RAMAN AND INFRARED SPECTROSCOPIC STUDIES OF NOVEL POLY-AZA CHAINS

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ABSTRACT

The preliminary results concerning the synthesis, the structural and spectroscopic studies of a new series of linear poly-aza-molecules are reported in the present work. All the Raman spectra are characterized by a remarkable simplicity of the spectral features and exhibit a high degree of similitude with the spectra of polyene compounds.

INTRODUCTION

The number of linear conjugated macromolecules for which a detailed spectroscopic studies have been done, concern mainly those posseding C=C and C=C bonds¹: polydiacetylenes, polyacetylenes, carotenoids. In this work, we reported the preliminary results concerning the synthesis, the structural and spectroscopic studies of a new series of poly-aza molecules. The aza polymers are amorphous and insoluble materials. As a consequence the synthesis, the structure and the vibrational spectra of chain oligomers have been studied in an effort to deduce the fundamentals properties of the related polymers. The new molecules under study are the following :



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Some small single crystals of short chain molecules have been obtained and the X-ray structure determination have been realized or under study. Besides, polarized Raman spectra were carried out using micro-Raman spectrometer².

Experimental

Biacetyl dihydrazone $C_4H_{10}N_4 \frac{7}{2}$ and biacetyl hydrazone azine $C_6H_{16}N_6 \frac{8}{2}$ are obtained as previously described³. The polyaza-compounds are synthetized from $\frac{7}{2}$, $\frac{8}{2}$ starting materials according to a general procedure. A typical synthesis is described below.

The hydrazone (1 mol) is dissolved in anhydrous ethanol, the carbonyl compound, biacetyl monoxime or 2-pyridyl carboxaldehyde (2 mol) is added dropwise, and then the solution is heated under reflux for 12 h. Upon cooling, yellow crystals are deposited overnight. The product is recrystallized in high yield from hot ethanol. The microanalyzes and the mass-spectra of the isolated products are in good agreement with the following formulation. 1, $C_8H_{14}N_4O_2$; $2 C_{12}H_{20}N_6O_2$; $3, C_{16}H_{26}N_8O_2$; $4, C_{12}H_{10}N_4$; $5, C_{16}H_{16}N_6$; $6, C_{20}H_{22}N_8$; $7, C_4H_{10}N_4$; $8, C_8H_{16}N_6$.

Biacetyl dihydrazone <u>7</u> is readily recrystallized as well-formed pale yellow crystals. The X-ray structure was solved by the MULTAN method : quatratic system, a = b = 12.177 (9) c = 4.116 (2) Å. Space group $P4_2/n \equiv c_{4h}^4$, Z = 4. The symmetric centre of the molecule $c_4H_{10}N_4$ is in general position c_1 .

The single-crystals of <u>7</u> were too small for conventional polarized Raman study, so the polarized Raman spectra have been recorded using the Raman microprobe $MOLE^2$. A well-formed rectangular parallelepipedic crystal with dimensions 0.450 x 0.180 \times 0.132 mm was mounted on the end of a fine needle and oriented by X-rays on a goniometer.

Results

The X-ray data indicate for the precursor $(\underline{7})$ of the poly-aza-compounds a molecular symmetry C_{2h} .



Although the X-ray structure of the poly-aza oligomers are not undertaken yet, it is probable that among the possible conformations, all the oligomers exhibit a planar backbone with a <u>trans</u> trans geometry in the solid state. In solution apparently no isomerization is detected by Raman and ¹H NMR spectroscopy.

Typical Raman spectra of the two sexta-aza molecules $\underline{3}$ and $\underline{6}$ are shown on figure 1. They are very similar to those of di and tetra-aza analogs. All the Raman spectra are characterized by a remarkable simplicity of the spectral features, the fact that this was due to the preresonant nature of the scattering. The strong bands were assigned by comparison with the spectra of model compounds to vibrational modes dominated by the stretching of the C=N and N-N bonds in the diaza-ane alternation sequence.

Only small changes in the wavenumbers and relative intensities of the two strongest lines were observed. The spectra are very similar to those of other polyene compounds (carotenoids, polyacetylenes, polydiacetylenes). We propose the following assignments.

The C=N stretching mode appears near 1550 cm⁻¹. The wavenumber decreases as the length of the chains increases 1560, 1556 and 1554 cm⁻¹ for aza-oxime derivatives and 1570, 1560 and 1560 cm⁻¹ for aza-pyridine derivatives. The shift in wavenumber can be related to the change in π -electron delocalization in the polyaza-molecules. The doublet observed in the spectra of 5 and 6 can be assigned to a Fermi resonance between C=N stretching mode and an harmonic of γ C-H mode obser ved at 780 cm⁻¹ in the infrared spectra of these compound. For oxime derivatives an additional band observed at 1632 cm⁻¹ can be assigned to terminal C=NOH group stretching.

The medium lines observed in the spectral range, $1300-1400 \text{ cm}^{-1}$, can be assi-



: Raman spectra of products 6 and 3

gned to methyl group deformations and some characteristic lines of pyridine are visible in this region for pyridine derivatives.

In view of the chemical structure of the poly-aza-molecules, two lines respectively assigned to C-C and N-N stretching are expected, however we observe only one line near 1064 $\rm cm^{-1}$. As the force constant should be relatively similar in these conjugated chain, it is not surprising that the two stretching vibrations are coupled in a same vibrational mode. The shift observed for this line (1053, 1065 and 1064 cm^{-1}) for the oxime derivatives 1, 2, 3 respectively and (1000, 1041 and 1067 cm^{-1}) for the pyridine derivatives 4, 5, 6 respectively, is related to an increase of the C-C, N-N bond order resulting to an increase of π delocalization. For other polyene chains we observe an opposite behaviour as the observed mode result from an admixture of C-C stretching and C-H bending⁴. The breathing mode of pyridine ring are observed near 998 $\rm cm^{-1}$.

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