

## Nitrogen-15 NMR of Pyridine in High Magnetic Fields\*

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The  $^{15}\text{N}$  NMR of pyridine was studied in the liquid and solid state. In the liquid the spin-lattice relaxation time  $T_1$  was studied from  $-60$  to  $+55^\circ\text{C}$  at 14 and 30 MHz. At low temperature, the two most important relaxation mechanisms are relaxation due to anisotropic chemical shift and intermolecular dipole-dipole interaction. The small contribution of intramolecular dipole-dipole interaction of  $^{15}\text{N}$  with protons was determined by making use of correlation times  $\tau_c$  obtained from  $^{13}\text{C}$  relaxation rates, which were also measured. At higher temperatures, relaxation by spin-rotation interaction becomes important. Analysis of the relaxation data shows that the anisotropy of the motion in liquid pyridine is rather small. The principal elements of the chemical shift tensor were obtained from powder spectra at  $-105^\circ\text{C}$  by FT NMR:  $\sigma_{xx} = -313 \pm 10$  ppm,  $\sigma_{yy} = -94 \pm 10$  ppm,  $\sigma_{zz} = +469 \pm 10$  ppm relative to liquid pyridine. From these values the following spin-rotation components were calculated:  $C_{xx} = 16.5 \pm 1$  kHz,  $C_{yy} = 11.5 \pm 1$  kHz,  $C_{zz} = -0.6 \pm 1$  kHz. In both cases the  $z$ -axis is perpendicular to the molecular plane.

### I. INTRODUCTION

Measurements of  $^{15}\text{N}$  spin-lattice relaxation times are scarce in the literature; because of the low natural isotopic abundance (0.365%) and the small magnetic moment ( $-0.28304 \mu_0$ ),  $^{15}\text{N}$  signals are extremely weak. Lippmaa *et al.* (1, 2) have shown that intramolecular dipole-dipole interaction (DDI) (e.g.,  $\text{C}_6\text{H}_5\text{NH}_2$ ) and spin-rotation interaction (e.g.,  $\text{C}_6\text{H}_5\text{NO}_2$ ) are dominant relaxation processes for  $^{15}\text{N}$ . As long as the  $^{15}\text{N}$  nucleus is shielded by surrounding atoms of the same molecule, or  $^{15}\text{N}$  is attached to protons, as in the case of  $\text{NH}_3$  studied by Litchman and Alei (3), intermolecular DDI is not an important relaxation mechanism.

In pyridine ( $\text{C}_6\text{H}_5\text{N}$ ), we can predict that intramolecular DDI will be small because of the  $r_{\text{N-H}}^{-6}$  distance dependence ( $r_{\text{N-H}}$  is the distance between the ring protons and the nitrogen in this case). On the other hand, the distance of protons of other molecules can be rather small because of the interaction of these protons with the nonbonding orbital at the nitrogen. This gives rise to an intermolecular DD relaxation mechanism, which could be predominant. In combination with  $^{13}\text{C}$  relaxation studies—from which we get the correlation times  $\tau_c$  of the angular reorientation of the pyridine ring—we are able to separate the intramolecular DD relaxation term for the  $^{15}\text{N}$ .

Another important purpose of this study is the investigation of the magnetic-field-dependent relaxation rate due to the  $^{15}\text{N}$  anisotropic chemical shift. Measurements of  $^{13}\text{C}$  spin-lattice relaxation have shown that only in few cases (4-6) does relaxation due to anisotropic chemical shift (ACS) play a role because usually intramolecular DDI is dominant or the ACS is small. Therefore, for  $^{13}\text{C}$  it is often necessary to work

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with deuterated molecules (7) to be able to separate the contribution of relaxation due to the anisotropy of the chemical shift. For  $^{15}\text{N}$ , it should be possible to observe relaxation due to ACS more easily, because in contrast to  $^{13}\text{C}$ , it is not bound directly to a proton in many interesting cases. Nevertheless, temperature-dependent studies of  $^{15}\text{N}$  relaxation times over a larger magnetic field range, similar to  $^{13}\text{C}$  (4, 5, 7), have not been reported so far.

Interpretation of the relaxation data is considerably simplified if the ACS is obtained independently from solid-state measurements. Therefore, we have also determined the ACS from the powder spectra of solid pyridine using Fourier transform techniques. In addition, it is then possible to obtain the spin-rotation constants.

## II. ANISOTROPIC CHEMICAL SHIFT AND SPIN-ROTATION INTERACTION

In previous cases, linear molecules (4) and spherical molecules (5) have been considered. Pyridine is an asymmetric rotor, but the principal axes systems of the chemical shift tensor  $\hat{\sigma}$ , the spin rotation tensor  $\hat{C}$  for  $^{15}\text{N}$ , and the moment of inertia tensor  $\hat{\theta}$  still coincide because of the symmetry of the molecule. In addition, we can now make use of the individual elements of the  $\hat{\sigma}$  tensor obtained from solid-state measurements. Therefore it is necessary to give a generalized analysis here.

Usually  $\hat{\sigma}$  is represented as the sum of a diamagnetic part  $\hat{\sigma}^d$  and a paramagnetic part  $\hat{\sigma}^p$ :

$$\hat{\sigma} = \hat{\sigma}^d + \hat{\sigma}^p. \quad [1]$$

Chemical shift data from high-resolution NMR measurements are an average of the diagonal elements of the shielding tensor, giving for the average shielding

$$\sigma_{\text{av}} = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz}). \quad [2]$$

Nevertheless, for each element  $\sigma_{ii}$ , Eq. [1] is also valid. As long as the principal axes of the three tensors  $\hat{\sigma}$ ,  $\hat{C}$ ,  $\hat{\theta}$  are parallel (see above), we can express the paramagnetic parts  $\sigma_{ii}^p$  in terms of only one spin rotation constant: (8)

$$\sigma_{ii}^p = \frac{e^2}{6mc^2} \left\{ \frac{3c}{e\mu_0 g_K} \theta_i C_{ii}^K - 2 \sum_{\alpha}' \frac{Z_{\alpha}}{r_{\alpha}^3} (j_{\alpha}^2 + k_{\alpha}^2) \right\}, \quad i, j, k = x, y, z \text{ cyclic.} \quad [3]$$

Here,  $C_{ii}^K$  is a component of the spin-rotation tensor<sup>1</sup> for the K-nucleus we are considering,  $\theta_i$  is the component of the moment of inertia of the molecule in the direction of the principal inertial axis,  $i$ ,  $\mu_0$  and  $g_K$  are nuclear magneton and nuclear  $g$ -factor of the Kth nucleus ( $g_K(^{15}\text{N}) = -0.567$ ),  $e$  the electronic charge,  $m$  the electronic mass, and  $c$  velocity of light. The prime on the summation indicates  $\alpha \neq K$ , and  $Z_{\alpha}$  is the charge on the  $\alpha$ th nucleus in the molecule while  $r_{\alpha}$  is the internuclear vector between the Kth and the  $\alpha$ th nuclei with length  $r_{\alpha}$  and the components  $j_{\alpha}$  and  $k_{\alpha}$ .

For the diamagnetic part, we use the approximate formulae given by Flygare and Goodisman (9)<sup>2</sup>

$$\sigma_{ii}^d = \sigma_{\text{av}}^d(\text{free atom}) + \frac{e^2}{3mc^2} \sum_{\alpha}' \frac{Z_{\alpha}}{r_{\alpha}^3} (j_{\alpha}^2 + k_{\alpha}^2), \quad [4]$$

<sup>1</sup>  $C_{ii}^K$  is an element of the spin-rotation tensor defined by  $\mathcal{H}_{\text{SR}} = \vec{hI} \hat{C}^K \vec{J}$ . Thus spin-rotation constants obtained from molecular beam data have to be multiplied by  $2\pi$  to be used in our notation.

<sup>2</sup> Using the more recent expressions given by Gierke and Flygare (9b) would complicate the analysis considerably. For pyridine, the corrections for  $\sigma^d$  (9b) would change the values for  $\sigma_{ii}$  by less than 2%.

where  $\sigma_{av}^d$  (free atom) is the diamagnetic shielding of the free atom. From combinations of Eqs. [3] and [4] we get

$$\sigma_{ii} = \sigma_{av}^d(\text{free atom}) + \frac{|e|}{2mc\mu_0 g_K} \Theta_i C_{ii}^K \quad [5]$$

and for the isotropic value  $\sigma_{av}$

$$\sigma_{av} = \sigma_{av}^d(\text{free atom}) + \frac{|e|}{6mc\mu_0 g_K} \sum_i \Theta_i C_{ii}^K. \quad [6]$$

$\sigma_{av}$  is given on an absolute scale and therefore difficult to obtain. However, it is not necessary to know the parameter  $\sigma_{av}^d$  (free atom) in order to make use of Eq. [6]. It can be eliminated with a reference compound whose spin-rotation tensor is known experimentally and whose relative isotropic shift  $\delta$  can be determined experimentally.

For  $^{15}\text{N}_2$ , the spin-rotation constant  $C_{N_2}$  as well as the relative isotropic shift  $\delta$  is known (10). For the linear molecule  $^{15}\text{N}_2$ , Eq. [6] reduces to

$$\sigma_{Av}(^{15}\text{N}_2) = \sigma_{av}^d(\text{free atom}) + \frac{|e|}{3mc\mu_0 g_K} \Theta_{N_2} C_{N_2}. \quad [7]$$

The individual components of  $\hat{\sigma}$  are also known relative to the reference compound:

$$\delta_i = \sigma_{av}(^{15}\text{N}_2) - \sigma_{ii}(^{15}\text{N-Pyridine}). \quad [8]$$

In our approximation, each  $\delta_i$  can be related to a single element of the spin rotation tensor  $C_{ii}$ . By substituting Eq. [5] for  $\sigma_{ii}$  and solving for  $C_{ii}$ , we obtain

$$C_{ii} = \frac{2}{3\Theta_i} \left( \Theta_{N_2} \cdot C_{N_2} - \frac{3\delta_i mc\mu_0 g_K}{|e|} \right). \quad [9]$$

In order to make use of Eq. [9], we should not only know the principal elements of  $\hat{\sigma}$  but also the orientation of the principal axis system of  $\hat{\sigma}$  relative to the molecule.

Independent of these considerations, the elements of  $\hat{\sigma}$  and  $\hat{C}$  also enter into the expressions for the relaxation rates due to ACS,  $1/T_1^{\text{CS}}$ , and due to spin-rotation interaction,  $1/T_1^{\text{SR}}$ .

A separation of the contributions of the individual tensor components to the relaxation rates is not possible in general. Therefore, we can only hope to get information about one parameter for the anisotropy of the chemical shift and one for the anisotropy of the spin rotation tensor. In contrast to relaxation due to ACS, even an isotropic spin-rotation tensor gives rise to a relaxation mechanism. Therefore, we can extract another parameter describing the  $\hat{C}$  tensor from our relaxation data.

For  $\sigma_{zz} > \sigma_{yy} \approx \sigma_{xx}$ , we will define  $\Delta\sigma = \sigma_{zz} - 1/2(\sigma_{yy} + \sigma_{xx}) = \sigma_{\parallel} - \sigma_{\perp}$ . The relaxation rate due to ACS (11) is given by

$$\frac{1}{T_1^{\text{CS}}} = \frac{2}{15} (\omega \cdot \Delta\sigma)^2 \cdot \tau_c^{\text{eff}}. \quad [10]$$

The complete expression  $1/T_1^{\text{CS}}$  contains an asymmetry parameter  $\eta$  (11) which we have omitted for simplicity because  $1/T_1^{\text{CS}}$  is quite insensitive against  $\eta$ . Thus for  $\eta \leq 0.5$ , we can always treat the system as if it was axially symmetric ( $\eta = 0$ ). The Larmor

frequency is  $\omega$ , and  $\tau_c^{\text{eff}}$  is the effective correlation time for angular reorientation. Expressions for the effective correlation time in this case have been given by several authors (12-14):

$$\tau_c^{\text{eff}} = \tau_{c\perp} \{1 - (3(\rho - 1)/(5 + \rho)) \sin^2 \beta \cdot (1 - (3(\rho - 1)/(2(2\rho + 1))) \sin^2 \beta)\}, \quad [11]$$

where  $\rho$  is the ratio of the correlation times of reorientation perpendicular and parallel to the symmetry axis ( $\rho = \tau_{c\perp}/\tau_{c\parallel}$ ) and  $\beta$  is the angle between the molecular vector of interest and the symmetry axis of the rotational diffusion tensor.

For the spin-rotation tensor, we shall define  $C_{zz} = C_{\parallel}$  and  $C_{\perp} = 1/2(C_{xx} + C_{yy})$ . It will be shown later that the unique axes of the almost axially symmetric tensors  $\hat{\sigma}$ ,  $\hat{C}$ , and  $\hat{\theta}$  are parallel. Therefore, we can use the expressions for the relaxation rate due to spin-rotation interaction for symmetric rotors as derived by Bender and Zeidler (15):

$$\frac{1}{T_1^{\text{SR}}} = \frac{2\Theta_{\parallel}^2}{3\hbar^2} C_{\parallel}^2 D_{\parallel} + \frac{4\Theta_{\perp}^2}{3\hbar^2} C_{\perp}^2 D_{\perp}. \quad [12]$$

$\hbar$  is Planck's constant divided by  $2\pi$ . The expression [12] can be generalized easily if the restriction of axial symmetry is removed but the principal axes systems of  $\hat{C}$ ,  $\hat{\theta}$ , and the diffusion tensor remain parallel (see above):

$$\frac{1}{T_1^{\text{SR}}} = \frac{2}{3\hbar^2} \{\Theta_{xx}^2 C_{xx}^2 D_{xx} + \Theta_{yy}^2 C_{yy}^2 D_{yy} + \Theta_{zz}^2 C_{zz}^2 D_{zz}\}. \quad [12a]$$

This can be seen using the derivation of Bender and Zeidler (15) and setting  $C_{zz} = C_{\parallel}$ ,  $C_{xx} = C_{\perp} + a$ ,  $C_{yy} = C_{\perp} - a$  with  $a = 1/2(C_{xx} - C_{yy})$ . Equation [3] of (15) then reads (notation as in (15)):

$$\begin{aligned} \hbar \mathcal{H}_1(t) = & \hbar C_{\parallel} I^0 \omega^0(t) - \hbar C_{\perp} \{I^{-1} \omega^{+1}(t) + I^{+1} \omega^{-1}(t)\} \\ & + \hbar a \{I^{+1} \omega^{+1}(t) + I^{-1} \omega^{-1}(t)\}. \end{aligned}$$

With this form of the Hamiltonian, the derivation of  $1/T_1^{\text{SR}}$  can be performed in exactly the same way as described in (15) and results in Eq. [12a]. For the rotational diffusion constants  $D_i$ , we have (14)

$$D_i = \frac{kT}{\Theta_i} (\tau_j)_i, \quad [13]$$

where  $(\tau_j)_i$  is the angular-velocity correlation time about the  $i$ th axis. Combining Eqs. [12] and [13] we get

$$\frac{1}{T_1^{\text{SR}}} = \frac{2kT}{3\hbar^2} (\Theta_{\parallel} C_{\parallel}^2 \tau_{j\parallel} + 2\Theta_{\perp} C_{\perp}^2 \tau_{j\perp}) \quad [14]$$

In the diffusion limit,  $\tau_j$  and  $\tau_c$  are related by

$$(\tau_j)_i \cdot (\tau_c)_i = \frac{\Theta_i}{6kT}. \quad [15]$$

For  $\tau_{j\parallel}$ , we then get the expression

$$\tau_{j\parallel} = \rho \cdot \frac{\Theta_{\parallel}}{\Theta_{\perp}} \cdot \tau_{j\perp}, \quad \rho = \frac{\tau_{c\perp}}{\tau_{c\parallel}}. \quad [16]$$

Now the correlation times can be eliminated by multiplication of the individual relaxation rates:

$$\left(\frac{1}{T_1^{\text{SR}}} \cdot \frac{1}{T_1^{\text{CS}}}\right) = \frac{2(\omega\Delta\sigma)^2}{135\hbar^2} (\rho\theta_{\parallel}^2 C_{\parallel}^2 + 2\theta_{\perp}^2 C_{\perp}^2). \quad [17]$$

Moreover, for  $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp}$ , we get an expression from Eq. [5]

$$\Delta\sigma = \frac{|e|}{2mc\mu_0 g_K} (\theta_{\parallel} C_{\parallel} - \theta_{\perp} C_{\perp}). \quad [18]$$

Besides the individual relaxation rates  $1/T_1^{\text{SR}}$  and  $1/T_1^{\text{CS}}$ , the spin-rotation constants, the anisotropic chemical shift  $\Delta\sigma$ , the moments of inertia of the molecule (which are well-defined for simple liquids), the constant  $\rho$  also enters the analysis. We shall see later how we get information about  $\rho$  from the comparison of the correlation times  $\tau_c$  from the analysis of the relaxation rates due to DDI for the ring  $^{13}\text{C}$  and relaxation due to ACS for the  $^{15}\text{N}$ .

### III. EXPERIMENTAL

The  $^{15}\text{N}$ -pyridine sample (50 per cent isotopically enriched) was obtained from Isocommerz G.m.b.H., Leipzig, DDR. The sample was degassed by several freeze-pump-thaw cycles. The NMR probes operating at 14, 30, and 32 MHz as well as the measurement procedure for the liquid phase have been described before (7, 16, 17). At 32 MHz, the corresponding magnetic field for  $^{15}\text{N}$  is about 74.2 kG. Measurements in the liquid phase were made down to  $-60^\circ\text{C}$  showing that the sample can be supercooled far below the melting point ( $-42^\circ\text{C}$ ). In the solid phase ( $-105^\circ\text{C}$ ), measurements were carried out using normal Fourier transform and signal-averaging techniques. Since the relaxation time in the liquid phase is much shorter than in the solid state, the sample was polarized in the liquid. Then the sample was frozen down for several minutes before measuring. After that, the sample was melted again starting a new cycle. Sixty four runs were accumulated.

### IV. RESULTS AND DISCUSSION

In Fig. 1 the experimental  $^{15}\text{N}$  and  $^{13}\text{C}$  spin-lattice relaxation rates for pyridine are plotted vs temperature. For  $^{15}\text{N}$ , in addition to the data for 14 and 30 MHz, the extrapolated curve for  $\nu = 0$  MHz is also shown. This curve was obtained from a plot of the relaxation rate vs the square of the frequency. Equation [10] shows that the relaxation rate due to ACS is proportional to the square of the resonance frequency. The validity of this dependence was demonstrated experimentally (see e.g. for  $^{13}\text{C}$  (4, 5) and for  $^{15}\text{N}$  in nitrobenzene (18)).

All of the  $^{15}\text{N}$  relaxation rates show a more or less pronounced curvature when plotted logarithmically vs  $1/T$  ( $T$  = temperature), suggesting that, in addition to ACS and dipole-dipole coupling, spin-rotation interaction also contributes to the relaxation rates. Certainly, the relaxation rate for DDI,  $1/T_1^{\text{DD}}$ , consists of an intramolecular part,  $1/T_1^{\text{DD}}(\text{intra})$ , and an intermolecular one,  $1/T_1^{\text{DD}}(\text{inter})$ :

$$1/T_1^{\text{DD}} = 1/T_1^{\text{DD}}(\text{intra}) + 1/T_1^{\text{DD}}(\text{inter}). \quad [19]$$

The relaxation rate  $1/T_1^{\text{DD}}(\text{intra})$  can be calculated if we know the correlation time for angular reorientation  $\tau_c$ . From the  $^{13}\text{C}$  relaxation rates for the ring carbons, we get

information about  $\tau_c$ . It has been shown (7, 16) that the  $^{13}\text{C}$  relaxation rates for ring carbons are solely determined in very good approximation by intramolecular DDI between the carbon and the directly attached proton. This holds even at a frequency of 61 MHz, where our measurements were performed. For this dipolar relaxation rate, we can write (11) (see also (16))

$$1/T_1^{\text{DD}}(^{13}\text{C}) = \frac{4}{3} \gamma_{^{13}\text{C}}^2 \gamma_{\text{H}}^2 \hbar^2 S(S+1) r_{\text{C-H}}^{-6} \tau_c \quad [20]$$

with  $r_{\text{C-H}} = 1.085 \text{ \AA}$  and  $S$  the proton spin.

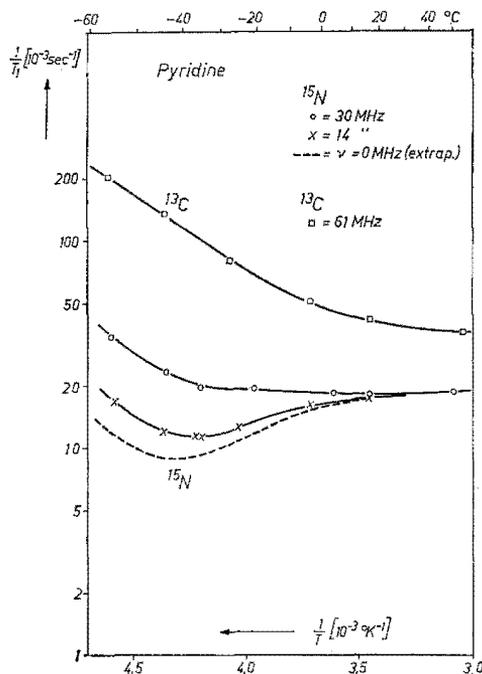


FIG. 1.  $^{15}\text{N}$  and  $^{13}\text{C}$  relaxation rates in pyridine. The dashed line was extrapolated from the frequency dependence of the  $^{15}\text{N}$  relaxation rates (see text).

So with the  $^{13}\text{C}$  relaxation rates shown in Fig. 1, we are able to calculate the correlation times  $\tau_c$ . The measured  $^{13}\text{C}$  relaxation rates (Fig. 1) are an average over all ring carbons. Because of the relatively poor homogeneity of our superconducting magnet, we are not able to distinguish between the different carbons. The differences of the relaxation rates for the individual carbons should be small<sup>3</sup> because the diffusion tensor in a good approximation should be almost the same as for benzene which has a sixfold symmetry axis perpendicular to the plane of the ring. The internuclear vectors describing the intramolecular DD coupling of  $^{15}\text{N}$  with the aromatic protons also lie in the plane of the molecule. Therefore, the correlation times for the intramolecular DD re-

<sup>3</sup> This is further supported by the values for the  $^{13}\text{C}$  relaxation times given in (6):  $T_1 = 19.1, 18.2,$  and  $17.0$  sec for  $\alpha, \beta,$  and  $\gamma$  carbon, respectively, temperature unspecified (probably  $38^\circ\text{C}$ , undegassed sample). Our averaged values are  $24$  sec at  $17^\circ\text{C}$  and  $27.5$  sec at  $55^\circ\text{C}$ . This shows that the effect of dissolved oxygen cannot be neglected.

laxation should be the same for  $^{15}\text{N}$  and  $^{13}\text{C}$ . Table 1 gives the correlation times  $\tau_c$  calculated for the measured  $^{13}\text{C}$  relaxation rates for some temperatures.

TABLE 1

CORRELATION TIMES AND SEPARATED  $^{15}\text{N}$  RELAXATION RATES IN LIQUID PYRIDINE.  $\tau_c$  IS AN AVERAGE CORRELATION TIME IF THE VECTOR OF INTEREST LIES IN THE PLANE OF THE RING.  $\tau_{c\perp}$  AND  $\tau_{j\perp}$  DESCRIBE THE MOTION OF THE AXIS PERPENDICULAR TO THE MOLECULAR PLANE

$T(^{\circ}\text{C})$	$\tau_c(\text{sec})$	$\tau_{c\perp}(\text{sec})$	$\tau_{j\perp}(\text{sec})$	$1/T_1^{\text{DD}}$ (intra) ( $\text{sec}^{-1}$ )	$1/T_1^{\text{CS}}$ (30 MHz) ( $\text{sec}^{-1}$ )
55	$1.65 \cdot 10^{-12}$	—	—	$2.04 \cdot 10^{-4}$	—
17	$1.89 \cdot 10^{-12}$	—	—	$2.34 \cdot 10^{-4}$	—
-4	$2.32 \cdot 10^{-12}$	—	—	$2.87 \cdot 10^{-4}$	$(3.6 \pm 1) \cdot 10^{-3}$
-25	$3.02 \cdot 10^{-12}$	$4.0 \cdot 10^{-12}$	$1.75 \cdot 10^{-14}$	$3.73 \cdot 10^{-4}$	$8.6 \cdot 10^{-3}$
-41	$5.66 \cdot 10^{-12}$	$6.2 \cdot 10^{-12}$	$1.20 \cdot 10^{-14}$	$7.00 \cdot 10^{-4}$	$1.3 \cdot 10^{-2}$
-55	$8.71 \cdot 10^{-12}$	$1.03 \cdot 10^{-11}$	$7.72 \cdot 10^{-15}$	$1.07 \cdot 10^{-3}$	$2.2 \cdot 10^{-2}$

In order to calculate  $1/T_1^{\text{DD}}$ (intra) for  $^{15}\text{N}$  from Eq. [20], we have to replace  $\gamma_{^{13}\text{C}}$  by  $\gamma_{^{15}\text{N}}$  and  $r_{\text{C-H}}$  by  $r_{\text{N-H}} = 2.135 \text{ \AA}$ . Furthermore, we have to multiply the resulting rate by a factor of two because of the two equivalent nearest-neighbor protons. (Because of the  $r^{-6}$  distance dependency, we can neglect the other protons.) The relaxation rates  $1/T_1^{\text{DD}}$ (intra) for  $^{15}\text{N}$  are given in Table 1.

The rate  $1/T_1^{\text{DD}}$ (inter) is substantially more difficult to estimate. In Fig. 1, the curve for  $\nu = 0 \text{ MHz}$  shows a relaxation rate minimum at a temperature of  $-41^{\circ}\text{C}$ . If we assume that at this temperature the relaxation rates due to spin-rotation interaction,  $1/T_1^{\text{SR}}$ , and DDI,  $1/T_1^{\text{DD}}$ , are equal, we get

$$1/T_1^{\text{SR}} = 1/T_1^{\text{DD}} = 4.4 \cdot 10^{-3} \text{ sec}^{-1} \text{ (at } -41^{\circ}\text{C)}.$$

With the calculated value  $1/T_1^{\text{DD}}$ (intra) (Table 1) at  $-41^{\circ}\text{C}$  and Eq. [19], we get for  $1/T_1^{\text{DD}}$ (inter) =  $3.4 \cdot 10^{-3} \text{ sec}^{-1}$  and for the ratio  $T_1^{\text{DD}}$ (intra)/ $T_1^{\text{DD}}$ (inter) = 5.3. This means that the relaxation rate due to *intermolecular* DDI is about five times larger than the one due to *intramolecular* DDI, or at least 85% of the dipolar rate is given by intermolecular DDI. We shall see later that this is a lower limit.

In Table 1 are also given the relaxation rates  $1/T_1^{\text{CS}}$  for 30 MHz and temperatures between  $-4$  and  $-55^{\circ}\text{C}$ . Now with Eq. [10] and the effective correlation times  $\tau_c$  found from the dipolar rate of the  $^{13}\text{C}$  measurement (shown in Table 1), we can calculate a tentative value for the anisotropy of the chemical shift  $\Delta\sigma$  noting that the correct value of  $\tau_c^{\text{eff}}$  for the chemical shift relaxation is probably larger because of the anisotropy of the motion (see below). We obtain an upper limit  $\Delta\sigma = 707 \text{ ppm}$ .

We have measured  $\Delta\sigma$  also directly from frozen solid pyridine. Figure 2 shows the powder pattern of the  $^{15}\text{N}$  in pyridine, typical for a nonaxially-symmetric chemical shift tensor. It can be seen in Fig. 2 that the frequency splitting due to ACS far exceeds the dipolar line broadening. Thus for  $^{15}\text{N}$  it will be possible to measure chemical shift anisotropies, even without decoupling techniques (19), in ordinary protonated samples in many cases if one works in high magnetic fields such as 75 kG. The spectrum (Fig. 2)

was taken at  $-105^{\circ}\text{C}$ , the central frequency was 31.985 MHz. The points are the measured intensity values while the curve was obtained by a computer fit giving  $\sigma_{xx} = -313$  ppm,  $\sigma_{yy} = -94$  ppm,  $\sigma_{zz} = 469$  ppm, and  $\sigma_{av}(\text{solid}) = 20.6$  ppm relative to liquid pyridine<sup>4</sup>. For further analysis, we treat the  $^{15}\text{N}$   $\hat{\sigma}$ -tensor in pyridine as if it was axially symmetric, the unique axis being the z-axis. With our definition above, we get  $\Delta\sigma = 672$  ppm. The comparison of the values for  $\Delta\sigma$  we get from solid pyridine and from the relaxation rate  $1/T_1^{\text{CS}}$  of the liquid shows only a small difference. Thus we can conclude that the molecular motion in liquid pyridine is not highly anisotropic. Comparison

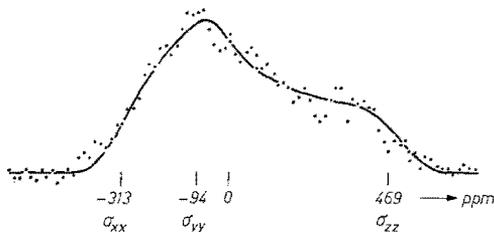


FIG. 2.  $^{15}\text{N}$  powder spectrum in pyridine at 32 MHz and  $-105^{\circ}\text{C}$ , reference liquid pyridine.

with the ACS for the corresponding carbons in benzene ( $\Delta\sigma_{^{13}\text{C}} = 180$  ppm (21)) shows that  $\Delta\sigma$  is much larger for nitrogen. This is also the case for  $^{15}\text{N}$  in nitrobenzene ( $\Delta\sigma = -398$  ppm) which should be compared with the  $^{13}\text{C}$  in the isoelectric benzoate ion (23) [see (18)].

From the powder spectrum we have only determined the diagonal elements of the chemical shift tensor but not the assignment of the individual elements to the principal axes. The nitrogen atom in pyridine forms two  $\sigma$ -bonds to the neighboring carbon atoms and is involved in the aromatic  $\pi$ -system. For carbons involved in the  $sp^2$  bonds and  $\pi$ -systems, a number of  $^{13}\text{C}$  chemical shift tensors have been studied (20–23). In all cases the most shielded  $\sigma$  component  $\sigma_{zz}$  was found perpendicular to the  $sp^2$  plane. We therefore assume that this is also the case for  $^{15}\text{N}$  in pyridine. This means that the unique axis of the  $\hat{\sigma}$  tensor is perpendicular to the molecular plane and thus parallel to the unique axis of the almost axially symmetric moment of inertia tensor. In order to calculate  $\tau_c^{\text{eff}}$  for relaxation through ACS from Eq. [11], we thus have to set  $\beta = 0^{\circ}$  which gives  $\tau_c^{\text{eff}} = \tau_{c\perp}$ . With the value  $\Delta\sigma = 672$  ppm from the solid-state measurement and the experimental relaxation rates  $1/T_1^{\text{CS}}$ , we can now obtain  $\tau_c^{\text{eff}} = \tau_{c\perp}$  by use of Eq. [10]. In Table I values  $\tau_{c\perp}$  are given for three temperatures. Together with the values for  $\tau_c$  obtained from the dipolar relaxation, we calculate an average ratio of  $\tau_{c\perp}/\tau_c = 1.2$ .

The quantity  $\tau_c$  can also be expressed in terms of  $\tau_{c\perp}$  and  $\rho$  by use of Eq. [11], where we have to set  $\beta = 90^{\circ}$  in this case. We then obtain  $\rho = \tau_{c\perp}/\tau_{c\parallel} = 1.4$ . This supports our statement above that the anisotropy of the motion is small. (For comparison, in benzene  $\rho = 3$  (24).) Actually, we should consider two different correlation times  $\tau_{c\perp}$ , one defined by the twofold axis through the nitrogen and the center of the molecule, and the other in the molecular plane perpendicular to the first one. The calculated moment of inertia around the first axis is  $\theta_1 = 1.436 \cdot 10^{-38}$  g-cm<sup>2</sup>, around the other  $\theta_2 = 1.427 \cdot 10^{-38}$  g-cm<sup>2</sup> (while the moment of inertia around the axis perpendicular to the molecular plane

<sup>4</sup> We have used the convention  $\sigma_{xx} \leq \sigma_{yy} \leq \sigma_{zz}$  for the principal axis system (20).

is  $\theta_z = \theta_{\parallel} = 2.816 \cdot 10^{-38} \text{ g-cm}^2$ ). Because the two moments of inertia are nearly the same, we can assume that both correlation times  $\tau_{c\perp}$  are equal in good approximation. From Eq. [15] and the values  $\tau_{c\perp}$  in Table 1, we can calculate  $\tau_{j\perp}$ ; the results are given in Table 1. Equation [15] is only valid if  $(\tau_j)_i \ll (\tau_c)_i$ . In Table 1 we see that this condition is fulfilled and the diffusion model should be a good description at the lower temperatures. Equation [16] gives a formula for the calculation of  $\tau_{j\parallel}$ .

For the calculation of the spin-rotation constants  $C_{ii}$ , from Eq. [9] we make use of the fact that the two moments of inertia are almost equal  $\theta_1 \approx \theta_2 \approx \theta_{\perp}$ . Therefore, it is not necessary to know which one of the  $\sigma$  components  $\sigma_{xx}$  or  $\sigma_{yy}$  belongs to  $\theta_1$  and which one to  $\theta_2$ . With a spin-rotation constant  $C_{N_2} = (22 \pm 1) \cdot 2\pi \text{ kHz} = (138.23 \pm 6.3) \text{ kHz}$  (10), a moment of inertia  $\theta_{N_2} = 1.5 \cdot 10^{-39} \text{ g-cm}^2$ , and a relative isotropic shift  $\delta = -8 \text{ ppm}$  (10) between  $^{15}\text{N}_2$  and  $^{15}\text{N}$  in liquid pyridine, we get from Eq. [9] for the components of the spin-rotation tensor the values given in Table 2. Values for  $C_{\perp}$  and  $\Delta\sigma$  defined above are also given. The absolute values of the components  $C_{ii}$  depend strongly on  $C_{N_2}$ . On the other hand, even an error of several ppm for  $\delta_i$  does not change  $C_{ii}$  appreciably.

TABLE 2  
CHEMICAL SHIFT AND SPIN-ROTATION  
TENSOR IN PYRIDINE.  $z$ -AXIS PERPENDI-  
CULAR TO THE MOLECULAR PLANE

	ppm		kHz
$\hat{\sigma}_{xx}$	$-313 \pm 10$	$C_{xx}$	$16.5 \pm 1$
$\hat{\sigma}_{yy}$	$-94 \pm 10$	$C_{yy}$	$11.5 \pm 1$
$\hat{\sigma}_{zz}$	$+469 \pm 10$	$C_{zz}$	$-0.6 \pm 1$
$\Delta\sigma$	$672 \pm 20$	$C_{\parallel} = C_{zz}$	$-0.6 \pm 1$
		$C_{\perp}$	$14 \pm 1$

Independently, we can obtain values for  $C_{\parallel}$  and  $C_{\perp}$  from our relaxation data by use of Eqs. [17] and [18]. We note that according to Eq. [17], the product of the relaxation rates should be temperature independent. The uncertainty in the rate  $1/T_1^{\text{CS}}$  is small because it was obtained from the frequency dependence of the total relaxation rate. To estimate the rate  $1/T_1^{\text{SR}}$  is much more difficult. At a temperature of  $-41^\circ\text{C}$ , we had already assumed above  $1/T_1^{\text{DD}} = 1/T_1^{\text{SR}}$  for  $\nu = 0 \text{ MHz}$ . Therefore, at this temperature, we get the product  $(1/T_1^{\text{CS}} \cdot 1/T_1^{\text{SR}})^{1/2} = 7.6 \cdot 10^{-3} \text{ sec}^{-1}$ . If we assume that at a temperature of  $-4^\circ\text{C}$  the relaxation rate for the curve  $\nu = 0 \text{ MHz}$  in Fig. 1 is due only to spin-rotation interaction, we get a very similar value for the product  $(1/T_1^{\text{CS}} \cdot 1/T_1^{\text{SR}})^{1/2} = 7.4 \times 10^{-3} \text{ sec}^{-1}$ . This value together with  $\Delta\sigma = 672 \text{ ppm}$  and Eqs. [17] and [18] results in spin-rotation constants  $C_{\perp} = 24.4 \text{ kHz}$  and  $C_{\parallel} = 4.6 \text{ kHz}$ . The agreement with the values we find from the  $\hat{\sigma}$  components in the solid is not very good, especially compared with results we obtained for  $^{15}\text{N}$  in nitrobenzene (18). It should be noted that the discrepancy is even worse if  $\sigma_{zz}$  is not assigned to the axis perpendicular to the plane of the ring. In pyridine, the values from the relaxation rates are too large. Essentially, two reasons can be given for this. As we see from Fig. 2, in the pyridine case we do not really have an axially symmetric shift tensor. The more important reason, however, is the uncertainty

of the relaxation rate  $1/T_1^{\text{SR}}$ . In order to obtain agreement with the spin-rotation constants given in Table 2, this rate must be smaller than we assumed so far by a factor of two. The frequency-independent relaxation rate is the sum of  $1/T_1^{\text{SR}} + 1/T_1^{\text{DD}}$ . The dipolar rate is dominated by the *intermolecular* contribution. Then the correlation times relevant for  $1/T_1^{\text{SR}}$  and  $1/T_1^{\text{DD}}$  are not determined by the same rotational diffusion process. This would only be true for  $1/T_1^{\text{SR}}$  and  $1/T_1^{\text{DD}}$ (intra). Therefore, it is difficult to determine  $1/T_1^{\text{SR}}$  from our data, and the discrepancy noted above is not surprising. In fact, we get agreement if we assume that the dipolar rate is somewhat larger than we had estimated before. This means that even at temperatures up to +30°C, the rate due to intermolecular DDI cannot be completely neglected compared with the spin-rotational relaxation rate. This also means that about 90 per cent of the dipolar rate is due to the *intermolecular* contribution. This statement is possible only because we have combined frequency-dependent  $^{15}\text{N}$  relaxation studies with solid-state  $^{15}\text{N}$  and  $^{13}\text{C}$  relaxation measurements.

#### V. SUMMARY AND OUTLOOK

Our results can be summarized as follows:

(1) We have demonstrated that in favorable cases  $^{15}\text{N}$  anisotropic chemical shifts can be determined in the solid without decoupling if one works in high magnetic fields such as 75 kG.

(2) Comparison of the relaxation mechanisms in liquids for  $^{15}\text{N}$  and  $^{13}\text{C}$  shows that basically the same mechanisms are operative. Detailed analysis shows, however, that the relative importance of the individual mechanisms is different for the two nuclei. In particular, relaxation due to anisotropic chemical shift is much more important for  $^{15}\text{N}$ . The dipolar relaxation rate is not always dominated by the intramolecular contribution. We have seen that in pyridine the intermolecular dipole-dipole interaction gives a significant contribution to the total relaxation over the whole temperature range measured and strongly dominates the dipolar rate. It can be anticipated that intermolecular dipole-dipole interaction will be important for other nitrogens with nonbinding orbitals if no protons are directly attached.

(3) The present study of pyridine shows that detailed information can be gathered by combining  $^{15}\text{N}$  and  $^{13}\text{C}$  measurements in the solid and liquid state.

(4) We have demonstrated that anisotropic chemical shift is an important relaxation mechanism for  $^{15}\text{N}$  in pyridine. The relaxation rate due to ACS can easily be determined from frequency-dependent  $T_1$  measurements, even in protonated samples. A similar situation can be anticipated for other aromatic heterocycles which are of great biological importance.  $^{15}\text{N}$  relaxation measurements can then be used to study dynamic properties of biological interest. This is possible because, from the relaxation rates and the known values for  $\Delta\sigma$ , we obtain the correlation times  $\tau_c$  without further assumptions (see Eq. [10]). This has considerable advantages over studying  $^{14}\text{N}$ : (a) Because of the low natural abundance, it is possible to use  $^{15}\text{N}$  as a label, and (b) in biological systems, the correlation times are often in a range  $\tau_c \approx 1/\omega_0$  giving the maximum relaxation rate. For  $^{14}\text{N}$ , where quadrupolar relaxation is dominant, the corresponding  $T_1$  will be of the order of a few  $\mu\text{sec}$  only, as calculated from the known quadrupole coupling constant (25) for pyridine. This makes signal detection difficult because the corresponding linewidth is of the order of several hundred kHz. For  $^{15}\text{N}$ , on the other hand, the minimum  $T_1$  can be calculated from our data to be about 0.1

sec, corresponding to a linewidth of the order of 10 Hz only, meaning relatively favorable conditions for signal averaging.

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