# Proton Magnetic Resonance and Molecular Motion in Solid Methyl-Piperidines and Piperazines

R. Schüler, L. Brücher, and W. Müller-Warmuth

Institut für Physikalische Chemie der Universität Münster

(Z. Naturforsch. **32 a**, 882–885 [1977]; received June 24, 1977)

The $^1$H-NMR spin-lattice relaxation time and lineshape in solid 2-, 3-, and 4-methyl-piperidine, in 2- and N-methyl-piperazine, and in NN′-dimethyl-piperazine has been measured from low temperatures to the melting point. For all cases, the experimental data can be described by classical rotation of the methyl group. Activation energies governing this motion are between 9 and 14 kJ/mole. Second moments are reduced from about 25 G$^2$ to 17 G$^2$. No further line-narrowing was observed.

## 1. Introduction

This nuclear magnetic resonance (NMR) investigation of methyl substituted piperidines and piperazines in the solid state is part of a more general study of internal motion of methyl groups attached to ring systems. But, while quantum mechanical tunnelling has been found in nearly all aromatic molecular crystals studied so far [1–4], the NMR data from saturated rings containing nitrogen can be described by classical rotation. The potential barrier to internal rotation is therefore thought to have an important intramolecular contribution. Values for the barriers by experiment and comparison of many different ring systems and structures should be of help in a better theoretical understanding of the origin and magnitude of the potential hindering the motion. The measurements reported here are proton spin-lattice relaxation times and second moments of NMR lines for three isomeric methyl piperidines, $C_5H_{10}N \cdot CH_3$, for 2- and N-methyl-piperazine, $C_4H_9N_2 \cdot CH_3$, and for NN′-dimethyl-piperazine, $C_4H_8N_2 \cdot (CH_3)_2$. For all six materials important nuclear relaxation is generated by reorientation of the $-CH_3$ rotor group in the 110 – 250 K temperature range. Rigid lattice second moments are only observed at temperatures of 60 K or below.

## 2. Experimental Details and Results

The piperidines and piperazines were obtained in liquid or polycrystalline form from Fluka AG., of high purity grade. Some of the materials were further purified by distillation, and both water and oxygen were carefully removed from the specimens. Measurements of proton spin-lattice relaxation time were carried out at 48 MHz using a Bruker variable-frequency pulsed NMR spectrometer. $n \cdot 90^\circ - \tau - 90^\circ$ and in a few cases $90^\circ - \tau - 90^\circ$ or $180^\circ - \tau - 90^\circ$ pulse sequences were applied. For all cases and at all temperatures, the recovery of nuclear magnetization was found to be purely exponential within experimental error. A unique relaxation time $T_1$ could therefore be attributed to each compound at each temperature.

Broad-line absorption spectra were registered with a homemade spectrometer consisting essentially of a bridge arrangement working at 10 MHz followed by phase-sensitive detection. The sample was placed in a variable temperature helium flow cryostat. Second moments $M_2$ were calculated from both the derivative and the absorption curves themselves using computer programs. At low temperatures, $T_1$ became very long and the signal-to-noise ratio was poor. In order to improve the sensitivity, $10^{-2}$ to $10^{-1}$ mole % of the free radical 2,2,6,6-tetramethyl-piperidin-ol-4-oxyl-1 was added to the (liquid) sample as impurity which shortens the re-

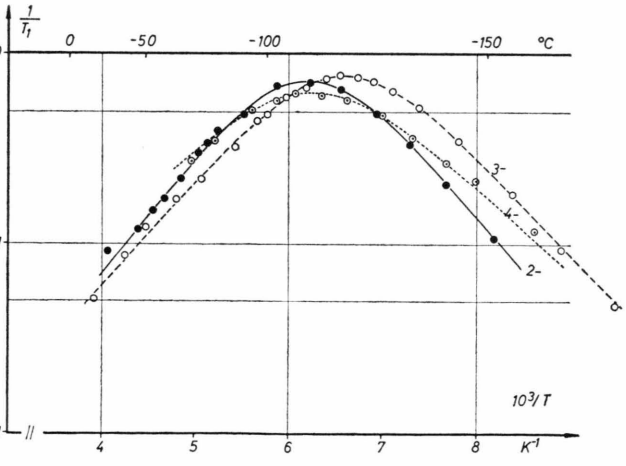


Fig. 1. The variation of proton spin-lattice relaxation rate $1/T_1$ with reciprocal temperature for 2-, 3-, and 4-methyl-piperidine. The lines are theoretical curves as described in the text.

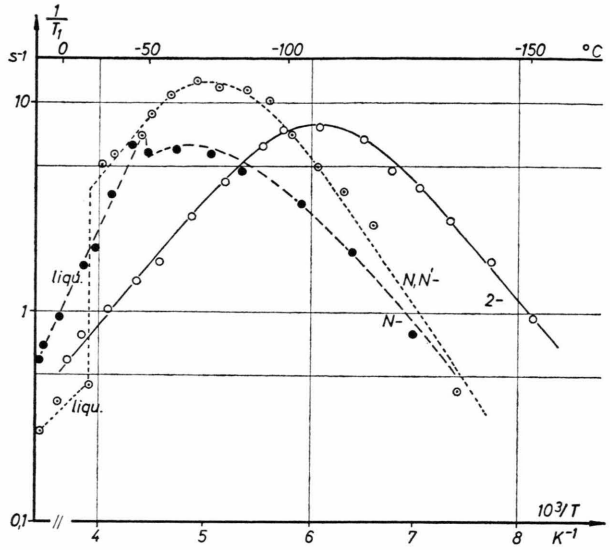


Fig. 2. The variation of proton spin-lattice relaxation rate $1/T_1$ with reciprocal temperature for 2-, and N-methyl-piperazine, and for MN'-dimethyl-piperazine. The lines are theoretical curves as described in the text.

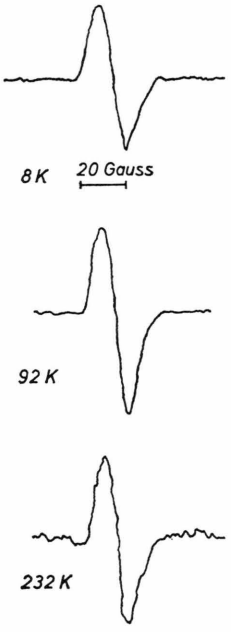


Fig. 3. Examples of the first derivative of the proton NMR absorption spectra of 2-methyl-piperazine obtained at 10 MHz and various temperatures.

laxation time. A series of experiments was performed to make sure that the lineshape remained unaffected by this procedure.

The results of the $T_1$ measurements are shown in Figs. 1 and 2. In each of the figures, the full or

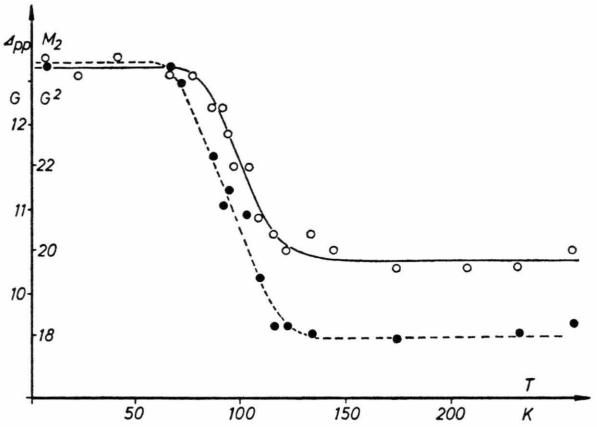


Fig. 4. Example of the observed peak to peak width of the derivative spectrum, $\Delta p\,p$ (○), and of the truncated second moment $M_2$ (●) for 2-methyl-piperazine versus temperature.

dotted line is a calculated line obtained from the analysis of the next paragraph.

Example broad-line-spectra of one compound at three temperatures are given in Figure 3. The second moments of the absorption lines are listed in Table 1 of the next paragraph. Figure 4 shows the variation of linewidth and second moment with temperature for an example.

## 3. Analysis and Discussion

In all cases the variation of $1/T_1$ with reciprocal temperature exhibits a symmetrical curve with a single maximum. This is characteristic of proton relaxation produced by the random reorientation of methyl groups. The experimental results can be analyzed in terms of the well-known semiclassical relaxation expression [5]

$$\frac{1}{T_1} = C\left[\frac{\tau_c}{1+\omega^2\tau_c^2} + \frac{4\tau_c}{1+4\omega^2\tau_c^2}\right], \qquad (1)$$

where $\omega/2\pi$ = resonance frequency, and $\tau_c$ = correlation time of the random motion. The curves of Figs. 1 and 2 are computer fits of the data using Eq. (1) and a simple Arrhenius law for the correlation time

$$\tau_c = \tau_c^0\, e^{E_A/RT}. \qquad (2)$$

The computer program minimized the relative differences between calculated and observed $T_1^{-1}$ data, and the best values of the activation energy $E_A$, and of $C$ and $\tau_c^0$ were thus obtained. They are listed in Table 1.

Table 1. Experimental [Eq. (1)] and theoretical values for $C$ [Eq. (3)], data for $\tau_c^0$ and $E_A$ [Eq. (2)] derived from $T_1$, and values for the rigid lattice and reduced second moments.

| | $C\text{exp} \cdot 10^{-9}/\text{s}^{-2}$ | $C_{th} \cdot 10^{-9}/\text{s}^{-2}$ | $\tau_c^0 \cdot 10^{12}/\text{s}$ | $E_A$/kJ/mol | $M_2^{rl}/\text{G}^2$ | $M_2^{red}/\text{G}^2$ |
|---|---|---|---|---|---|---|
| 2-methyl-piperidine | 1.55 | 1.80 | 0.3 | 11.7 | 25.6 | 19.5 |
| 3-methyl-piperidine | 1.61 | 1.80 | 0.5 | 10.5 | 24.7 | 18.3 |
| 4-methyl-piperidine | 1.31 | 1.80 | 1.8 | 9.2 | 25.5 | 18.4 |
| 2-methyl-piperazine | 1.65 | 2.0 | 0.3 | 12.1 | 24.4 | 17.9 |
| N-methyl-piperazine | 1.31 | 2.0 | 4.8 | 10.5 | 28.2 | 17.5 |
| NN′-dimethyl-piperazine | 2.65 | 3.4 | 0.4 | 14.2 | — | 16.2 |

There is an excellent agreement between the measurement points and the calculated curves over the whole temperature range. No asymmetry was found. Variation of frequency confirms the validity of Eq. (1) to describe the experimental results. The quantity $C$ in Eq. (1) can be expressed by the gyromagnetic ratio $\gamma$, the proton-proton distance $b = 1.79$ Å, and by the ratio, $N_{CH_3}/N_H$, of the number of methyl protons and the total number of protons [6, 7]

$$C = \frac{9}{20} \frac{\gamma^4 \hbar^2}{b^6} \cdot \frac{N_{CH_3}}{N_H} . \qquad (3)$$

Validity of Eq. (3) supposes that rapid spin diffusion occurs to relax the piperidine or piperazine protons via reorientation of the methyl protons. Comparison between $C$ values obtained experimentally and those calculated from Eq. (3) yields agreement within 10 to 30%, see Table 1. As in the case of ketones [7] and ethers [8], but different from n-alkanes [6], $C_{exp}$ looks systematically a little bit too small.

Recently it was shown [9] that in a polycrystalline solid, where the random reorientation of methyl groups is the dominant relaxation mechanism, actually the relaxation is a sum of two exponentials, resulting from a dynamical coupling between the nuclear magnetization and the rotational polarization. In this experiment, independent upon the way of performance, within the limits of accuracy, no deviation from exponentiality could be observed, and $T_1$ is the apparent time constant of the signal recovery. The Emid-Wind effect may, however, cause systematic errors, which could explain differences between $C_{exp}$ and $C_{th}$ not only for the present study. Since no difference in the slope of $\ln {T_1}^{-1}$ versus $T^{-1}$ for $\omega\tau_c \ll 1$ and $\omega\tau_c \gg 1$ has been found, the activation energy is probably not very much influenced by this effect.

The values of activation energy $E_A$ in Table 1 between 9 and 14 kJ/mole agree well with measured data in straight-chain hydrocarbons [5–8], where tunneling is absent. In most materials $E_A$ is slightly smaller than the theoretical value of 12.5 kJ/mole for the barrier height in ethane. The activation energy seems to increase as the reorienting methyl group approaches the nitrogen in the ring. It is the largest for the material which contains two $CH_3$ per molecule.

The order of magnitude of $\tau_c^0$ agrees with the reciprocal rate of rotation to be expected for a methyl fragment in the gas phase. The maximum of the proton relaxation rate occurs at higher temperature when $CH_3$ is attached to N rather than to a C-atom.

The last two columns of Table 1 contain the experimental second moments observed at temperatures below and above the step-like variation with temperature (see Fig. 4 as an example). The values of $M_2^{rl}$ are not very much different from those obtained for cyclohexane [10] (26 G²) or cycloheptane [11] (27 G²). Since crystal structures have not been determined, the second moment expected for a rigid lattice can only be estimated by adding up the contributions of each structural group [12]. In methyl-piperidine, the $CH_3$ group contains 3/13 of the protons, its second moment is 22 G². The $CH_2$ groups contain 8/13 of the protons and here the value of 18 G² is used. For the remaining two protons a contribution of 3 G² is assumed. This leads to

$$M_2^{rl} = \tfrac{3}{13}22 + \tfrac{8}{13}18 + \tfrac{2}{13}3 + M_2^{inter} = 16.6\ \text{G}^2 + M_2^{inter} .$$

For similar materials [10, 11], $M_2^{inter}$ was assumed to be approximately 9 G², yielding a final value of 25 – 26 G², which agrees well with the present experiment. Corresponding estimates for the three piperazines are 24 G², 27 G² and 29 G², respectively.

The variation of $M_2$ with temperature shows in agreement with the $T_1$-data that the only motion fast enough to average out the dipolar broadening is the random rotation of $CH_3$ groups about the $C_3$ axes. This reduces the contribution of the methyl groups generally by a factor of 1/4. Corresponding values of $M_2^{red}$ would be 22, 20, 23, and 21 $G^2$ for the three piperidines, 2-methyl-piperazine, N-methyl-piperazine, and NN′-dimethyl-piperazine, respectively. The experimental data show that also part of $M_2^{inter}$ is averaged out. A reasonable assumption may be that the intermolecular contribution is reduced proportionally; values of $M_2^{red}$ are then smaller by 2 to 3 $G^2$.

The step-like reduction of the linewidth or of the observed $M_2$ is often employed in order to extract the correlation time with associated activation energy from the absorption curves. In the present case (as in many others), such an attempt has failed completely, independently on whether the linewidth method [13] or the second moment method [14] was used. One reason for this is the shape of the absorption line, which is neither Gaussian nor Lorentzian, nor does it change from Gaussian to Lorentzian.

Application of the universal expression of Mehring for the rigid lattice half intensity half linewidth [15],

$$\delta = \sqrt{\frac{\pi}{2}} \sqrt{\frac{M_2}{\mu - 1.87}} \tag{4}$$

with $\mu = M_4/M_2^2$, shows that for the materials studied: $\mu < 3$ (Gaussian: $\mu = 3$, Lorentzian: $\mu > 3$). As compared with a Gaussian, the lineshape looks steeper or slightly flattened at the top. Line narrowing causes $\mu$ to become nearly 3.

A reasonable estimate for the activation energie from the reduction of the linewidth is, however, the simple Waugh-Fedin expression [16],

$$E_a \approx 0.156\, T_c \tag{5}$$

($T_c$ in K, $E_a$ in kJ/mole). The temperature $T_c$, where line narrowing occurs are 62, 79, and 92 K, respectively, for 4-methyl-piperidine, 2-methyl-piperazine, and NN′-dimethyl-piperazine, for example. Application of Eq. (5) yields 9.7, 12.3, and 14.4 kJ/mole. These values agree very well with those of Table 1 which have been obtained from $T_1$ measurements.


[1] W. Müller-Warmuth, R. Schüler, A. Kollmar, and M. Prager, Proc. XIX Ampere Congress, Heidelberg 1976, page 345.
[2] J. Haupt and W. Müller-Warmuth, Z. Naturforsch. **23 a**, 208 [1968]; Z. Naturforsch. **24 a**, 1066 [1969].
[3] P. S. Allen and A. Cowking, J. Chem. Phys. **49**, 789 [1968].
[4] J. U. von Schütz, W. Güttler, and H. C. Wolf, Z. Naturforsch. **28 a**, 69 [1973].
[5] E. Stejskal and S. Gutowsky, J. Chem. Phys. **28**, 388 [1958].
[6] J. E. Anderson and W. P. Slichter, J. Phys. Chem. **69**, 3099 [1965].
[7] K. P. A. M. van Putte, Trans. Faraday Soc. **65**, 1709 [1969].
[8] K. Grude, J. Haupt, and W. Müller-Warmuth, Z. Naturforsch. **21 a**, 1231 [1966].
[9] R. A. Wind, S. Emid, J. F. J. M. Pourquié, and J. Smidt, J. Phys. C = Solid State Phys. **9**, 139 [1976].
[10] E. R. Andrew and R. G. Eades, Proc. Roy. Soc. **A 216**, 398 [1953].
[11] J. R. Brookeman and F. A. Rushworth, J. Phys. C = Solid State Phys. **9**, 1043 [1976].
[12] H. S. Gutowsky and L. H. Meyer, J. Chem. Phys. **21**, 2122 [1953].
[13] H. S. Gutowsky and G. E. Pake, J. Chem. Phys. **18**, 162 [1950].
[14] E. R. Andrew and J. Lipofsky, J. Magn. Res. **8**, 217 [1972].
[15] M. Mehring, High Resolution NMR Spectroscopy, in NMR Basic Principles and Progress, Bd. 11, Springer-Verlag, Berlin 1976.
[16] J. S. Waugh and E. I. Fedin, Solid State Phys. Moskau **4**, 2233 [1962].