

Cyclotetraphosphanes: Geometry, $^1J(\text{PP})$ Nuclear Magnetic Resonance Coupling Constants, and Phosphorus Chemical Shift Anisotropy. A Nuclear Magnetic Resonance Study in Liquid Crystals

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Abstract: The ^{31}P $\{^1\text{H}\}$ or $\{^{19}\text{F}\}$ NMR spectral analysis of five cyclotetraphosphanes $(\text{RP})_4$ ($\text{R} = \text{CH}_3$, *t*-Bu, *i*-Pr, C_2H_5 , $\text{c-C}_6\text{H}_{11}$) oriented by means of nematic phases is reported. The NMR spectrum in oriented phase allows us unambiguously to assign a tetrameric formula to the compounds under study. The ring puckering has been measured and shows a good agreement with x-ray data. The $^1J(\text{PP})$ values which are unobservable in isotropic phase have been measured. The phosphorus chemical shift shows a large anisotropy which ranges from 130 ($\text{R} = \text{CF}_3$) to 172 ppm ($\text{R} = i\text{-Pr}$).

The structure and ring size of cyclopolyposphanes $(\text{PR})_n$ has been, for a long time, a matter of dispute as illustrated by the lasting uncertainty about the structure of the various forms of "phosphobenzene", $(\text{C}_6\text{H}_5\text{P})_n$,¹⁻⁴ and by the controversy over the first reported cyclotriphosphane, $(\text{C}_2\text{F}_5\text{P})_3$.^{5,6} Since a few years, however, the advent of Fourier transform ^{31}P NMR with large band decoupling of all other nuclei has provided a very reliable tool for the identification of these cyclopolyposphanes in solution.^{4,7,8} Thus, the unambiguous analysis, in terms of an AA'BB'C system, of the complex ^{31}P (other nuclei decoupled) spectra observed for $(\text{CH}_3\text{P})_5$,⁹ $(\text{CF}_3\text{P})_5$,¹⁰ and $(\text{C}_2\text{H}_5\text{P})_5$ ¹¹ have established unequivocally the five-membered ring structure of these compounds in solution. There is also little doubt that the other cyclopolyposphanes $(\text{C}_6\text{H}_5\text{P})_5$,⁴ (*i*-PrP)₅, and (*n*-BuP)₅,⁷ which present also a complex $^{31}\text{P}\{^1\text{H}\}$ spectrum between +10 and -30 ppm, have a five-membered ring structure. On the other hand, the identification and analysis of A_2B systems in the ^{31}P chemical shift range 120-180 ppm elucidated the controversy about the existence of the three-membered ring $(\text{C}_2\text{F}_5\text{P})_3$ ¹² and established the existence of several other cyclotriphosphanes.¹³ In the case of cyclotetraphosphanes, the phosphorus substituents can realize a symmetrical trans alternation and accordingly the ^{31}P NMR spectrum with decoupling of all other nuclei in the molecule shows a single line. The occurrence of the ^{31}P signal in the chemical shift range 50-80 ppm is indicative of a four-membered ring structure¹² but it does not establish unequivocally this structure. Information from other sources should be sought before reaching a definitive conclusion. It must be pointed out that a six-membered ring (e.g., $(\text{PC}_6\text{H}_5)_6$) cyclopolyposphane will also show a single line $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum which can only be differentiated from that of a four-membered ring by the ^{31}P chemical shift value. On the other hand, the single line phosphorus NMR spectrum does not contain any information concerning the $J(\text{PP})$ coupling constants.

In a recent paper,¹⁴ we have shown that much more information can be obtained by recording the ^{31}P spectra of cyclotetraphosphanes oriented by the nematic phase of liquid crystals. We report here the comparative study of several compounds of this family $(\text{PR})_4$ with $\text{R} = \text{C}_2\text{H}_5$, *i*-C₃H₇, *t*-C₄H₉, *c*-C₆H₁₁, and CF_3 . Such a study not only establishes the existence of the four-membered ring in solution, but gives geometrical information concerning the ring puckering, the value of the $^1J(\text{PP})$ NMR coupling, which is not accessible

from isotropic solution, and information concerning the phosphorus chemical shift tensor, for which only the trace is obtained in the isotropic liquid phase. The data collected here, along with the ones already reported for (*t*-BuP)₄ and $(\text{CF}_3\text{P})_4$, allow a more comprehensive discussion of the substituent effects on the ring structure and on the NMR parameters.

Experimental Section

Materials. Tetraisopropylcyclotetraphosphane, (*i*-C₃H₇P)₄, tetracyclohexylcyclotetraphosphane, (*c*-C₆H₁₁P)₄, and tetra-*tert*-butylcyclotetraphosphane, (*t*-BuP)₄,¹⁴ were prepared by the method of Henderson et al.¹⁵ Tetraethylcyclotetraphosphane was obtained by the same method; the crude reaction mixture distilled at a pot temperature of 250-300 °C yields a 50:50 mixture of the tetramer and pentamer which was used without further fractionation. $(\text{C}_2\text{H}_5\text{P})_4$ has been described previously by Baudler et al.^{13b} Perfluorotetramethylcyclotetraphosphane was prepared according to Mahler and Burg¹⁶ and the NMR study was performed on a 40:60 mixture of the tetramer and pentamer.

Spectra. $^{31}\text{P}\{^1\text{H}\}$ and $^{31}\text{P}\{^{19}\text{F}\}$ NMR spectra were obtained in the Fourier transform mode on a Varian Associates XL-100.15 spectrometer operating with a fluorine or proton external lock. The broad band noise decoupling was performed using the spectrometer gyrocode system. Chemical shift were measured relative to internal 85% phosphoric acid and by using the indirect referencing method.¹⁷ The nematic solvents used are the commercially available phase IV and V (Merck) *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA) Kodak and *N*-(*p*-ethoxybenzylidene)-*p*-butylaniline (EBBA) (Kodak-Eastman). Samples were prepared using 5-mm NMR sample tubes and were degassed before sealing in vacuo. In the variable temperature experiment, the spectrometer dial is calibrated with a thermocouple placed inside a solvent contained in a dummy NMR tube. A precision of ± 1 °C is expected.

NMR Spectral Analysis. X-ray diffraction studies of several cyclotetraphosphanes $(\text{PR})_4$, $\text{R} = \text{CF}_3$,¹⁸ C_6H_{11} ,¹⁹ C_6F_5 ,²⁰ have shown that these compounds adopt in the solid state a folded ring structure with pseudoequatorial substituents as depicted in Figure 1. The x-ray structure reveals that in the solid state these molecules adopt a conformation of D_{2d} symmetry ($\text{R} = \text{CF}_3$, space group $P4_2/nmc$) or very close to it. This symmetry has been used to analyze the four-spin system displayed by the ^{31}P NMR spectrum of the five tetracyclophosphanes under study when dissolved in a liquid crystal.

The NMR spectrum of partially oriented molecules in the presence of a static magnetic field H_0 is described by the spin Hamiltonian \mathcal{H} .²¹

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

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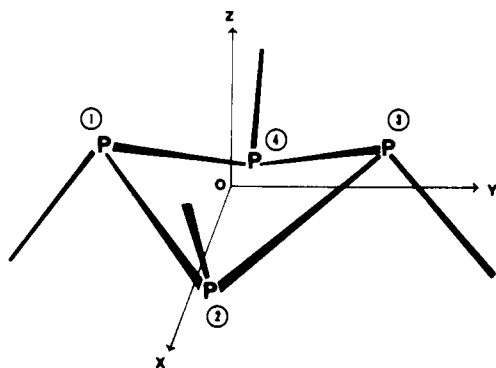


Figure 1. Cyclotetraphosphane ring structure.

Table I. Values of the Dipolar and Spin-Spin Coupling (Hz) between Phosphorus Nuclei in Cyclotetraphosphanes (RP)₄^b

R	Solvent	T, °C	J ₁₂	D ₁₂	D ₁₃
CF ₃ ^a	BEPC-MBBA	39	100.6	52.6	30.2
C ₂ H ₅	MBBA-EBBA	39	112.6	54.6	30.4
<i>i</i> -C ₃ H ₇	MBBA-EBBA	35	123.3	93.8	46.9
<i>t</i> -C ₄ H ₉ ^a	BEPC-MBBA	39	148.4	71.0	32.0
<i>c</i> -C ₆ H ₁₁	EBBA	50	116.3	95.5	50

^a Reference 14. ^b The uncertainty on the *J* and *D* values is ±0.5 Hz.

Owing to the presence of a *S*₄ symmetry axis, one needs only one ordering parameter *S*_{zz}.²²

Using the axes orientation shown in Figure 1, one obtains $\nu_i = (H_0/2\pi)\gamma_P(1 - \sigma_i - 2/3\Delta\delta_i S_{zz})$. γ_P is the phosphorus magnetogyric ratio, σ_i one-third of the trace of the phosphorus chemical shift tensor, and $\Delta\sigma_i$ the chemical shift anisotropy:

$$\Delta\sigma_i = \sigma_{zz}^i - 1/2(\sigma_{xx}^i + \sigma_{yy}^i) \quad (2)$$

*D*_{*ij*} is given by

$$D_{ij} = 1/3(J_{zz}^{ij} - 1/2(J_{xx}^{ij} + J_{yy}^{ij}))S_{zz} - \frac{\hbar^2\gamma_P^2}{2\pi} (Z_{ij}^2 - 1/2(X_{ij}^2 + Y_{ij}^2))S_{zz}/r_{ij}^5 S_{zz} \quad (3)$$

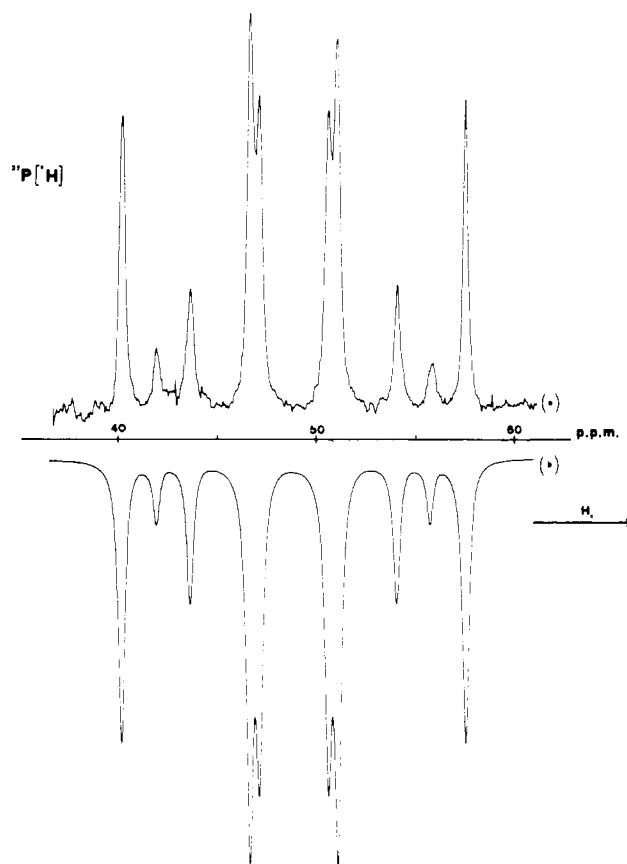
*X*_{*ij*}, *Y*_{*ij*}, *Z*_{*ij*} are the components of the vectors joining atoms *i* and *j* along the 0*X*, 0*Y*, 0*Z* axes, respectively. *J*_{*rs*}^{*ij*} (*r*, *s* = *x*, *y*, *z*) are the spin-spin coupling tensor components.

The *D*_{2d} symmetry factorization of the A₄ phosphorus spin system gives $\Gamma(A_4) = 6A_1 + B_1 + 3B_2 + 3E$. The symmetry factorization combined with the commutation rule [$\sum_i I_{zi}, \mathcal{H}$] = 0 allows the calculation of all the spectral transitions. Figure 2 shows a typical ³¹P{¹H} NMR spectrum of a cyclotetraphosphane oriented by means of a liquid crystal. It can be noticed that the phosphorus nuclei in the 1,3 position (Figure 1) are fully magnetically equivalent²³ and therefore the ²*J*(PP) spin-spin coupling cannot be observed.²⁴ In contrast, adjacent phosphorus nuclei are not fully magnetically equivalent and the spectrum does yield the ¹*J*(PP) values. Table I shows the NMR parameters obtained from the analysis of the spectra along with the results previously obtained for (CF₃P)₄ and (*t*-BuP)₄.¹⁴

Discussion of the Results

A. Ring Shape. The *D*_{*ij*} expression is made up of two terms: one which represents the potential contribution of the spin-spin coupling anisotropy, and another which is only dependent upon geometrical factors. The relative magnitude of these two terms is a priori unknown. The spin-spin coupling anisotropy contribution has been shown to be negligible in the case of proton-proton couplings, and also in case of phosphorus-phosphorus couplings.^{25,26} Assuming that the *J*_{*ij*} anisotropy does not contribute to *D*_{*ij*}, one easily obtains (Figure 3)

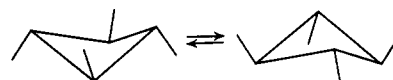
$$D_{12} = \frac{1 - \tan^2 \alpha}{d^3(2 + \tan^2 \alpha)^{5/2}} S_{zz} \quad \text{and} \quad D_{13} = \frac{S_{zz}}{16d^3} \quad (4)$$

Figure 2. Fourier transform ³¹P {¹H} NMR spectrum of (P-*i*-C₃H₇)₄ dissolved in a 1:1 mixture of EBBA-MBBA. Acquisition time 4 s; 1000 scans.

From the ratio of these two expressions, the folding angle of the ring (α) can be obtained. Table II gives the ring folding angle and the corresponding P-P-P bond angle calculated from the *D*₁₂/*D*₁₃ ratio for the cyclotetraphosphanes under study. Each value shown in Table II is the average resulting from five measurements of *D*₁₂ and *D*₁₃ on NMR spectra recorded at different temperatures thus corresponding to different values of the *S*_{zz} ordering parameter.

Comparison of the values obtained from the nematic phase NMR spectra with the values obtained from x-ray structure determination shows a consistent agreement between the two methods and justifies the assumption that the contribution of the spin-spin coupling anisotropy to the *D* value is negligible. The results of Table II indicate a decrease of the folding angle of the four-membered ring with the increasing bulk of the substituent. Such an effect is particularly illustrated by the decrease in the α value in the sequence from R = C₂H₅ to R = *i*-C₃H₇ and *t*-C₄H₉.

It must be pointed out that the results would be compatible with a rapid interconversion of the cyclotetraphosphane ring between two identical forms as indicated below. However, such



a conformational process would require a ring inversion and a bond inversion at the phosphorus in order to maintain the R group in the more favorable equatorial orientation. Since the bond inversion at the phosphorus is slow at room temperature on the NMR time scale in diphosphanes,^{27,28} it is more reasonable to consider that the four-membered ring is conformationally rigid with the four substituents lying in the equatorial position as observed in the solid state by x-ray diffraction.

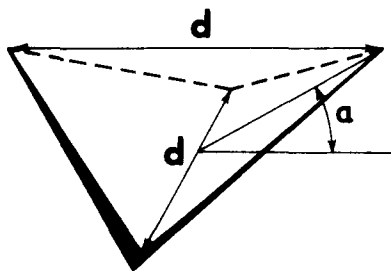


Figure 3. Geometrical parameters d and α used for ring shape characterization.

Table II. Ring Folding Angle α (deg) and PPP Bond Angle Obtained in Cyclotetraphosphanes^c

(PR) ₄	CF ₃	C ₂ H ₅	<i>i</i> -C ₃ H ₇	<i>t</i> -C ₄ H ₉	<i>c</i> -C ₆ H ₁₁
Exp	24.8	23.6 (2)	20.9 (2)	18.2 (2)	22.1 (2)
RX	24.4 (2) ^a				22.5 (2) ^b
PPP \angle	84.5 (1)	84.9 (1)	86.1 (1)	87.0 (1)	85.6 (1)

^a Reference 18. ^b Reference 19. ^c The uncertainty in the last digit is given in parentheses.

Value uncertainties of the ring folding and of the P-P-P bond angles (Table II) have been calculated by taking account only of NMR line positions (0.5 Hz). However, it should be pointed out that recent work on the NMR spectral analysis of molecules dissolved in liquid crystals has shown the importance of considering vibrational corrections, in the case of direct coupling between bonded atoms.²⁹ The direct dipole-dipole interaction D_{ij} between two nuclei can be written as $D_{ij} = S \langle 1/r_{ij}^3 \rangle$. S is the orientation parameter, and the brackets denote the averaging over the vibrational motion of the two nuclei with respect to each other. The $\langle 1/r_{ij}^3 \rangle$ include terms due to harmonic and anharmonic motions. Such a correction requires a knowledge of the normal vibration modes and coordinates of the molecules under study. Unfortunately, the very few IR and Raman studies which reported the Raman and vibrational assignments of symmetrical cyclotetraphosphanes³⁰ were in fact dealing with other cyclopolyphosphanes. For example, *n*-propyl¹⁵ and *n*-butylcyclopolyphosphanes are pentamers and not tetramers as previously reported.¹² Owing to the good agreement between the α puckering angle obtained by liquid crystal NMR study and x-ray structure determination (R = CF₃; R = C₆H₁₁) we assume that the vibrational correction will not introduce errors larger than that due to the NMR line positions.

B. ¹J(PP) NMR Coupling Constants. The NMR spectral analysis of the nematic phase spectra of cyclotetraphosphanes gives an easy access to the isotropic value of the ¹J(PP) spin-spin coupling constants. These values would be very difficult to obtain from the isotropic phase spectra since this would require the analysis of complex [AX_n]₄ systems. It should be noticed that the ¹J(PP) coupling constants in cyclotetraphosphanes must be considered as ¹J and ³J coupling constants, and should be compared only cautiously with other ¹J(PP) values as the ³J(P-P-P) values can be as large as 30 Hz.²⁶

The analysis of the spectra gives the relative signs of D and J couplings, but the absolute signs of the ¹J(PP) couplings cannot be obtained. As all the ¹J(PP) values reported up to now are shown to be negative³¹ we shall assume that this is also true for the cyclotetraphosphanes under study. The magnitude of the ¹J(PP) couplings can be considered as being under the influence of essentially two parameters, the phosphorus atom hybridization state^{31,32,33} and the adjacent phosphorus lone pair orientation.^{9,10,28,34} For the cyclotetraphosphanes, the $|^1J(PP)|$ value increases as the β PPP bond angle increases

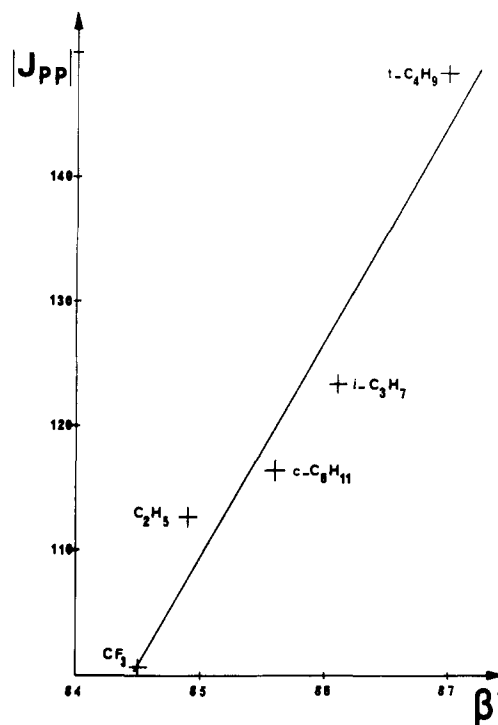


Figure 4. ¹J(PP) NMR coupling constant dependence vs. the PPP bond angle (β) in cyclopolyphosphanes.

(Figure 4). Such a tendency seems to be quite general for cyclopolyphosphanes and diphosphanes. A least-squares fitting gives a $\Delta J/\Delta\beta$ value of 17.4 Hz/deg. Such a linear correlation of ¹J(PP) vs. β is probably only valid in a small range of the β angle and must be restricted to four-membered rings in which the adjacent phosphorus lone pairs are in a trans relationship. An extrapolation to six-membered ring cyclopolyphosphanes ($\beta \sim 95^\circ$)³³ will lead to an unacceptable value of 200 Hz as compared to an experimental value of 107 Hz,²⁶ which is smaller than the one observed in cyclotetraphosphanes.

C. Phosphorus Chemical Shift. In combining the chemical shift measurements of a molecule dissolved in an isotropic liquid and oriented by means of liquid crystals, one can obtain information concerning the chemical shift tensor components σ_{rs} . In order to get a better understanding of the different factors which may influence the phosphorus chemical shift, it seems interesting to perform the σ_{rs} measurements in series of molecules, as the screening constant measured in isotropic phase is one-third of the trace of the σ tensor ($\sigma_{iso} = 1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$). Previous studies have shown that in organophosphorus molecules, the σ tensor components may differ by more than hundreds of parts per million.^{14,28,36-39}

The isotropic ³¹P chemical shift of cyclopolyphosphanes has been found to be indicative of ring size and linearly dependent upon the average endocyclic P-P-P bond angle.^{7,12} The greater the ring strain, as measured by the endocyclic phosphorus bond angle β , the more upfield the chemical shift, in qualitative agreement with the extremely high-field chemical shift of 488 ppm for the strained P₄ tetrahedron. In the present study which reports the ³¹P chemical shift values (Table III) in a small range of PPP bond angle ($\Delta\beta \sim 3^\circ$) the same trend is observed for the ³¹P chemical shift vs. β (Figure 5). However, the spread out of the points of Figure 5 shows that it would be illusive to try to obtain precise geometrical information from the ³¹P screening constant of cyclotetraphosphanes (PR)₄ even in considering R groups chemically similar (e.g., C₂H₅, *i*-C₃H₇, *t*-Bu).

The NMR spectrum of an oriented molecule which possesses a symmetry axis of order three or higher (S₄ in the present

Table III. ^{31}P Chemical Shift δ ,^a Chemical Shift Temperature Factor a , and Chemical Shift Anisotropy ($\Delta\sigma$) of Cyclotetraphosphanes^c

(PR) ₄ R	δ , ppm 30 °C	Temp range, °C	$ S_{zz} $	a , ppm °C ⁻¹	$\Delta\sigma$, ppm
CF ₃	76.71	9.5	0.0950	-0.057	129 ± 15
		41. 3.	0.0616 0.1144		
C ₂ H ₅	68.70	39.	0.0845	0.050	169 ± 15
		11.	0.1646		
<i>i</i> -C ₃ H ₇	62.40	46.	0.0982	-0.046	172 ± 15
		10.5	0.1473		
<i>t</i> -C ₄ H ₉	58.38	55.5	0.0877	-0.052	167 ± 15
<i>c</i> -C ₆ H ₁₁ ^b	69.50				

^a The ^{31}P chemical shifts are given in parts per million high field to a 85% solution of phosphoric acid and correspond to solutions in benzene. ^b The low solubility of this compound precluded its variable temperature study. ^c The temperature range of the NMR study in oriented phase along with the corresponding ordering parameters is also reported.

case) depends on only one ordering parameter S_{zz} . The resonance frequency in the isotropic phase ν_{iso} and in the anisotropic phase ν_{anis} are related by

$$\nu_{\text{iso}} - \nu_{\text{anis}} = \frac{H_0}{2\pi} \gamma_P^2 \frac{2}{3} S_{zz} (\sigma_{\parallel} - \sigma_{\perp})$$

$$\text{with } \sigma_{\parallel} = \sigma_{zz} \text{ and } \sigma_{\perp} = \frac{\sigma_{xx} + \sigma_{yy}}{2}$$

The chemical shift tensor components refers to the molecular coordinates system (Figure 1). The $\Delta\sigma$ value ($\sigma_{\parallel} - \sigma_{\perp}$) can be obtained from the slope of a plot of the ordering parameter which can be varied by varying the temperature vs. the corresponding nematic chemical shift. Extrapolation to $S_{zz} = 0$ should in the absence of a discontinuity in the solvent effect upon phase transition yield the isotropic chemical shift. However, one must take into account the temperature dependence of the phosphorus chemical shift.^{37,40-42} This temperature dependence of the phosphorus chemical shift has been accounted for by a linear correction $\nu = \nu_0 + aT$. The a values have been obtained by measuring at different temperatures the ^{31}P chemical shift of the molecules under study dissolved in the melted liquid crystal used for nematic measurements. In Table III are reported the temperature coefficients a , the $\Delta\sigma$ values along with the temperature range in which the anisotropic studies have been performed, and the corresponding S_{zz} values.

It has been shown that this method of temperature variation can lead to serious discrepancies when compared with the results obtained by use of the smectic phase in which the ordering parameter S_{zz} can be changed by means of a sample orientation change instead of a temperature change.⁴³ However, in the present study, it has been checked on one compound (PtBu)₄ that the $\Delta\sigma$ value obtained by use of a smectic phase is in good agreement with the one obtained by use of a nematic phase (145 vs. 167 ppm).

The correct geometry of the ring has been obtained with D , J , and S_{zz} of the same sign; thus as J is very probably negative, S_{zz} is also negative. The resonance of the cyclotetraphosphane oriented in the liquid crystal is observed at higher frequency than in the isotropic liquid; thus $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$ is positive.

It must be pointed out that in the present case, due to only C_s local symmetry, the molecular axes of Figure 1 do not coincide with the coordinates system which diagonalize the

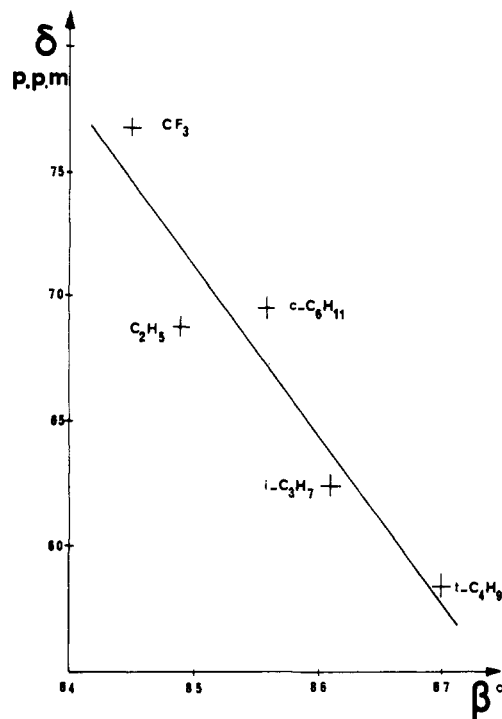


Figure 5. ^{31}P NMR chemical shift dependence vs. the PPP bond angle (β) in cyclotetraphosphanes.

phosphorus chemical shift tensor. These axes would be obtained by a rotation of angle ϕ around the x axis. Such a rotation to a new coordinate system (designated axis system $\alpha\beta\gamma$) yields the following for the shielding tensor:

$$\sigma_{\alpha\alpha} = \sigma_{xx}$$

$$\sigma_{\beta\beta} = \sigma_{yy} \cos^2 \phi - 2 \sigma_{yz} \sin \phi \cos \phi + \sigma_{zz} \sin^2 \phi$$

$$\sigma_{\beta\gamma} = (\sigma_{yy} - \sigma_{zz}) \sin \phi \cos \phi + \sigma_{yz} (\cos^2 \phi - \sin^2 \phi)$$

$$\sigma_{\gamma\gamma} = \sigma_{yy} \sin^2 \phi + 2 \sigma_{xy} \cos \phi \sin \phi + \sigma_{zz} \cos^2 \phi$$

The angle would be determined by canceling the $\sigma_{\beta\gamma}$ term ($\tan 2\phi = -(\sigma_{yy} - \sigma_{zz})/2\sigma_{yz}$) but only σ_{zz} is known from the present experiments.

However, it is interesting to note that the $\Delta\sigma$ values referred to the molecular axes on Figure 1 are fairly large and very similar for the three compounds with an alkyl group attached to the phosphorus. The smaller $\Delta\sigma$ value observed for $R = \text{CF}_3$ is opposite to what is observed in phosphine molecules PR_3 where the chemical shift anisotropy is higher for electronegative R groups.³⁶

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On the Molecular Structure of Beryllocene

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Abstract: A conformational analysis of beryllocene, $\text{Be}(\text{C}_5\text{H}_5)_2$, was executed based on ab initio standard single determinant MO theory with an STO-3G minimal basis. The study concentrated on two contradictory experimental models. One was the gas-phase electron diffraction model of $\text{Be}(\text{C}_5\text{H}_5)_2$, an asymmetrical sandwich structure in which the metal atom can occupy two alternate positions on the fivefold rotation axis, $h_1 = 1.472 \text{ \AA}$ from one ring and $h_2 = 1.903 \text{ \AA}$ from the other. The second model was the x-ray crystallographic slip-sandwich structure, in which one of the two parallel rings has slipped sideways by about 1.2 \AA , apparently producing a σ -bonded and a π -bonded ring system. The results of our calculations indicate that the gas-phase diffraction structure is 14–18 kcal/mol less stable in the STO-3G approximation than a symmetrical sandwich or a model which is similar to the x-ray structure, but has nonparallel rings. STO-3G calculations probably are too approximate to definitely rule out any conformation of a beryllium compound in a comparison of this kind. But it is possible to use these results as a basis for speculation that the vapors of $\text{Be}(\text{C}_5\text{H}_5)_2$ consist of a complicated conformational equilibrium with σ - π and σ - σ tautomerism which contains conformers in which the Be atom forms a π bond to one ring and a σ bond to the other. It is not unlikely that the radial distribution of this equilibrium is compatible with the experimental radial distribution observed by gas electron diffraction. This study points in a striking way to the usefulness of hybrid experimental and theoretical procedures in structural studies of gaseous molecules.

Introduction

The molecular structure which has been proposed for beryllocene (I), $\text{Be}(\text{C}_5\text{H}_5)_2$, in order to explain its vapor phase electron diffraction data^{1,2} is probably one of the most remarkable low-weight structural designs which are known. The Almenningen, Bastiansen, and Haaland (ABH) model of beryllocene^{1,2} describes the compound as a sandwich complex with two planar, symmetrical, parallel, and staggered C_5H_5 rings with a vertical ring-ring distance $h = 3.375 \text{ \AA}$. The CH skeleton of this model belongs to point group D_{5d} ; the complete molecule has the lower group C_{5v} , since the beryllium atom may occupy two alternative positions on the fivefold rotation axis, $h_1 = 1.472 \text{ \AA}$ from one ring and $h_2 = 1.903 \text{ \AA}$ from the other. Thus, the most characteristic feature of the ABH model for beryllocene is a double minimum potential energy curve for beryllium with the ability of the metal to tunnel between its two equilibrium positions.

In subsequent investigations Fritz and Sellmann³ claimed that the ABH structure was also found for I by analysis of its IR spectrum. Similar conclusions were reported by McVicker

and Morgan,⁴ who compared the IR condensed state spectrum of I to its vapor phase data. In direct contrast to this the earlier IR study of I by Fritz and Schneider⁵ seemed to favor an angular structure for this compound and inferred the presence of two equivalently bonded ligands. The semiempirical MO calculations by Sundbom⁶ indicated that the ABH structure might correspond to an energy minimum. But it was also warned⁶ that the shape of the energy curve depended strongly on the values chosen for some of the empirical parameters so that more refinements were needed to make a really conclusive statement. Lopatko, Klimenko, and Dyatkina⁷ used a somewhat more advanced semiempirical MO LCAO SCF procedure to calculate the electronic structure of I in a PNDO approximation taking into account all the valence electrons of beryllium and the $2p_z$ atomic orbitals of all the carbon atoms using a Slater-type basis set. The conclusion of these authors was that the asymmetrical conformation of I, C_{5v} , was energetically more favored than its symmetric form, D_{5d} .

In 1972 Wong, Lee, Chao, and Lee (WLCL)⁸ studied the crystal structure of I by x-ray diffraction at $-120 \text{ }^\circ\text{C}$ and