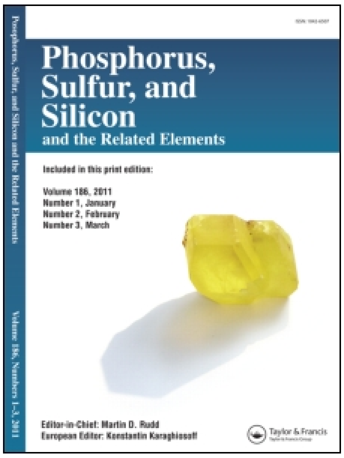

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# LINEAR SHORT-CHAIN CHLOROPHOSPHAZENES. SYNTHESES, $^{31}P$, $^{15}N$-NMR AND RAMAN SCATTERING CHARACTERIZATIONS

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Two classes of short-chain linear chlorophosphazenes have been synthesized in high degree of purity, $Cl_3PN(PCl_2N)_nP(X)Cl_2$ (X = O, $n$ = 0, 1, 2, 3; $X$ = $S$, $n$ = 0, 1) and $[Cl_3PN(PCl_2N)_nPCl_3]$ [Y] (Y = $Cl^-$, $n$ = 0, 1; Y = $PCl_6^-$, $n$ = 0, 1, 2). New routes of synthesis were employed for some compounds. All these molecular and ionic compounds were characterized by $^{31}P$, $^{15}$ N-NMR and Raman scattering at room temperature. A $^{31}P$-NMR study of the molecular compounds $Cl_3PN(PCl_2N)_nP(X)Cl_2$ as a function of temperature shows a coalescence phenomenon near 220K for two compounds, $Cl_3PN(PCl_2N)_2P(O)Cl_2$ and $Cl_3PN(PCl_2N)_3P(O)Cl_2$ demonstrating the flexibility of the PN backbone. The Raman scattering provides evidence for planar cis-trans molecular conformation in the melt and in the solution as well as in the solid state for all the molecular compounds.

*Key words:* Chlorophosphazenes; $^{31}P$-NMR; $^{15}N$-NMR; Raman scattering.

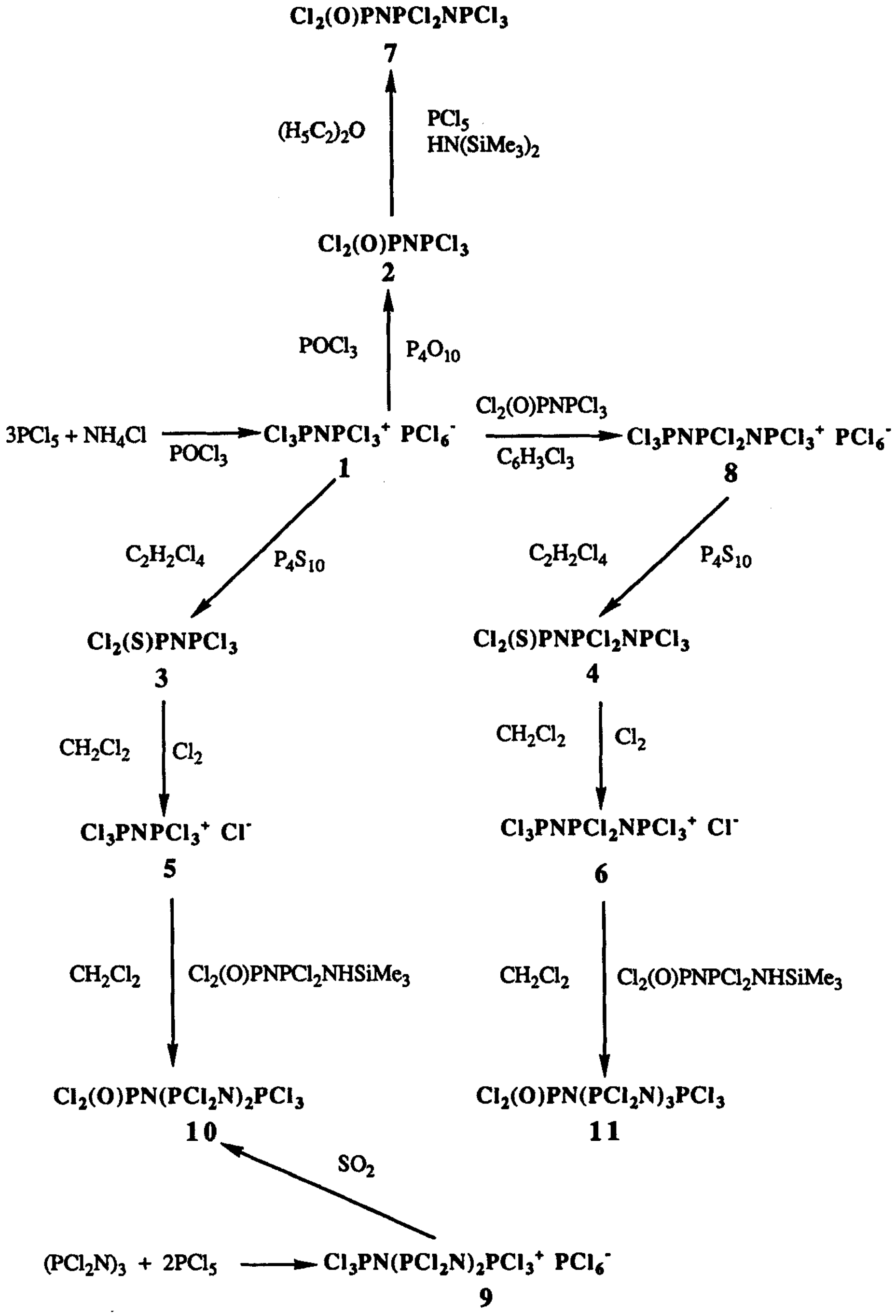
## INTRODUCTION

Polyphosphazenes, $(PR_2N)_n$, represent a new family of organomineral polymers with unusual properties.[1-9] Depending on the nature of the side groups, R, the polymers possess a wide range of applications.[10-14] These polymers are obtained by replacing the chlorine atoms of the polydichlorophosphazene, $(PCl_2N)_n$, by various organic nucleophiles.[1,2,15]

Several processes have been reported for the preparation of $(PCl_2N)_n$.[15-21] The most recent one is based upon polycondensation of the monomeric phosphoranimine, $Cl_3PNP(O)Cl_2$, which occurs with elimination of phosphorylchloride, $P(O)Cl_3$.[19-22]

Some linear short-chain molecules have been identified by $^{31}P$-NMR spectroscopy during the polycondensation reaction.[22]

In order to isolate the intermediate present in this process, we have chosen existing synthetic routes for most of the compounds and new specific routes for some short-chain oligomers. In the present work we report the synthesis and the characterization of the linear short-chain oligomers by $^{31}P$, $^{15}N$-NMR and Raman scattering at room and low temperature. The motivation behind this study is twofold: Firstly, to provide the NMR and vibrational characteristics of the isolated compounds to compare them with the spectroscopic measurements made during the polycondensation process.[22] Secondly, to study the conformation and the flexibility of the (PN) backbone as a function of the chain length.


$Cl_2(O)PNPCl_2NPCl_3$
7
$(H_5C_2)_2O$
$PCl_5$
$HN(SiMe_3)_2$
$Cl_2(O)PNPCl_3$
2
$POCl_3$
$P_4O_{10}$
$3PCl_5 + NH_4Cl$
$POCl_3$
$Cl_3PNPCl_3^+ PCl_6^-$
1
$Cl_2(O)PNPCl_3$
$C_6H_3Cl_3$
$Cl_3PNPCl_2NPCl_3^+ PCl_6^-$
8
$C_2H_2Cl_4$
$P_4S_{10}$
$C_2H_2Cl_4$
$P_4S_{10}$
$Cl_2(S)PNPCl_3$
3
$Cl_2(S)PNPCl_2NPCl_3$
4
$CH_2Cl_2$
$Cl_2$
$CH_2Cl_2$
$Cl_2$
$Cl_3PNPCl_3^+ Cl^-$
5
$Cl_3PNPCl_2NPCl_3^+ Cl^-$
6
$CH_2Cl_2$
$Cl_2(O)PNPCl_2NHSiMe_3$
$CH_2Cl_2$
$Cl_2(O)PNPCl_2NHSiMe_3$
$Cl_2(O)PN(PCl_2N)_2PCl_3$
10
$Cl_2(O)PN(PCl_2N)_3PCl_3$
11
$SO_2$
$(PCl_2N)_3 + 2PCl_5$
$Cl_3PN(PCl_2N)_2PCl_3^+ PCl_6^-$
9

**Scheme I**

## RESULTS AND DISCUSSION

### *Syntheses*

All the compounds listed in the Scheme I were synthesized according to the previously reported procedures[23–27] (see experimental section). However a new route was developed for the preparation of $[Cl_3PNPCl_2NPCl_3][PCl_6]$ (**8**) which arises from thermal treatments of (**1**) and (**2**). In the same way $Cl_3PN(PCl_2N)_2P(O)Cl_2$ (**10**) and $Cl_3PN(PCl_2N)_3P(O)Cl_2$ (**11**) were obtained using a new method based upon reaction of (**2**) with $HN(SiMe_3)_2$ followed by treatment of the intermediate formed with (**5**) and (**6**), respectively.

All these compounds have been characterized by microanalysis and $^{31}P$ NMR. $^{15}N$ NMR spectra were recorded in the natural abundance for the more soluble compounds (**2**), (**7**) and (**10**) whereas all the compounds were characterized by Raman scattering in the bulk, the melt or solution phases.

### *$^{31}P$, $^{15}N$-NMR Study*

The $^{31}P$-NMR spectra of the ionic compounds (**1**), (**5**), (**6**), (**8**) and (**9**) were carried out at room temperature; their study at low temperature is difficult because of their poor solubility in the usual solvents. The NMR data (Table I) which are in accordance with those previously published[24,25,28,29] indicate a high degree of purity of all compounds. These results point out the selectivity of the synthetic processes

TABLE I

Phosphorus-31 chemical shifts, δ (in ppm) and coupling constants, J (in Hz) of the ionic linear short-chain chlorophosphazenes in $CD_3NO_2$

| Compounds | $\delta_{1=1'}$ | $\delta_{2=2'}$ | $^2J_{12}$ | $^4J_{12'=1'2}$ |
|---|---|---|---|---|
| $Cl_3{}^1PN^{1'}PCl_3{}^+$ | +21.0 | | | |
| $Cl_3{}^1PN^2PCl_2N^{1'}PCl_3{}^+$ | +16.8 | -8.4 | 43.9 | |
| $Cl_3{}^1PN^2PCl_2N^{2'}PCl_2N^{1'}PCl_3{}^+$ | +16.3 | -8.3 | 27.5 | 16.6 |
| $PCl_6{}^-$ | -297.0 | | | |

TABLE II

Phosphorus-31 chemical shifts, δ (in ppm) and coupling constants, J (in Hz) at 233 K of the molecular linear short-chain chlorophosphazenes in $CDCl_3$

| Compound | $\delta_1$ | $\delta_2$ | $\delta_3$ | $\delta_4$ | $\delta_5$ | $^2J_{12}$ | $^2J_{23}$ | $^4J_{13}$ | $^2J_{34}$ | $^4J_{24}$ | $^2J_{45}$ | $^4J_{35}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Cl_3{}^1PN^2P(O)Cl_2$ | -1.0 | -10.1 | | | | 20.3 | | | | | | |
| $Cl_3{}^1PN^2P(S)Cl_2$ | +1.0 | -33.6 | | | | 0.0 | | | | | | |
| $Cl_3{}^1PN^2PCl_2N^3P(O)Cl_2$ | +6.6 | -18.2 | -9.0 | | | 32.7 | 27.2 | 5.0 | | | | |
| $Cl_3{}^1PN^2PCl_2N^3P(S)Cl_2$ | +5.2 | -18.0 | +35.4 | | | 36.3 | | | | | | |
| $Cl_3{}^1PN^2PCl_2N^3PCl_2N^4P(O)Cl_2$ | +7.5 | -14.3 | -18.3 | -9.0 | | 36.0 | 41.5 | 5.7 | 31.3 | 8.0 | | |
| $Cl_3{}^1PN^2PCl_2N^3PCl_2N^4PCl_2N^5P(O)Cl_2$ | +8.5 | -14.1 | -15.1 | -19.5 | -9.2 | 35.8 | 42.6 | 6.5 | 38.6 | 8.9 | 27.8 | 5.6 |

used throughout the present work. The $^{31}P$ NMR spectra are in good agreement with all *trans* conformation of the cation $[Cl_3PN(PCl_2N)_2PCl_3]^+$ as determined in the solid state by X-ray data.[30,31]

Although the $^{31}P$ NMR spectra of the molecular compounds have previously been extensively studied[31–36] no coalescence phenomenon has been observed. Our experiments were carried out with the help of a high field spectrometer, (161.977 MHz) between 223 and 298 K in two solvents: chloroform and diethyl ether. The main trends of the NMR data of the compounds (**2**), (**3**), (**4**), (**7**), (**10**) and (**11**) are as follows:

—Significant variation of chemical shifts (δ) and related coupling constants (J) as a function of temperature, especially for the signal assigned to the end group $PCl_3$, (Table II).

—Narrowing of the lines at low temperature.

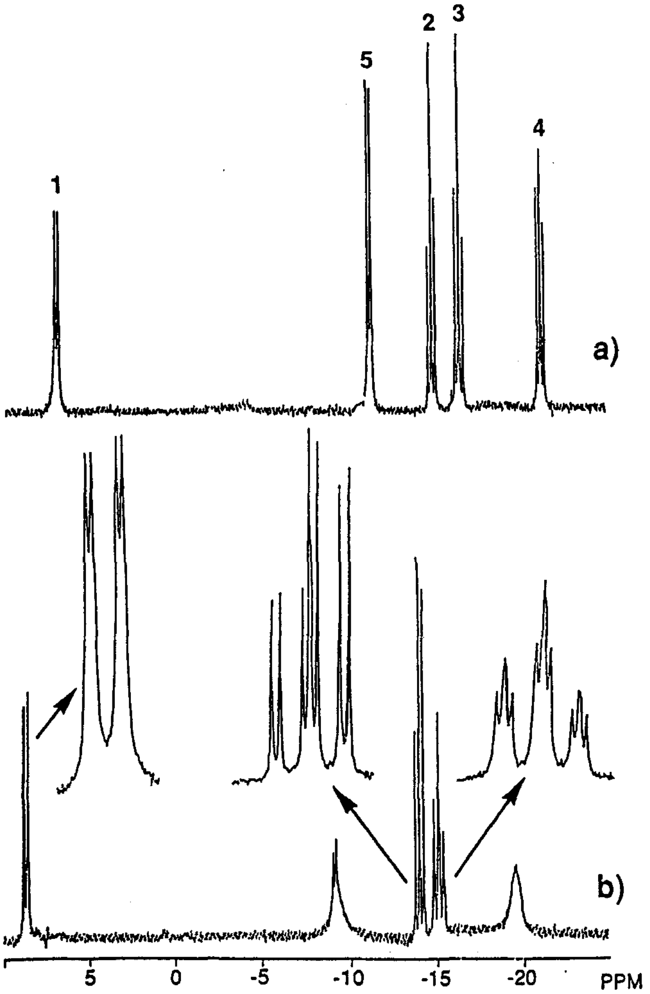


FIGURE 1 $^{31}P$-NMR spectra of $Cl_3{}^1PPN^2PCl_2N^3PCl_2N^4PCl_2N^5P(O)Cl_2$ in $CDCl_3$. a) at 298 K, b) at 223 K.

TABLE III

Nitrogen-15 chemical shifts, $\delta$ (in ppm) and coupling constants, J (in Hz) of some molecular linear short-chain chlorophosphazenes in $C_6D_6$

| Compounds | $\delta_\alpha$ | $\delta_\beta$ | $\delta_\gamma$ | $J_{\alpha 1}$ | $J_{\alpha 2}$ |
|---|---|---|---|---|---|
| $Cl_3{}^1PN_\alpha{}^2P(O)Cl_2$ | -239 | | | 15.2 | 1.7 |
| $Cl_3{}^1PN_\alpha{}^2PCl_2N_\beta{}^3P(O)Cl_2$ | -248.2 | -248.2 | | | |
| $Cl_3{}^1PN_\alpha{}^2PCl_2N_\beta{}^3PCl_2N_\gamma{}^4P(O)Cl_2$ | -248.4 | -255.5 | -249.6 | | |

These phenomena were interpreted by Thomas *et al.*[34] and Schilling *et al.*[35,36] as due to the temperature variation. Further, according to Deutsch *et al.*,[37] the temperature effect should be weaker for rigid compounds. The experimental data indicate possible conformational changes of the molecules. Indeed, chemical shifts and coupling constants are sensitive to the $\pi$-bond symmetry around the phosphorus.[38] The torsional motions would improve the $\pi$-bond symmetry and cause significant variations of $\delta$, J and the line width of the signals.

In the case of (**2**), (**3**), (**4**), and (**7**) no coalescence phenomenon was observed in the temperature range studied. This behavior is in good agreement with low energy barriers of internal rotations calculated for (**2**)[39] which were recently re-evaluated by MNDO calculation.[40,41] On the contrary coalescence phenomena were observed near 220 K in chloroform for (**10**) and (**11**) (Figure 1) for the signals assigned to $P(O)Cl_2$ and the $-PCl_2-$ adjacent group. This phenomenon illustrates the hindered internal rotation of the $P(O)Cl_2$ end group. Due to the solute or/and solvent solidification significant spectrum could not be obtained at lower temperature. Cooling to lower temperature is possible using the diethyl ether; however the coalescence phenomenon probably occurs at lower temperature in this solvent.

The calculated energy barriers corresponding to the isomerization from *cis-trans* to all *trans* are too high to lead to facile rotation around the $PCl_2N$ bonds in the chain. Consequently, the linear phosphazene backbone can be considered as rigid in the time scale of the NMR, except the two end groups. The stable conformation of the backbone in solution appears to be the *cis-trans* conformation as determined in the solid state by X-ray data[31] and expected from MNDO calculation.[40,41]

$^{31}P$-NMR characterization was completed by a natural abundance $^{15}N$-NMR study of the most soluble compounds. The experimental data are listed in Table III. The better resolution obtained for (**1**) (doublet of doublets) permits the calculation of a value of the coupling constant $J_{\alpha 2}$ (Table III) which is in accordance with those obtained for the $^{15}N$-labelled compound.[35,42] For (**7**) and (**10**) the determination of different coupling constants is not possible considering the complexity of the spectra. The signal $N_\beta$ observed in the case of (**10**) can be compared with those of the high polymer $(PCl_2N)_n$.[43]

Several linear short-chain molecules have been studied by $^{31}P$ NMR technique. This study at low temperature completes the previous studies at room temperature.[31] The relationship of the $^{31}P$ NMR spectra of the short-chain species to the high polymer is obvious. Even when only three phosphorus atoms are present in the chain (dimer) the spectrum (Table II) closely resembles that of a linear high

TABLE IV
Wavenumbers of the characteristic Raman bands of the molecular linear short-chain chlorophosphazenes

| Compounds | | | | | Assignments |
|---|---|---|---|---|---|
| (2) | (3) | (7) | (4) | (10) | |
| 1337 m | 1304 vw | 1323 vw | 1347 vw | | νP=N |
| | | | 1270 s | | |
| 1261 vs | | 1237 m | | 1247 vw | νP=O |
| | | 847 vw | | 862 vw | |
| | 803 m | | 840 m | | νP-N |
| 779 w | | 767 vw | 768 m | 764 vw | |
| | 677 m | | 674 s | | νP=S |
| | | 628 m | | 630 vw | |
| | 610 m | | 613 s | | |
| 600 m | | 600 w | | | |
| | 588 m | | 580 m | | |
| 558 m | | 552 w | | 563 vw | νaPCl$_3$, νaPCl$_2$ |
| 526 m | 517 m | 528 m | 520 m | | |
| 508 m | | | 507 m | 504 m | |
| | | 490 m | 494 m | 489 w | |
| 455 vs | 453 vs | 473 vs | 459 vs | 464 vs | |
| | | 435 s | 438 s | 440 w | νsPCl$_3$, νsPCl$_2$ |
| 400 m | 424 m | | 400 m | 413 s | |
| 357 vw | | 354 s | 354 m | 377 m | |
| | 349 s | | | 347 w | δaPCl$_3$, δaPCl$_2$ |
| | | 310 m | 331 vs | | |
| 303 m | 286 m | | | | |
| 270 m | | 271 m | 273 m | 274 m | |
| 262 s | | | 264 m | 263 w | δsPCl$_3$, δsPCl$_2$ |
| | 248 m | 246 m | 251 m | 249 m | |
| 231 s | | 237 s | | 232 m | ρPCl$_3$, ρPCl$_2$ |
| | | 227 m | 219 m | 219 m | |
| 209 s | 208 vs | | | | |
| 184 m | 171 m | 186 m | 178 m | 169 m | Torsions |
| | | 164 s | | | |
| 161 s | 151 vs | 153 vs | 158 vs | 146 s | |

s: strong, v: very, w: weak, m: medium
ν: stretch, δ: deformation, ρ: rock, s: symmetric, as: antisymmetric

polymer. $^{31}$P NMR spectrum of the polymer consists of a sharp singlet at $\delta = -16$ ppm.[43]

The $^{31}$P NMR spectra of these isolated short oligomers confirm the identification of the intermediates observed during the polycondensation study of the monomer, $Cl_3PNP(O)Cl_2$.[22] The $^{31}$P NMR spectra recorded during the polycondensation reaction result mainly of a combination from those of linear oligomers and the reactivity of these oligomers depends on the chain length and may be correlated to the chemical shifts of the $PCl_3$ and $P(O)Cl_2$ end groups.

TABLE V

Wavenumbers of the characteristic Raman bands of the ionic linear short-chain chlorophosphazenes

| Compounds | | | | | Assignments |
|---|---|---|---|---|---|
| (1) | (5) | (8) | (6) | (9) | |
| 832 vw | | 847 vw | | 860 vw | |
| | 806 m | | | 808 vw | νP-N |
| | | 781 vw | 772 w | | |
| | | | 761 w | 764 vw | |
| 635 vw | 637 m | 636 w | | 635 vw | |
| | 626 s | | | 627 vw | |
| 615 vw | | 612 w | 616 m | 612 vw | νaPCl$_3$, νaPCl$_2$ |
| | 601 s | 609 w | 607 m | | |
| | 580 m | | | | |
| 468 s | | 466 vs | 464 vs | 460 vs | |
| 452 m | | 453 m | | | νsPCl$_3$, νsPCl$_2$ |
| | 415 vs | | | 414 w | |
| | | 405 m | 406 m | | |
| 358 vs | | 352 vs | | 352 vs | νsPCl$_6^-$ |
| | 347 m | | 349 s | | |
| | | 336 s | | | δaPCl$_3$, δaPCl$_2$ |
| | | | | 319 m | |
| 288 m | | | | | |
| 276 s | | 268 s | | 265 s | δPCl$_6^-$ |
| 248 m | 254 vs | | 256 m | | δsPCl$_3$, δsPCl$_2$ |
| 240 s | | 237 s | | 241 m | δPCl$_6^-$ |
| | | | 233 m | | |
| | | | 219 m | | |
| 214 m | 210 m | 209 m | 214 s | 213 w | ρPCl$_3$, ρPCl$_2$ |
| 205 m | 181 m | 177 m | | | |
| 168 s | | | 169 m | | |
| 158 m | 158 vs | 161 s | 164 m | 160 m | Torsions |
| 153 s | | | 147 s | | |
| | | 138 s | | 132 m | |
| | 112 m | | | | |
| | 61 m | | | | Lattice modes |
| | 49 vs | | | | |
| | 32 vs | | | | |

s: strong, v: very, w: weak, m: medium

ν: stretch, δ: deformation, ρ: rock, s: symmetric, as: antisymmetric

### *Raman Scattering Study*

Several reports concerning Raman scattering studies of cyclic chlorophosphazenes[44–47] were published whereas only two publications dealed with linear polyphosphazenes[48,49] and no publication concerning the linear short-chain chlorophosphazenes was found. Among the vibrational methods the Raman scattering is the most suitable technique to study the chlorophosphazenes which are highly sensitive to moisture. The synthesis of the linear short-chain molecules in high degree of purity leads to good quality Raman spectra of the isolated compounds in the melt, solution as well as in the solid state. The Raman spectra of the isolated short-chain molecules can be used to identify the intermediates formed during the polycondensation reaction of $Cl_2(O)PNPCl_3$ which occurs at 510 K. The Raman technique can be used with glass vessels for liquid or solid phases and may be

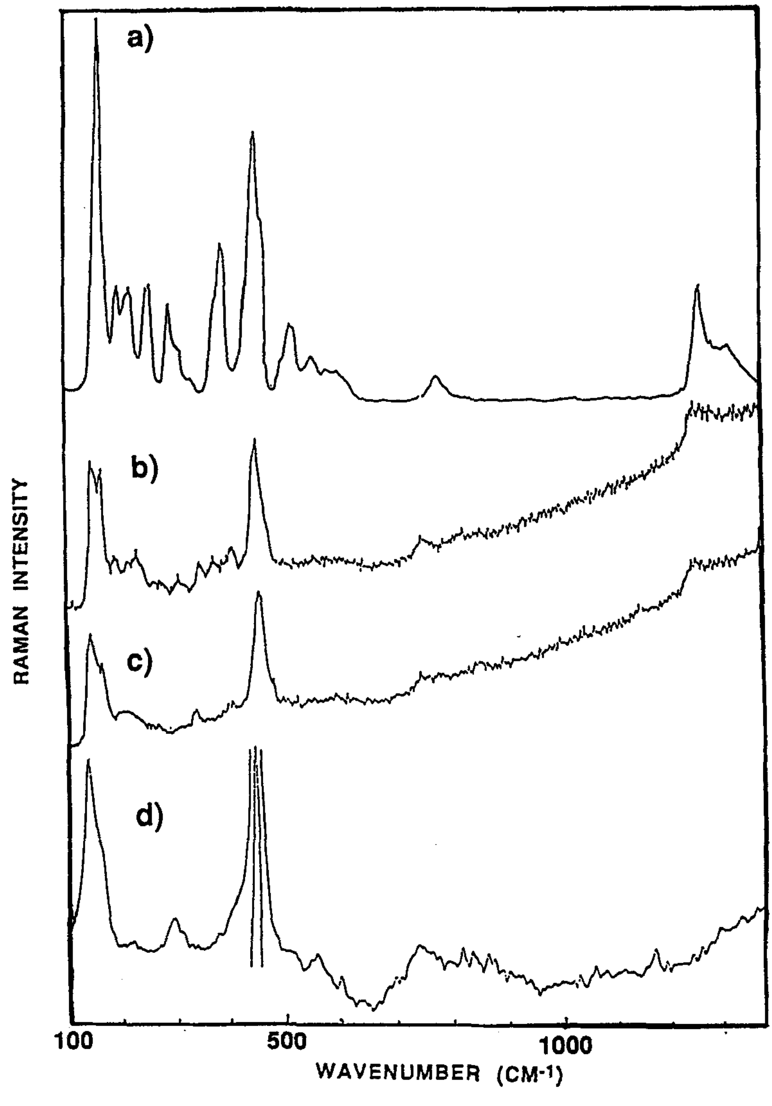


FIGURE 2 Raman spectra of molecular linear short-chain chlorophosphazenes and polydichlorophosphazene. a) $Cl_2(O)PNPCl_3$ at 340 K, b) $Cl_2(O)PNPCl_2NPCl_3$ at 340 K, c) $Cl_2(O)PNPCl_2NPCl_2NPCl_3$ at 340 K, d) $(PCl_2N)_n$ at 298 K (Reference 50).

adapted to the in situ measurement at high temperature. Spectra of **(1)**–**(10)** were recorded in the melt or solution and solid state at room and low temperature. The observed frequencies and assignments of the normal modes of the most characteristic groups based on the force field calculations developed for some linear short-chain compounds[40,41] in Tables IV and V are given.

The Raman spectrum of $Cl_2(O)PNPCl_3$ in the melt was interpreted on the basis of a OPNP planar skeleton with two stable rotamers as found in the solid state.[31] The PN stretching modes are observed for all compounds, in the range 1310–1375

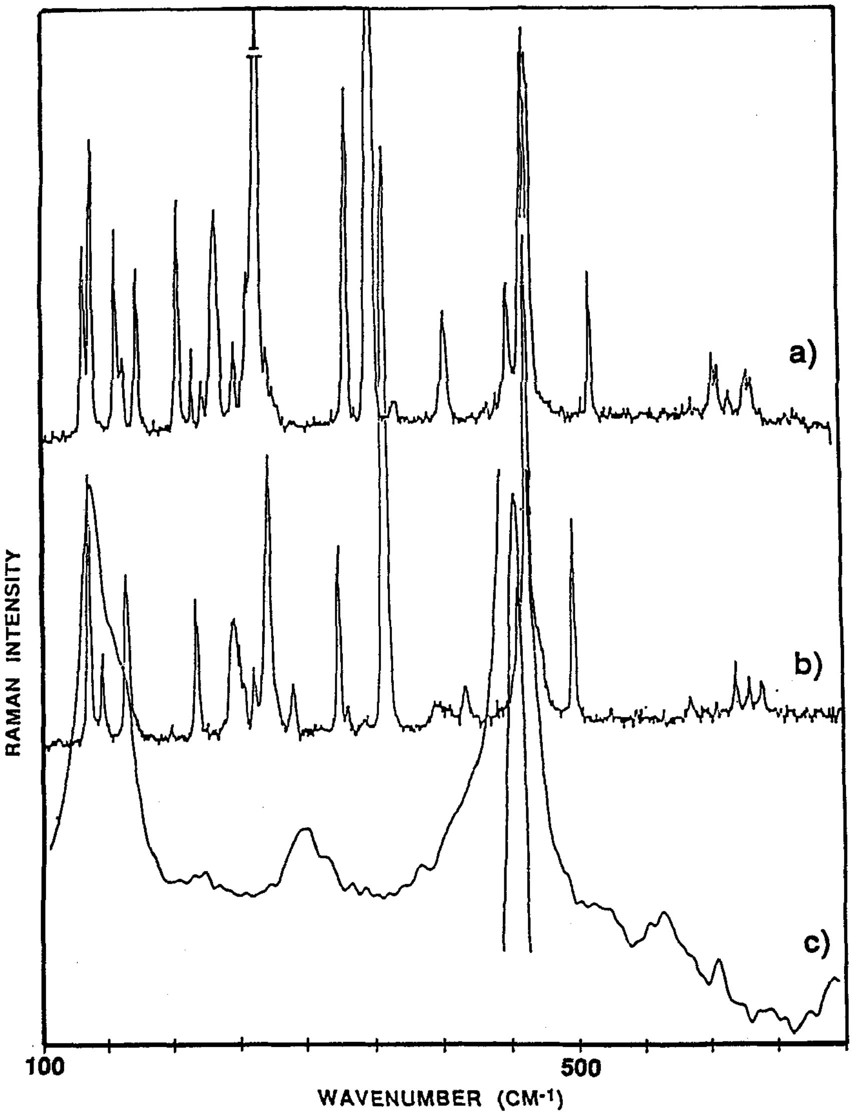


FIGURE 3 Raman spectra of ionic linear short-chain chlorophosphazenes and polydichlorophosphazene. a) $[Cl_3PNPCl_2NPCl_3][PCl_6]$ at 298 K, b) $[Cl_3PNPCl_2NPCl_2NPCl_3][PCl_6]$ at 298 K, c) $(PCl_2N)_n$ at 298 K (Reference 50).

$cm^{-1}$ and 760–860 $cm^{-1}$ for $\nu P = N$ and $\nu P - N$, respectively. In the case of the ionic compounds the $\nu_{as}PN$ vibrations have a very weak Raman intensity whereas the $\nu_s PN$ modes can be better identified. For the molecular compounds, supplementary characteristic bands are attributed to $\nu$ P = O and $\nu$ P = S stretching modes at 1230–1270 $cm^{-1}$ and 660–680 $cm^{-1}$, respectively. The main PCl vibrations of $PCl_2$ and $PCl_3$ groups were observed around 600 $cm^{-1}$ ($\nu_{as}PCl_2$) and 450 $cm^{-1}$ ($\nu_s PCl_2$). The depolarisation ratios of the Raman bands observed in the melt and solution are in good agreement with a nearly planar PN skeleton for all compounds under study. The striking analogy between the Raman spectra obtained in the melt or solution and in the solid state indicates analogous molecular structure in the different phases. This result is in good agreement with X-ray determination performed for some compounds.[31] The comparison between the Raman spectra of the molecular compounds $Cl_2(O)PN(PCl_2N)_nPCl_3$ and those of a high polymer exhibits an analogy (Figure 2) which is not found for the ionic analogs $Cl_3PN(PCl_2N)_nPCl_3^+$, at least for the short oligomers (Figure 3). The main difference between the molecular and ionic short-chain compounds arises from their different conformations, *cis-trans* in the former and *trans-trans* in the latter. This difference progressively disappears with increasing chain length.

## *Concluding Remarks*

The synthesis of two series of linear short-chain chlorophosphazenes, $Cl_2(O)PN(PCl_2N)_nPCl_3$ and $Cl_3PN(PCl_2N)_nPCl_3^+$ in high degree of purity permits the $^{31}P$ and $^{15}N$ NMR studies. In addition, the high purity of the compounds allowed to obtain high-quality Raman spectra which are very characteristic of these compounds.

The $^{31}P$-NMR study as a function of the temperature provides evidence for a coalescence phenomenon in relation to internal rotation of the $P(O)Cl_2$ end group. The resemblance between the $^{31}P$-NMR spectra of the molecular oligomers and high polymer indicates that the molecular oligomers are better models for the high polymer than the cyclic and ionic compounds. The comparison of respective Raman spectra puts in evidence the resemblance between the *cis-trans* structure of the linear molecules and of the polymer.

## EXPERIMENTAL

*Syntheses.* All the reactions were carried out under an inert atmosphere to avoid hydrolysis. The reactants used in these syntheses are commercial products and all solvents were dehydrated by distillation or by treatment with molecular sieves.

*$[Cl_3PNPCl_3][PCl_6]$* (**1**). Compound (**1**) was synthesized from $PCl_5$ (47.56 g, 0.228 mol) and $NH_4Cl$ (4.07 g, 0.076 mol) in $POCl_3$ (42.5 ml) by the method of Seglin[23] and was purified by washing twice with $CCl_4$. The final product was vacuum dried (0.1 Torr). (**1**) was characterized by $^{31}P$-NMR (Table I) and Raman spectroscopy (Table IV). Yield: 95%.

Anal. $P_3NCl_{12}$: Calc.: P, 17.45; N, 2.62; Cl, 79.92
Found: P, 17.72; N, 2.72; Cl, 79.88

*$Cl_3PNP(O)Cl_2$* (**2**). Species (**2**) was prepared in two steps.[23] The first one is the same as (**1**). After formation of (**1**), $P_4O_{10}$ (0.13 mol equiv. per 1 mol of initial $PCl_5$) was added and the mixture heated for 2 h at 85°C. After cooling at room temperature, $POCl_3$ was removed by rotary evaporation and

the product purified by vacuum distillation. (**2**) was characterized by $^{31}$P, $^{15}$N-NMR (Tables II and III) and Raman spectroscopy (Table V). Yield: 94%.

Anal. $P_2NOCl_5$: Calc.: P, 23.01; N, 5.19; Cl, 65.86
Found: P, 23.27; N, 5.30; Cl, 65.93

*$Cl_3PNPCl_2NP(O)Cl_2$* (**7**). (**7**) was synthesized by the method of Riesel.[27] $HN(Si(CH_3)_3)_2$ (21 ml, 0.100 mol) was added dropwise to (2) (27.2 g, .100 mol) in $(C_2H_5)_2O$. The mixture was refluxed for 3 h. After cooling to room temperature, $PCl_5$ (20.85 g, 0.100 mol) was added and the reaction mixture refluxed for another 3 h. The solvent was removed and the solid purified by vacuum distillation (0.05 Torr, 140–145°C). (**7**) was characterized by $^{31}$P, $^{15}$N-NMR (Tables II and III) and Raman spectroscopy (Table V). Yield: 80%.

Anal. $P_3N_2OCl_7$: Calc.: P, 24.12; N, 7.26; Cl, 64.46
Found: P, 24.02; N, 7.36; Cl, 64.30

*$[Cl_3PNPCl_2NPCl_3][PCl_6]$* (**8**). An equimolar mixture of (**1**) (49.7 g, 0.093 mol) and (**2**) (25.14 g, 0.093 mol) in $C_6H_3Cl_3$ (75 ml) was heated to 180–195°C for 12 h. During this period we observed the $POCl_3$ clearing. The pasty solid obtained after cooling at room temperature was dissolved in $C_2H_2Cl_4$ and precipitated in $CCl_4$. This procedure was repeated twice, the solid product washed twice by petroleum ether and dried under vacuum (0.1 Torr). (**8**) was characterized by $^{31}$P-NMR (Table I) and Raman spectroscopy (Table IV). Yield: 80%.

Anal. $P_4N_2Cl_{14}$: Calc.: P, 19.11; N, 4.31; Cl, 76.57
Found: P, 19.29; N, 4.49; Cl, 76.58

*$Cl_3PNP(S)Cl_2$* (**3**) *and* *$Cl_3PNPCl_2NP(S)Cl_2$* (**4**). (**3**) and (**4**) were synthesized by the same general procedures. (**1**) (for (**3**)) or (**8**) (for (**4**)) was treated by $P_4S_{10}$ (0.337 mol equiv. per 1 mol equiv. of (**1**) or (**8**) in $C_2H_2Cl_4$). The reaction mixture was refluxed for 3 h. The solvent and $PSCl_3$ formed were removed by rotary evaporation and the solid product purified by vacuum distillation (0.1 Torr, 88°C for (**3**) and 0.05 Torr, 140–146°C for (**4**)). (**3**) and (**4**) were characterized by $^{31}$P-NMR (Table III) and Raman spectroscopy (Table V). Yield: 95% for (**3**) and 80% for (**4**).

Anal. $P_2NSCl_5$: Calc.: P, 21.71; N, 4.90; Cl, 62.10
Found: P, 21.41; N, 4.69; Cl, 62.57
$P_3N_2SCl_7$: Calc.: P, 23.16; N, 6.97; Cl, 61.89
Found: P, 23.20; N, 6.81; Cl, 61.65

*$[Cl_3PNPCl_3][Cl]$* (**5**) *and* *$[Cl_3PNPCl_2NPCl_3][Cl]$* (**6**). (**5**) and (**6**) were prepared by passing $Cl_2$ (g) over (**3**) (for (**5**)) or (**4**) (for (**6**)) in $CH_2Cl_2$. The reaction was complete when a brown-red colour appeared.[24] The solvent and $SCl_2$ formed were removed and the solid purified by successive washing with petroleum ether and drying under vacuum. (**5**) and (**6**) were characterized by $^{31}$P-NMR (Table I) and Raman spectroscopy (Table IV). Yield: 75%.

Anal. $P_2NCl_7$: Calc.: P, 19.10; N, 4.31; Cl, 76.57
Found: P, 19.05; N, 4.20; Cl, 76.35
$P_3N_2Cl_9$: Calc.: P, 21.11; N, 6.20; Cl, 72.53
Found: P, 20.88; N, 6.30; Cl, 71.75

*$[Cl_3PN(PCl_2N)_2PCl_3][PCl_6]$* (**9**). Compound (**9**) was synthesized from $(PCl_2N)_3$ (10.8 g, 0.031 mol) and $PCl_5$ (18.3 g, 0.058 mol) by the method of Moran.[25] (**9**) was characterized by $^{31}$P-NMR (Table I) and Raman spectroscopy (Table IV). Yield: 74%.

Anal. $P_5N_3Cl_{16}$: Calc.: P, 20.26; N, 5.49; Cl, 74.25
Found: P, 20.13; N, 5.88; Cl, 74.78

*$Cl_3PN(PCl_2N)_2P(O)Cl_2$* (**10**) *and* *$Cl_3PN(PCl_2N)_3P(O)Cl_2$* (**11**). Species (**10**) and (**11**) were synthesized by the same general process. (**1**) was treated by $HN(Si(CH_3)_3)_2$ (1 mol equiv. per 1 mol equiv.) in $CH_2Cl_2$. The reaction mixture was refluxed for 3 h. After cooling at room temperature, 1 mol equiv. of (**5**) (for (**10**)) or (**6**) (for (**11**)) was added and the reaction mixture refluxed for 10–12 h. The solvent and $ClSi(CH_3)_3$ were removed under vacuum. (**10**) and (**11**) were obtained as colorless liquids. (**10**) was characterized by $^{31}$P, $^{15}$N-NMR (Tables II and III) and Raman spectroscopy (Table V). (**11**) was characterized only by $^{31}$P-NMR (Table II). Yield: 70%.

| | | |
|---|---|---|
| Anal. $P_4N_3OCl_9$: | Calc.: | P, 24.72; N, 8.37; Cl, 63.70 |
| | Found: | P, 24.43; N, 8.16; Cl, 63.57 |
| $P_5N_4OCl_{11}$: | Calc.: | P, 25.02; N, 9.03; Cl, 63.03 |
| | Found: | P, 25.60; N, 9.86; Cl, 63.45 |

*NMR Spectroscopy.* $^{31}P$ and $^{15}N$-NMR spectra were recorded at room and low temperature with WP 400 spectrometer operating in the Fourier transform mode at 161.977 and 40.561 MHz, respectively. Chemical shifts were referred to external 85% $H_3PO_4$ for $^{31}P$ or $CH_3NO_2$ for $^{15}N$.

*RAMAN Spectroscopy.* Raman spectra were recorded by using the dispersive technique on a triple-monochromator spectrometer Dilor model RTI 30 at various temperatures ranging from 77 K to 370 K with liquid or solid samples. The instrument is equipped to accumulate spectra. The Raman scattering was excited by using argon laser lines (457.9, 488.0, 514.5 nm) with a power of 100–200 mW. The slit widths were typically 4 and 1.5 $cm^{-1}$ for the liquid and solid samples, respectively. The sloping background in the Raman spectra was not corrected.

*Elementary Analyses.* The microanalysis of P, N and Cl elements of all compounds under study was realized at the microanalysis central service of the C.N.R.S., Vernaison, France.

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