

# $^{13}\text{C}$ NMR RELAXATION AND MOLECULAR STRUCTURE. $^{13}\text{C}$ SPIN-LATTICE RELAXATION AND ROTATIONS OF METHYL GROUPS IN N,N-DIMETHYLFORMAMIDE

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Received 19 February 1975

Revised manuscript received 29 April 1975

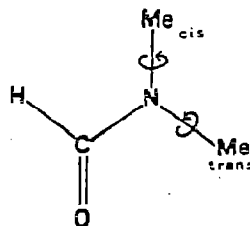
Rotational rates of the two methyl groups in N,N-dimethylformamide were calculated using Woessner's equation from  $^{13}\text{C}$  spin-lattice relaxation values at low temperatures. The rotation of the *cis* methyl group was found to be more hindered than that of the *trans* methyl group.

## 1. Introduction

The recent development of the pulsed Fourier transform method in nuclear magnetic resonance spectroscopy makes it possible to determine easily spin-lattice relaxation times ( $T_1$ ) of naturally abundance carbon-13 nuclei in organic molecules. Study of spin-lattice relaxation times gives information about the tumbling motion and the internal rotation of the molecules. Since carbon atoms are more centrally situated than hydrogen atoms in most organic molecules, the experimentally obtained relaxation times of carbon-13 nuclei give more direct information about the molecular conformation than those of hydrogen which are considerably influenced by intermolecular hydrogen-hydrogen interactions.

To date, spin-lattice relaxation times of many compounds involving the methyl group have been studied [1-6]. The rotation of the methyl group, however, was discussed only qualitatively in these reports. A theoretical study of the nuclear spin-lattice relaxation in molecules with an internal motion has been made by Woessner et al. [7], who treated axially symmetric ellipsoid molecules. On the other hand, Wallach et al. [8] have studied the anisotropic molecular rotation in liquid N,N-dimethylformamide (DMF) by the nuclear magnetic resonance technique and have reported that in this molecule there takes place an approximately axially symmetric motion at low temperatures.

This report presents the results of the first quantitative study of fast internal rotations of methyl groups in DMF by carbon-13 spin-lattice relaxation techniques.



## 2. Experimental

DMF of commercial origin was distilled before use. 20 V% deuteriochloroform was added for the deuterium lock. The sample was completely degassed with a high vacuum system and was sealed in a special 8 mm o.d. sample tube for the  $T_1$  measurement.  $^{13}\text{C}$  NMR spectra were recorded on a NEVA NV-14 spectrometer operating at 15.087 MHz with a Varian 620/L computer for a pulsed FT mode. Spin-lattice relaxation times were determined by the usual  $180^\circ - \tau - 90^\circ$  pulse sequence method. The pulse delay time was set at greater than five times the longest  $T_1$  to be measured. 8-16 free induction decays were accumulated. The error range in the  $T_1$  measurements was better than  $\pm 5\%$ . The nuclear Overhauser enhancement factor (NOE) was determined by dividing the

Table 1  
NOE factors of DMF

$T(^{\circ}\text{C})$	<i>cis</i> Me	<i>trans</i> Me	CO
23.6	2.5	1.9	2.1
-33.1	3.0	2.9	2.5

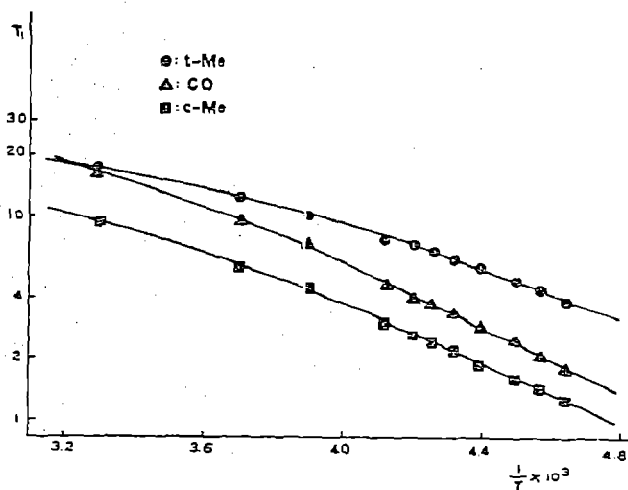


Fig. 1.  $\log T_1$  versus  $1/T$  plots of N,N-dimethylformamide.

integrated peak intensities in  $^1\text{H}$  decoupled  $^{13}\text{C}$  spectra by the total integrated band intensities in non-decoupled  $^{13}\text{C}$  spectra. In this case, the pulse interval was also longer than  $5 T_1$  for the slowest relaxing carbon. The accumulation was made 90 times for the decoupled spectra and 720 times for the non-decoupled spectra. The temperatures were determined by a calibrated copper-constantan thermocouple.

### 3. Results and discussion

The  $T_1$  of the *trans* methyl carbon in DMF is known to be considerably longer than that of the *cis* methyl carbon at room temperature [6]: the  $T_1$  values from our measurements are 17.1 s for *trans* methyl carbon and 11.4 s for *cis* methyl carbon at  $31.0^{\circ}\text{C}$ . In order to obtain the contribution of the spin-rotation mechanism to the methyl relaxation, the nuclear Overhauser enhancement factors were determined. The results are given in table 1. It was found that the contribution of the spin-rotation mechanism cannot be neglected at room temperature, especially in the

Table 2  
Relaxation times, correlation times, and the rates of methyl group rotation in DMF at  $-57.6^{\circ}\text{C}$  ( $\phi = 49^{\circ}$ )

	$T_1$ (s)	$\tau_c$ (s)	$k$ ( $\text{s}^{-1}$ )
<i>cis</i> Me	1.3	$1.2 \times 10^{-11}$	$3.9 \times 10^{10}$
<i>trans</i> Me	4.3	$3.6 \times 10^{-12}$	$6.5 \times 10^{10}$
CO	1.8	$2.5 \times 10^{-11}$	—

*trans* methyl carbon. The fact that the NOE value for the *trans* methyl carbon is smaller than that for the *cis* methyl carbon strongly suggests that the rotation of the *trans* methyl group is faster than the *cis* methyl group. To reduce the spin-rotation contribution,  $T_1$ 's were measured at low temperatures (fig. 1 and table 2). The ratio of the  $T_1$  of the *trans* methyl carbon to the *cis* methyl becomes greater as the temperature is decreased. NOE factors at  $-33.1^{\circ}\text{C}$  show that the carbons of the two methyl groups are relaxed predominantly by the dipole-dipole mechanism. Thus at temperatures below  $-33.1^{\circ}\text{C}$ , a discussion about the  $T_1$  values can be made by taking account of this mechanism only. The correlation times  $\tau_c$  can be calculated from the observed  $T_1$  values by the well known equation:

$$1/T_1^{\text{dd}} = \hbar^2 \gamma_{\text{H}}^2 \gamma_{\text{C}}^2 \sum_i (N_i/r_i^6) \tau_c, \quad (1)$$

where  $r$  is the internuclear distance between the proton and the carbon to be considered, which is calculated from the already known bond distances and bond angles of formamide and dimethylamine [9]. The correlation time  $\tau_c$  can be related to the rate of the methyl rotation and self-diffusion constants in accordance with Woessner's equation (2) [7],

$$\tau_c = \frac{1}{4} \frac{(3 \cos^2 \theta - 1)^2}{6 D_{\perp} + R} + \frac{3 \sin^2 \theta \cos^2 \theta}{5 D_{\perp} + D_{\parallel} + R} + \frac{3}{4} \frac{\sin^4 \theta}{2 D_{\perp} + 4 D_{\parallel} + R}, \quad (2)$$

since in DMF there takes place an approximately prolate symmetric top motion at low temperatures [8]. When the axes of the self-diffusion tensor of DMF are set as in the literature [8] (fig. 2),  $D_{\perp} \equiv D_y$ ,  $\approx D_z$  and  $D_{\parallel} \equiv D_x$  in the temperature range from  $-30^{\circ}\text{C}$  to  $-58^{\circ}\text{C}$ .  $R = \frac{3}{2} k$  ( $k$ : the rate of rotation of

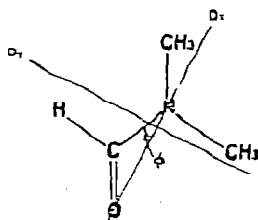


Fig. 2. Axes of the self-diffusion tensor of DMF.

the methyl group) and  $\theta$  is the angle between the principal diffusion axis and the N-Me bond. We estimate the angle ( $\phi$ ) between the principal diffusion axis and the amide N-CO bond to be in the range from  $42^\circ$  to  $49^\circ$  at low temperatures [8]. Thus  $\theta$  is in the ranges shown below:

$$\theta = 5-12^\circ \text{ for } \textit{cis} \text{ methyl,}$$

$$= 103-96^\circ \text{ for } \textit{trans} \text{ methyl.}$$

Using the self-diffusion constants estimated from Wallach's results [8], the rotational rate constants of *cis* and *trans* methyl groups in DMF at low temperatures ( $-30.6$  to  $-57.6^\circ\text{C}$ ) can be calculated from eq. (2). The results are given in table 2 and the Arrhenius plots for the methyl rotations are shown in fig. 3. In the calculation at every  $\phi$  and temperature, the rotational rate of the *trans* methyl group was found to be more rapid than that of the *cis* methyl group. The activation energies obtained for the methyl rotations are as follows:

$$EA = 3.9 \pm 0.3 \text{ kcal/mole for } \textit{cis} \text{ methyl,}$$

$$= 2.7 \pm 0.6 \text{ kcal/mole for } \textit{trans} \text{ methyl.}$$

The activation energies remain almost the same when the calculations are made with  $\phi = 42-49^\circ$ . Thus it can be safely said that the rotation of the *cis* methyl group is more strongly hindered than that of the *trans* methyl in liquid DMF, although some ambiguity in  $\phi$  makes the rate constant data rather scattered in the Arrhenius plots, and the errors obtained in rotational barriers are somewhat large. The rotational barriers of the two methyl groups in DMF have not been reported until now. The activation energies obtained in this work seem reasonable, since the barriers to rotation of the methyl groups in dimethylamine and trimethylamine were reported to be 3.6 and 4.4 kcal/mole by infrared [10] and microwave [11] spec-

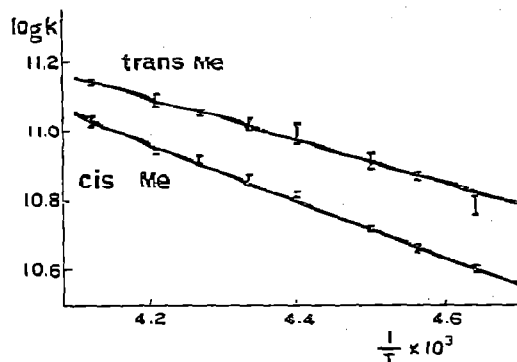


Fig. 3. Arrhenius plots of rotational rate constants for the two methyl groups in DMF.

troscopic studies, respectively. The higher rotational barrier in the *cis* methyl group than that in the *trans* methyl is unexpected, since, from a simple steric hindrance point of view, the rotation of the *trans* methyl group is considered to be more restricted by the carbonyl oxygen than that of the *cis* methyl by the formyl hydrogen. It will be worthwhile studying the reason for this interesting difference in the rotational barriers of the two methyl groups in N,N-dimethylformamide in the future.

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