eckert, C. S. Liang and G. D. Stucky, *J. Phys. Chem.*, **93**, 452 (1989).
12. J. H. Hillier and V. R. Saunders, *J. Chem. Soc (A)*, 2475 (1970).
13. J. H. Letcher and J. R. van Wazer, *J. Chem. Phys.*, **45**, 1916 (1966).
14. C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).
15. C. P. Cheng and T. L. Brown, *J. Am. Chem. Soc.*, **102**, 6418 (1980).