Anisotropy of the ^{1}J(PSe) Spin–Spin Coupling. X-ray and Liquid Crystal NMR Study of Se=P(CH$_3$)$_3$

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Abstract: The X-ray diffraction study and the NMR study (^{13}C, ^{31}P) of Se=P(CH$_3$)$_3$ oriented by means of liquid crystals are reported. Comparison of the phosphorus–selenium bond lengths obtained by the two methods shows that the ^{1}J(PSe) spin–spin coupling is highly anisotropic ($J_{\parallel} - J_{\perp} = -680 \pm 180$ Hz).

The interaction of nuclear spins consists of a direct dipolar coupling $\mathcal{D}$ and an indirect interaction via the electrons J. The appropriate Hamiltonian for the interaction of nuclei A and B of angular momentum I_A and I_B is $\mathcal{H}_{AB} = I_A(\overline{\mathcal{D}} + \bar{J})I_B$. $\overline{\mathcal{D}}$ is a symmetric traceless tensor which cancels out in isotropic liquid. In an anisotropic medium, the dipole interaction does not average to zero and it can provide information on the molecular geometry. $\bar{J}$ is a nonsymmetric tensor of which only the trace ($J = {}^{1}\!/_{3}\sum_{\alpha} J_{\alpha\alpha}$) can be measured in isotropic phase. The $\bar{J}$ tensor has in general nine components; however, the molecular symmetry may reduce this number.[2] NMR spectra recorded in liquid crystals can provide information on the values of the $\bar{J}$ tensor components.

Most of the NMR studies of molecules oriented by means of liquid crystals[3,4] have been focused on measurements of molecular geometry and of chemical-shift anisotropy.[5,6] Fewer studies have been directed toward the measurement of the $\bar{J}$ tensor anisotropy.[7-10]

From a relativistic analogue of Ramsey's theory of nuclear spin–spin coupling,[11] it is predicted that the coupling anisotropy would increase as one goes lower in the periodic table. In the course of our studies on the NMR spectral parameters of phosphorus-containing molecules, it was shown that the ^{1}J(PC)[12] and ^{1}J(PP)[13] have a negligible anisotropy. However, such a conclusion does not seem to be general and a large ^{1}J(PP) anisotropy was suggested from solid-state study in $Ag_4P_2O_6$.[14] Thus it seemed interesting to examine ^{1}J spin–spin couplings involving phosphorus and nuclei of higher Z value.

We wish to present here evidence for the existence of a large anisotropy of the ^{1}J(PSe) coupling as obtained from the NMR spectral analysis (^{13}C, ^{31}P) of the triply ^{13}C labeled trimethylphosphine selenide. To extract evidence for the existence of ^{1}J(PSe) anisotropy from an NMR study requires an accurate value of the P=Se bond length. Thus, an X-ray diffraction study was undertaken on the same molecule and is reported here. The present study provides also the opportunity to discuss the relative accuracy of the geometrical data obtained from NMR liquid crystal study and from X-ray diffraction on the same molecule.

Previous studies have already been published on the NMR study of Se=P(CH$_3$)$_3$ oriented in nematic[12] or smectic phase,[15] but only the geometry (CPC bond angle) without vibration corrections and the phosphorus chemical shift anisotropy were reported.

Experimental Section

Trimethylphosphine selenide was obtained by the direct combination of selenium with trimethylphosphine in vacuo.[16] The triply ^{13}C labeled molecule was synthesized starting from the labeled trimethylphosphine which was obtained from the Laboratoire des Molécules Marquées, C.E.A., Saclay, France.

A. X-ray Structure. Single crystals of Se=P(CH$_3$)$_3$ were grown by sublimation under vacuum and mounted in a glass capillary under nitrogen. From the Weissenberg photographs the space group was assumed to be $P2_1$ or $P2_1/m$ ($0k0$ absent for k odd). The cell dimensions were refined by a least-squares fitting of the angular position of 25 reflections and are reported along with other crystal data in Table I.

The intensity of 1108 independent reflections ($2° < \theta < 30°$) were collected on a Enraf-Nonius CAD-4 diffractometer equipped with a carbon monochromator for the Mo Kα radiation. Three check reflections (0 6 0; 3 0 $\bar{5}$; 0 0 $\bar{5}$) were recorded periodically and showed no drop-off in intensity during the data collection. The data were corrected for Lorentz and polarization factor but not for absorption.

The structure was solved by the Patterson method and the statistic test showed the centrosymmetric space group $P2_1/m$. The Patterson function allowed the location of the P, Se, and C atoms. One of the carbons lies on the $y = {}^{1}\!/_{4}$ mirror plane. The hydrogen atoms were localized from a Fourier difference map. Full-matrix least-squares refinement[17] with anisotropic parameters for all atoms except hydrogens, which are kept fixed with a B factor equal to 6 Å^2, on 379 reflections ($F_o > F_{max}/10$) led to final error indices $R_w = |\sum w(F_o - F_c)^2/\sum wF_o^2|^{1/2} = 0.057$ and $R = \sum|F_o - F_c|/\sum|F_o| = 0.048$. The positional and thermal parameters of the nonhydrogen atoms are given in Table II, and those of the hydrogen atoms are in Table III.

B. NMR Studies. The nematic medium used was Merck "phase V", eutectic mixture of azoxy compounds of undisclosed composition. The trimethylphosphine was directly added to gray selenium (99.9%, Prolabo) by transfer under vacuum in the NMR sample tube in order to prevent any loss of labeled compound. After reaction, the liquid crystal was added with an approximate proportion of 6% (in weight) of solute. The sample was degassed over many freeze-pump-thaw cycles and then sealed.

The spectra were recorded on a Varian XL.100.15 pulsed NMR spectrometer, equipped with a 5-mm ^{31}P probe, with external ^{19}F lock. The pulse control and Fourier transform unit is an Informatek-Varian calculator with 32K memory. The ^{13}C and ^{31}P spectra were recorded with broad band proton decoupling.

IR spectra were recorded on a CsBr IR 5A Beckman spectrophotometer, in a 0.2-mm liquid cell. Solvents were benzene and acetonitrile Uvasol Merck.

Discussion

X-ray Molecular Structure. The bond lengths and bond angles are presented in Table IV, and a stereoview of the molecule is shown in Figure 1. The molecule lies on a mirror plane, with a staggered conformation of the methyl groups around the P-C bonds. The P-C bond lengths are equal within the error limits, but the molecule shows a slight distortion from the C_{3v} symmetry when considering the phosphorus bond angles. Although a C_3 structure for gaseous X=P(CH$_3$)$_3$ molecules cannot be positively eliminated, the electron-diffraction results[18,19] and microwave results[20] are generally consistent with a C_{3v} model. For solids S=P(CH$_3$)$_3$ a partial X-ray analysis[21] has established a $P2_1/m$ space group, with the molecule lying on a mirror plane (C_s symmetry) which is

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Table I. Crystal Data for Trimethylphosphine Selenide

formula	C_3H_9PSe	$a = 6.453\ (1)$ Å
mol wt	155.04	$b = 7.806\ (1)$ Å
monoclinic		$c = 6.586\ (1)$ Å
space group	$P2_1/m$	$\beta = 90.46\ (1)°$
$F(000)$	152	$V = 331.74$ Å^3
d_{calcd}	1.552	
d_{obsd}	1.54 (2)	

similar to the present observation. For these molecules, although the intermolecular atomic distances are larger than the sum of the corresponding van der Waals radii,[22] it is difficult to determine if the departure from the C_{3v} symmetry which is observed in the solid state is due to a packing effect or if the C_s symmetry corresponds to the energy minimum of the isolated molecule.

The average P-C bond distance (1.786 (14) Å) is close to the one observed in S=P(CH$_3$)$_3$ (1.793 Å). Similar PC bond lengths are also observed in these two molecules by electron diffraction, 1.819 and 1.818 Å, respectively.[18,19] The average values of the CPC bond angle are similar from electron diffraction and X-ray measurements in S=P(CH$_3$)$_3$, 104.5 and 104.8°, respectively. For Se=P(CH$_3$)$_3$ a slightly larger value is observed in the solid state, 105.7 vs. 104.8°.

The P=Se bond length (2.111 Å) is very close to the one measured on other phosphines,[23] but larger than the distance reported for triethylphosphine selenide (1.963 Å).[24] However, this last value corresponds to the first P=Se bond distance measured in a phosphine molecule, and it was obtained with a small number of reflections. The uncertainty which results in the distance (0.1 Å) shows that the difference between Se=P(Et)$_3$ and Se=P(CH$_3$)$_3$ is probably not significant.[25]

NMR Results. A. NMR Spectral Analysis. Trimethylphosphine selenide exhibits a threefold symmetry on the NMR time scale; thus its NMR spectrum in oriented phase will require the determination of only one orientation parameter, S_{zz}.[26] All the spectra discussed in this section are proton decoupled. The spectrum of a partially oriented AX$_3$ system (A phosphorus, X carbon) has been described previously.[27,28] When selenium-containing molecules are considered (AKX$_3$ system, K selenium), the A part shows two 1:3:3:1 quartets (splitting $|J(AX) + 2D(AX)|$) separated by $|J(AK) + 2D(AK)|$. D(PC) and D(PSe) contain the dipolar couplings and a contribution from the anisotropy of the indirect couplings J. In the case under study (C_3 symmetry), D(PC) and D(PSe) are given by the following expressions:

$$D(\mathrm{PC}) = \frac{1}{3}\,\Delta J(\mathrm{PC})S_{zz} + \frac{h}{4\pi^2}\,\gamma_\mathrm{P}\gamma_\mathrm{C}\,\frac{(2\sin^2\alpha/2 - 1)}{r_\mathrm{PC}{}^3}\,S_{zz} \tag{1}$$

$$D(\mathrm{PSe}) = \frac{1}{3}\,(J_\parallel(\mathrm{PSe}) - J_\perp(\mathrm{PSe}))S_{zz} + \frac{h}{4\pi^2}\,\gamma_\mathrm{Se}\gamma_\mathrm{P}\,\frac{1}{r_\mathrm{PSe}{}^3}\,S_{zz} \tag{2}$$

where ΔJ(PC) denotes a contribution arising from the $\bar{J}$(PC) tensor anisotropy; $J_\parallel$(PSe) and $J_\perp$(PSe) are the parallel and perpendicular contribution to the spin-spin coupling ($J_\parallel = J_{zz}$; $J_\perp = (J_{xx} + J_{yy})/2)$; γ_C, γ_P, and γ_Se are the ^{13}C, ^{31}P, and ^{77}Se magnetogyric ratios, respectively; r_PC and r_PSe are the phosphorus-carbon and phosphorus-selenium bond distances; α is the CPC bond angle (Figure 2).

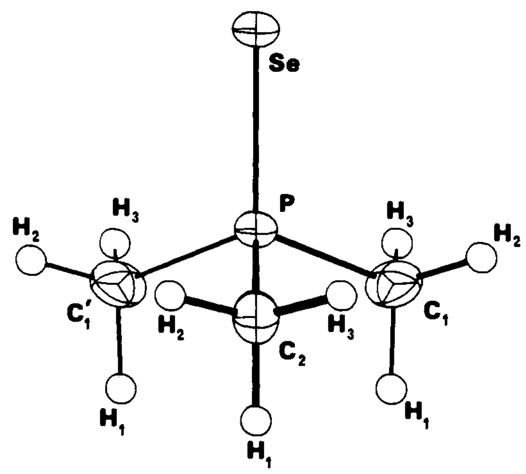

Figure 1.

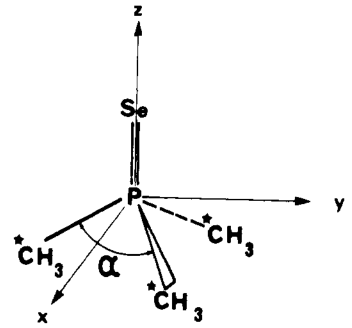

Figure 2.

From the ratio of the purely dipolar contribution $\mathcal{D}$(PC) and $\mathcal{D}$(CC) ($\mathcal{D}$(PC)/$\mathcal{D}$(CC)), a CPC bond angle value (105.0 ± 0.2°)[12] was obtained which is in good agreement with the one determined by electron diffraction (104.8 ± 0.3°)[19] and X-ray crystallography (average value 105.7°).

Our goal in the present study is to compare the r_PSe bond length values obtained from the X-ray analysis and from the NMR study through the knowledge of S_{zz} and D_PSe (formula 2 above). If a discrepancy exists between the values obtained by these two methods, we would be able to conclude the presence of a sizable J(PSe) and indirect spin-spin coupling anisotropy in Se=P(CH$_3$)$_3$.

There are two main factors which may influence the experimentally deduced magnitude of the indirect nuclear spin-spin coupling. Firstly, the isotropic part of the indirect coupling may be solvent dependent; secondly, the observed direct polar interaction will depend upon $\langle r_{ij}{}^{-3}\rangle$; thus a vibration correction must be done.

B. ^1J(PSe) Value. In order to obtain the D(PSe) value from the line splitting $|J(\mathrm{PSe}) + 2D(\mathrm{PSe})|$ one must know the ^1J(PSe) spin-spin coupling. For a large majority of nuclei, the

Table II. Fractional Atomic Coordinates and Thermal Parameters with Estimated Standard Deviations (All ×10^4) for Nonhydrogen Atoms

	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
P	6667 (4)	2500	3100 (6)	165 (8)	164 (7)	244 (11)	0	8 (7)	0
Se	3396 (2)	2500	3043 (3)	156 (3)	193 (3)	464 (7)	0	−2 (3)	0
C(1)	7755 (17)	4346 (17)	1909 (18)	265 (26)	269 (28)	449 (40)	−66 (24)	−5 (27)	135 (28)
C(2)	7735 (25)	2500	5608 (23)	379 (49)	188 (30)	268 (43)	0	−22 (38)	0
C′(1)	7755 (17)	654 (17)	1909 (18)	265 (26)	269 (28)	449 (40)	−66 (24)	−5 (27)	135 (28)

Table III. Fractional Atomic Coordinates (×10^4) for Hydrogen Atoms, Thermal Parameter B = 6 Å^2

	X	Y	Z
$H_1(C_1)$	9462	4309	2045
$H_2(C_1)$	7204	5517	2662
$H_3(C_1)$	7328	4389	308
$H_1(C_2)$	9451	2500	5530
$H_2(C_2)$	7247	1357	6434
$H_3(C_2)$	7247	3643	6434
$H_1(C'_1)$	9462	691	2045
$H_2(C'_1)$	7204	−517	2662
$H_3(C'_1)$	7328	611	308

Table IV. Bond Distances (Å) and Bond Angles (deg) in $Se{=}P(CH_3)_3$

P-Se	2.111 (3)	Se-P-C_2	112.86 (4)
P-C_1	1.787 (13)	Se-P-C_1	113.28 (5)
P-C_2	1.784 (16)	C_1-P-C'_1	107.44 (6)
		C_2-P-C'_1	104.86 (5)

Table V. ^1J(PSe) NMR Coupling in Different Solvents at 28 °C

solvent	C_6D_6	$C_6D_5CD_3$	$CDCl_3$	CD_2Cl_2	CD_3CN
^1J(PSe), Hz	709	711	684.4	689.0	684.4

J couplings are independent of solvent and temperature in the absence of conformational mobility. However, several cases have been reported where the NMR couplings vary by a large extent by changing the solvent.[10] In particular were reported both a solvent and a temperature dependence for ^1J(PSe).[29] A list of the ^1J(PSe) values obtained at infinite dilution in various solvents for $Se{=}P(CH_3)_3$ is given in Table V. The presence of an aromatic ring in the solvent molecule results in an increase in $|^1J(PSe)|$. The variations observed cannot be accounted for by intermolecular exchange,[30] as the ^1J(PSe) values are independent of the concentration. One could also consider a possible conformational effect. The examination of the ν(P=Se) stretching frequency, which is known to lie in the 500-400-cm^{-1} region,[31] shows only one single band at 442 cm^{-1} which does not shift when changing the solvent. It must be pointed out that the same frequency value is observed in the solid state. A least-squares analysis of the ^1J(PSe) values measured as a function of temperature, for the solvents reported in Table V, leads to linear variation with similar temperature coefficients ($\Delta J/\Delta t$ = −0.3 Hz deg^{-1}).

Three kinds of experiments have been undertaken in order to determine ^1J(PSe) for the molecules oriented in the liquid crystal. They lead to very close values.

In a first experiment, ^1J(PSe) has been measured in the melted liquid crystal above the clearing point. With a $\Delta J/\Delta t$ slope equal to the one observed in other solvents (−0.3 Hz deg^{-1}), one obtains by extrapolation a ^1J(PSe) value of 698.5 Hz at 28 °C. Secondly, in an NMR tube, the anisotropic phase of $Se{=}P(CH_3)_3$ (20 mg) oriented in Merck V (400 μL) is destroyed by adding toluene (25 μL). The ^{31}P NMR spectrum of the solution which is now isotropic shows a ^1J(PSe) value of 701.5 Hz at 28 °C. In a third experiment, the NMR tube is spun about an axis perpendicular to the magnetic field. The behavior of a nematic phase in such a situation was noted first by Lippman,[32,33] who reported that there exists a critical speed above which the orientation disappears. In our case, the splitting between the selenium satellite lines of the [^{1}H]^{31}P NMR spectrum gradually increases with the rotation speed to reach a ^1J(PSe) limit value of 700 Hz at 28 °C. Thus, from the three measurements reported, we can deduce that the ^1J(PSe) value is equal to 700 (±1.5) Hz in the Merck V phase at 28 °C.

The results of NMR spectral analysis of $Se{=}P(CH_3)_3$ oriented in the nematic Merck phase V at two different temperatures are presented in Table VI.

C. Vibration Corrections. Analysis of the NMR spectra of molecules partially oriented in liquid crystals gives values of the direct dipolar spin-spin interaction averaged over molecular motion. Thus, to obtain the geometrical parameters corresponding to the zero-point motion of the molecule, corrections must take into account the molecular vibrations. Such corrections have been made following the treatment developed by Lucas.[34] The necessary Raman spectra and normal coordinates were taken from the literature.[35] The $\alpha_{ij}\alpha'_{ij}/r_{ij}^5$ quantities, where α_{ij} represents the X, Y, Z components (Figure 2) of the r_{ij} vector connecting the nuclei i and j, have been calculated from the X-ray data, and are quoted in Table VII along with the corrections calculated according to formula (11) given by Lucas.[34a]

For a C_{3v} symmetry problem, the dipolar contribution between nuclei i and j to the splitting is equal to

$$\mathcal{D}_{ij} = \frac{h\gamma_i\gamma_j}{4\pi^2}\frac{Z_{ij}^2 - \frac{1}{2}(X_{ij} + Y_{ij})^2}{r_{ij}^5}S_{zz}$$

In the present case, it comes out

$$\mathcal{D}(\mathrm{PC}) = -\frac{h\gamma_\mathrm{P}\gamma_\mathrm{C}}{4\pi^2}\frac{1 - 2\sin^2\alpha/2}{r_\mathrm{PC}^3}S_{zz}$$

$$\mathcal{D}(\mathrm{CC}) = \frac{h\gamma_\mathrm{C}^2}{4\pi^2}\frac{1}{2r_\mathrm{PC}^3\sin^3\alpha/2}S_{zz}$$

$$\mathcal{D}(\mathrm{PSe}) = \frac{h\gamma_\mathrm{P}\gamma_\mathrm{Se}}{4\pi^2}\frac{S_{zz}}{r_\mathrm{PSe}^3}$$

When comparing the uncertainties due to the line position in the NMR spectra (0.5 Hz) and the one due to the molecular vibrations (Table VII) on the internuclei couplings, it appears that the latter is negligible. Thus, the vibration corrections turn out to be unimportant in the determination of $Se{=}P(CH_3)_3$ structure by NMR study in a liquid crystal. With the assumption that the $\bar{J}$(PC) and $\bar{J}$(CC) tensors have a negligible anisotropy, one can identify the direct dipole-dipole coupling $\mathcal{D}$ with the D values which are readily obtained from the NMR spectral analysis. The D(PC)/D(CC) ratio[12] gives a CPC bond angle value of 105 ± 0.2°, which is only slightly smaller than the average CPC value obtained by X-ray diffraction (105.7 ± 0.4°). Thus, there is no detectable anisotropic contribution to the ^1J(PC) indirect coupling constant.

D. J(PSe) Indirect Spin Coupling Anisotropy. If one assumes that $^1\bar{J}$(PSe) tensor is isotropic, by taking the CPC bond angle value obtained from the D(PC)/D(CC) ratio[12] and the r(PC) average bond distance measured by X-ray diffraction, the D(PC)/D(PSe) allows us to calculate the P=Se bond distance r(PSe). From the values of Table VI, it comes out r(PSe) = 2.33 ± 0.06 Å. Such a value is considerably larger than the one obtained from X-ray measurement (r(PSe) = 2.11 Å). The assumptions concerning the r(PC) bond lengths and the CPC bond angle seem perfectly reasonable; a modification of these geometrical parameters cannot explain the discrepancy observed between the r(PSe) values measured by NMR and X-ray diffraction. One may question the assumption made concerning the C_3 symmetry assumed for the molecule under study, in the liquid state; such a conformation is observed on the NMR time scale, but it is not necessarily the one corresponding to the ground state of the molecule. However, the Raman data are in agreement with such a symmetry and a similar symmetry is found in the liquid state for trimethylphosphine oxide and trimethylarsine selenide.[36] On the other hand, it has been shown that certain molecules may adopt more than one averaged orientation in the nematic phase of the solvent.[37] This can lead to erroneous deduction of geometry, but, as the CPC bond angle measured by NMR is in good agreement with the value obtained by other techniques, this explanation is rejected.

Table VI. Results from $[^1H]^{31}P$ NMR Spectral Analysis of $Se{=}P(CH_3)_3$ Dissolved in the Nematic Merck V Phase at 28 and 33 °C[a]

t, °C	$\lvert J + 2D\rvert$(PC)	J(PC)	D(PC)	$\lvert J + 2D\rvert$(PSe)	J(PSe)	D(PSe)
28	21.0	+48.5	34.7	608.	−698.5	45.3
33	20.3	+48.5	34.4	609.	−700	46.5

[a] The values are given in hertz.

The explanation we propose to account for the large discrepancy between the r(PSe) bond distance measured by NMR liquid crystal and X-ray crystallography in $Se{=}P(CH_3)_3$ is the presence of a large anisotropy of the ^1J(PSe) indirect spin-spin coupling.

From the comparison of the experimentally measured D(PSe)/D(PC) ratio to its calculated expression in which the J(PSe) anisotropy has been taken into account, but not the J(PC) anisotropy, one may calculate the ΔJ(PSe) anisotropy through the expression

$$\frac{D(\mathrm{PSe})}{D(\mathrm{PC})} = \left(\frac{\Delta J}{3} + \frac{h}{4\pi^2}\frac{\gamma_P\gamma_{Se}}{r_{PSe}{}^3}\right)\Bigg/\frac{h}{4\pi^2}\frac{\gamma_P\gamma_C}{r_{PC}{}^3}\left(1 - 2\sin^2\alpha/2\right)$$

In this calculation, the geometrical data are taken from the X-ray structure determination. The whole assumption of this calculation is that there is no significant change in the molecular geometry in going from the solid state to the liquid state. One obtains by taking into account only the uncertainty due to the NMR line position $\Delta J = J_{\parallel}(\mathrm{PSe}) - J_{\perp}(\mathrm{PSe}) = -680 \pm 60$ Hz.

Another contribution to the uncertainty in the J(PSe) spin coupling anisotropy may be due to a perturbation of the molecular geometry by the nematic solvent. Molecules of high symmetry (either cubic or tetrahedral) which should experience no orientation when dissolved in liquid crystals in fact do.[38] The observed orientation has been interpreted as resulting from a slight distortion of the solute molecule by the anisotropic pressure exerted by the anisotropic solvent environment. Similarly solvent effects on internuclear distance ratio of the order of 1% have been detected in benzene and acetylene[39] and attributed to molecular deformation. If in the present study on $Se{=}P(CH_3)_3$ one assumes a 1% modification in the PSe bond distance as due to the nematic solvent effect, an uncertainty of 120 Hz is obtained on the J(PSe) spin coupling anisotropy.

From the isotropic value of J(PSe) $((J_{\parallel}(\mathrm{PSe}) + 2J_{\perp}(\mathrm{PSe}))/3 = -700$ Hz), which is of negative sign,[40] it comes out $J_{\parallel}(\mathrm{PSe}) = -1153 \pm 120$ Hz and $J_{\perp}(\mathrm{PSe}) = -473 \pm 60$ Hz. The uncertainty in the J values includes both the one due to the NMR spectral analysis and a 1% modification of the PSe bond distance which may result from the interaction of the solute molecule with the liquid-crystal solvent.

Thus, combining the X-ray structural data and the NMR spectral analysis of $Se{=}P(CH_3)_3$ one may conclude that the indirect ^1J(PSe) NMR coupling exhibits a large anisotropy. In the previous NMR liquid crystal studies reported up to now and concerned with the NMR coupling involving phosphorus nuclei, the J values are generally assumed or shown to be isotropic.[41,42] However, a large anisotropy has been reported from a solid-state study on $Ag_4P_2O_6$.[14]

Among the different terms which contribute to the nuclear spin-spin interaction (Fermi contact, orbital, spin-orbital, spin dipolar-Fermi contact), the Fermi contact term will have no orientation dependence to the applied magnetic field.[2,43] Thus, the contribution of other terms than the Fermi contact becomes important for ^1J(PSe). At the present stage of our knowledge of the nature of the P=Se chemical bond, it is difficult to predict which among the three other terms contributes the most to the anisotropy.

The indirect spin-spin coupling anisotropy, which has been examined in only a few cases, is important for a better understanding of the coupling mechanism which is usually discussed by considering only the trace of the $\bar{J}$ tensor and not its individual components. The experimental determination of the $\bar{J}$ tensor components will also provide a good test for the several kinds of calculation which have been proposed to account for the spin-spin coupling values.

Table VII. Corrections on the X^2/r^5, Y^2/r^5, Z^2/r^5 Quantities Corresponding to the P-C and P-Se Vectors as Due to Molecular Vibrations in $Se{=}P(CH_3)_3$[a]

bond vector		X-ray value, Å^{-3}	correction, Å^{-3}
PC	X^2/r^5	1.504×10^{-1}	1.80×10^{-4}
	Y^2/r^5	0	$<10^{-6}$
	Z^2/r^5	2.5118×10^{-2}	-2.1×10^{-6}
P=Se	Z^2/r^5	1.063×10^{-1}	6.5×10^{-5}

[a] The equilibrium distances correspond to the X-ray data. The direction of the axes refers to Figure 2.

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Supplementary Material Available: A table of calculated and observed structure factors (4 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Centre d'Etudes Nucléaires de Grenoble, ERA CNRS no. 674; (b) Université Libre de Bruxelles.
(2) A. D. Buckingham and I. Love, *J. Magn. Reson.*, **2**, 338 (1970).
(3) P. Diehl and G. L. Khetrapal, "NMR Basic Principles and Progress," Vol. 1, P. Diehl, E. Fluck, and R. Kosfeld, Eds., Springer-Verlag, West Berlin, 1969.
(4) J. W. Emsley and J. C. Lindon, "NMR Spectroscopy Using Liquid Crystal Solvents," Pergamon Press, Oxford, 1975.
(5) B. R. Appelman and B. P. Dailey, *Adv. Magn. Reson.*, 7 (1974).
(6) C. L. Khetrapal and A. C. Kunwar, *Adv. Magn. Reson.*, **9** (1977).
(7) T. R. Krugh and R. A. Bernheim, *J. Chem. Phys.*, **52**, 4942 (1970).
(8) C. Schumann, H. Dreeskamp, and K. Hildenbrand, *J. Magn. Reson.*, **18**, 97 (1975).
(9) R. von Boeckh, G. Graff, and R. Ley, *Z. Phys.*, **179**, 285 (1964).
(10) J. Jokisaari, K. Räisänen, L. Lajunen, A. Passoja, and P. Pyykkö, *J. Magn. Reson.*, **31**, 121 (1978); J. Jokisaari, and K. Räisänen, *Mol. Phys.*, **36**, 113 (1978).
(11) P. Pyykkö, *Chem. Phys.*, **22**, 289 (1977).
(12) J. P. Albrand, A. Cogne, and J. B. Robert, *Chem. Phys. Lett.*, **48**, 524 (1977).
(13) J. P. Albrand, A. Cogne, and J. B. Robert, *Chem. Phys. Lett.*, **42**, 498 (1976).
(14) A. R. Grimmer, R. Peter, and E. Fechner, *Z. Chem.*, **109**, 3 (1978).
(15) A. Montana, N. Zumbulyadis, and B. P. Dailey, *J. Am. Chem. Soc.*, **99**, 4290 (1977).
(16) R. R. Renshan and F. K. Bell, *J. Am. Chem. Soc.*, **43**, 918 (1921).
(17) W. R. Busing, K. O. Martin, and H. A. Levy, ORFLX-3, Report ORNL 59-4-37, Oak Ridge, Tenn., 1971.
(18) C. J. Wilkins, K. Hagen, L. Hedberg, Q. Shen, and K. Hedberg, *J. Am. Chem. Soc.*, **97**, 6352 (1975).
(19) E. J. Jacob and S. Samdal, *J. Am. Chem. Soc.*, **99**, 5656 (1977).
(20) D. R. Lide Jr. and D. E. Mann, *J. Chem. Phys.*, **29**, 914 (1958).
(21) P. G. Eller and P. W. R. Corfield, *Chem. Commun.*, 105 (1971).
(22) L. Pauling, "The Nature of the Chemical Bond," 3rd ed., Cornell University Press, Ithaca, N.Y., 1960.
(23) T. S. Cameron, K. D. Howlett, and K. Miller, *Acta Crystallogr., Sect. B*, **34**, 1639 (1978); T. S. Cameron and B. Dahlen, *J. Chem. Soc., Perkin Trans 2*, 1737 (1975).
(24) M. Van Meerssche and A. Leonard, *Acta Crystallogr.*, **12**, 1053 (1959).
(25) Dr. M. Van Meerssche (Louvain University), with whom this problem was discussed, perfectly agrees with the fact that from his measurements, made 20 years ago on a disordered structure and with a limited number of reflections (160), an uncertainty of about 4σ will result in the P=Se bond distance. Thus, his P=Se value is in line with the recently reported values. We wish to thank Dr. M. Van Meerssche for his interesting comments

concerning this problem.
(26) A. Saupe, Z. *Naturforsch. A*, **20**, 572 (1965).
(27) A. D. Buckingham and J. A. Pople, *Trans. Faraday Soc.*, **59**, 2521 (1963).
(28) R. A. Bernheim, D. J. Hoy, T. R. Krugh, and B. J. Lavery, *J. Chem. Phys.*, **50**, 1350 (1969).
(29) J. W. Stec, *Phosphorus*, **2**, 97 (1972).
(30) D. H. Brown, R. J. Cross, and R. Keat, *J. Chem. Soc., Chem. Commun.*, 708 (1977).
(31) L. C. Thomas, "Interpretation of the Infra Red Spectra of Organophosphorus Compounds", Heyden, London, 1974.
(32) H. Lippman, *Ann. Phys.* (*Leipzig*), **1**, 157 (1958).
(33) P. G. de Gennes, "The Physics of Liquid Crystals," Clarendon Press, Oxford, 1974.
(34) (a) M. J. D. Lucas, *Mol. Phys.*, **22**, 147 (1971); (b) *ibid.*, **22**, 233 (1971); (c) *ibid.*, **23**, 825 (1973).
(35) H. Rojhantalab, J. N. Wibler, and C. J. Wilkins, *Spectrochim. Acta, Part A*, **32**, 519 (1976).
(36) F. Choplin and G. Kaufmann, *Spectrochim. Acta, Part A*, **26**, 2113 (1970).
(37) P. Diehl, H. Reinhold, A. S. Tracey, and E. Wullschleger, *Mol. Phys.*, **30**, 1781 (1975).
(38) L. G. 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, *ibid.*, **18**, 344 (1975).
(39) P. Diehl, H. Bösiger, and H. Zimmerman, *J. Magn. Reson.*, **33**, 113 (1979); P. Diehl, S. Sykora, W. Niederberger, and E. E. Burnel, *ibid.*, **14**, 260 (1974).
(40) W. McFarlane and J. A. Nash, *Chem. Commun.*, 913 (1969).
(41) N. Zumbulyadis and B. P. Dailey, *Chem. Phys. Lett.*, **26**, 777 (1973); **27**, 633 (1974).
(42) J. D. Kennedy, W. McFarlane, and B. Wrackmeyer, *J. Mol. Struct.*, **30**, 125 (1976).
(43) N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).

Macrocyclization of Poly(thiaethylene)

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Abstract: Cyclization of an acyclic poly(thiaethylene) chain to form $(CH_2CH_2S)_x$ has been studied by Monte Carlo methods for even x ranging from 4 to 24. Unperturbed acyclic chains are assumed to behave in accord with a rotational isomeric state treatment which incorporates first- and second-order interactions. The most readily formed macrocycle is that with $x = 6$, in harmony with results obtained in the poly(oxyethylene) series. However, cyclization at all x considered is found to be more difficult for poly(thiaethylene) than for the equivalent poly(oxyethylene). The greater difficulty in cyclization of poly(thiaethylene) can be attributed to the increase in C–X bond length and decrease in C–X–C angle when X is changed from an oxygen to a sulfur atom. Large macrocycles in both series have similar asymmetries, as measured by ratios of averaged principal moments of the inertia tensors.

Cyclic poly(oxyethylenes), $(CH_2CH_2O)_x$, are of great interest because certain members of this series form strong, selective complexes with cations.[1-5] As a consequence, cyclic poly(oxyethylenes) have been promoted as models for biological cation transport and for use in fractionation of cations. Stable complexes with cations are also formed by certain cyclic poly(thiaethylenes), $(CH_2CH_2S)_x$.[6,7] Members of this series form complexes which exhibit optical and redox properties reminiscent of those observed with blue copper proteins.[6]

Considerable effort has been expended in development of synthetic procedures which produce high yields of these macrocycles. In most cases the final step is an intramolecular reaction of $Y(CH_2CH_2X)_{x-1}CH_2CH_2X^-$, where X is an oxygen or sulfur atom and Y is a suitable leaving group.[1,2,8,9] Yields in the oxygen series go through a maximum when x is 6. A yield as high as 93% has been reported for preparation of $(CH_2CH_2O)_6$.[8] Occurrence of a maximum at $x = 6$ is in harmony with the properties of unperturbed acyclic poly(oxyethylenes). Simultaneous occurrence of a zero end-to-end distance and proper angular correlation of terminal bonds is more probable when x is 6 than for any other even x in the range 4–20.[10] A template effect arising from the presence of potassium ions in the reaction mixture may also contribute to the high yield for $(CH_2CH_2O)_6$. Cyclization tends to become more difficult when oxygen atoms are replaced by sulfur atoms. Macrocycles for which x is 6 illustrate this point. While yields for the oxygen-containing macrocycle are reported to be as high as 93%, those for the sulfur-containing macrocycle are only 25–35%.[9] Lower yields in the sulfur-containing series are also observed when the macrocycle formed contains an aromatic ring.[11-13]

One objective here is to assess whether the reduced tendency for cyclization seen with the sulfur-containing polymers might arise from a decrease in the probability for a zero end-to-end distance in the unperturbed acyclic chain. A second goal is to determine how substitution of sulfur for oxygen atoms alters average configuration-dependent properties for macrocycles actually formed. These objectives are met by first constructing a rotational isomeric state model for poly(thiaethylene). This model is similar to one recently described in preliminary form by Abe.[14] Subsequent development is based on an adaptation of Flory's macrocyclization theory[15] used previously to investigate cyclization of poly(oxyethylene).[10,16]

Conformational Energies

Geometry. Lengths of 1.10, 1.53, and 1.82 Å were used for C–H, C–C, and C–S bonds, respectively. The first two values are those appropriate for poly(methylene)[17] and poly(oxyethylene),[18] while that for the C–S bond is the one found in cysteine.[19] A length 0.005 Å shorter has been used for the C–S bond in poly(thiaethylene).[14] The C–S–C and C–C–S angles were 102 and 114°, respectively.[14]

Conformational Energy Calculations. Conformational energy was calculated as the sum of 6–12 potentials and intrinsic torsional potentials. Parameters for 6–12 potentials were formulated in the manner described by Brant et al.[20] Polarizabilities, effective number of electrons, and van der Waals radii were the following: carbon atom, 0.93 Å^3, 5, 1.70 Å; hydrogen atom, 0.42 Å^3, 0.9, 1.20 Å; sulfur atom, 0.34 Å^3, 16, 1.80 Å. Carbon and hydrogen atom parameters are those used by Brant et al.,[20] while sulfur atom parameters are from Scheraga.[19] Intrinsic torsional potentials were $(\Delta E_\varphi/2)(1 - \cos 3\varphi)$, where φ is taken to be zero for a trans placement. Barrier heights were 2.8 kcal mol^{-1} for C–C bonds[17] and 2.0 kcal mol^{-1} for C–S bonds.[19] Conformational energies were calculated at 10° intervals for variable dihedral angles. Terminal methyl groups were always oriented to yield a trans

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