

NUCLEAR MAGNETIC RESONANCE OF ORGANOPHOSPHORUS MOLECULES ORIENTED IN LIQUID CRYSTAL

J.P. Albrand and J.B. Robert *

Laboratoire de Chimie Organique Physique, Département de Recherche Fondamentale,
Equipe de Recherche Associée au C.N.R.S. n° 674, Commissariat à l'Energie Atomique,
85 X, F-38041 GRENOBLE CEDEX, France.

Abstract

It is explained how the recording of ^{31}P NMR spectra in a liquid crystal phase can provide much more experimental data than the same spectra recorded in an isotropic liquid. These additional data include the measurement of indirect spin couplings which are not accessible in the isotropic liquid phase, the obtention of geometrical parameters and the measurement of the anisotropy of the chemical shift and indirect spin-coupling tensors. The results obtained by this method are illustrated by the study of simple phosphorus molecules oriented by means of nematic phases. Geometrical data obtained compare favorably with the data derived from other methods. Examples of large anisotropy of the chemical shift tensor and of the $^1\text{J}(\text{PSe})$ spin coupling are also reported.

In the last decade, there has been an enormous increase in the use of ^{31}P nuclear magnetic resonance for the study of the various organic, inorganic and biological structures containing phosphorus. The ^{31}P nucleus was already easily observable, possessing a relatively high magnetogyric ratio γ (2/5 of the proton value) and a spin 1/2 present with a 100 % natural abundance (Table 1).

TABLE 1. N.M.R. Properties of the ^{31}P nucleus. (1)

Spin	1/2
Magnetogyric ratio	$\gamma/10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ 10.8290
NMR frequency ^a	40.481 MHz
Relative receptivity ^b	0.0663

a : Scaled such that ^1H is at 100 MHz ; b : Relative to the proton receptivity.

The introduction of Fourier Transform NMR with broad band decoupling of protons has now brought the ^{31}P NMR sensitivity to a level comparable to the one routinely achieved for ^1H NMR. However, in spite of the high degree of sophistication attained in the recording of ^{31}P NMR spectra, the only information obtained in most cases is the resonance frequency of one or several lines and a few values of the indirect spin-spin couplings of the phosphorus with other nuclei.

In this communication, we aim to explain why the information is reduced to such an extent when the NMR spectra are recorded in isotropic liquid phases, and to show on a few examples how the information may be largely extended by recording the NMR spectra of molecules partially oriented in the matrix of a liquid crystal (2). The method was first introduced by Saupe and Englert (3)(4)(5).

* Faculty member of the Université Scientifique et Médicale de Grenoble.

NMR PARAMETERS IN ISOTROPIC AND ANISOTROPIC ENVIRONMENT

The most commonly examined NMR parameters in chemistry are the screening constant σ and the indirect spin-spin coupling J . These two quantities which appear as scalars in isotropic phases are in fact dependent upon the orientation of the molecule with respect to the external magnetic field B_0 and must be described by second rank tensors with nine independent components in general. The number of independent components of these tensors $\bar{\sigma}$ and \bar{J} can be reduced according to the molecular symmetry (6).

The spatial dependence of the screening constant σ means that in a given magnetic field B_0 , the magnetic field B experienced by a given nucleus i (Figure 1a) has for full expression :

$$\begin{pmatrix} B_x \\ B_y \\ B_z \end{pmatrix} = \begin{bmatrix} 1-\sigma_{xx} & -\sigma_{xy} & -\sigma_{xz} \\ -\sigma_{yx} & 1-\sigma_{yy} & -\sigma_{yz} \\ -\sigma_{zx} & -\sigma_{zy} & 1-\sigma_{zz} \end{bmatrix} \begin{pmatrix} B_{0x} \\ B_{0y} \\ B_{0z} \end{pmatrix}$$

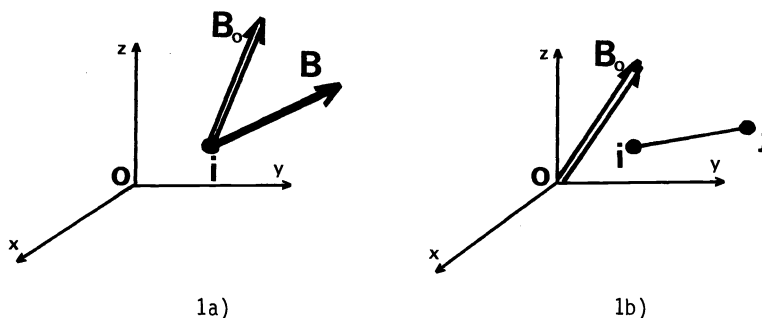


Fig. 1 : O_x, O_y, O_z represent a coordinate system attached to the molecule under study. B_0 is the applied magnetic field.

If one considers a polycrystalline sample, where the molecules have different but fixed orientations with respect to B_0 , one will observe a broad band signal, which is the envelope of all the different resonance frequencies experienced by the same type of nucleus in the different molecular orientations. In an isotropic liquid, due to the rapid tumbling of the molecules, the screening tensor $\bar{\sigma}$ is averaged to a scalar quantity σ which is equal to the trace of $\bar{\sigma}$, $\sigma = 1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$. The magnetic field experienced by a given nucleus is then $B = B_0(1-\sigma)$. Therefore, all the information concerning the individual components of the $\bar{\sigma}$ tensor is lost.

The same situation holds for the indirect spin-spin coupling \bar{J} which is also a second rank tensor and the scalar value measured in the isotropic liquid phase is in fact : $J = 1/3(J_{xx} + J_{yy} + J_{zz})$. The tensorial nature of \bar{J} means that the spin-spin coupling between two nuclei i and j will depend upon the orientation of \vec{r}_{ij} , the vector connecting the two nuclei, with respect to the magnetic field B_0 (Fig. 1b).

The third interaction we will consider here is the direct dipolar interaction \mathcal{D}_{ij} between a pair of nuclei i and j . This interaction which is the analog of the classical interaction between two magnets can be written :

$$\hbar^2 \gamma_i \gamma_j \left(\frac{\vec{I}_i \cdot \vec{I}_j}{r_{ij}^3} - \frac{3(\vec{I}_i \cdot \vec{r}_{ij})(\vec{I}_j \cdot \vec{r}_{ij})}{r_{ij}^5} \right)$$

$$\text{or } \hbar^2 \gamma_i \gamma_j \vec{I}_i \cdot \bar{\mathcal{D}}_{ij} \cdot \vec{I}_j \text{ in tensor notation}$$

γ_i and γ_j are the magnetogyric ratios of the nuclei i and j of spins \vec{I}_i and \vec{I}_j , \vec{r}_{ij} is the vector joining the two nuclei. The $\bar{\mathcal{D}}_{ij}$ tensor has a zero trace and, as a result, the dipolar interaction vanishes under conditions of rapid isotropic molecular reorientation. Thus, in isotropic liquid phase NMR, all information concerning the molecular geometry which could be obtained through the dipolar interaction is lost. The dipolar interaction still contributes to the total relaxation rate of the nuclei, but in the case of phosphorus, the presence, in general, of several relaxation mechanisms (dipolar, spin-rotation, chemical shift anisotropy) (7)(8) makes it a very difficult task to obtain accurate information on the internuclear distances from relaxation data in the liquid phase.

All these tensorial interactions which average to a scalar value in isotropic liquids are evidently contained in the solid state spectra. However, in that case, the dipolar interactions are so large, that the spectra show very broad line signals and it becomes very difficult to obtain any detailed information on the smaller $\bar{\sigma}$ and \bar{J} interaction without first getting rid of the dominant dipolar interaction. This task requires highly sophisticated decoupling techniques, using pulse sequences which have only been applied to a limited number of phosphorus containing molecules (9).

The use of a liquid crystal solvent constitutes an interesting compromise between the simplicity of the spectra in isotropic liquids and their complexity in the solid state. Different sorts of liquid crystal solvents can be used to induce a privileged average orientation of the solute with respect to the B_0 external magnetic field. The most widely used liquid crystals for high resolution NMR studies are nematic phases, which consist of long rod shaped molecules. Magnetic fields cause an alignment of the longest axes of the molecules or the direction of smallest diamagnetic susceptibility parallel to the field. The motion of a solute molecule in such an ordered matrix is anisotropic enough to let subsist a preferential average orientation and hence results in non zero intramolecular averaged dipolar couplings. Yet the relative motion of the solute molecules remains fast enough so that intermolecular dipolar interactions completely average to zero. Thus, one observes well resolved spectra which are dependent on the reduced average of the intramolecular dipolar couplings and independent of the intermolecular interactions.

We shall present examples of information which can be obtained through the NMR spectral analysis of molecules oriented in liquid crystals, namely indirect spin-spin coupling between isochronous nuclei, molecular geometry, chemical shift and spin-spin coupling anisotropy.

OBTENTION OF INDIRECT SPIN-SPIN COUPLING BETWEEN ISOCHRONOUS NUCLEI

We shall start our review of experimental data by an unusual aspect of the use of NMR of molecules dissolved in liquid crystals. In cyclopolyphosphanes $(PR)_n$ containing an even number of phosphorus atoms, like cyclotetraphosphanes or cyclohexaphosphanes, it has been experimentally observed that all the phosphorus nuclei are isochronous (10). Thus the (decoupled from other nuclei) ^{31}P NMR spectrum is a single line pattern (A_n) in isotropic phase. The phosphorus-phosphorus spin-spin coupling cannot be obtained. Undecoupled ^{31}P spectra could possibly be used to reach the $J(PP)$ values but these undecoupled spectra would in general be much too complex to be analyzed.

In the ordered phase, we have a different situation because the Hamiltonian \mathcal{H} needed for the NMR spectral analysis differs from the isotropic one by additional terms :

$$\mathcal{H} = \sum_i (1-\sigma_i) I_{zi} + \sum_{i<j} (J_{ij} + 2D_{ij}) I_{zi} I_{zj} + \frac{1}{2} \sum_{i<j} (J_{ij} - D_{ij})(I_i^+ I_j^- + I_i^- I_j^+) \quad (1)$$

σ_i and J_{ij} represent one third of the trace of the screening tensor of nucleus i and of the indirect spin-spin coupling between nuclei i and j respectively.

D_{ij} is a more complex quantity which contains a contribution from the direct dipolar interaction and from the \bar{J}_{ij} tensor components.

Due to this particular expression of the Hamiltonian \mathcal{H} , where the $I_{zi}I_{zj}$ and $(I_i^+ I_j^- + I_i^- I_j^+)$ terms have a different coefficient conversely to the case of the Hamiltonian in isotropic phase, the spectrum of an A_n spin system may exhibit a multi-line pattern instead of a singlet. The spectrum will be independent of the J_{ij} isotropic values only when the isochronous nuclei i and j have the same J and D values with any other nuclei in the spin system. For example, in cyclotetraphosphanes, the phosphorus nuclei on opposite sides of the ring fulfill this condition (Fig. 2) since $J_{12}=J_{13}$ and $J_{24}=J_{34}$, adjacent nuclei

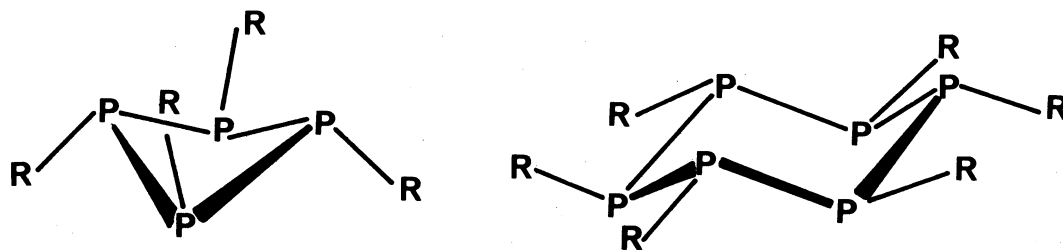


Fig. 2. Cyclotetraphosphane

Cyclohexaphosphane

do not fulfill it since $J_{13} \neq J_{23}$ and $J_{14} \neq J_{24}$. Therefore, the ^{31}P spectrum in oriented phase will depend on the $^1\text{J}(\text{PP})$ coupling but not on the $^2\text{J}(\text{PP})$ value. In the case of cyclohexaphosphanes, the spectrum will depend on the three internuclei spin-spin couplings $^1\text{J}(\text{PP})$, $^3\text{J}(\text{PP})$, $^3\text{J}(\text{PP})$. From the NMR spectral analysis of $\text{P}(\text{C}_6\text{H}_5)_6$ (Fig. 3), the following values are obtained (11) :

$$^1\text{J}(\text{PP}) = \mp 107 \text{ Hz} ; \quad ^2\text{J}(\text{PP}) = \pm 32 \text{ Hz} ; \quad ^3\text{J}(\text{PP}) = \mp 30 \text{ Hz}$$

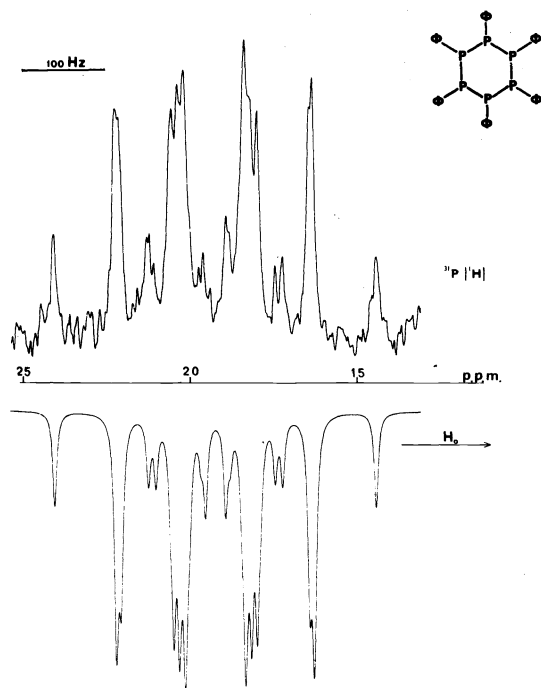


Fig. 3. Experimental and calculated (^1H) ^{31}P NMR spectrum of $(\text{PC}_6\text{H}_5)_6$ oriented in a nematic phase.

The $^1\text{J}(\text{PP})$ coupling which is probably of negative sign (12) is the smallest absolute value observed for a phenyl substituted cyclopolyphosphane (13). Such a value, which corresponds to a nearly trans diaxial orientation of the phosphorus lone pairs (14), is in agreement with the angular dependence shown in a calculation on P_2H_4 . It was found that $^1\text{J}(\text{PP})$ vary from -152 Hz to $+10 \text{ Hz}$ when the torsional angle between the phosphorus lone pairs directions increases from 0° to 180° (15).

Similarly, the one line ^{31}P proton decoupled spectrum of cyclotetraphosphanes $(\text{PR})_4$ dissolved in isotropic phase becomes a multiplet in nematic phase from which the $^1\text{J}(\text{PP})$ coupling is easily obtained. When various substituents R are considered (C_2H_5 ; $\text{C}-\text{C}_6\text{H}_{11}$; $i-\text{C}_3\text{H}_7$; $t-\text{C}_4\text{H}_9$) one observed an increase of the $^1\text{J}(\text{PP})$ absolute value with the P-P-P bond angle (16).

GEOMETRICAL INFORMATION

As mentioned in the introduction, the direct internuclear dipolar couplings \mathcal{D}_{ij} observed in a molecule dissolved in a liquid crystal are values averaged over all the possible orientations of the molecule in the anisotropic phase. The average orientation of a rigid molecule may be described by a 3×3 matrix S (4)(5). The definition of a matrix element is $S_{pq} = 1/2 \langle 3 \cos \phi_p \cos \phi_q - \delta_{pq} \rangle$, where the p, q indices refer to the x, y, z axes of a cartesian coordinates system attached to the molecule, ϕ_p and ϕ_q are the angles between these molecular axes and the magnetic field direction. From the definition of the S matrix elements, it clearly appears that S is symmetric and traceless. Thus, the S matrix will have five independent components in the general case. However, the number of S_{pq} independent terms may be reduced by molecular symmetry. For example, if a molecule has a C_n symmetry axis with $n > 2$, only one S_{pq} value is needed to define the order matrix S (4).

The measured dipolar coupling values can be used to write equations where the unknowns are the S_{pq} terms and the internuclei distances. Thus, in a C_{3v} symmetry molecule, the measurement of n distinct dipolar couplings will give access to $n - 1$ geometrical informations which are ratios of the internuclear distances. If only one dipolar coupling is measured, assuming the internuclear distance will give access to the unique orientation term S_{zz} .

The first phosphorus compounds, which have been studied by NMR in the nematic phase, were indeed simple molecules with a C_{3v} symmetry like PH_3 , PF_3 , POF_3 , PSF_3 (17), $P(\overset{O}{\parallel}C_6H_5)_3$ (18), $P(N(CH_3)_2)_3$ (19).

As an illustration, we will discuss here the results obtained for trimethylphosphine derivatives $X = P(CH_3)_3$ ($X =$ lone pair, O, S and Se) (20)(21)(22). Molecules triply labelled with ^{13}C have been used to obtain two dipolar coupling data on the rigid part of the molecules. With complete proton decoupling, the phosphorus and carbon nuclei form a simple AX_3 spin system. Assuming that the indirect spin couplings $^1J(P-C)$ and $^2J(C-P-C)$ are isotropic, the C-P-C bond angles α can be obtained from the $\mathcal{D}(PC)/\mathcal{D}(CC)$ ratio of the phosphorus-carbon and carbon-carbon dipolar couplings (Fig. 4).

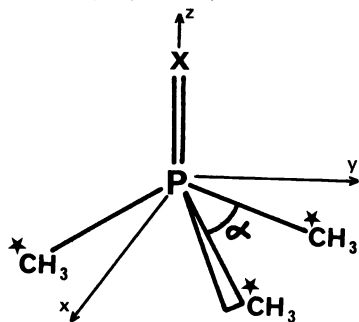


Fig. 4. Representation of the $X = P(CH_3)_3$ molecules ($X =$ lone pair, O, S, Se) along with the choice of the molecular axis system. The three ^{13}C are ^{13}C .

The vibrational corrections (23) have been taken into account and appear to be negligible, compared to the errors resulting from uncertainties in the line positions in the NMR spectra. The α bond angle values obtained by NMR are shown in Table 2, along with the values obtained using other experimental techniques.

TABLE 2. CPC bond angle α in $X = P(CH_3)_3$ molecules, as measured by NMR in nematic phases and by other techniques (m.w. microwave, e.d. electron diffraction, X-ray X-ray diffraction).

X	lone pair	O	S	Se
α (deg.) NMR	99.2 ± 0.2	105.7 ± 0.2	104.7 ± 0.2	105.0 ± 0.2
α (lit)	99.1	104.7	104.4	104.8
	m.w. (24)	e.d. (25)	e.d. (25)	e.d. (26)

It is evident that the results obtained by NMR in oriented phases are closely comparable to the ones obtained by other techniques. Other examples, where the study of the ^{31}P NMR spectrum in the nematic phase, gives access to geometrical information, are given by cyclotetraphosphanes $(PR)_4$ and cyclohexaphosphanes $(PR)_6$. In the case of cyclotetraphosphanes, the ^{31}P spectrum in the nematic phase is in agreement with the D_{2d} symmetry shown in Fig. 2. The analysis of this spectrum yields two dipolar couplings $_{12}$ and $_{13}$ and the ratio of these two values can be related to an angle α characterizing the degree of folding of the four-membered ring (16). Table 3 shows the results obtained for cyclotetraphosphanes bearing various substituents (16), along with the data obtained by X-ray diffraction for $(PCF_3)_4$ (27), $(PC-C_6H_{11})_4$ (28) and $(P-t-C_4H_9)_4$ (29). The two methods give very similar results.

TABLE 3. Ring folding α (deg) obtained in cyclotetraphosphanes $(PR)_4$. The uncertainty in the last digit is given in parentheses.

R	CF_3	C_2H_5	$i-C_3H_7$	$t-C_4H_9$	$C-C_6H_{11}$
α (deg) NMR	24.8(2)	23.6(2)	20.2(2)	18.2(2)	22.1(2)
RX	24.4(2)			17.6(3)	22.5(2)

A good agreement between X-ray (14) and NMR (11) structural data is also observed for the cyclohexaphosphane $P(C_6H_5)_6$. All these results tend to indicate that in acyclic phosphanes and in cyclopolyphosphanes, the $^1J(PC)$ and $^1J(PP)$ indirect spin-couplings have a negligible anisotropy.

Thus, in the case of highly symmetrical phosphorus molecules, NMR in nematic phases appears to be a reliable method to get information on the molecular geometry. It is often necessary to work with labelled molecules in order to get dipolar couplings involving the non fluxional part of the molecule. In the examples reported here, the vibration corrections are negligible but there exist in the literature several cases where they may become important (30). Difficulties may arise also from the existence of several orientations of the solute molecule in the ordered phase (31) or from modifications of the molecular geometry under the pressure exerted by the liquid crystal phase (32).

CHEMICAL SHIFT ANISOTROPY

As it was pointed out in the introduction, the NMR chemical shift of a given nucleus in a molecule is dependent upon the molecular orientation with respect to the external magnetic field B_0 . The magnetic field experienced by a nucleus i is given by $B = (1 - \bar{\sigma})B_0$, where $\bar{\sigma}$ is a second rank tensor which may have nine independent components. Most attempts to rationalize phosphorus chemical shifts (33)(34) are based on data which have been obtained in isotropic phases where only the trace of the chemical shift tensor $\bar{\sigma}$ can be measured. Knowledge of the the individual components of the $\bar{\sigma}$ tensor allows a better understanding of the influence of several factors such as geometry, electronegativity of the substituents, presence of π electron systems .. on the phosphorus chemical shift. This has been clearly illustrated by studies of several organophosphates mono and diesters. In these compounds, the components of the ^{31}P $\bar{\sigma}$ tensor are significantly more sensitive to the chemical or stereochemical environment than their isotropic counterpart (35)(36).

A molecule dissolved in a liquid crystal has a preferred average orientation with respect to the external magnetic field B_0 , and thus its resonance frequency ν_{aniso} will be different from the one observed in an isotropic phase ν_{iso} . For example, in a molecule of C_{3v} symmetry :

$$\frac{\nu_{\text{iso}} - \nu_{\text{aniso}}}{\nu_0} = \frac{2}{3} (\sigma_{\parallel} - \sigma_{\perp}) S_{zz}$$

$(1 - \sigma_{\parallel})B_0$ and $(1 - \sigma_{\perp})B_0$ represent the magnitude of the magnetic field at the nucleus under study when B_0 is parallel and perpendicular to the C_3 axis respectively.

An elegant use of smectic phases has been developed to measure easily the chemical shift anisotropy $\Delta\sigma = (\sigma_{\parallel} - \sigma_{\perp})$ (37). However, problems of solubility frequently preclude its use.

The measurement of the $\Delta\sigma$ value in nematic solvents is based on the following technique. By changing the temperature, the S_{zz} order parameter is changed. Extrapolation of the ν_{aniso} resonance frequency to the $S_{zz} = 0$ value allows the determination of ν_{iso} in a medium similar to the one in which ν_{aniso} is measured. The $\Delta\sigma$ values measured by this technique in $X = P(CH_3)_3$ (20)(21)(22) ; $X = P(C_6H_5)_3$ (38) and $X = PF_3$ (17c, 17d) ($X =$ lone pair, O, S, Se) are shown in Table 4. The absolute shielding values σ_{\parallel} and σ_{\perp} are based on phosphine, PH_3 , shielding which is assumed to be known accurately from ab initio calculations (39) and molecular beam experiments (40).

The accumulation of similar data will probably provide a good help in understanding and perhaps even predicting the trends observed in phosphorus chemical shifts.

It can be seen from the values quoted in Table 4 that $\Delta\sigma$ is, in general, fairly large and shows a striking increase when going from the three coordinate phosphorus compounds to the tetracoordinate ones. The largest values are observed for the phosphine oxides. It is interesting to note that the difference in the chemical shift observed for $O = P(CH_3)_3$ by changing the orientation of the magnetic field from parallel to perpendicular to the C_3 axis of the molecule, is greater than the chemical shift difference observed in the isotropic phase between $P(CH_3)_3$ and $O = P(CH_3)_3$. Except for the phosphine oxide, the benzene ring π -electron system does not affect significantly the chemical shift anisotropy. It is also worth noting that for the $X = P(CH_3)_3$ and $X = P(C_6H_5)_3$ compounds, σ_{\parallel} remains almost constant except for the oxide. A reverse situation seems to prevail in $X = PF_3$ molecules where a large increase in σ_{\parallel} is observed when going from PF_3 to $O = PF_3$ and $S = PF_3$.

Further investigations on similar series of simple organophosphorus compounds are needed and it will be interesting to compare the results with the recent calculations of the chemical shift tensor anisotropy in organophosphorus molecules (41)(42).

TABLE 4. Components (σ_{\parallel} , σ_{\perp}) of the chemical shift tensor σ of $X = P(CH_3)_3$, $X = P(C_6H_5)_3$ and $X = PF_3$ (X lone pair, O, S, Se). σ denotes the trace of the tensor ($\sigma = \frac{\sigma_{\parallel} + 2\sigma_{\perp}}{3}$), $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$. The values are given in p.p.m.

X		X = P(CH ₃) ₃	X = P(C ₆ H ₅) ₃	X = PF ₃
lone pair	σ	404	364	
	σ_{\parallel}	409	379	357
	σ_{\perp}	401	356	175
	$\Delta\sigma$	8	23	182
O	σ	308	329	
	σ_{\parallel}	424	516	594
	σ_{\perp}	250	236	260
	$\Delta\sigma$	174	280	334
S	σ	311	315	
	σ_{\parallel}	386	390	610
	σ_{\perp}	274	278	149
	$\Delta\sigma$	112	112	461
Se	σ	347	323	
	σ_{\parallel}	414	392	
	σ_{\perp}	314	289	
	$\Delta\sigma$	100	103	

SPIN-SPIN COUPLING ANISOTROPY

The indirect spin-spin coupling is also a second rank tensor \bar{J} which may have nine independent components. Due to the rapid tumbling of the molecule, only the trace of the \bar{J} tensor is accessible from the NMR spectral analysis in isotropic liquids. The dependence of the spin-spin coupling J_{ij} between nuclei ij upon the angle defined by the r_{ij} vector, and the magnetic field B_0 is difficult to measure in the solid state, where the dipolar coupling D_{ij} is largely dominant. However, an example of large anisotropy has been reported for $^1J(PP)$ from a solid state study of $Ag_4P_2O_6$ (43).

The NMR study of a molecule oriented in a liquid crystal may provide information on the anisotropy of the \bar{J} tensor. The method usually applied may be summarized as follows. In the nematic phase NMR spectrum, the dipolar couplings measured using equation (1) are in fact the sum of two terms :

$$D_{ij} = D_{ij}^{dir} + D_{ij}^{ind}$$

D_{ij}^{dir} is the pure dipolar contribution which depends only on the geometry. D_{ij}^{ind} depends on the individual components of the spin-spin coupling tensor \bar{J}_{ij} . This D_{ij}^{ind} contribution cancels out when the \bar{J}_{ij} tensor is isotropic. Thus, the obtention of accurate geometrical data relies heavily on the anisotropy of J being negligible and conversely the obtention of information on the anisotropy of J relies on the observation of a significant discrepancy (that is larger than experimental errors) between the geometry derived by oriented NMR and the actual geometry known from a reliable source. It is this way of reasoning which was followed above in the section concerning the obtention of geometrical information and the agreement between the data derived from NMR and from other experimental methods, led us to conclude that in the molecules studied, the $^1J(PH)$ (17a), $^1J(PC)$, $^2J(CC)$ $^1J(PP)$ tensors have a negligible anisotropy.

Recent theoretical investigations predicted a large anisotropy of \bar{J} for nuclei of high atomic number (44)(45). Such a prediction is supported by recent experimental results (45). This suggested to us the examination of the $^1J(PSe)$ coupling. From the NMR spectral analysis of the trimethylphosphane selenide $Se = P(CH_3)_3$ dissolved in a nematic phase, assuming that $^1J(PSe)$ is isotropic, one obtains a $r(PSe)$ bond distance (2.33 Å) (22), which is fairly different from the $r(PSe)$ value measured from X-ray diffraction (2.11 Å). This large discrepancy between the two $r(PSe)$ values lead us to conclude that there exists a large anisotropy for the $^1J(PSe)$ coupling. Assuming that all the discrepancy is due to the anisotropy, a simple analysis yields : $J_{\parallel}(PSe) = -1153 \text{ Hz} \pm 120 \text{ Hz}$; $J_{\perp}(PSe) = -473 \text{ Hz} \pm 60 \text{ Hz}$ where J_{\parallel} and J_{\perp} represents the spin spin coupling when the magnetic field B_0 is parallel and perpendicular to the C_3 axis of the molecule respectively (46).

Among the different terms which contribute to the indirect spin-spin coupling (Fermi-contact, orbital, spin-orbital, spin dipolar-Fermi contact), the Fermi contact will have no orientation dependence upon the applied magnetic field (6). Thus, the contribution of other terms than the Fermi contact becomes important for $^1J(\text{PSe})$. The \bar{J} tensor anisotropy which has been examined in a few cases only thus appears as an important factor for a better understanding of the coupling mechanism.

CONCLUSION

The few examples given above show that ^{31}P NMR in liquid crystal phases can be a powerful technique for the obtention of structural data on simple phosphorus containing molecules, which possess at least a three fold symmetry axis. The accuracy and reliability of the geometrical parameters derived from the measured dipolar couplings, require that the anisotropy of the indirect spin couplings is negligible. The examples given here show that this seems to be verified in the case of the indirect spin couplings involving light nuclei like ^1H , ^{13}C , ^{15}N , ^{31}P . The study in nematic phases can give also an easy access to the anisotropy of the ^{31}P chemical shift. The values obtained are however more prone to errors than the values measured in smectic phases (37) or in the solid state (9).

Finally, a close comparison of the geometries determined by X-ray diffraction and by NMR in the nematic phase may, in favorable cases, give some indication about the anisotropy of the indirect spin coupling tensor. This remains a useful source of information considering how difficult it is to obtain this information from solid state NMR studies.

REFERENCES

1. R. K. Harris, Chem. Soc. Rev. **5**, 1 (1976) ; R. K. Harris and B.E. Mann, NMR and the Periodic Table, Academic Press, London (1978).
2. G. W. Gray, Molecular Structure and the properties of Liquid Crystals, Academic Press, London (1962).
3. A. Saupe and G. Englert, Phys. Rev. Lett. **11**, 462 (1963) ; Z. Naturforsch. **19a**, 172 (1964)
4. P. Diehl and C. L. Khetrapal, in NMR Basic Principles and Progress vol. 1, 1. P. Diehl, E. Fluck and R. Kosfeld editors, Springer-Verlag, Berlin (1969).
5. J.W.Emsley and J.C. Lindon, NMR Spectroscopy using liquid crystal solvents, Pergamon Press, London (1975).
6. A. D. Buckingham and I. Love, J. Magn. Reson. **2**, 338 (1970).
7. T. C. Farrar and E. D. Becker, Pulse and Fourier Transform NMR, Academic Press, New York (1971), ch. 4
8. R. K. Harris and E. M. Mc Vicker, J. Chem. Soc. Faraday II **2291** (1976) ; N. J. Koole, A. J. De Koning and M. J. De Bie, J. Magn. Reson. **25**, 375 (1977, and references cited in.
9. U. Haeblerlen, High Resolution NMR in Solids, Advances in Magnetic Resonance, supplement 1, Academic Press, New York (1976) ; M. Mehring, High Resolution NMR Spectroscopy in Solids, NMR Basic Principles and Progress, vol. 11, Springer Verlag, Berlin (1976).
10. T. J. Dupont, L. R. Smith and J. L. Mills, J.C.S. Chem Comm. **1001** (1974) ; J. L. Mills, in Homoatomic Rings, Chains and Macromolecules of Main Group Elements, A. L. Theinhold editor, Elsevier, New York (1977).
11. J. P. Albrand, A. Cogne and J. B. Robert, Chem. Phys. Letters **42**, 498 (1976).
12. E. G. Finer and R. K. Harris, in Progress in Nuclear Magnetic Resonance Spectroscopy vol. 6, J.W. Emsley, J. Feeney and L. H. Sutcliffe editors, Pergamon Press, Oxford (1971).
13. M. Baudler, B. Carlsohn, B. Kloth and D. Koch, Z. Anorg. allg. Chem. **432**, 67 (1977) ; M. Baudler, J. Vesper, B. Kloth, D. Koch and H. Sandmann, ibid. **431**, 39 (1977).
14. J. J. Daly, J. Chem. Soc. A **4789** (1965) ; ibid. **428** (1966).
15. J. P. Albrand, D. Gagnaire, H. Faucher and J. B. Robert, Chem. Phys. Letters **38**, 521 (1976).
16. J. P. Albrand, A. Cogne and J. B. Robert, J. Amer. Chem. Soc. **100**, 2600 (1978).
17. a) N. Zumbulyadis and B. P. Dailey, Mol. Phys. **27**, 633 (1974) ; b) N. Zumbulyadis and B. P. Dailey, ibid. **26**, 777 (1973) ; c) P. K. Bhattacharyya and B. P. Dailey, ibid. **28**, 209 (1974) ; d) A. J. Montana, N. Zumbulyadis and B. P. Dailey, J. Chem. Phys. **65**, 4756 (1976).

18. A. Cogne, J. B. Robert, L. Wiesenfeld and R. Tyka, Org. Magn. Reson., in the press.
19. A. Cogne, J. B. Robert, and L. Wiesenfeld, Chem. Phys. Letters **57**, 627 (1978).
20. J. D. Kennedy and W. McFarlane, J. Chem. Soc. Chem. Comm. 666 (1976).
21. A. J. Montana, N. Zumbulyadis and B. P. Dailey, J. Amer. Chem. Soc. **99**, 4290 (1977).
22. J. P. Albrand, A. Cogne and J. B. Robert, Chem. Phys. Letters **48**, 524 (1977).
23. M. J. D. Lucas, Mol. Phys. **22**, 147 (1971) ; **22**, 233 (1971) ; **23**, 825 (1972).
24. D. R. Lide Jr. and D. E. Mann, J. Chem. Phys. **29**, 914 (1958).
25. C. J. Wilkins, K. Hagen, L. Hedberg, Q. Shen and K. Hedberg, J. Amer. Chem. Soc. **97**, 6352 (1975).
26. E. J. Jacob and S. Samdal, J. Amer. Chem. Soc. **99**, 5656 (1977).
27. G. J. Palenik and J. Donohue, Acta Cryst. **15**, 564 (1962).
28. J. C. J. Bart, Acta Cryst. B **25**, 762 (1969).
29. J. P. Albrand, A. Grand and J. B. Robert, unpublished results.
30. S. Šykora, J. Vogt, H. Bösigler and P. Diehl, J. Magn. Reson. **36**, 53 (1979).
31. P. Diehl, M. Reinhold, A. S. Tracey and E. Wullschlegler, Mol. Phys. **30**, 1781 (1975).
32. L. C. Snyder and S. Meiboom, J. Chem. Phys. **44**, 4057 (1966) ; A. J. Montana and B. P. Dailey, J. Magn. Reson. **22**, 117 (1976) ; D. Bailey, A. D. Buckingham, F. Fujiwara and L. W. Reeves, J. Magn. Reson. **18**, 344 (1975).
33. M. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark and J. R. van Wazer, ³¹P Nuclear Magnetic Resonance, in Topics in Phosphorus Chemistry, volume 5, John Wiley, New York (1967).
34. D. Purdela, J. Magn. Reson. **5**, 23 (1971).
35. T. Terao, S. Matsui and K. Akasaka, J. Amer. Chem. Soc. **99**, 6136 (1977).
36. S.J. Kohler and M.P.Klein, Biochemistry **15**, 967 (1976).
37. A. J. Montana and B. P. Dailey, Mol. Phys. **30**, 1521 (1975) ; J. Magn. Reson. **21**, 25 (1976) ; **22**, 117 (1976) ; J. Chem. Phys., **66**, 989 (1977).
38. J. B. Robert and L. Wiesenfeld, J. Magn. Reson., in the press .
39. S. Rothenberg, R.H.Young and H.F.Schaefer III, J. Amer. Chem. Soc., **92**, 3243 (1970).
40. P. B. Davies, R. M. Neuman, S. C. Wofsy and W. Klemperer, J. Chem. Phys., **55**, 3564 (1971).
41. J. Ridard, B. Levy and Ph. Millié, Mol. Phys. **36**, 1025 (1978).
42. F. Ribas Prado, C. Giessner-Prettre, B. Pullman and J. P. Daudey, J. Amer. Chem. Soc. **101**, 1737 (1979).
43. A. R. Grimmer, R. Peter and E. Fechner, Z. Chem. **109**, 3 (1978).
44. P. Pyykkö, Chem. Phys. **22**, 289 (1977).
45. C. Schumann, H. Dreeskamp and K. Hildenbrand, J. Magn. Reson. **18**, 97 (1975) ; J. Jokisaari, K. Räsänen, L. Lajunen, A. Passoja and P. Pyykkö, ibid., **31**, 121 (1978); J. Jokisaari and K. Räsänen, Mol. Phys. **36**, 113 (1978).
46. A. Cogne, A. Grand, J. Laugier, J. B. Robert and L. Wiesenfeld, J. Amer. Chem. Soc., in the press.