Internal Rotation of Methyl Groups in *NN*-Dimethylamides studied by Nuclear Magnetic Resonance Methods

Adam Gryff-Keller* and Leszek Poppe
Chemistry Department, Technical University, 00-664 Warszawa, Poland

The diffusion constants for anisotropic reorientation and internal rotation rates of methyl groups in DMF have been recalculated using longitudinal relaxation times for ^{14}N, ^{17}O, ^{2}H, ^{13}C, and quadrupolar parameters available in the literature. Within the framework of an isotropic reorientation model the rates of internal rotation of CH_2D groups in *NN*-di([^{2}H]methyl)-formamide, -benzamide, and -2-methoxybenzamide have been determined on the basis of ^{14}N and ^{2}H relaxation data. It seems that generally in *NN*-dimethylamides internal rotation of the *E*-methyl group is more hindered than that of the *Z*-methyl group.

The phenomenon of different nuclear magnetic relaxation rates of nuclei in methyl groups in the *E*- and *Z*-configurations in *NN*-dimethylamides is well documented.[1–8] However, two different opinions on the origin of the phenomenon have been formulated. Some authors[1–3] claim that the only reason for the observed differences is the anisotropic reorientation of amide molecules in solution. Others consider the different internal rotation rates of methyl groups to be the main reason for the phenomenon.[4,5] Recently, even the concept of anisotropic rotational diffusion of the dimethylformamide (DMF) molecule has been questioned.[9] Unfortunately, the only quantitative work which could solve this controversy[4] contains a mistake which makes its results inconclusive. Thus, we have found it desirable to calculate once again the rotational diffusion tensor for the DMF molecule and then to calculate the internal rotation rates of methyl groups on the basis of available data. Moreover in order to generalize the results we have interpreted our orginal data for *NN*-di([^{2}H]methyl)-formamide (**1**), -benzamide (**2**), and -2-methoxybenzamide (**3**).

Results and Discussion

Reorientation of DMF Molecule and Internal Rotation of its Methyl Groups.—The quantitative description of the reorientation of the DMF molecule as a neat liquid was given by Wallach and Huntress.[1,2] They based their calculation on longitudinal relaxation data for ^{17}O, ^{14}N, and formyl ^{2}H nuclei in isotopically substituted molecules and on quadrupolar parameters for those nuclei in analogous compounds taken from the literature. The authors assumed that the DMF molecule behaves like a planar rotor with the rotational diffusion tensor characterized by three diffusional constants D_x, D_y, D_z and angle θ defining the direction of main rotational diffusion axis OX within the molecular plane (Figure 1). Since the problem is mathematically underdetermined their results were given in the form of functional dependences of D_x, D_y, and D_z on the angle θ (Figure 2c). Qualitatively, the same results were obtained by Daragan[10] on the basis of ^{17}O, ^{14}N, and ^{13}C relaxation data.† Currently available quadrupolar parameters for ^{14}N and ^{2}H in [$^2H_7$]DMF[11] differ from those applied by Wallach and Huntress.[1] So we decided to repeat their calculation using experimental data contained in Table 1 and the geometry of the DMF molecule reported in refs. 11 and 12. The longitudinal relaxation time for quadrupolar nuclei can be related to diffusional parameters by equation (1)[1,2] where $D_R = 3(D_xD_y + D_xD_z + D_yD_z)$ and $D_s = (D_x + D_y + D_z)/3$.

$$\frac{1}{T_{1q}} = \frac{3}{160}\frac{2I+3}{I^2(2I-1)}\left(\frac{e^2Qq_{z'}}{\hbar}\right)^2\frac{1}{D_R}\left\{[4D_z + (\eta'+1)^2D_y + (\eta'-1)^2D_x]\cos^2\varphi + [4D_z + (\eta'+1)^2D_x + (\eta'-1)^2D_y]\sin^2\varphi - \frac{4}{3}\eta'^2\frac{(D_x-D_y)^2}{(D_z+D_s)}\cos^2\varphi\sin^2\varphi\right\} \tag{1}$$

The quadrupolar parameters $e^2Qq_{z'}/h$ and $\eta' = (eq_{x'}/h - eq_{y'})/eq_{z'}$ in Table 1 and equation (1) are defined by assuming that the main axis of the electric field gradient tensor, perpendicular to the molecular plane, is labelled z'. φ denotes the angle between the field gradient x' and the main diffusional rotation axis X. Using equation (1) and experimental data for ^{17}O, ^{14}N, and formyl ^{2}H we obtained the results shown in Figure 2a. On the basis of those results the value of the dipolar relaxation time T_{1dd} for carbonyl ^{13}C in the DMF molecule can be calculated using equation (2)[14] where φ denotes the angle between the diffusional axis X and the C–H vector.

$$\frac{1}{T_{1dd}} = \frac{\gamma_H^2\gamma_C^2}{r_{CH}^6}\frac{3}{4D_R}\left[(D_x + D_s)\cos^2\varphi + (D_y + D_s)\sin^2\varphi - \frac{(D_x-D_y)^2}{(D_z+D_s)}\cos^2\varphi\sin^2\varphi\right] \tag{2}$$

The comparison of the calculated value T_{1dd} with the experimental one (Table 1) does not, unfortunately, lead to a unique solution since the choice of any set of D_x, D_y, D_z, and θ values from Figure 2a invariably gives a value of $T_{1calc.}$ close to the experimental one. This is not surprising since the electric field gradient on the formyl ^{2}H nucleus is almost cylindrically symmetrical and its axis is close to the C–H bond direction.[11] As a result the relaxation data for ^{13}C and ^{2}H nuclei are interdependent within experimental error. For completeness we also performed the calculation of

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† The treatment of the data in ref. 10 may give rise to some reservations. The author calculated the effective correlation times for N–CH_3 vectors assuming an isotropic reorientation model and then used the values to calculate rotational diffusion parameters within the anisotropic reorientation model. Such a procedure seemed to be adequate. Moreover at higher temperatures the averaging of relaxation times for ^{13}C in CH_3 groups due to rotation about C(O)–N bond should be considered.[5,8]

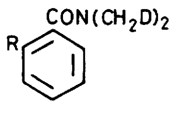
Table 1. Literature data for relaxation times at 40 °C and quadrupolar parameters for particular nuclei in DMF used in our calculations

Nucleus	T_1/s	$e^2Qq_{z'}/h^{-1}$(MHz)	η′	Ref.	Orientation of x[a]
^{14}N	2.15×10^{-3}	-3.26 ± 0.15	-0.41 ± 0.06	10, 11	$\measuredangle[x, C(O)\text{–}N] = 28 \pm 15°$
^{17}O	5.83×10^{-3}	-10.48[b]	1.36[b]	10, 13	$x \parallel C{=}O$
^{2}H	1.3	-0.111	-2.55	1, 11	$\measuredangle(x, C\text{–}D) = 5 \pm 2°$
$^{13}C_{C=O}$	28.9[c]			5	
$^{13}C_{E\text{-}CH_3}$	13.1[c]			5	
$^{13}C_{Z\text{-}CH_3}$	28.6[c]			5	

[a] In-plane main axis of electric field gradient at the given nucleus. [b] Data concerning H_2CO. [c] Dipolar relaxation times (T_{1dd}) calculated in original paper from total T_1 and NOE enhancement coefficient.

$HCON(CH_2D)_2$

(1)



(2) R = H

(3) R = OCH3

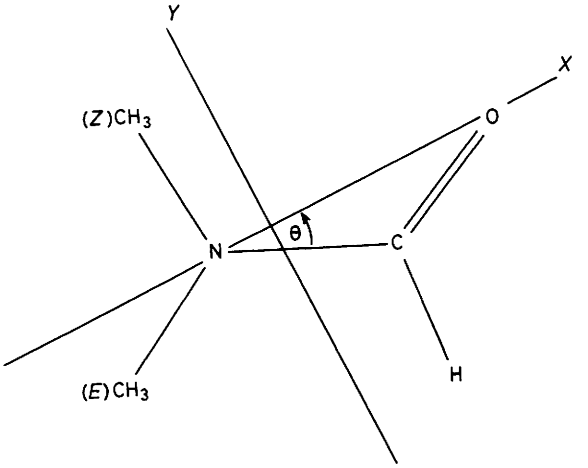


Figure 1. The position of the main diffusional axes in the plane of the DMF molecule

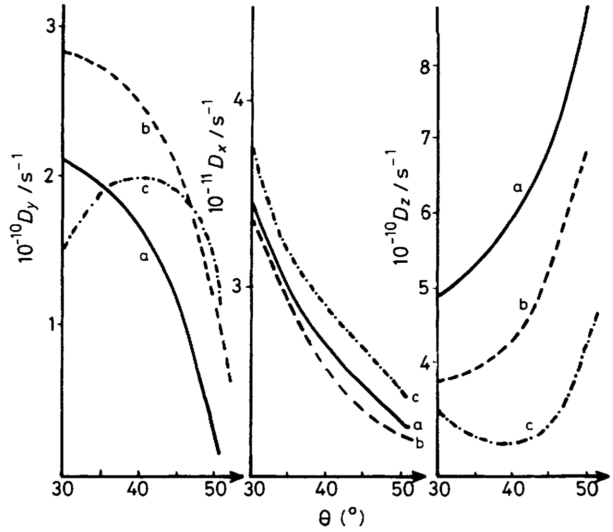


Figure 2. Diffusional constants for DMF molecule (neat liquid; 40 °C) calculated on the basis of a, relaxation and quadrupolar constants for ^{14}N, ^{17}O, and formyl ^{2}H nuclei (Table 1), b, relaxation and quadrupolar constants for ^{14}N, ^{17}O, and carbonyl ^{13}C nuclei (Table 1), c, quadrupolar parameters used by Wallach and Huntress[1]

diffusional parameters on the basis of T_{1q} data for ^{17}O, ^{14}N, and T_{1dd} for carbonyl ^{13}C nuclei (Figure 2b). The comparison of the plots in Figure 2 clearly shows that numerical values of diffusional parameters are very sensitive to experimental data used in the calculation. Nevertheless they unequivocally support the previously formulated[1,10] conclusion that the reorientation of the DMF molecule is strongly anisotropic. The fastest rotation is about the X axis, the direction of which is close to that of the dipole moment and to that of the smallest moment of inertia. The opposite statement formulated recently[9] seems to be an overhasty one. It is mainly based on the observation that the correlation times calculated from T_{1q} data for ^{14}N and ^{17}O nuclei are equal. This result does not exclude anisotropy of reorientation and moreover is strongly biased by the specific choice of the values of quadrupolar parameters for those nuclei. The criticism formulated by Burgar *et al.*[9] toward values of quadrupolar parameters for ^{17}O in DMF used by Wallach and Huntress,[1] which apparently invalidate the results of their work, is unjustified. Differences between values used in refs. 1 and 9 are predominantly caused by different labelling of the main axes of electric field gradient at that nucleus.

The estimation of the rotational diffusion tensor of the DMF molecule makes possible the calculation of the rotation rate of its CH_3 groups. As a source of information on this process one can use T_{1dd} data for methyl ^{13}C nuclei (Table 1). The dependence of T_{1dd} relaxation times on the parameter D_i characterizing the internal rotation rate of the methyl group, on the diffusion tensor of overall reorientation, and on the geometry of the molecule is given by equation A1 in ref. 1 derived by Wallach and Huntress. Despite the formula being exceptionally long its numerical solution to give D_i values is straightforward. The exact, single values of rotational diffusion parameters are not known, nevertheless the estimation of the internal rotation rates of methyl groups is possible since calculations based on various sets of D_x, D_y, and D_z from Figures 2a and b give the values of the rotation rates of CH_3 groups falling in a relatively narrow range (Table 2). Table 2 also contains the values of activation potentials V_0 for methyl-group rotations calculated from equation (3)[15] where $D_{io} = \sqrt{kT/I}$ and represents the rate of free methyl rotation at a

$$D_i = D_{io}e^{-V_0/RT} \qquad (3)$$

given temperature (I = moment of inertia involved). Thus there is no doubt that the different relaxation behaviour of the E- and Z-methyl groups is caused by a large difference of internal rotation rates rather than by anisotropic tumbling.

We also performed the calculation of methyl rotation rates following the idea of Nakanishi and Yamamoto[4] who treated

Table 2. Overall and internal diffusion constants at 40 °C and activation potentials V_0 for methyl group rotations in DMF

Planar rotor						
$10^{-10}D_x$/s^{-1}	$10^{-10}D_y$/s^{-1}	$10^{-10}D_z$/s^{-1}	$10^{-11}D_i^E$/s^{-1}	$10^{-11}D_i^Z$/s^{-1}	V_0^E/kJ mol^{-1}	V_0^Z/kJ mol^{-1}
31 ± 5	2.2 ± 0.6	4.8 ± 1	1.8 ± 0.4	7.7 ± 0.6	10.1 ± 0.6	6.3 ± 0.3
	Symmetrical top					
	$10^{-10}D_\perp$/s^{-1}	$10^{-10}D_\parallel$/s^{-1}				
	3.5	30	1.9 ± 0.2	8.1 ± 0.2	10 ± 0.3	6.2 ± 0.1
		Spherical top				
		$10^{-10}D_0$/s^{-1}				
		5 ± 0.4	3.4 ± 0.4	25 ± 5	8.5 ± 0.3	3.4 ± 0.5

the DMF molecule as a symmetrical rotor for which $D_\parallel \equiv D_x$ and $D_\perp \equiv (D_z + D_y)/2$. In our calculation we used formula 8 from ref. 15 (Nakanishi and Yamamoto[4] used formula 7 from ref. 15 in the same situation which in our opinion is inapplicable in the case under consideration). A comparison of the results contained in Table 2 shows that the adopted simplification of reorientation model hardly affects the calculated values of the rotation rates of the methyl groups.

Applicability of Isotropic Diffusion Model in Investigations of Methyl Group Rotation.—As opposed to the case of the DMF molecule in which the reorientation can be described as a rotational diffusion of the planar rotor, for the remaining molecules investigated in this work, the reorientation would be accurately described only within the framework of a fully anisotropic rotor model including additionally the non-rigidity of the molecule. Such a treatment would be, however, extremely troublesome and to our knowledge has never been used in practice. On the other hand one can find many papers in which, in order to calculate the rate of the methyl group rotation, the isotropic reorientation model was assumed even for molecules of a shape very far from spherical (*e.g.* 1-methylnaphthalene,[16] 1-acetylpyrene, or a porphyrin [17,18]). Such treatment is of course an approximation but in many cases it may be the only practical one. In general it is difficult within that treatment to estimate the accuracy of the data obtained for methyl group rotation. By use of the results the in the preceding section we are now able to test whether the assumption of isotropic tumbling introduces prohibitively large errors into the final results.

Within this model the effective correlation time for the ^{13}C nucleus τ_{eff} is related to internal D_i and overall D_0 diffusion constants as expressed by equation (4)[15] where $A =$

$$\tau_{eff} = \frac{A}{6D_0} + \frac{B}{6D_0 + D_i} + \frac{C}{6D_0 + 4D_i} \qquad (4)$$

$1/4(3\cos^2\Delta - 1)^2$, $B = 3/4\sin^2 2\Delta$, $C = 3/4\sin^4\Delta$, and Δ is the tetrahedral angle. The isotropic diffusion constant was calculated by two independent ways. On the basis of the ^{14}N n.m.r. linewidth $w_{1/2} = 1/\pi T_{1q} = 165 \pm 10$ Hz and using equation (5)[14] we obtained $D_0 = 5.3 \times 10^{10}$ s^{-1}. Secondly,

$$D_0 = 1/16\left(\frac{e^2Qq_z}{\hbar}\right)^2 (1 + \eta^2/3)T_{1q} \qquad (5)$$

using the hydrodynamic model of molecular tumbling of Gierer and Wirtz[19] and adopting viscosity $\eta = 0.7386$ cP, molecular volume[20] $V_m = 128.5$ Å^3, and microviscosity coefficient $f_r = 0.163$, a value of $D_0 = 4.6 \times 10^{10}$ s^{-1} was obtained, in reasonable agreement with the previous estimate. The D_i values for methyl group rotations, obtained within this model, are in Table 2. It is obvious that these values are strongly affected by oversimplification of the reorientation model and by the inaccuracy of the estimate of D_0. For instance much better agreement between the D_i values obtained from anisotropic and isotropic models of reorientation, namely at 40 °C $D_i^Z = 11 \times 10^{11}$ s^{-1} and $D_i^E = 1.8 \times 10^{11}$ s^{-1}, would be achieved assuming $D_0 = 8 \times 10^{10}$ s^{-1}. That value seems also to be reasonable taking into account that for $\theta = 35°$ $D_s = 1/3(D_x + D_y + D_z) = 12.6 \times 10^{11}$ s^{-1}. Thus in the light of the results it seems that as long as the D_i values are treated as semi-quantitative estimates, the assumption of the isotropic reorientation model in the calculation of the CH_3 group rotation is quite acceptable.

Methyl Group Rotations in NN-*Di*([^{2}H]*methyl*)*amides.*—Some qualitative observations for compounds (**1**)—(**3**) were reported and discussed in our previous paper.[6] Now on the basis of line-shape analysis of the ^{1}H n.m.r. signals of CH_2D groups we have determined longitudinal quadrupolar relaxation times for deuterons and then with the aid of equation 3B.6 from ref. 14 we have calculated effective correlation times for C–D vectors. The appropriate NQCC values for [$^2H_2$]DMF (157 and 178 kHz for *E*- and *Z*-methyl deuterons, respectively) have been taken from ref. 11 and the standard value 165 kHz has been used in the case of benzamides.[3] In view of the results obtained in the previous section the isotropic model of reorientation for the evaluation of methyl group rotation rates has been assumed. In order to use equation (4) we had to estimate D_0 values for compounds (**1**)—(**3**). Those values for room temperature were calculated on the basis of ^{14}N n.m.r. linewidths [700 ± 100 and 1 400 ± 200 Hz for (**2**) and (**3**), respectively]. For (**2**) and (**3**) we adopted the NQCC values for ^{14}N equal to 3.9 MHz as measured for *NN*-dimethylbenzamide.[21] The D_0 constants obtained were extrapolated to low temperatures using the Gierer and Wirtz equation.[19] The value obtained for compound (**2**) is comparable with the results obtained for the similar compounds nitrobenzene[22] and toluene.[23] Also the activation potentials calculated for methyl group rotation in (**1**) (Table 3) are in good agreement with the values calculated independently for non-deuteriated DMF (Table 2). The rotation rate of the *Z*-methyl group in (**2**) is very fast in comparison with the overall reorientation, so the relaxation rate for the *Z*-deuteron is controlled by the rate of the latter's movement[3] ($\tau_{eff} \simeq 0.11/$

Table 3. Relaxation times for ^2H nuclei in *E*- and *Z*-CH_2D groups of amides (**1**)—(**3**) and internal rotation rates for CH_2D groups calculated assuming isotropic reorientation model. Activation potentials are given in the form $V_0 + \Delta V_0$ where V_0 is the mean value and ΔV_0 the experimental maximal deviation

Amide	T/K	$T_{1_q}{}^E$/s	$T_{1_q}{}^Z$/s	$\tau_{eff}{}^E$/ps	$\tau_{eff}{}^Z$/ps	$10^{-10}D_0$/s^{-1}	$10^{-11}D_i{}^E$/s^{-1}	$10^{-11}D_i{}^Z$/s^{-1}	$V_0{}^E$/kJ mol^{-1}	$V_0{}^Z$/kJ mol^{-1}
(**1**)	308	2.2 ± 0.15	4.2 ± 0.2	1.2	0.5	5.3	3.1	28	9 ± 0.5	3.2 ± 0.5
	241	0.76 ± 0.05	1.8 ± 0.1	3.6	1.2	1.9	0.94	20		
	228	0.50 ± 0.05	1.3 ± 0.1	5.4	1.6	1.5	0.50	12		
(**2**)	242	0.52 ± 0.04	0.72 ± 0.04	4.8	3.4	0.6	2.4	17	7.4 ± 0.5	3.1
	228	0.42 ± 0.03	0.65 ± 0.04	5.9	3.8	0.48	2.0	Rotation very fast		
	218	0.28 ± 0.02	0.52 ± 0.04	8.8	4.8	0.38	0.98			
(**3**)	242	0.58 ± 0.04	0.73 ± 0.04	4.3	3.4	0.54	5.2	Rotation very fast	5.3 ± 0.2	
	228	0.46 ± 0.03	0.58 ± 0.04	5.4	4.3	0.42	4.6			
	218	0.38 ± 0.03	0.48 ± 0.03	6.5	5.2	0.35	3.8			

$6D_0$. In the case of (**3**) the effective correlation time for the deuteron in the *Z*-methyl group is even shorter than the calculated limiting value $0.11/6D_0$ which is probably the result of an overestimation of D_0 for that compound. Such an error may easily arise since the reorientation of (**3**) is presumably anisotropic whereas D_0 is calculated on the basis of T_1 for one nucleus only. On the other hand one may suppose that the *Z*-methyl group in (**3**) as in (**2**) rotates very fast so that the D_0 constant may be estimated from formula $D_0 = 0.11/6\tau_{eff}$. The D_0 values estimated in that way were used in the calculation of D_i for the *E*-methyl group rotation in (**3**) (Table 3).

In summary, we conclude that such large differences in the relaxation behaviour of *E*- and *Z*-methyl groups in compounds (**2**) and (**3**) could not arise solely from the anisotropy of reorientation of amide molecules. This opinion is also supported by previously discussed observations[6] about the influence of viscosity of solvents and structure of amide on ^1H n.m.r. line shapes. Thus all the data presently available point out that, in the liquid phase, the rotation rates of *E*- and *Z*-CH_3 groups in *NN*-dimethylamides are different and that the *Z*-CH_3 group rotates faster than the *E*-CH_3 group.

Experimental

Syntheses of (**1**)—(**3**) are described elsewhere.[6]

Samples of 0.2M solutions of (**1**)—(**3**) in $CDCl_3$ containing small amounts of cyclopentane as a resolution standard and tetramethylsilane were carefully degassed and sealed. The ^1H n.m.r. spectra were recorded on a Tesla BS 487C spectrometer (80 MHz; continuous wave) in the Institute of Drugs, Medical Academy, Warsaw (sweep rate 0.1 Hz s^{-1}; scale 0.1 Hz mm^{-1}). The temperature was controlled by a methanol standard. All the measurements were repeated on a Varian XL 100 pulsed spectrometer in the Institute of Organic Chemistry, Munich University. In each case 10 scans were accumulated and the Fourier transform spectrum contained 830 points on 50 Hz (*ca.* 0.06 Hz per point).

The ^{14}N n.m.r. spectra of 0.8M solutions of (**1**)—(**3**) in $CDCl_3$ were measured in the Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, with a Varian HR60A spectrometer. The method is described in ref. 24.

The T_{1q} values for deuterons in CH_2D groups of (**1**)—(**3**) were determined by the method described in detail in ref. 25. The experimental spectra were visually compared with a series of theoretical ones calculated for different T_{1q} values. In order to include the field inhomogeneity effect, the theoretical line shapes[26] were convoluted with the Lorentzian curve, the widths of which were evaluated on the basis of the cyclopentane signal. Calculations were performed with the aid of the SNMRS program written in FORTRAN 4 using a Cyber CDC175 computer, Leibnitz Counting Center, Munich.

Calculation of Diffusion Constants for DMF.—The right-hand side of equation (1) after division by D_z is expressed in terms of variables: $p = D_x/D_z$, $q = D_y/D_z$, and parameter θ. This system of three equations was reduced to a system of two. The latter was solved for each chosen value of $\theta = 28$—$52°$ in 2° steps by the method of trial and error. Substitution of the p and q values obtained to one of the initial equations gave D_z, $D_x = p \cdot D_z$ and $D_y = q \cdot D_z$. All the above calculations and those of methyl group rotation rates were done on the programmable pocket calculator, Sharp PC1211

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