

RAMAN STUDY OF CONFORMATIONAL DISORDER IN n-PrNH₃X (X = Cl, Br, I)

H. HAGEMANN and H. BILL

Groupe de Physico-Chimie du Solide, Université de Genève, 30, quai E. Ansermet,
CH-1211 Geneva 4 (Switzerland)

J. MAREDA

Département de Chimie Organique, Université de Genève, 30, quai E. Ansermet,
CH-1211 Geneva 4 (Switzerland)

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ABSTRACT

We have obtained the room temperature Raman spectra of the three salts n-PrNH₃X (X = Cl, Br and I). The concentration of *gauche* isomers increases when passing from the chloride to the iodide. We have evaluated experimentally the lattice contribution to the energy difference between *gauche* and *anti* conformers. A force field calculation yielded an energy difference of 0.85 kcal mol⁻¹ between the two conformations of the propylammonium moiety.

INTRODUCTION

The room temperature crystal structure of the n-propylammonium halides has been found to be tetragonal with space group *P4/nmm* (*Z* = 2) [1]. It is characterized by free rotation of the organic cation. Analysis of the structure factors in n-PrNH₃Cl [1] showed configurational isomerism.

In a more recent NMR study [2] on n-PrNH₃Cl, the dynamical disorder in the room-temperature phase was investigated. The second moment analysis revealed a relatively fast chain rotation about its long axis with independent methyl- and ammonium-group rotations. The activation energy of the chain rotation is found to be 2.5 kcal mol⁻¹, and thus this rotation is hindered. These conclusions have been obtained assuming that only *anti* isomers exist in n-PrNH₃Cl, in contrast to the results of the X-ray study. The authors of this NMR study suggested a vibrational analysis of the conformation of the propylammonium group in n-PrNH₃Cl.

In the course of investigations on the vibrational spectra of the alkylammonium halides [3], we decided to study the Raman spectra of n-PrNH₃X (X = Cl, Br, I) to obtain additional information on the conformation of the propylammonium ion.

EXPERIMENTAL

$n\text{-PrNH}_3\text{Cl}$ (Fluka, Switzerland) was vacuum dried and used without further purification. $n\text{-PrNH}_3\text{X}$ ($\text{X} = \text{Br}, \text{I}$) were obtained by reacting an aqueous solution of n -propylamine with aqueous HX . After evaporation of the water, the powders were vacuum dried. $n\text{-PrNH}_3\text{I}$ was additionally washed with ether to remove impurities of molecular iodine.

All the samples were finely ground and sealed in glass capillaries.

The Raman spectra were obtained using the laboratory assembled spectrometer described in ref. 3. All the measurements were performed at room temperature with the 488 nm line of the argon ion laser.

RESULTS AND DISCUSSION

The room temperature Raman spectra of $n\text{-PrNH}_3^+$ in H_2O and of polycrystalline $n\text{-PrNH}_3\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were measured. The solution spectrum is in agreement with the results reported by Edsall in 1937 [4].

Figure 1 shows the Raman spectra of solid $n\text{-PrNH}_3\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in the range 800 to 1100 cm^{-1} . The simplest spectrum belongs to the chloride and the two transitions at 876 and 1049 cm^{-1} may be assigned to C—C stretching vibrations pertaining to the *anti* isomer. These values agree fairly well with the corresponding modes at 837 and 1058 cm^{-1} in liquid n -butane [5]. The band at 997 cm^{-1} has been assigned to an NH_3 rocking mode [3]. The additional transitions observed at 822, 950, 1015 and 1076 cm^{-1} in $n\text{-PrNH}_3\text{I}$ are assigned to the *gauche* isomer by analogy with the results reported for liquid n -butane [5].

We observe thus an increase of *gauche* isomers in the solid state when passing from the chloride to the iodide in the solids $n\text{-PrNH}_3\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). The solution spectrum exhibits transitions pertaining to both *gauche* and *anti* isomers.

Using the intensity ratio of the 876 and 822 cm^{-1} lines, we have evaluated the energy difference between the two conformations with the help of the relation

$$I(\textit{gauche})/I(\textit{anti}) = C \times \exp(-\Delta E/RT)$$

Assuming further that ΔE can be split into two components, i.e. ΔE_{int} which is equal to the internal energy difference of an individual molecule and ΔE_{ext} which accounts for the lattice contribution to the total energy difference, and assuming additionally that in the solution on a time average $\Delta E_{\text{ext}} = 0$, we can evaluate ΔE_{ext} for the three halides by

$$I(\textit{gauche})/I(\textit{anti}) \{\text{solid}\} \times I(\textit{anti})/I(\textit{gauche}) \{\text{solution}\} = \exp(-\Delta E_{\text{ext}}/RT)$$

The results of this evaluation are given in Table 1, together with the two tetragonal lattice parameters [1] for $n\text{-PrNH}_3\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$). Table 1 shows that the lattice parameter a is mainly affected by the size of the halogen.

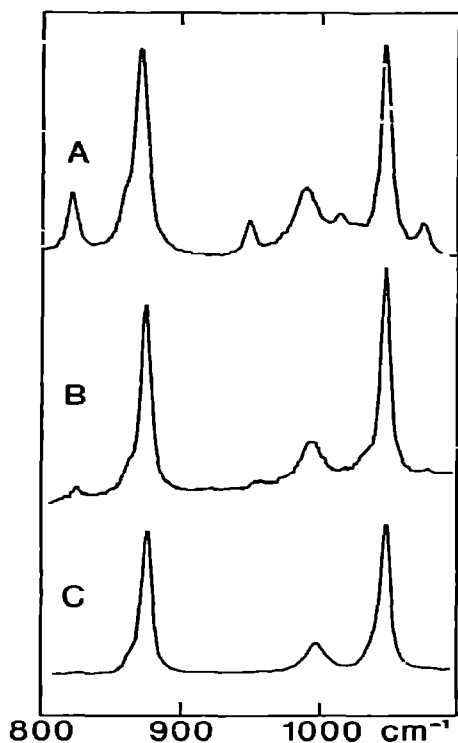


Fig. 1. Room temperature Raman spectra of powdered $n\text{-PrNH}_2\text{X}$ between 800 and 1100 cm^{-1} . (A) $\text{X} = \text{I}$, $\lambda = 514.5 \text{ nm}$ (0.2 W), resolution 2 cm^{-1} ; (B) $\text{X} = \text{Br}$, $\lambda = 488 \text{ nm}$ (0.2 W), resolution 2 cm^{-1} ; (C) $\text{X} = \text{Cl}$, $\lambda = 488 \text{ nm}$ (0.3 W), resolution 3 cm^{-1} .

ΔE_{ext} can be correlated to this parameter through an experimental relation

$$\Delta E_{\text{ext}} \propto (\alpha - \alpha_0)^{-1} \text{ where } \alpha_0 = 5.9 \text{ \AA}$$

This relation suggests a simple steric hindrance of the conformational equilibrium.

TABLE 1

Room temperature tetragonal lattice parameters (space group $P4/nmm$, $Z = 2$) of $n\text{-PrNH}_2\text{X}$ ($\text{X} = \text{Cl}$, Br , I) [taken from ref. 1] and lattice energy contribution to the conformational equilibrium. The values in parentheses indicate the evaluated experimental error.

X	a Å	c Å	ΔE_{ext} kcal mol ⁻¹
Cl	6.220	7.377	2.5 (0.4)
Br	6.497	7.380	1.43 (0.2)
I	6.931	7.332	0.84 (0.1)

We executed force-field calculations on the propylammonium group using Allinger's program MM2 [6, 7]. The standard force-field of this program was used [6]. In order to determine the relative energy of possible rotamers, the rotational barrier around the central carbon-carbon bond was computed.

The energy profile (shown in Fig. 2) was obtained by incrementing the dihedral angle $\tau(\text{C}-\text{C}-\text{C}-\text{N})$ by 5° starting from 180° (*anti*-form). All remaining degrees of freedom were optimized.

As can be anticipated, the eclipsed-form is located on the top of a barrier of $3.65 \text{ kcal mol}^{-1}$ where $\tau = 120^\circ$. Corresponding within 5° to the *gauche*-form, the second minimum is detected for $\tau = 65^\circ$. In terms of relative energy, the *gauche* rotamer is less stable than the *anti*-form by $0.85 \text{ kcal mol}^{-1}$. This value was obtained on searching by varying only one dihedral angle (τ). Multidimensional grid search could further reduce the energy difference between the *gauche* and the *anti* conformer.

It should be pointed out that our results for the propylammonium group are in qualitative agreement with those obtained by Allinger et al [8, 9] for the isoelectronic n-butane (barrier $3.35 \text{ kcal mol}^{-1}$, *gauche* form $0.67 \text{ kcal mol}^{-1}$).

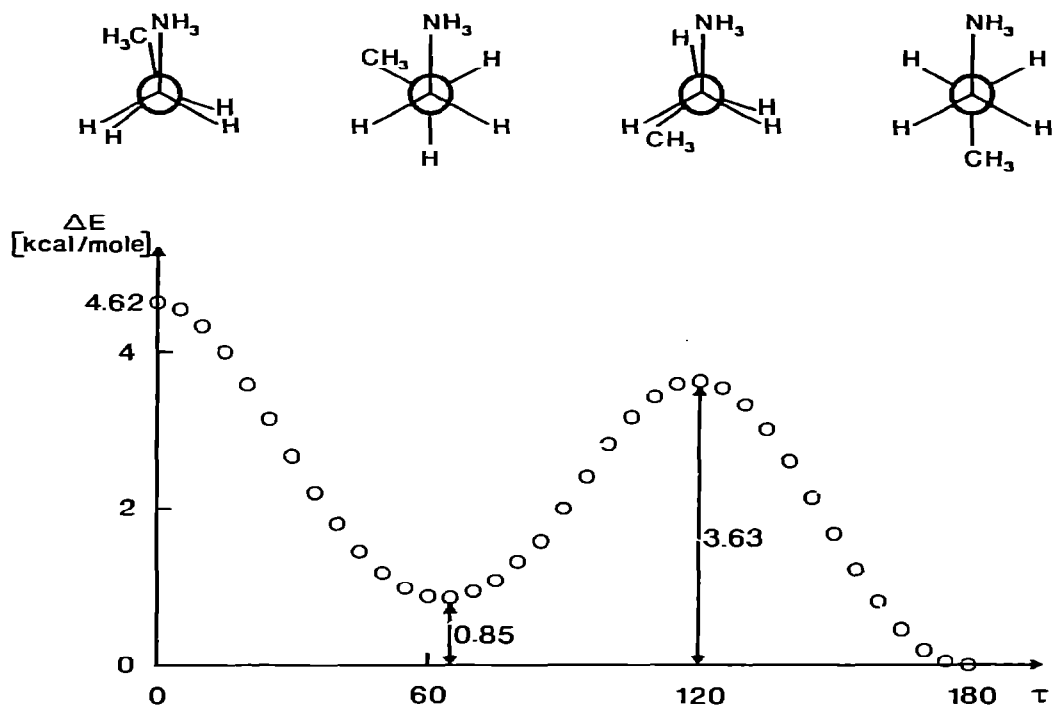


Fig. 2. Energy profile corresponding to internal rotation about the central carbon-carbon bond in the n-propylammonium group calculated using Allinger's program MM2 [6, 7].

Using the calculated value of ΔE_{int} ($0.85 \text{ kcal mol}^{-1}$), one obtains at room temperature a concentration ratio *gauche/anti* of 0.43. This value may be compared with the observed intensity ratio $I(832 \text{ cm}^{-1})/I(873 \text{ cm}^{-1})$ in the solution spectra of the propylammonium group (concentration 10% by weight). This ratio is found to be 0.71 at room temperature.

Considering that the Raman intensity is only proportional to the concentration and that the force field calculations remain approximate, we may qualitatively justify observing mainly ΔE_{int} in the solution spectra. Additional measurements of solution spectra as a function of temperature are in progress to obtain an experimental value of ΔE_{int} .

As suggested in the NMR study [2], we may now evaluate the concentration of *gauche* isomers in solid $n\text{-PrNH}_3\text{Cl}$. Using the calculated value of ΔE_{int} ($0.85 \text{ kcal mol}^{-1}$) and the experimental value of ΔE_{ext} ($2.5 \text{ kcal mol}^{-1}$), we obtain at room temperature the concentration ratio *gauche/anti* of 0.03. The relative *gauche* population is thus almost negligible. This result supports the analysis of the NMR spectra [2], but contradicts the crystallographic analysis [1].

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