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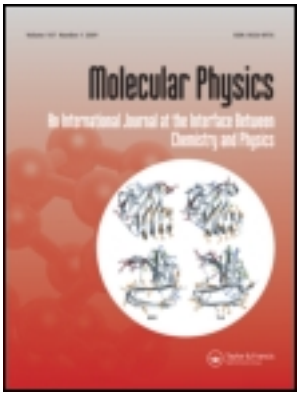

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Nuclear relaxation and molecular properties

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MOLECULAR PHYSICS, 1971, VOL. 22, NO. 2, 273–287

Nuclear relaxation and molecular properties Part V. Molecular dynamics of liquid pyridine from ^{2}D and ^{14}N nuclear quadrupolar relaxation†

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(*Received* 28 *June* 1971)

The dynamic structure of liquid pyridine has been studied by analysing the deuterium and nitrogen ^{14}N quadrupolar relaxation data of selectively labelled substances. The molecular motions are anisotropic; the anisotropy changes from ' solid like ' (faster rotation about the axis perpendicular to the molecular plane) to ' gas like ' (faster rotation about an in-plane axis) behaviour as the temperature increases. The 'solid like ' region extends over most of the temperature range where pyridine is liquid (at *ca.* atmospheric pressure). At low temperatures the molecular re-orientations may be described as a rotational diffusion process. Some indication of a possible motional coherence is found.

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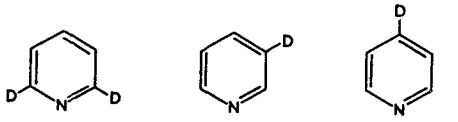
1. INTRODUCTION

The analysis of nuclear relaxation data is a powerful method for studying the microdynamic properties of liquids [2].

For nuclei with spin $I \geqslant 1$, relaxation occurs principally through the quadrupolar mechanism, i.e. modulation of the interaction between the nuclear quadrupole moment and the electric field gradient at the nucleus, by the molecular motions. Quadrupolar relaxation (QR) data are thus particularly well suited for analysis, as the other relaxation mechanisms may be neglected (except when strongly paramagnetic substances are present). In addition, the problem is further simplified by the fact that translational motions do not contribute to the process. Thus, *quadrupolar labelling* is a powerful tool for studying the details of molecular rotational motions. Recent studies of ^{2}H, ^{14}N, ^{17}O, and ^{35}Cl QR times lead to a detailed description of anisotropic molecular re-orientation in acetonitrile [3], CCl_3CN [4], dimethylformamide [5], methylacetylene [6], chloroform [7], isobutylene [8] and ND_3 [33].

We present here a study of the molecular re-orientation in liquid pyridine using deuterium and nitrogen-14 QR time measurements on specifically labelled molecules: the α, α'-d_2(I), β-d_1(II) and γ-d_1(III) pyridines§:



(I) α,α'-d_2 (II) β-d_1 (III) γ-d_1

† For previous papers in this series, see [1].

‡ Equipe de Recherche Associée au C.N.R.S.

§ In the following, one may assume that the isotope effects on molecular properties in pyridine and in I, II and III are negligible (see also the moments of inertia [25]).

Pyridine is a particularly interesting molecule since it exhibits the anisotropy of molecular re-orientations of a ' flat ' molecule (very different cross-sections in the molecular plane and in a plane perpendicular to the molecule).

2. Results

The temperature dependence of the QR times T_q of the α, β and γ deuterons in I, II and III and of the nitrogen-14 nucleus has been measured for pure liquid pyridine between $-20°C$ and $+80°C$. At 30°C, the deuterium relaxation times are respectively equal to 1·14, 1·17 and 1·20 s for the α, β and γ positions. The differences are not significant and the three relaxation times may be considered as being equal. The mean value, 1·17 s, is slightly higher than the values measured for d_5-pyridine by spin–echo (1·04 s; [9]) and by adiabatic fast passage (1·11 s; [10]) methods. At 25°C, the ^{14}N relaxation time is 1·65 ms (literature values: 1·70, 1·49, 1·62, 1·48 ms [11]).

In the extreme narrowing conditions (which are fulfilled here) one has [12]

$$T_q^{-1}=\frac{3}{8}\left(\frac{e^2q_zQ}{\hbar}\right)^2\left(1+\frac{\eta^2}{3}\right)\tau_q \tag{1}$$

(q_z: main component of the electric field gradient with asymmetry parameter $\eta=(q_x-q_y)/q_z$ at the nucleus with nuclear quadrupole moment Q; x, y, z is the principal axis system which diagonalizes the field gradient tensor).

Considering the molecular motion represented by the quadrupolar correlation time τ_q as a thermally activated process and using the Eyring rate equation gives

$$\tau_q^{-1}=KT\exp(-\Delta G^{\neq}/RT), \tag{2}$$

where $K=k_Bf/h$ (k_B Boltzmann's constant; h: Planck's constant; f: frequency factor, taken equal to unity) and $\Delta G^{\neq}$ is the free energy of activation of the correlation time for molecular re-orientation.

The temperature dependence $T_q/T=f(1/T)$ of the ^2D and ^{14}N QR times is shown in figure 1.

Using $\Delta G^{\neq}=\Delta H^{\neq}-T\Delta S^{\neq}$, one has

$$\log(T_q/T)=K'-\frac{\Delta H^{\neq}}{4\cdot57\,T} \tag{3}$$

with

$$K'=\log K-\log\frac{3}{8}\left(\frac{e^2q_zQ}{\hbar}\right)^2\left(1+\frac{\eta^2}{3}\right)+\frac{\Delta S^{\neq}}{4\cdot57}. \tag{4}$$

If the quadrupolar coupling constant χ ($\chi=e^2qQ/h$ in Hz) and the asymmetry parameter η in equation (1) are known, a plot of $\log(T_q/T)=f(1/T)$ should be a straight line whose slope and intercept, respectively, yield the enthalpy of activation $\Delta H^{\neq}$ and the entropy of activation $\Delta S^{\neq}$.

No accurate measurements of the α, β and γ deuteron quadrupolar coupling constants χ_D in pyridine are presently available.

Measurements on completely deuterated pyridine in nematic phase gave

$$\chi_\alpha=206\pm12\text{ kHz},\qquad \chi_\beta=211\pm12\text{ kHz},\qquad \chi_\gamma=199\pm12\text{ kHz, [13]}$$

whereas in similar conditions compound II gave $\chi_\beta=197\pm8$ kHz [14]. Calculations using an *ab initio* wave function [15] for pyridine yield $\chi_D\sim280$ kHz

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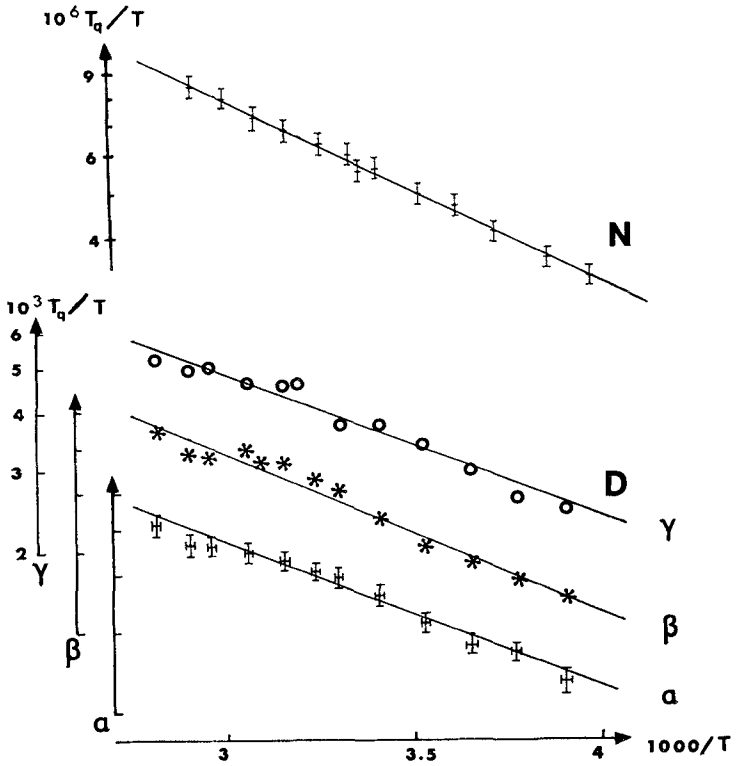

Figure 1. Temperature dependence log $(T_q/T)=f(1/T)$ of the α, β, γ deuterium and nitrogen-14 nuclear quadrupolar relaxation times in liquid pyridine (T : °K; T_q : s).

and $\eta_D=0\cdot03$ whatever the position of the deuteron on the pyridine ring [16 a]. Such calculations are expected to give reliable relative values of χ even if the absolute values obtained are in error because of a low quality wave function [16 b]. The values $\chi_D=193$ kHz ($\eta_D=0$) and $\chi_D=194$ kHz $-196\cdot5\pm1\cdot3$ kHz have been obtained from N.M.R. studies of deutero-benzene in the solid state [17] and in nematic phase respectively [18]. The results presented here have been obtained with $\chi_D=193$ kHz and $\eta_D=0$; we have checked that using the other possible values cited above does not alter our results (see also below). The values

$$\chi_N=4\cdot88 \text{ MHz } (\eta_N=0\cdot405) \text{ [19] and } \chi_N=4\cdot584 \text{ MHz } (\eta_N=0\cdot396) \text{ [20]}$$

have been obtained for the nitrogen quadrupolar coupling constant in pyridine in the gas phase and in the solid state respectively.

As in other cases it has been found that the quadrupolar coupling constants are similar in the solid state and in the liquid phase [21, 22], we have used the solid state values of χ_N and η_N [20] for liquid pyridine.

It is then possible to calculate the activation parameters $\Delta H^{\neq}$, $\Delta S^{\neq}$ and $\Delta G_{343}{}^{\neq}$ (at 303°K) for the QR times of the α, β, γ deuterons and of the ^{14}N nucleus from a log $(T_q/T)=f(1/T)$ plot using equations (3) and (4). The values obtained are listed in table 1.

It is seen that the temperature dependence and the corresponding activation parameters of the ^2D and ^{14}N relaxation times, although not very different,

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	$\Delta H^{\neq}$ (kcal/mole)	$\Delta S^{\neq}$ (e.u.)	$\Delta G_{303}{}^{\neq}$ (kcal/mole)
D_α	1·4	0·0	1·4
D_β	1·55	+0·5	1·4
D_γ	1·4	+0·2	1·4
^{14}N	1·8	+1·3	1·5
D_a	2·8	+0·4	2·7
D_b	2·5	−0·4	2·6
D_c	0·4	−6·4	2·3
$D_\parallel$	0·4	−6·4	2·3
$D_\perp$	2·5	−0·1	2·5

Table 1. Activation parameters of the deuterium (D_α, D_β, D_γ) and nitrogen-14 nuclear quadrupolar relaxation times obtained from the temperature dependence shown in figure 1, and activation parameters of the rotational diffusion constants D_a, D_b, D_c, $D_\parallel$ and $D_\perp$ obtained from the temperature dependence shown in figure 3 (see also text).

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point nevertheless to the presence of anisotropic motion in liquid pyridine, independently from any reorientational model. In order to further analyse the details of molecular reorientation it is necessary to assume a theoretical motional model and to check its compatibility with the experimental results. We shall successively consider a rotational diffusion model and an inertial rotation model.

3. Discussion

3.1. *Rotational diffusion model*

In the rotational diffusion model, the molecular motions are described by a rotational diffusion tensor. In the molecular principal axis system a, b, c, which diagonalizes the diffusion tensor, the re-orientations are represented by three diffusion constants D_a, D_b and D_c with respect to the a, b and c axes.

Describing the molecular motions by D_a, D_b and D_c, the relaxation time of a quadrupolar nucleus is given by

$$\frac{1}{T_q}=\frac{3}{40}\left[\frac{2I+3}{I^2(2I-1)}\right]\left(\frac{e^2qQ}{\hbar}\right)^2 f(\mathbf{\Omega}, \mathbf{D}), \tag{5}$$

where $f(\mathbf{\Omega}, \mathbf{D})$ is the function describing the re-orientations and depending on the angles $\mathbf{\Omega}$ between rotational diffusion and field gradient axes, and on the rotational diffusion tensor $\mathbf{D}$; I is the nuclear spin. For a planar asymmetric rotor-like pyridine and for a nucleus of spin 1, the expression of the quadrupolar relaxation time in the diffusional principal axis system is given by [23]:

$$\begin{aligned}\frac{1}{T_q}=\frac{3}{32D_{\mathrm{R}}}\left(\frac{e^2q_zQ}{\hbar}\right)^2\Big\{&[4\,D_a+(\eta-1)^2\,D_b+(\eta+1)^2\,D_c]\cos^2\Phi\\&+[4\,D_b+(\eta-1)^2\,D_a+(\eta+1)^2\,D_c]\sin^2\Phi\\&-\frac{1}{3}(\eta-3)^2\left[\frac{(D_a-D_b)^2}{(D_c+D_s)}\right]\cos^2\Phi\sin^2\Phi\Big\},\end{aligned} \tag{6}$$

with

$D_R = 3(D_a D_b + D_b D_c + D_c D_a)$,

$D_s = (1/3)(D_a + D_b + D_c)$,

Φ: angle between the in-plane principal axes z of the field gradient and a of the diffusion tensor.

Neglecting the isotope effects, the diffusional principal axis system is taken as shown in figure 2 (with the c axis perpendicular to the molecular plane)†. For the nitrogen nucleus (spin 1), the angle Φ is zero as q_z^N lies along the a axis [24]. Then, introducing $\Phi = 0°$ and $\eta = 0{\cdot}396$ [20] in equation (6) the expression for the nitrogen quadrupolar relaxation time is

$$\frac{1}{T_N} = \frac{3\pi^2}{8\,D_R}\chi_N{}^2(4\,D_a + 0{\cdot}3648\,D_b + 1{\cdot}9488\,D_c) \tag{7}$$

with $\chi_N = (e^2 q_z{}^N Q_N/h) = 4{\cdot}584$ MHz.

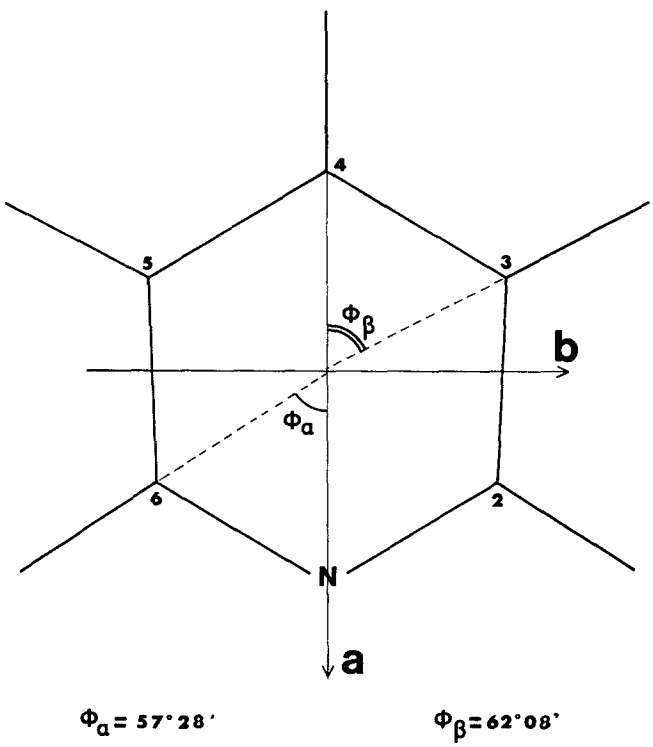

Figure 2. Geometry and principal axis system a, b, c, (c axis perpendicular to the molecular plane) of the pyridine molecule.

For the deuterium nuclei (spin 1), q_z^D may be considered as lying along the C–D bond axis. The angles Φ depend on the position α, β or γ of the deuterium atom on the pyridine ring. Using the experimental geometry of the molecule [25] (figure 2) one has $\Phi_\alpha = 57°\,28'$, $\Phi_\beta = 62°\,08'$, $\Phi_\gamma = 0°$. Then, with these values for Φ and with $\eta_D = 0$, equation (6) leads to the expressions for the

† In fact we shall see below that pyridine may be considered to a good approximation as being a planar symmetric rotor (see also the moments of inertia [25]).

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quadrupolar relaxation time of the α, β and γ deuterons:

$$\frac{1}{T_{D_\alpha}}=\frac{9\pi^2}{8\,D_R}\chi_D{}^2\left[0\cdot2892\,(D_a+D_s)+0\cdot7108\,(D_b+D_s)-0\cdot2056\,\frac{(D_a-D_b)^2}{D_c+D_s}\right], \quad (8)$$

$$\frac{1}{T_{D_\beta}}=\frac{9\pi^2}{8\,D_R}\chi_D{}^2\left[0\cdot2185\,(D_a+D_s)+0\cdot7815\,(D_b+D_s)-0\cdot1707\,\frac{(D_a-D_b)^2}{D_c+D_s}\right], \quad (9)$$

$$\frac{1}{T_{D_\gamma}}=\frac{9\pi^2}{8\,D_R}\chi_D{}^2(D_a+D_s) \quad (10)$$

with $\chi_D=193$ kHz.

We thus have a system of four equations with three unknowns, the three diffusion constants D_a, D_b and D_c. This system has been solved at several temperatures ($-20°$ to $+80°$C in steps of $10°$) using the relaxation times given by the activation straight lines of figure 1 and taking into account 5 per cent errors for the relaxation times of D and N.

At each temperature, a set of values (10 to 30) of the diffusion constants is obtained on which a statistical analysis has been performed (see §5 for more details). At 30°C, the results are as follows†: $D_a=7\cdot3$, $D_b=8\cdot2$ and $D_c=14\cdot6\times10^{10}\,s^{-1}$.

The difference between D_a and D_b is small and becomes significant only at low temperatures. We have already seen above (see also figure 1) that the relaxation times of the deuterons are practically the same for the three positions on the pyridine ring. We may thus consider that within the temperature range studied, the reorientations about the a and b axis are isotropic and that the pyridine molecule is almost a planar (oblate) symmetric rotor. Its motions are then described by two rotational diffusion constants: $D_\parallel$ for the rotations about an axis parallel to the former c axis and $D_\perp$ for the rotations about an in-plane axis, perpendicular to the $\parallel$ axis.

Equations (7)–(10) now become

$$\frac{1}{T_N}=\frac{3\pi^2}{2}\chi_N{}^2\,\frac{4\cdot3648\,D_\perp+1\cdot9488\,D_\parallel}{12\,D_\perp(D_\perp+2\,D_\parallel)}, \quad (11)$$

$$\frac{1}{T_D}=\frac{3\pi^2}{2}\chi_D{}^2\,\frac{5\,D_\perp+D_\parallel}{12\,D_\perp(D_\perp+2\,D_\parallel)}. \quad (12)$$

We thus have a system of two equations with two unknowns. The T_D values used for solving this system have been taken as the mean of the three values measured for the α, β and γ positions. At 30°C, the following values are obtained: $D_\perp=8\cdot5\times10^{10}\,s^{-1}$ and $D_\parallel=13\cdot3\times10^{10}\,s^{-1}$‡. Figure 3 shows a semi-logarithmic

† Introducing $\chi_{D\alpha}=206$ kHz, $\chi_{D\beta}=211$ kHz, $\chi_{D\gamma}=199$ kHz one obtains, respectively, 8·2, 6·7 and 19·0 $10^{10}\,s^{-1}$ for D_a, D_b, D_c at 30°C.

‡ Calculations with $\chi_D=197$ kHz, $\eta_D=0$ give $D_\perp=8\cdot0\times10^{10}$ and $D_\parallel=15\times10^{10}\,s^{-1}$. If we take $\eta_D=0\cdot06$ and $\chi_D=181$ kHz as suggested by Fung and Wei [26] for C_6D_6 one finds that whereas $D_\perp$ increases with temperature (4 to $31\times10^{10}\,sec^{-1}$ from $-20°$ to $+80°$C), a negative $\Delta H^{\neq}$ is obtained for $D_\parallel$ (6 to $4\cdot1\times10^{10}\,s^{-1}$ from $-20°$ to $+80°$C). When χ_D larger than 193 kHz is used $\Delta H^{\neq}$ for $D_\parallel$ increases slightly. Thus, whereas the anisotropic character of the motion is not affected, the intersection region of the curves in figure 3 is displaced slightly towards higher temperatures when the value of χ_D is increased.

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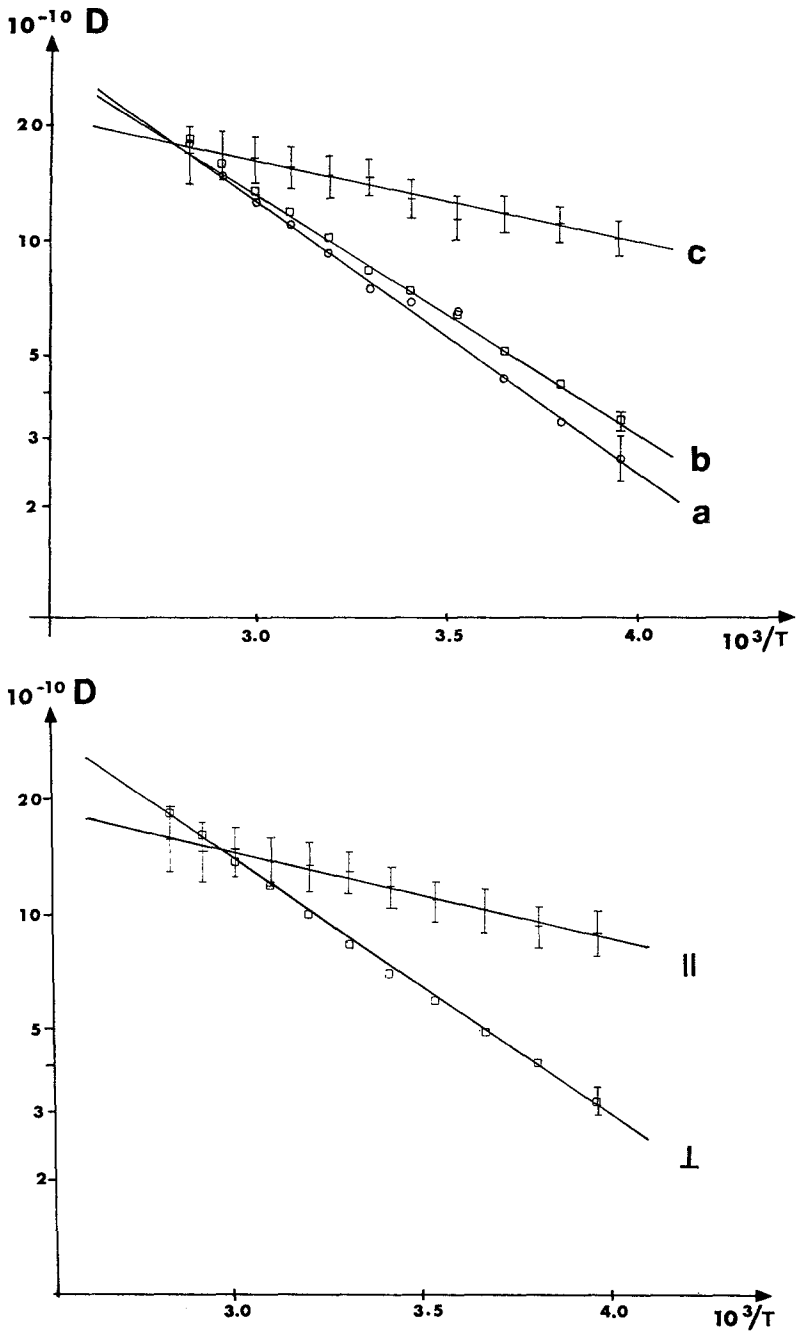

Figure 3. *Above:* Semi-logarithmic plot of the temperature dependence of the principal diffusion constants D_a, D_b and D_c in pyridine (D: s^{-1}; T: °K); *Below:* semi-logarithmic plot of the temperature dependence of $D_{\parallel}$ and $D_{\perp}$ in pyridine (D: s^{-1}; T: °K).

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plot of the temperature dependence $D=f(1/T)$. Using the Eyring rate equation the activation parameters $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the rotational diffusion constants may be obtained:

$$D=KT\exp(-\Delta G^{\neq}/RT). \tag{13 a}$$

$\Delta H^{\neq}$ and $\Delta S^{\neq}$ are obtained in the normal way from a plot $\log(D/T)=f(1/T)$. One has

$$\log D=10\cdot 32+\log T-(\Delta H^{\neq}/4\cdot 57\ T)+(\Delta S^{\neq}/4\cdot 57) \tag{13 b}$$

The results are given in table 1.

Using an Arrhenius law of activation, one has

$$D=D_0\exp(-E_a/RT), \tag{14}$$

where E_a is the Arrhenius activation energy and D_0 the frequency factor. E_a and D_0 may be obtained from a plot of $\log D=f(1/T)$. The results are given in table 2 together with some literature data.

Compound	$E_{a\parallel}$ (kcal/mole)	$E_{a\perp}$ (kcal/mole)	$D_{\parallel}$ (s^{-1})†	$D_{\perp}$ (s^{-1})†	T (°C)	Ref.
Pyridine	1·0	3·1	$1\cdot 3\times 10^{11}$	$8\cdot 5\times 10^{10}$	30°	Present work
CH_3CN	0·7	2·0	$1\cdot 6\times 10^{12}$	$1\cdot 6\times 10^{11}$	30°	[3]
CH_3CN	0·8	1·7	$1\cdot 2\times 10^{12}$	$1\cdot 35\times 10^{11}$	25°	[3]
$CH_3C\equiv CH$	0·5	1·7	$1\cdot 83\times 10^{12}$	$1\cdot 3\times 10^{11}$	−30°	[6]
$HCCl_3$	0·7	1·6	$1\cdot 8\times 10^{11}$	$0\cdot 96\times 10^{11}$	20°	[7]

† At temperature T.

Table 2. Arrhenius activation energy and rotational diffusion constant for various liquids.

From the results in tables 1 and 2 and in figure 3 it is seen that within the rotational diffusion model, the molecular motions of pyridine in the liquid phase are *anisotropic*, the re-orientations being at 30°C about twice as fast about the axis perpendicular to the molecular plane (D_c or $D_{\parallel}$) as about an in-plane axis (D_a, D_b or $D_{\perp}$). This relatively small factor may explain why anisotropic reorientation has not been detected in measurements performed at room temperature.

The anisotropy of the motions increases at lower temperatures (at −20°C: $D_a=2\cdot 7$, $D_b=3\cdot 3$, $D_c=10\cdot 1\times 10^{10}$; s^{-1}; see figure 3) as one comes nearer to the solid state (m.p. −42°C) where one expects rotation about the c or $\parallel$ axis to be largely predominant as in solid benzene [27, 28]. As the temperature is raised above 30°C one approaches an *isotropic region* at about 60–90°C. At higher temperatures the anisotropy is expected to be *reversed*: $\parallel$ rotations become *slower* than $\perp$ rotations as is found in the gas phase.

It is probable that in liquid benzene [29, 30] the molecular re-orientations are also anisotropic and comparable to those in pyridine, but a detailed analysis using deuterium relaxation in C_6D_6 is not possible, since there is only one kind of nucleus and there are two unknowns ($D_{\parallel}$ and $D_{\perp}$). It is worth noting that the D_c (or $D_{\parallel}$) motions are largely entropically controlled (table 1); this may

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indicate some coherence of the re-orientations in pyridine, as it seems to be the case in benzene [28, 31].

The data in table 2 also show that the diffusion constants for pyridine resemble those of a rigid molecule like chloroform; however, when internal rotations are present as in CH_3CN and $CH_3C{\equiv}CH$ much faster rotation about the internal rotation axis is observed. The E_a values are comparable, but their significance is not clear and they may be quite inaccurate [32–34].

3.2. *Inertial rotation model*

In this model, molecular re-orientation in liquids is treated as gas-like rotation. *Unconditional inertial rotation* has been treated within classical mechanics [35] and a general quantum mechanical formulation has been given recently [36]. It assumes that the intermolecular viscous forces are weak enough to let any molecule rotate inertially for some time in an homogeneous lattice.

However, this model is found to be incomplete, and it is necessary to use a *conditional inertial rotation* model in order to describe the experimental results, especially the temperature dependence. The structure of the lattice becomes important as it is assumed that inertial rotation only takes place at the site of lattice defects. Such a process is non-markovian, the probability of inertial-rotation depending on the preliminary formation of a defect in the liquid structure at the site of the molecule [37] (see also the original Anderson treatment [38]). Only the case of a ' simple defect ' (condensed and expanded lattices where the molecule respectively cannot and can rotate inertially) has been treated in detail, but it has been pointed out, that defects of different structure should be considered in a complete theory, as they are expected to contribute to different modes of inertial rotation [37]. We shall now apply this ' simple defect ' model to pyridine, assuming that it is a symmetrical rotor, since only this case has been considered theoretically [37].

With the assumption that the population of defects P_D increases with temperature and that their formation is an activated process, the quadrupolar relaxation time of a spin 1 nucleus is given by [37]:

$$\frac{1}{T_q}=\frac{3}{8\sqrt{\pi}}\left(\frac{eqQ}{\hbar}\right)^2\left(\frac{\pi I_\perp}{3kT}\right)^{1/2}\left(\frac{\alpha}{1+2\alpha}\right)^{1/2}f(\theta,\alpha)P_D^{-1}, \tag{14}$$

with

$$\alpha=I_\perp/I_\parallel \tag{15}$$

the ratio of the moment of inertia about an axis perpendicular to the symmetry axis, to the moment of inertia about the symmetry axis:

$$f(\theta,\alpha)=\frac{9}{4}\left(\frac{\sin^4\theta}{1+2\alpha}\right)+\frac{18\sin^2\theta\cos^2\theta}{5+\alpha}+\frac{1}{4}(1-3\cos^2\theta)^2 \tag{16}$$

(θ: angle between the molecular symmetry axis and the axis of the field gradient)

$$P_D=P\exp(-E_a/RT) \tag{17}$$

(P is a constant; E_a: activation energy of defect formation, i.e. lattice expansion).

In the case of pyridine, with $\theta_D=\theta_N=0$, $\chi_D=193$ kHz, $\chi_N=4\cdot584$ MHz, $I_\perp=1\cdot41\times10^{-38}$ g cm^2† and $I_\parallel=2\cdot84\times10^{-38}$ g cm^2 [25] the temperature

† $I_\perp$ is taken as the average of I_a ($1\cdot39\times10^{-38}$ g cm^2) and I_b ($1\cdot44\times10^{-38}$ g cm^2) [25].

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dependence of the deuterium and nitrogen quadrupolar relaxation times are

$$T_D^{-1} = 1 \cdot 82\, P^{-1} T^{-1/2} \exp(E_a/RT) \tag{18}$$

or

$$\log(T_D/T^{1/2}) = -\log(1 \cdot 82/P) - (E_a/4 \cdot 57\, T), \tag{19}$$

and

$$\log(T_N/T^{1/2}) = -\log(1024/P) - (E_a/4 \cdot 57\, T). \tag{20}$$

In fact, as the nitrogen asymmetry parameter η_N is not zero, equations (14) and (20) do not strictly apply. However, the contribution of η_N is probably small and we shall assume here that as a first approximation, equation (20) may be used.

The slope and intercept of a plot $\log(T_D/T^{1/2}) = f(1/T)$ respectively yield: $E_a = 1 \cdot 8$ kcal/mole and $P = 2 \cdot 3$. From a similar plot of $\log(T_N/T^{1/2}) = f(1/T)$, $E_a = 2 \cdot 1$ kcal/mole and $P = 3 \cdot 4$ is obtained. The constant P is related to the activation entropy of lattice formation. In the 'simple defect' theory, the values of P obtained from deuterium and nitrogen nuclear relaxation should be the same. However, as was already stated above for the rotational diffusion model, it is not known whether or not the differences in E_a and P values obtained from T_D and T_N are significant, since activation parameters may be quite inaccurate [32–34].

3.3. *Discussion of the validity of the two re-orientation models*

In order to test the applicability of the *rotational diffusion model*, the following parameter (χ test) has been used [3–5, 8, 23]:

$$\chi_i = (\tau_d/\tau_f)_i = (5/18\, D_i)(kT/I_i)^{1/2}, \tag{21}$$

where $(\tau_d)_i = 1/6\, D_i$ is the experimental correlation time of a diffusional rotor for re-orientation about the axis i and $(\tau_f)_i = (5I_i/3kT)^{1/2}$ is the theoretical re-orientation time in the gas phase of a spherical free rotor having a moment of inertia I_i about the axis i.

If $\chi_i \gg 1$ the reorientations are adequately described by the rotational diffusion model (small-angle Brownian diffusion). When $\chi \simeq 1$ the inertial effects predominate and the molecule undergoes large-angle inertial re-orientation. For $\chi \gtrsim 5$, the reorientation angle is $\lesssim 5°$, whereas for $\chi \lesssim 3$ the angle is $\gtrsim 10°$ [4]. The results for pyridine are listed in table 3.

Thus: (1) the re-orientation of the pyridine molecule in the liquid state about an axis in the molecular plane is adequately described by the rotational diffusion model at low temperatures (χ_a, χ_b, $\chi_\perp > 1$); however the inertial contribution becomes important as one approaches the boiling point. (2) The motion

T (°K)	χ_a	χ_b	χ_c	$\chi_\perp$	$\chi_\parallel$
253·0	16·5	13·2	3·1	13·4	3·4
303·0	6·6	5·8	2·3	5·6	2·5
353·0	2·8	2·7	2·2	2·7	2·3
388·5	2·1	2·1	2·0	1·8	2·0

Table 3. Values of the χ parameter for reorientation of pyridine at different temperatures ($T = 388 \cdot 5$K: boiling point).

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about the c or $\parallel$ axis is less well described by the diffusion model; reorientation occurs through angular jumps of about 15°; inertial effects become more and more important with respect to frictional force as the temperature increases. (3) Purely inertial effects would lead to faster reorientation about an in-plane axis since $(\tau_f)_\perp < (\tau_f)_\parallel$, whereas one finds $(\tau_d)_\perp > (\tau_d)_\parallel$. Thus, the relative rates of the $\perp$ and $\parallel$ motions are in the reverse order with respect to the free rotor in the gas phase, but the inertial contribution is large or dominant for that re-orientational mode ($\parallel$) which corresponds to the larger moment of inertia ($I_\parallel$).

The different E_a and P values obtained above by applying the '*simple defect*' *conditional inertial rotation model* probably point to the inability of this model to describe the reorientations of pyridine molecule in liquid phase. The 'simple defect' model is sufficient for describing the motions in liquid ammonia [37]. Both ammonia and pyridine (in the present approximation) are symmetrical rotors which are expected to display anisotropic motion about $\parallel$ and $\perp$ axes. Thus, in both cases, it would be necessary to use a 'double defect' model, in which the formation of two kinds of expanded lattices, each permitting one type of motion, would have to be considered. However, the success of the 'simple defect' model in the case of ammonia may be understood by noting that the ammonia molecule is a more spherical-like symmetric rotor, and thus the defects contributing to the two motions ($\parallel$ and $\perp$) are of more similar structure and shape than in the case of the flat pyridine molecule.

It is probable that a model with *two types of defects* of different structures and shapes might describe adequately the motions of the pyridine molecule. The attractive feature of the conditional inertial rotation model is that it separates the intrinsic properties of the free molecule (inertial effects) from those imposed upon it by the presence of neighbouring molecules in a condensed lattice (frictional effects). At the limit, in the rigid lattice of the solid state, only the motion about the symmetry axis is still possible (down to quite low temperatures), the other one being efficiently quenched by the absence of appropriate defects†.

The analogies between pyridine and benzene pointed out above, agree with and strengthen the previous conclusion that inertial effects do not dominate the molecular re-orientations in liquid benzene [29, 30]; they indicate however that this conclusion applies principally to the motion about an in-plane axis.

3.4. *Comparison with dielectric relaxation data*

If molecular re-orientation occurs by a rotational Brownian motion the nuclear spin and dielectric relaxation times are related by $\tau_{\text{diel}} = 3\,\tau_{\text{spin}}$. On the other hand, if the molecule undergoes large angle jumps $\tau_{\text{diel}} = \tau_{\text{spin}}$ [2]. Correcting for the field effect, dielectric relaxation measurements lead to a microscopic relaxation time of $5 \cdot 1 \times 10^{-12}$ s for liquid pyridine at +20°C [41]. Using our nuclear relaxation data one calculates $\tau_\parallel = 1 \cdot 4 \times 10^{-12}$ s, $\tau_\perp = 2 \cdot 3 \times 10^{-12}$ s at the same temperature, and $3\tau_\parallel = 4 \cdot 2 \times 10^{12}$ s and $3\tau_\perp = 6 \cdot 9 \times 10^{-12}$ s. At +60°C one has: $\tau_{\text{diel}} = 3 \cdot 45 \times 10^{-12}$ s [42, 43], which agrees well with our results: $3\tau_\parallel \sim 3\tau_\perp = 3 \cdot 1 \times 10^{-12}$ s.

Thus the rotational diffusion model is valid for the molecular re-orientations in liquid pyridine at +20°C. In addition, τ_{diel} is nearer to $3\tau_\parallel$ than to $3\tau_\perp$; this may

† Molecular rotation in the solid state has been observed in a number of carbocyclic and heterocyclic molecules [39], and especially in pyridinium salts [40].

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arise in part from the fact that only the motions about one $\perp$ axis (the b axis; figure 2) contribute to electric dipole relaxation.

4. Conclusion

The results discussed in the previous sections lead to the following conclusions:

(1) The molecular reorientations in liquid pyridine are *anisotropic*.

(2) The temperature dependence of the motional anisotropy shows three regions:

(*a*) An extended *solid-like region* at low temperatures (*ca.* $-42°$ to $+60°$C), where the molecular rotations about the axis perpendicular to the molecular plane are faster than the motions about an in-plane axis, such as in solid benzene;

(*b*) An *isotropic region* where inertial and frictional effects compensate each other is reached at higher temperatures (*ca.* 60–90°C)†.

(*c*) A *gas-like region* just below the boiling point, where the motions about an in-plane axis are now faster than those about the perpendicular axis, as in the free rotor.

Thus the dynamic behaviour of liquid pyridine bridges the gap between the solid and the gas state motions.

(3) The *ratios* of the extrapolated re-orientation times $(\tau_d)_i$ at the boiling point agree very well with the ratios of the free rotor re-orientation times $(\tau_f)_i$. One has

$$(\tau_d)_b/(\tau_d)_a = 1\cdot02, \qquad (\tau_f)_b/(\tau_f)_a = 1\cdot02.$$

$$(\tau_d)_c/(\tau_d)_a = 1\cdot37, \qquad (\tau_f)_c/(\tau_f)_a = 1\cdot43.$$

This gives some more confidence in the reality of the observed behaviour.

(4) In the temperature range studied, pyridine may be considered to a good approximation as a *planar symmetric rotor*. The motions about the two in-plane axes become significantly different only at low temperatures.

(5) The motions about the in-plane axes appear to be mainly enthalpically determined, whereas the motions about the perpendicular axis display a dominant entropic contribution (table 2). The large negative entropy of activation found in this last case might be an indication of the presence of some *motional coherence* during the re-orientation process. This would agree nicely with the concerted motions found for benzene in the solid state for rotation about the six-fold axis [28].

(6) The molecular motions may be described as a *rotational diffusion process*. However, this model is less valid at high temperatures and especially for the rotations about the perpendicular axis (angular jumps of about 15°).

It is clear that a study of the kind presented here depends strongly on experimental accuracy as well as on the theoretical model used. The present results lead to a coherent and reasonable picture of the *dynamic structure* of liquid pyridine. A confirmation of the results obtained and a detailed discussion of the activation parameters, of the change of motional anisotropy with temperature and of the validity and generality of the resulting re-orientation picture, has to await further studies of planar rotors in the liquid phase‡.

† Because of experimental inaccuracies, the position of this region is not known with precision.

‡ Such studies of other planar nitrogen heterocycles are presently under way in this laboratory.

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5. Experimental section

5.1. *Equipment and measurements*

^2D *spin lattice relaxation times* were measured by the spin–echo method at 12 MHz using a 90°–90° pulse sequence. The spin–echo equipment used has been described elsewhere by Goldhammer and Zeidler [9]. Temperature variation (−20° to +80°C) and stabilization (within ±1°C) was achieved by circulating water or methanol from an ultra-thermostat through the copper probe head.

^{14}N *spin lattice relaxation times* have been measured by the spin–echo technique at 6 MHz using 90°–90° or 180°–90° pulse sequences on a Bruker B–KR 304 S spectrometer. The signal to noise ratio was improved by accumulating 400 to 600 spectra with the aid of a NUCLEAR CHICAGO memory accessory.

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5.2. *Data analysis*

The ^2D and ^{14}N relaxation times were not measured at exactly the same temperature, the values used for the calculations (see equations in text) were obtained by interpolation by means of the regression line passing through the experimental points obtained from the measurements at different temperatures.

For each temperature, all possible combinations of the diffusion constants D_a, D_b, D_c in the area 10^9 to 10^{12} s^{-1} for D_a and D_b and in the area 10^{10} to 10^{13} s^{-1} for D_c were tested, using a 10 per cent step between two successive values of a given diffusion constant.

All sets of D_i values giving ^2D and ^{14}N relaxation times within 5 per cent of the experimental value were considered as satisfactory. A statistical analysis was performed on the resulting 20 to 30 sets of D_i values; maximal, minimal and means values, and standard deviations were obtained. Least squares lines were drawn through the resulting values (see figure 3); the D_i values at any temperature in the range may be obtained from equation (13 *b*) and the activation parameters listed in table 1.

The data analysis has been performed using a set of programmes written for an IBM 360–65 computer. The calculations require *ca.* 3 min computer time for each temperature. A typical result is shown below:

	D_a	D_b	D_c
	(in units of 10^{10} s^{-1})		
Mean value	7·3	8·2	14·6
Standard deviation	1·0	0·7	1·6
Maximum	8·8	9·7	17·5
Minimum	3·5	7·3	11·9

5.3. *Samples: substrates*

5.3.1. *Preparation of substrates*

The selectively deuterated pyridines were prepared according to an earlier publication [44] but on a larger scale. For example, 23·5 g (0·15 M) 3-bromo pyridine were added to a suspension of 52 g (0·8 M) zinc dust in 110 g D_2SO_4,

2N (98 per cent D) obtained by adding 10 g H_2SO_4 to 100 g D_2O (99·95 per cent D). This mixture was refluxed 2 hours with stirring. After cooling and addition of 100 g KOH, the mixture is steam extracted until the extracts are neutral. Decantation after addition of *ca.* 50 g KOH gives 9·5 g pyridine which is dried and distilled over KOH (yield: 6 g). NMR and mass spectroscopy indicate that position 3 is *ca.* 92 per cent deuterated, and that the amount of dideuterated products is lower than 1 per cent. The other substrates are prepared in a similar way starting with the corresponding bromo- or chloropyridine.

5.3.2. *Preparation of samples*

Anhydrous and oxygen-free samples were prepared in 8 mm O.D. sealed tubes on a vacuum line by the usual freeze–thaw technique and distillation over calcium hydride.

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