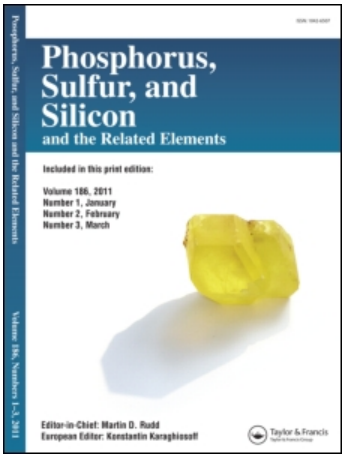

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Vibrational and Conformation Study in Short-Main Linear Dichlorophosphazenes

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VIBRATIONAL AND CONFORMATION STUDY IN SHORT-CHAIN LINEAR DICHLOROPHOSPHAZENES

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The availability of new high polymer based on a polyphosphazene backbone provides an opportunity for the exploration of the different parameters which induce the conformation of macromolecular chains. Information in needed for polydichlorophosphazenes to correlate solid state and solution properties with structural factors of the preferred conformation. Raman spectroscopy is a powerful tool to investigate the conformation change in solution as well as in the solid state. Until now, some X-ray structural data and vibrational studies have been performed for cyclic trimeric and tetrameric dichlorophosphazenes. Howerver, the cyclic systems do not appear as the best models for the polydichlorophosphazenes. Indeed, the constraints of a cyclic molecule induce differences in structural parameters and conformations.

Earlier, a number of short-chain analogues of macromolecular phosphazenes have been synthesized and some X-ray diffraction studies have been realized. In the present work, we describe experimental evidence for Raman spectra of two series of short-chain linear chlorophosphazenes in solution as well as in the solid state from 77 to 450 K :

$$Cl_2(O)P\,(\,N{=}PCl_2\,)_n\,N{=}PCl_3 \qquad n=0,1,2 \qquad (1)$$

$$[Cl_3P\,(N{=}PCl_2)_n\,N{=}PCl_3]^+\,Y^- \qquad n=0,1,2\ ;\ Y=Cl,\ PCl_6 \qquad (2)$$

The polarized Raman spectra were carried out in solution and/or in the fused state from 220 to 450 K, assigned according to the structural assumptions obtained from theoretical conformational studies and then compared with the 31 P NMR results. On the other hand, the Raman spectra of all the compounds were recorded using powder samples for 77 to 300 K. The data are interpreted using the X-ray analyses previously reported for some compounds under study.