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A Proton Magnetic Resonance Study of Rotational Motion of NH_3 Group in Solids

S. Ratković and S. Forsén*

Institute of Technology, Division of Physical Chemistry, Lund 7, Sweden

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The variations in PMR line parameters of taurine $[NH_3^+CH_2CH_2SO_3^-]$ and ε-aminocaproic acid $[NH_3^+(CH_2)_5COO^-]$ were studied in a wide temperature region. They were explained in terms of rotational motion of NH_3^+ group. The energy barriers hindering such a motion were calculated, and they are $V_0 = 5.0$ kcal mole^{-1} for taurine, and $V_0 = 9.0$ kcal mole^{-1} for ε-aminocaproic acid. The influence of hydrogen bond length N — H... O and position of NH_3^+ group in a molecule upon the extent of hindering, were shown.

INTRODUCTION

Proton magnetic resonance is one of the most valuable methods in studying mobility of whole molecules and separate atomic groups in solids. It is of special interest to investigate behaviour of the amino group in solid amino acids, keeping in mind their zwitterion configuration (NH_3^+) and the existence of N—H... O hydrogen bonds, which play an important role in hindering NH_3^+ rotation.

Of the amino acids containing an NH_3^+ group at one end of the molecule, only glycine[1,2] and β-alanine[1] were investigated using the PMR method. The conclusion was that rotation of the NH_3^+ group about its triad axis had a drastic effect upon the resonance line shape. The energy barriers hindering this process were calculated[3] for both compounds from the line width transitions.

It would be interesting to show how the hydrogen bond length and NH_3^+ position in a molecule can affect the amino group mobility. Toward this end we studied the PMR line width and second moment of taurine $NH_2CH_2CH_2SO_3H$ and ε-aminocaproic acid $[NH_2(CH_2)_5COOH]$ in a broad temperature interval. The physical properties of the molecules, mentioned above, were correlated with the barrier heights V_0 preventing NH_3^+ rotation.

EXPERIMENTAL

The measurements were done with polycrystalline samples of taurine and ε-aminocaproic acid (BDH products). The deuterated compound $ND_2(CH_2)_5COOD$, was prepared by repeated deuteration in an excess of heavy water.

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* Present address: Institute INEP, P. O. Box 46, Zemun, Yugoslavia.

The PMR spectra were recorded on a Varian wide line spectrometer (Model V 4200 B) using a steady magnetic field of 3.7 kgauss and radiofrequency of 15.8 MHz. Modulation amplitude of 1.5 gauss was in use, and r. f. amplitude was kept at a minimum to avoid the saturation effects.

The sample temperature was regulated by a special unit (Varian variable temperature accessory) and measured with a copper-constantan thermocouple, before and after running the PMR spectra. It was usually constant within 1^0 C.

The line widths ΔH_{max} were measured between two maxima of the derivative lines. To calculate second moments, the most symmetric spectra were chosen and the following formula[4] was applied: $\langle \Delta H^2 \rangle = -1/3 \int_{-\infty}^{+\infty} h^3 \left(\frac{dg}{dh} \right) dh$. The second moments were calculated by numerical integration, and corrections for modulation broadening[5] and proton signal from the probe were taken into account.

RESULTS

Taurine (2-Aminoethanesulphonic acid)

Okaya[6] has unambiguously shown by X-ray analysis that the taurine molecule has the zwitterion configuration in crystals, with the structural formula $NH_3^+ CH_2CH_2SO_3^-$, while the NH_3^+ and SO_3^- groups assume a *gauche* configuration around the central methylene linkage. From the point of view of magnetic dipoles interactions, the presence of a triangular group in the molecule must have a strong effect upon the shape of PMR lines.

The PMR spectra of taurine were recorded in an interval of temperature from -140^0 C to $+175^0$ C. The changes in second moment are shown in Fig. 1. The second moment at -140^0 C is about 30 gauss^2, and below this temperature one has to expect a constant value. But, it was difficult to record good spectra below -140^0 C, probably due to the effects of saturation. With increasing temperature the line narrows and the second moment decreases reaching a constant value of about 15 gauss^2. At higher temperatures there is an additional line narrowing, so that the second moment drops a further 5 gauss^2 and takes a value of 10 gauss^2 above $+100^0$ C.

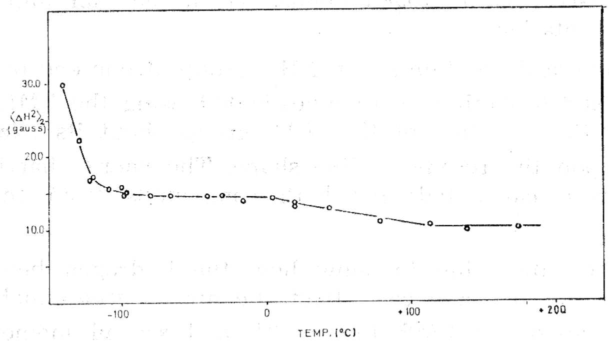

Fig. 1. Second moment temperature dependence for taurine.

ε-Aminocaproic acid

The results of crystallographic study[7] show that ε-aminocaproic acid possesses zwitterion structure $NH_3^+ (CH_2)_5COO^-$ and the molecules are held together by three N—H ... O hydrogen bonds.

We have done our PMR measurements in a temperature interval from —50° C up to the melting point of the compound (+202°C). The variations in line width are presented in Fig. 2. In the whole temperature region investigated the inner line width remains constant at 2.5 gauss, but width of the outer line changes drastically. Below room temperature the line width suddenly increases from 12.5 gauss and reaches a constant value of about 19 gauss at — 40° C. At higher temperatures it changes very slowly. Near the melting point a single line of 2.5 gauss width is observed.

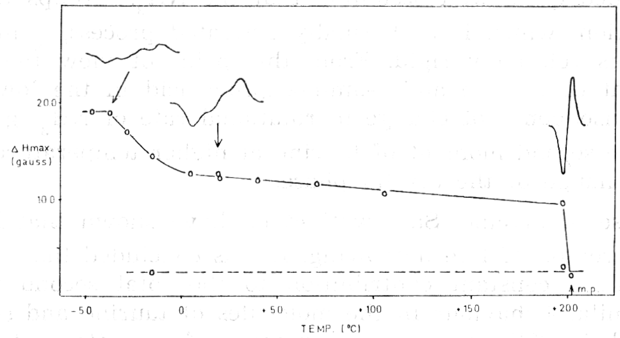

Fig. 2. The line width against temperature for ε-aminocaproic acid. The shapes of derivative lines at three different temperatures are shown.

— — — inner line
——— outer line

The same situation is more evident in Fig. 3 where we can follow changes in second moment as a function of temperature in the same interval. With increasing temperature above — 40° C, the second moment decreases from about 35 gauss^2 to 16.5 gauss^2 around + 50° C. When the compound starts

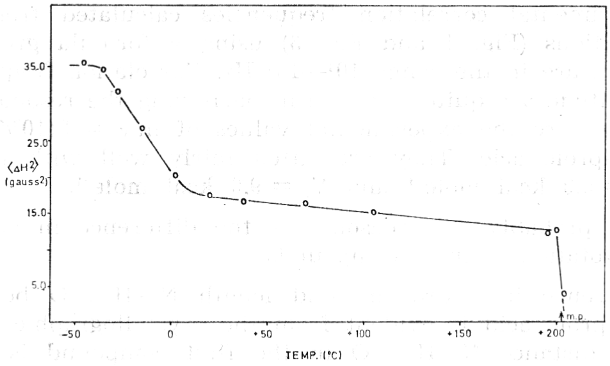

Fig. 3. The variation of second moment with temperature for ε-aminocaproic acid.

to melt, an abrupt change appears. The line narrowing results in a very sharp transition in the second moment. This is a consequence of increased molecular mobility and destroying of the crystal lattice.

We have also recorded room temperature PMR spectra of the deuterated compound $ND_2(CH_2)_5COOD$. The resulting line shape is characteristic of rigid CH_2 groups.

DISCUSSION

The observed variations in PMR line parameters of both compounds can be explained quite well assuming that the NH_3^+ groups take part in a rotational motion, which is a thermally activated process, while the rest of the molecule is relatively rigid. From this point of view the transition in second moment of taurine and ε-aminocaproic acid in the low temperature region is a consequence of change in rotational rate of NH_3^+ group. A small decrease in the second moment of taurine at higher temperatures is probably due to some change of the crystal phase.

In the case of glycine, Saraswati *et al.* have shown that NH_3^+ rotation was the main reason of line narrowing. It was concluded that the CH_2 group was rigid with a constant contribution to the total second moment. One can expect similar behaviour in the molecules of taurine and ε-aminocaproic acid. In fact their PMR spectra are composed of separate contributions from NH_3 and CH_2 atomic groups.

To evaluate the energy barriers hindering rotational motion of the NH_3^+ groups we apply a model proposed by Das[3], where the rotation around the triad axis of the amino rotor is understood as a movement in a threefold potential well. Then, the probability of transition from one potential well to the next can be found using the relation:

$$W = 3/2\,\pi \left(\frac{V_0}{2\,I_{eff}}\right)^{1/2} e^{-\frac{V_0}{KT}}$$

in which V_0 is an energy barrier and I_{eff} represents the effective moment of inertia of the NH_3 group, $I_{eff} = 5.14 \cdot 10^{-14}$ gcm^2. This probability of transition is, in fact, $W = 2\,\pi\nu_c$, so one can calculate theoretical functions $\ln \nu_c = f(10^3/T)$ for different values of V_0 (Fig. 4).

The experimental correlation frequencies calculated from the second moment transitions (Fig. 1 and Fig. 3) using a formula given by Powles and Gutowsky[8], are in the range 10^4—10^5 Hz. Correlation frequencies of this order of magnitude are quite effective in narrowing the resonance lines. The points in Fig. 4 are the experimental values of $\ln \nu_c = f(10^3/T)$ for taurine and ε-aminocaproic acid. They are fitted fairly well with the theoretical lines for $V_0 = 5.0$ kcal mole^{-1} and $V_0 = 9.0$ kcal mole^{-1}.

There are probably two reasons for the difference in energy barriers for the NH_3^+ rotation in these compounds:

1. A difference in hydrogen bond length N—H...O between taurine and ε-aminocaproic acid is evident from the crystallographic studies[6,7]. The average bond distance N—H...O in the first compound is 2.907 Å, and 2.765 Å in the second. This fact points out that the NH_3^+ group in ε-amino-

caproic acid is more hindered in rotation than the same group in taurine, giving as the result different values of V_0.

2. The other reason could be a variation in position of NH_3^+ group in the molecules of taurine and ε-aminocaproic acid, *i. e.* different length of the molecules. In larger molecules there is a higher probability for the NH_3^+ group to interact with adjacent bonds[3]. This interaction will have some effect in hindering rotation of the amino group.

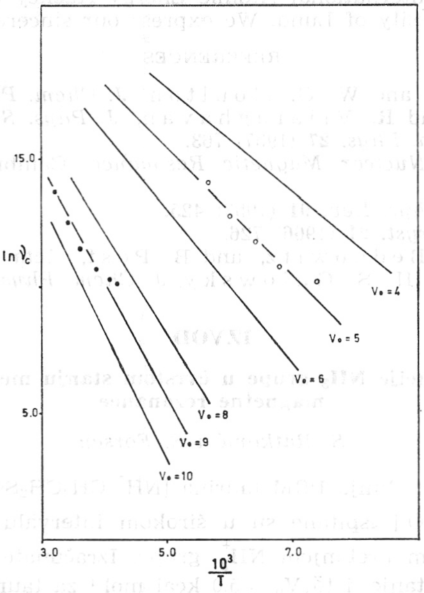

Fig. 4. Plot of correlation frequency ν_c against $10^3/T$ for various values of V_0. The points presented here, are calculated from the second moment transitions.
○ taurine $[NH_3^+CH_2CH_2SO_3^-]$
● ε-aminocaproic acid $[NH_3^+(CH_2)_5COO^-]$

It is interesting to compare the values of V_0 in the series of amino acids: glycine, β-alanine and ε-aminocaproic acid (Table I). The energy

TABLE I

Energy Barriers Hindering Rotation of NH_3 Groups in Some Solid Amino Acids

Compound	Structural formula	V_0 (kcal mole^{-1})
Taurine	$NH_3^+ (CH_2)_2SO_3^-$	5.0
Glycine	$NH_3^+ CH_2COO^-$	6.1*
β-alanine	$NH_3^+ (CH_2)_2COO^-$	8.0*
ε-aminocaproic acid	$NH_3^+ (CH_2)_5COO^-$	9.0

* Data from: T. P. Das, *J. Chem. Phys.* **27** (1957) 763.

barriers of the first two compounds have been calculated by Das from line width transitions. The barrier heights are 6.1 kcal, 8.0 kcal and 9.0 kcal per mole for the NH_3^+ rotation, if the group takes α, β and ε positions respectively. This trend in V_0 variation can be explained assuming that the probability of interaction between, the NH_3^+ group and adjacent bonds increases in the same direction.

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IZVOD

Proučavanje rotacije NH_3 grupe u čvrstom stanju metodom protonske magnetne rezonance

S. Ratković i S. Forsén

Promene parametara linija PRM taurina [NH_3^+ $CH_2CH_2SO_3^-$] i ε-aminokapronske kiseline [NH_3^+ $(CH_2)_5COO^-$] ispitane su u širokom intervalu temperature. Rezultati su objašnjeni rotacionim kretanjem NH_3^+ grupe. Izračunate su energetske barijere koje sputavaju ovo kretanje, i to $V_0 = 5.0$ kcal mol^{-1} za taurin i $V_0 = 9.0$ kcal mol^{-1} za ε-aminokapronsku kiselinu. Prikazan je i efekt dužine vodonične veze N — H . . . O te položaja NH_3^+ grupe u molekulu na veličinu energetskih barijera.

INSTITUTE OF TECHNOLOGY
DIVISION OF PHYSICAL CHEMISTRY
LUND 7

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