Hydrogen Bond Studies

42.* Proton Magnetic Resonance in Hydrazinium Hydrogen Oxalate

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Proton magnetic resonance spectra of polycrystalline $N_2H_5HC_2O_4$ have been studied from 190 to 340°K. As the temperature is changed from 210 to 280°K, the second moment of the resonance line decreases from 33 to 13 G^2. This is interpreted as due to the onset of reorientation of the NH_3 group with a rate which is fast in comparison with the line width ($> 10^5$ c/s).

A proton magnetic resonance study of $N_2H_5HC_2O_4$ has been published previously by Pratt and Richards[1] and by Deeley *et al.*[2] A considerable decrease in the second moment of the proton resonance line was observed when going from 122°K to room temperature indicating the onset of some kind of molecular reorientation. However, their report included only measurements at three different temperatures, and the present study was made to investigate the variation of the second moment in more detail. Furthermore, X-ray[3] and neutron[4] diffraction studies of $N_2H_5HC_2O_4$ have been completed at this Institute, and it is of interest to attempt to correlate the PMR and diffraction results.

EXPERIMENTAL

The hydrazinium hydrogen oxalate was prepared as described earlier.[3]

The proton resonance spectra of the polycrystalline sample were recorded at 16.0 Mc/s using a Varian Asc wide-line NMR spectrometer equipped with a 12″ magnet and a low proton background probe. The temperature of the sample was regulated by blowing nitrogen gas over the sample in a Dewar tube. The temperature was measured with a copper-constantan thermocouple inserted in the sample immediately before and after each run. The low-temperature device is described in more detail elsewhere.[5] The temperature drift while recording a spectrum was less than 1°C. The magnetic field was swept with a Fieldial unit (Varian Asc.), and the sweep rate, 1.5 − 2 G min⁻¹, was calibrated with a frequency counter. The audio frequency modulation amplitude was about 1.2 G, and the radio frequency amplitude was kept below the saturation level. Spectra were

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recorded from 190 to 340°K. Below 190°K, saturation effects prevented registration of useful spectra.

The experimental second moments were obtained from the recorded derivatives of the absorption lines by numerical integration and were corrected for modulation broadening.[6]
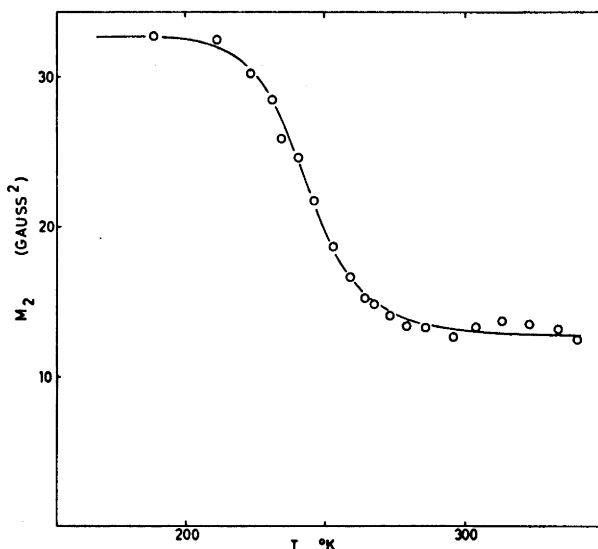

Fig. 1. The second moment of $N_2H_5HC_2O_4$ as a function of the temperature. Circles denote experimental values. The curve has been calculated for an $-NH_3$ reorientation barrier of 8.1 kcal/mol, as described in the text.

RESULTS AND DISCUSSION

The experimental second moment *versus* temperature is plotted in Fig. 1. The data may be interpreted in the following way.

1. $T < 210°K$

Below about 210°K, the second moment approaches a constant value of 33 G^2 which probably corresponds to a rigid structure or, expressed more properly, to a structure where molecular reorientations are slow compared to the line width of a rigid structure. The line width is then usually of the order of 10^5 c/s, which is comparable to the present value 0.8×10^5 c/s below 210°K.

A theoretical value of the second moment for a rigid arrangement of atoms has been calculated from the atomic coordinates obtained in the neutron diffraction study.[4] In this calculation the usual expression [7] for the second moment of a powdered sample was used, *i.e.*

$$M_2 = \tfrac{3}{5}\gamma_I^2\hbar^2 I(I+1)\tfrac{1}{n}\sum_{i=1}^{n}\sum_{i\neq j}1/r_{ij}^6 + \tfrac{4}{15}\gamma_s^2\hbar^2 S(S+1)\tfrac{1}{n}\sum_{i=1}^{n}\sum_{k}1/r_{ij}^6$$

where γ_1, γ_s, I and S are the gyromagnetic ratios and spins for ^{1}H and ^{14}N, respectively, and n is the number of protons/unit cell. The first sum is taken over all proton-proton distances r_{ij}, and the second sum over all proton-nitrogen distances r_{ik}. All proton-proton and nitrogen-proton interactions were considered for which the internuclear distance r was less than 6.0 Å. The contribution for $r > 6.0$ Å was estimated to be 0.4 G^2 by integration over a continuous distribution of protons. The total value thus obtained is 32.0 G^2, in good agreement with the experimental value.

2. $T > 210°$K

In the temperature interval 210 to 280°K there is a considerable decrease of the second moment, from 33 G^2 to 13 G^2. The magnitude of the decrease clearly indicates the onset of reorientation of the NH$_3$ group or the NH$_2$ group (or both) at a rate greater than 10^5 c/s. Since the neutron diffraction data [4] give definite proton maxima, the time spent by a nucleus in its equilibrium positions is evidently much longer than the time between two such positions.

The contribution to the second moment from a pair of spins at a fixed distance from one another is reduced by the factor $(3\cos^2\gamma - 1)^2/4$, if the pair is reorienting at a rate fast in comparison with the line width.[8] In this expression γ is the angle between the axis of rotation and the internuclear vector.

a. *Reorientation of the* $-NH_3$ *end*. Application of this formula to the N$-$H and H$-$H interactions within the NH$_3$ group gives a decrease of the second moment by 12.1 G^2. The effect of motion on the remaining intramolecular and the intermolecular interactions is harder to calculate, since the motion changes not only the orientations of the internuclear vectors, but also their lengths. However, an estimate of the effect can be made in the following way, provided the motion is of the nature described above in the present compound.

Consider a pair of spins undergoing reorientation between n different equilibrium configurations. The effect of motion on the contribution to the second moment from this pair is obtained by averaging $b = (3\cos^2\theta - 1)/r^3$ over the motion,[8] where θ is the angle between the internuclear vector and the external magnetic field. This average can be written

$$\langle b \rangle = \sum_{i=1}^{n} b_i$$

where b_i is $(3\cos^2\theta - 1)/r^3$ for the ith configuration. For a powder $\langle b \rangle^2$ should furthermore be averaged over all possible crystal orientations. It can then be shown that

$$\overline{\langle b \rangle^2} = \tfrac{2}{5}\frac{1}{n^2}\sum_{i=1}^{n}\sum_{j=1}^{n}\frac{3\cos^2 v_{ij} - 1}{r_i^3 \; r_j^3}$$

where v_{ij} is the angle between the internuclear vectors r_i and r_j for the configurations i and j. Application of this formula to the remaining intramolecular and intermolecular interactions with the NH$_3$ group gives an additional decrease of about 4.3 G^2. The expected total decrease in the second moment, caused by a reorienting NH$_3$ group, should then be 16.4 G^2. Naturally, too

much significance should not be attached to the exact value, since the model used in the above calculations is very much simplified.

b. *Reorientation of the* $-NH_2$ *end.* Reorientation of the $-NH_2$ group should have a rather small effect on the second moment: the hydrogen-bond pattern derived from the diffraction data is only consistent with 360° jumps about the $N-N$ axis, which leave all interatomic vectors effectively unchanged. However, such a reorientation must be coupled with a simultaneous reorientation of the $-NH_3$ end of a neighbouring hydrazinium ion, as the barrier is otherwise too high (see further below).

It is accordingly quite clear that the NH_3 group undergoes fast reorientations ($>10^5$ c/s) at room temperature, whereas it cannot be definitely concluded from the NMR data, whether or not the NH_2 group reorients (simultaneously with the NH_3 end).

Barrier for the reorientation of the NH_3 group

The energy barrier E restricting the reorientation of the NH_3 group has been estimated using the following assumptions. The temperature dependence of the reorientation frequency ν is given by

$$\nu = \nu_0\, e^{-E/RT}$$

The second moment M_2 is related to ν through the relation [8]

$$\nu = \alpha\gamma\sqrt{M_2}/\tan\left(\frac{\pi}{2}\frac{M_2 - M_2'}{M_2'' - M_2'}\right)$$

M_2' and M_2'' are the high- and low-temperature limits of the second moment, γ is the gyromagnetic ratio for protons, and α is a line-shape dependent constant, assumed for simplicity to be equal to 1 in this case.

The best fit between these two expressions and the experimental second moments was obtained by the least squares method for a barrier of 8.1 kcal/mol. The variation of M_2 with T thus obtained is shown in Fig. 1.

Comparison with other data

From the crystal structure of $N_2H_5HC_2O_4$, as determined by diffraction methods,[3,4] it is clear that the only type of motion that is likely to occur is a reorientation of the $-NH_3$ group or possibly a coupled reorientation of one $-NH_3$ group and the $-NH_2$ group to which it is hydrogen bonded. From the hydrogen-bond pattern it is immediately clear that isolated rotation of the $-NH_2$ end about the $N-N$ axis is quite impossible.

Calculations of the electrostatic and van der Waals interactions, recently made at this Institute,[9] for various orientations of the NH_2 and NH_3 groups in $N_2H_5HC_2O_4$ strongly support the above conclusions about the type of motion. Furthermore, the value obtained for the rotation barrier for the $-NH_3$ group was 7.5 kcal/mol, in surprisingly good agreement with the present investigation.

In the neutron diffraction study [4] a phase transition at about $-100°C$ is reported. This temperature is well below the temperature range of the NMR line width transition. Naturally, this does not exclude the possibility that the two transitions are related. The line width transition merely indicates that the reorientation rate passes through a certain region, and the motion may very well prevail down to the transition temperature observed in the diffraction study.

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