Investigation of Methyl Reorientations in 1,4-Dimethoxy-2,6-dimethylbenzene by NMR and Inelastic Neutron Scattering

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In this paper a solid state NMR relaxation study and inelastic neutron scattering (INS) experiments (the latter in the solid and liquid phase) are reported for a molecule containing methyl groups in different surroundings, namely 1,4-dimethoxy-2,6-dimethylbenzene. The results are compared with each other and with those of a liquid state NMR study reported earlier. It is found that in this way both the shapes and magnitudes of the various hindering potentials can be determined.

The result is that the methyl groups 1, 2 and 4 possess a threefold cosine-shaped potential with heights given by 7.7, 9.0 and 15.0 kJ/mol according to the solid state NMR measurements (from the INS study the values 7.5, 7.5 and 16.0 kJ/mol were obtained). For methyl group 6 a mixture of a three- and six-fold symmetry had to be taken into account in order to explain the experiments. Except for methyl group 4 the liquid state NMR results deviate from those obtained with the other two techniques. A possible cause for this discrepancy is discussed.

For the molecular structure it is concluded that the reorientations of the methyl groups 1 and 2 are influenced by mutual hindering and that the angle between the plane through the C_4–O–C bond and the aromatic plane is small, whereas for the C_1–O–C bond this angle is estimated to be about 70°.

1. Introduction

The random reorientations of methyl groups have been subject of many studies, using different spectroscopic techniques. The purpose of such investigations can be the motional mechanism itself, or/and the determination of the magnitude and shape of the hindering barrier governing the reorientation. This a.o. can contribute to a better knowledge of the conformation of the molecule to which the methyl group is attached. Among the spectroscopic techniques, available for the investigation of methyl reorientations, we have chosen inelastic neutron scattering (INS) and NMR.

Both methods have their own merits and limitations. With NMR the correlation time characterizing the reorientations can be obtained over a large range, from which the activation energy E_a can be determined. E_a is a measure for the barrier height, but neither the exact value of the height nor the shape of the hindering potential can be abstracted from it. With INS usually only the energy difference between the ground and first excited torsional level and/or the so-called tunnelling splitting of the ground level can be obtained. Hence the height of the barrier can be determined only if an assumption is made about the shape of the barrier. It has been demonstrated by Müller-Warmuth et al. [1] that a combined synthesis of NMR and INS can lead to a more accurate determination of the hindering potential than was possible with each method separately.

The purpose of this paper is threefold.

(i) In [1] molecules with one kind of methyl groups are considered. In this paper it will be investigated whether NMR and INS can also provide information about the hindering potentials in molecules containing methyl groups in different surroundings.

(ii) Recently theories about relaxation through methyl reorientation in solid state NMR have changed appreciably by the introduction of symmetry restricted spin diffusion [2], a phenomenon that has been overlooked so far. It has been shown that in this way discrepancies between the measurements and the traditional relaxation theory can be explained. However, up till now the new concept has not been applied to a study of the methyl group reorientation itself. To our knowledge the present study is the first one in which this will be accomplished.

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(iii) Usually the INS measurements are performed at relatively low temperatures in order to avoid life-time broadening of the peaks in the neutron spectra. It will be investigated whether it is also possible to obtain reliable information at higher temperatures. This opens the possibility, for instance, to compare the hindering barriers in the solid and liquid phase.

As the object of study the molecule 1,4-dimethoxy-2,6-dimethylbenzene (DMDMB) was chosen, see Figure 1. This was done because according to liquid state NMR results for a solution of this molecule [3] some very different barriers to methyl reorientation were present in this molecule. Hence one might expect readily resolved torsional transitions in the neutron spectra as well as separated maxima in the NMR Zeeman relaxation rate vs. inverse temperature curve. In order to be able to assign the different barriers to the methyl groups the experiments have been performed also on DMDMB where one or two methyl groups were deuterated.

The remainder of this paper consists of three sections. In Sect. 2 the solid state NMR experiments are discussed, while in Sect. 3 the INS work is discussed. In the last section the results of the different methods, including the liquid state NMR work, are compared and it is explored whether they can be combined to yield detailed information about the methyl reorientation.

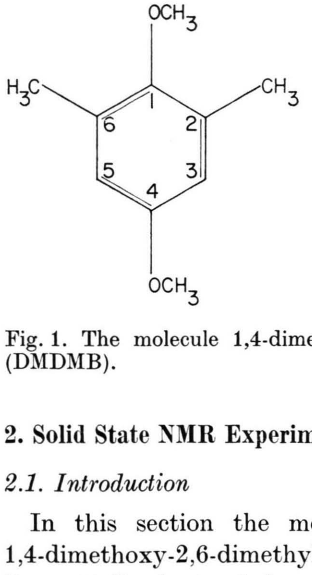

Fig. 1. The molecule 1,4-dimethoxy-2,6-dimethylbenzene (DMDMB).

2. Solid State NMR Experiments

2.1. Introduction

In this section the methyl reorientations of 1,4-dimethoxy-2,6-dimethylbenzene (DMDMB) and its partially deuterated compounds will be investigated in the solid phase by means of proton NMR. This has been done by measuring the Zeeman relaxation as a function of the temperature for a fixed value of the Larmor frequency.

The Zeeman relaxation is caused by the dipolar interactions between the various protons rendered time-dependent by the methyl reorientations. Moreover, the spin diffusion process, due to the time-independent dipolar interactions, plays an important role in those solids, where the relaxation rates of the various protons are unequal. This results, namely, in differences in local Zeeman temperatures during the relaxation process. The spin diffusion is an energy-conserving process which equalizes these temperatures on a time scale short compared with the spin-lattice relaxation times [4]. It has been found [2], that in solids containing reorienting methyl groups the efficiency of the spin diffusion is restricted due to the symmetry properties of these groups. Until recently this phenomenon had not been recognized, and the measurements were interpreted by the traditional relaxation theory, where complete spin diffusion was assumed. It has been shown [5] that this may lead to incorrect values of the correlation time. For an extensive treatment we refer to the references [6—10]. Here we shall confine ourselves to a brief summary of the results, emphasizing the relaxation of the Zeeman system.

2.2. Theory

We assume that the relaxation of DMDMB is governed by methyl groups with random rotations characterized by four correlation times τ_c, one τ_c value for each of the four types of CH_3 groups.

As usual we take into account the symmetry character of the groups, and classify the eight eigenstates of such a group in the presence of an external magnetic field H_0 according to the A, E^a and E^b irreducible representations of the point group C_3. It has been shown [7] that the following quasi constants of the motion can be distinguished: (i) the Zeeman system, defined as the population difference between energy levels splitted by the H_0 field; (ii) the dipolar system, defined as the population difference between levels splitted by the local dipolar fields; (iii) the rotational polarization system, defined as the population difference between the E^a and E^b species; and (iv) the tunnelling system, defined as the population difference between the A and $(E^a + E^b)$ species.

In general all these constants of the motion are dynamically coupled, resulting in a relaxation of each of these quantities governed by a weighted sum of 4 exponentials [7, 9]. In order to observe the spin-lattice relaxation the value of at least one of the above systems has to be brouhgt out of thermal equilibrium. In the following we only consider the auto relaxation rate A_z of the Zeeman system. It is assumed that only this system has been disturbed by one short r.f. pulse, e.g. a 90° pulse (for other preparation methods the observed relaxation may become different [5, 6]). In this case A_z is equal to the initial rate value of the observed non-exponential Zeeman relaxation.

A_z can be written as

$$A_z = (A_z)_{\text{intra}} + (A_z)_{\text{inter}}\,, \tag{1}$$

where $(A_z)_{\text{intra}}$ is due to the time-dependent dipolar interactions between protons belonging to a same methyl group, whereas $(A_z)_{\text{inter}}$ is due to the dipolar interactions between protons belonging to different groups. $(A_z)_{\text{intra}}$ is generally given by

$$\begin{aligned}(A_z)_{\text{intra}} = \frac{9}{40} K S p \{ & J(\omega_T + \omega_0) \\ & + J(\omega_T - \omega_0) + 4[J(\omega_T + 2\omega_0) \\ & + J(\omega_T - 2\omega_0)]\}\,, \quad K = \gamma^4 \hbar^2 / r^6\,. \end{aligned} \tag{2}$$

We shall briefly consider the different parameters of Equation (2):

(i) r is the intra-methyl proton-proton distance.

(ii) S is the so-called efficiency factor, which is given by a weighted sum over i, j of the matrix elements $|\langle\psi(i)|A(t)|\psi(j)\rangle|^2$, where $\psi(i)$ is the eigenfunction of the i-th torsional level and where $A(t)$ is the time-dependent spatial part of the dipolar interactions [11]. The weighting takes into account the occupations of the various levels. S varies between 0 and 1, and depends on the magnitude of the hindering barrier and the temperature. It is difficult to give explicit numbers for S. We shall confine ourselves by remarking that the larger the barrier height and/or the temperature, the more S approaches unity.

(iii) p accounts for the fact that the total number of protons N_H in a sample needs not be equal to the number of protons N_{Me} belonging to the methyl groups. This causes a reduction in A_z by the factor p, given by

$$p = N_{Me}/N_H\,. \tag{3}$$

(iv) $\omega_0/2\pi$ is the larmor frequency.

(v) $\omega_T/2\pi$ is the tunnelling frequency, which is a measure for the energy splitting between the A and E species of the group. For low temperatures, where almost only the ground torsional level is occupied, ω_T equals the tunnelling splitting Δ_0 of the level [11]. For increasing temperatures the tunnelling splittings of the various torsional levels become mixed, resulting in a decrease of ω_T [7, 12, 13, 14]. If the temperature is high enough, ω_T becomes zero. In this case Eq. (2) reduces to the well-known BPP formula [15]. The temperatures for which $\omega_T = \Delta_0$ respectively $\omega_T = 0$ depends on the shape and magnitude of the hindering barrier. Typical values are that for $T \lesssim 20$ K ω_T becomes close to Δ_0, whereas ω_T can be neglected for $T \gtrsim 60$ K [9].

(vi) $J(\omega)$ is the spectral density function characterizing the random motions of the methyl groups. We assume that $J(\omega)$ is given by the lorentzian function

$$J(\omega) = \tau_c/(1 + \omega^2 \tau_c^2)\,, \tag{4}$$

where τ_c is the correlation time.

At different temperatures different processes determine τ_c. At high temperatures τ_c is caused by the classical random hopping of the methyl protons over the hindering barriers. Usually τ_c is then supposed to be given by the Arrhenius equation:

$$\tau_c = \tau_0 \exp(E_a/k_B T)\,. \tag{5}$$

The activation energy E_a is taken equal to the barrier height [16], or the difference between the barrier height and the ground torsional level [17]. τ_0 is the correlation time at infinite temperature, given by [16]

$$\tau_0 = (4\pi/9)\sqrt{I/2E_a}\,, \tag{6}$$

where I denotes the moment of inertia of the methyl group. At lower temperatures the classical reorientations of the methyl groups due to random hopping over the barrier is inefficient [18], and the time-dependence in the positions of the protons is now caused by the tunnelling of these protons through the hindering barrier, rendered random because of non-magnetic transitions between the torsional levels. For very low temperatures ($T < 20$ K) only the transitions between the ground and first torsional level occur and τ_c is given by [11]

$$\tau_c = \tau_0' \exp(E_{10}/k_B T)\,. \tag{7}$$

The activation energy E_{10} is equal to the energy difference between these levels. The value of τ_0' is difficult to predict. Haupt [11] calculated that τ_0' is proportional to E_{10}^{-3}. For the case $E_{10} = 0.4$ kJ/mol he found that τ_0' is of the order of $5 \cdot 10^{-10}$ sec, which is in good agreement with the experimental value of $3 \cdot 10^{-10}$ sec, obtained for toluene.

At intermediate temperatures the random tunnelling due to non-magnetic transitions between the ground torsional level and higher torsional levels becomes important, so that the activation energy will become larger than E_{10} whereas τ_0 will become smaller.

We now return to Equation (1). Considering the term $(A_z)_{\text{inter}}$, it can be shown [9, 19] that this term can cause relaxation transitions between A and E states, resulting in spectral density functions $J(\omega_T \pm n\omega_0)$, and between E^a and E^b states, resulting in spectral density functions $J(n\omega_0)$, $n = 1, 2$.

Resuming, the following relaxation behaviour may be observed when the auto-relaxation rate A_z of the Zeeman system is measured for decreasing temperatures.

(i) For $T > 60$ K A_z usually displays a single maximum, which occurs for $\omega_0\tau_c = 0.616$. From the slopes on both sides of the maximum the activation energy E_a can be determined from which the barrier height can be estimated.

(ii) For $T < 60$ K ω_T is increasing to its final value Δ_0 which can be larger than the usual values of ω_0 for barrier heights lower than ca. 6 kJ/mol (for instance for a three-fold barrier with a height of 5.9 kJ/mol, $\Delta_0/2\pi$ is given by 95 MHz). Then, if ω_0 can be neglected in Eq. (2), a second maximum may occur for $\omega_T\tau_c = 0.616$, if τ_c is caused now by the random tunnelling. On the low temperature side of this maximum $\omega_T\tau_c \gg 1$, and so the inter-methyl contribution in Eq. (1) depending on $J(\omega_0)$ and $J(2\omega_0)$ may become dominant for the relaxation. This can give rise then to another maximum in A_z for $\omega_0\tau_c = 0.616$. Moreover, extra maxima can occur in the temperature region where $\omega_T \cong \omega_0$, $2\omega_0$ [9, 20] and for specific hindering potentials [21] so that especially the relaxation at low temperature can be difficult to interpret. We shall come back to this matter later on.

2.3. Experimental

We measured the auto-relaxation of the Zeeman system as a function of the temperature for the following compounds: 1,4-dimethoxy-2,6-dimethylbenzene (DMDMB), see Fig. 1; DMDMB with the CH_3 group 4 replaced by a CD_3 group (DMDMB-D4); DMDMB with the CH_3 1 replaced by a CD_3 group (DMDMB-D1); and DMDMB with both CH_3 groups 1 and 4 replaced by CD_3 groups (DMDMB-D1,4). All samples had a purity and a degree of deuteration both better than 98%. The temperature was varied between 290 K and 30 K, using a home-built bath cryostat. The Zeeman relaxation was measured by means of a home-built pulse spectrometer, operating at 28.1 MHz, using a $\pi/2 - \tau - \pi/2$ sequence, with a pulse duration of 5 μsec.

The results given in the next section have been obtained by taking the following into account:

(i) In case of non-exponential relaxation the initial rate value of the curve $\ln(M_0 - M_z)/M_0$ versus t (M_z is the magnetization and M_0 its thermal equilibrium value) has to be taken in order to obtain the value of the Zeeman auto-relaxation rate A_z [5]. This has as a consequence that the accuracy of the values becomes rather poor: 10 to 15% of its value (a more accurate procedure would be obtained by rotating the sample externally because then the non-exponentiality has disappeared [6], but to perform this as a function of the temperature was not possible at the time the experiments were carried out).

(ii) It has been shown extensively in [5] that for $\omega_0\tau_0 \ll 1$ the observed non-exponential relaxation can be used to determine the contribution of the inter-methyl relaxation to the total relaxation. This method has been applied.

(iii) It appeared that the relaxation behaviour as a function of the temperature depended on the way the samples were cooled down from the liquid to the solid phase. The freezing point of all samples is 244 K, but it was found that in case of fast cooling (0.5 to 1 K/sec) undercooling occurred up to 200 K. In that case a Zeeman relaxation was found which could only be explained by a distribution of correlation times [22]. From this it may be concluded that probably the material was in some form of glassy phase, where the hindering potentials of chemically identical methyl groups become different. The results of these measurements are beyond the scope of this paper, and will not be reported here. For small cooling velocities (0.1 to 0.2 K/sec) the chemical identical groups could be described a single correlation time as will become clear from the next section. Obviously now the material was in a polycrystallic phase (of an unknown crystal structure, however). We shall only consider the latter results.

We finally note that besides the Zeeman relaxation also the dipolar relaxation has been measured for the first three compounds. As the latter measurements only confirmed the results of the first ones, and did not provide new information, the dipolar relaxation will not further be considered.

2.4. The Measurements

Figure 2 shows the auto Zeeman relaxation rates of the four compounds in the temperature region $4.5 < 10^3/T < 34\ K^{-1}$.

We observe that for the compounds DMDMB and DMDMB-D1 three, for the other compounds two

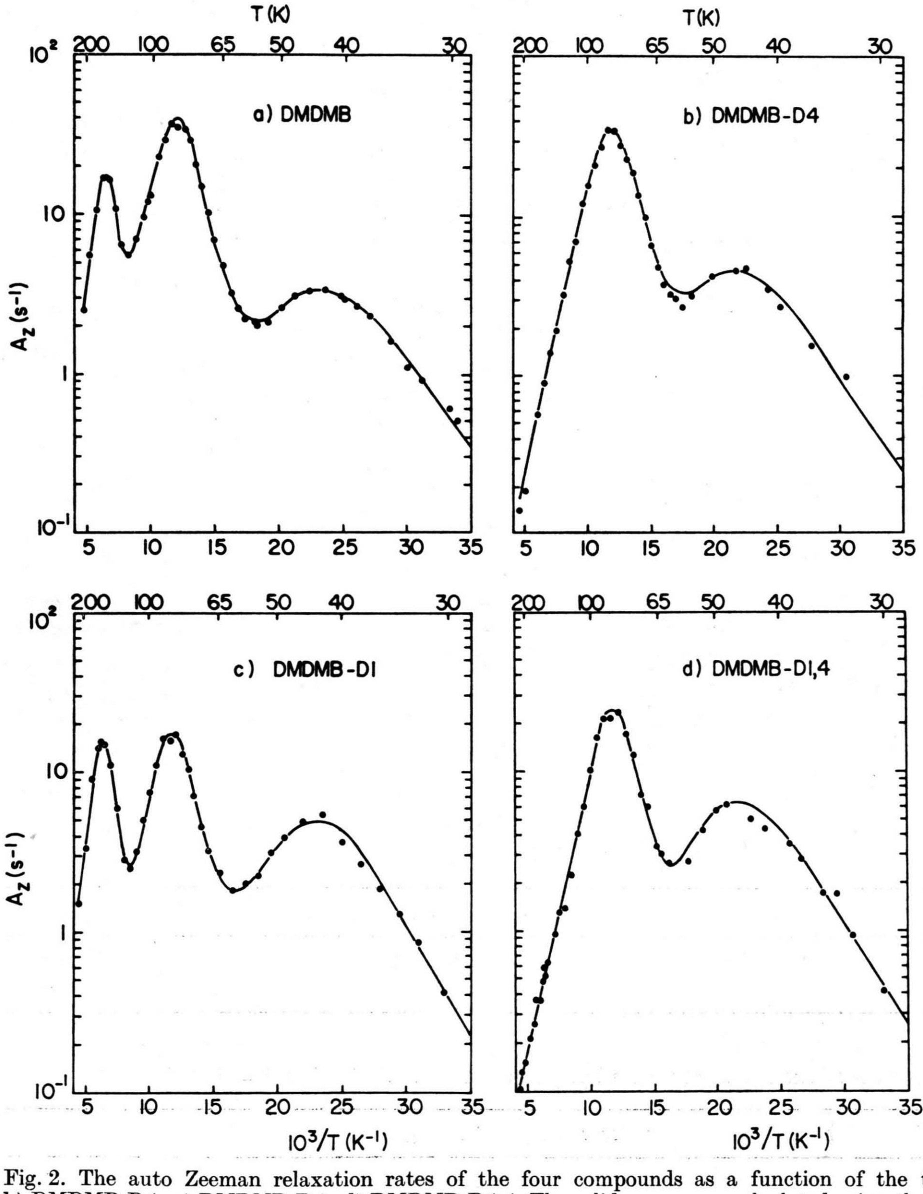

Fig. 2. The auto Zeeman relaxation rates of the four compounds as a function of the temperature. a) DMDMB; b) DMDMB-D4; c) DMDMB-D1; d) DMDMB-D1,4. The solid curves are calculated using the data of the Sections 2.4.1, 2.4.2 and 2.4.3.

relaxation maxima can be distinguished, occurring at respectively $10^3/T = 6.2\ K^{-1}$ (DMDMB and DMDMB-D1), $11.8\ K^{-1}$ and $23\ K^{-1}$ (all compounds).

The following can be deduced:

(i) The maximum at $10^3/T = 6.2\ K^{-1}$ is caused by the reorientations of the methylgroup 4.

(ii) The maximum value of A_z for $10^3/T = 11.8\ K^{-1}$ is for DMDMB and DMDMB-D4 approximately two times larger than for the other compounds. Hence, this maximum is caused by the reorientations of methyl group 1 and by one of the methyl groups 2 or 6. For convenience we define the latter group to be methyl group 2.

(iii) Deuteration of the methyl groups 1 or 4 does not cause a decrease in the relaxation maximum at $10^3/T = 23\ K^{-1}$ (in fact deuteration causes an increase in A_z, which can be explained by the increase in p). We conclude that this maximum is caused by the remaining methyl group 2 or 6. For convenience we define this group to be methyl group 6.

We shall consider the reorientations of the different methyl groups separately.

2.4.1. The Reorientation of Methyl Group 4

Table 1 gives the values of the different qualities governing the relaxation of DMDMB and DMDMB-D1 in the temperature region $4.5 < 10^3/T < 8\ K^{-1}$. The data were obtained after a correction of the relaxation for $10^3/T \gtrsim 7\ K^{-1}$ for the relaxation corresponding to the maximum at $10^3/T = 11.8\ K^{-1}$. This has been done by substracting the relaxation curve of DMDMB-D4 from that of DMDMB, respectively substracting the curve of DMDMB-D1,4 from that of DMDMB-D1. Here we have corrected for the difference in magnitudes of the relaxation curves for $10^3/T > 9\ K^{-1}$, which is mainly due to a change in the p-factor of the different compounds. The remaining relaxation curve has been interpreted by the Eqs. (1) and (2) after insertion of $\omega_T = 0$ (tunnelling effects can be neglected at the considered temperatures). We observe that E_a and τ_0 are very similar for both compounds. These quantities characterize the classical reorientation of the methyl group. $({}^{10}\log \tau_0)^{\text{theor}}$ has been calculated from Equation (6). The agreement with the experimental values is satisfactory. Further we observe that for both compounds the relative contribution of the intermethyl relaxation is about 30%, a reasonable number. Finally the value of S has been calculated assuming K to be given by $1.73 \cdot 10^{10}\ s^{-2}$, which follows from its definition in Eq. (2) after insertion for r the generally accepted value of $1.79 \cdot 10^{-10}$ m.

It follows that for DMDMB S is close to unity, whereas it is less for the partially deuterated compound. It is not obvious which phenomenon is responsible for this change.

2.4.2. The Reorientations of the Methyl groups 1 and 2

The relaxation of DMDMB-D1 and DMDMB-D1,4 in the temperature range $9 < 10^3/T < 16\ K^{-1}$ is governed by methyl group 2. The measurements have been interpreted with the Eqs. (1) and (2), again assuming that tunnelling still can be neglected, so that $\omega_T = 0$. The results are given in Table 2.

Table 1. The relaxation due to the reorientations of the methyl group of the 4-methoxy group. A = (DMDMB) − (DMDMB-D4); B = (DMDMB-D1) − (DMDMB-D1,4).

	p	E_a (kJ/mol)	${}^{10}\log \tau_0$	$({}^{10}\log \tau_0)_{\text{theor}}$	$(A_z)_{\text{inter}}/A_z$	KS (s^{-2})	S
A	3/14	13.4 ± 0.8	-12.8 ± 0.3	-13.3	0.3 ± 0.2	$(1.7 \pm 0.3) \cdot 10^{10}$	0.98
B	3/11	13.8 ± 0.8	-12.9 ± 0.3	-13.3	0.3 ± 0.2	$(1.1 \pm 0.2) \cdot 10^{10}$	0.64

Table 2. The relaxation due to the reorientations of the methyl group 2. A = DMDMB-D1; B = DMDMB-D1,4.

	p	E_a (kJ/mol)	${}^{10}\log \tau_0$	$({}^{10}\log \tau_0)_{\text{theor}}$	$(A_z)_{\text{inter}}/A_z$	KS (s^{-2})	S
A	3/11	7.9 ± 0.4	-13.3 ± 0.3	-13.2	0.3 ± 0.2	$(1.3 \pm 0.3) \cdot 10^{10}$	0.75
B	3/8	7.9 ± 0.4	-13.3 ± 0.3	-13.2	0.2 ± 0.1	$(1.5 \pm 0.3) \cdot 10^{10}$	0.87

Table 3. The relaxation due to the reorientations of the methyl group of the 1-methoxy group. A = DMDMB; B = DMDMB-D4.

	p	E_a (kJ/mol)	$^{10}\log \tau_0$	$(^{10}\log \tau_0)_{\text{theor}}$	$(A_z)_{\text{inter}}/A_z$	KS (s^{-2})	S
A	6/14	6.7 ± 0.5	-12.5 ± 0.4	-13.2	0.4 ± 0.2	$(1.8 \pm 0.3) \cdot 10^{10}$	1.04
B	6/11	6.7 ± 0.5	-12.5 ± 0.4	-13.2	0.2 ± 0.1	$(1.5 \pm 0.2) \cdot 10^{10}$	0.87

It is very likely that E_a and τ_0 characterize the classical reorientation again. The reorientation of methyl group 1 has been obtained from the measurements of DMDMB and DMDMB-D4 after substraction of the relaxation of methyl group 2. This has been done using the data of Table 2 and under the assumption that methyl groups 1 and 2 contribute equally to the relaxation. The results are given in Table 3. We observe that the reorientations of both methyl groups 1 and 2 are very similar. The values of S in the Tables 2 and 3 have been calculated using for K the value $1.73 \cdot 10^{10}\ s^{-2}$ again. The same result is obtained as in the previous section: $S \simeq 1$ for DMDMB and becomes less for the other compounds.

2.4.3. The Reorientation of Methyl group 6

For the compound DMDMB-D1,4 it is found that in the temperature region $4.5 < 10^3/T < 8\ K^{-1}$ the Zeeman relaxation rate, calculated with the data of Table 2, is smaller than has been observed experimentally.

We propose as an explanation that in this temperature region the relaxation is governed by the reorientations of both CH_3 groups 2 and 6.

The reorientations of one of the groups give rise to the relaxation maximum at $10^3/T = 11.7\ K^{-1}$ and the relaxation due to the reorientations of the other group can be determined by substraction of the relaxation strength, calculated using the data of Table 2, from the experimental data. The result is given in Figure 3.

We interpreted the data in the following way: first we use the Eq. (2) under the assumption that in this temperature region the extreme narrowing condition $\omega \tau_c \ll 1$ is fulfilled. Then the activation energy can be determined. The result is: $E_a = (4.4 \pm 1)$ kJ/mol. Secondly, as the maximum of this relaxation curve is not observed, it is not possible to determine τ_0 in the usual way. Therefore we use another approach: we assume that the relaxation constant K is given again by $1.73 \cdot 10^{10}\ s^{-2}$. Moreover, as $(A_z)_{\text{inter}}/A_z$ could not be determined in this case, we estimate this factor to be 0.2. S was taken to be 1. Then by comparing the experimental and calculated value at a specific temperature τ_0 can be determined. The result is that $^{10}\log \tau_0 = -12.5 \pm 0.4$, a value which is in rather good agreement to the value -13.1, obtained from Eq. (6) and $E_a = 4.4$ kJ/mol. (We remark that the relaxation of methyl group 6 is not visible in the relaxation of the other compounds, because there the relaxation in the temperature region $4.5 < 10^3/T < 8\ K^{-1}$ is enhanced by the reorientations of the methyl groups 1 and/or 4).

It has been stated in the beginning of this section, that methyl group 6 is also governing the relaxation of all compounds in the temperature region $17 < 10^3/T < 34\ K^{-1}$.

It can be calculated that the activation energies obtained from the relaxation for $17 < 10^3/T < 34\ K^{-1}$ are much smaller than 4.4 kJ/mol, obtained from the high temperature measurements. Moreover, the

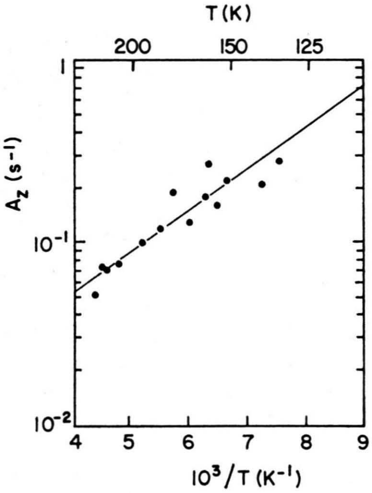

Fig. 3. The auto Zeeman relaxation rate of DMDMB-D1,4 in the temperature region $4.5 < 10^3/T < 8\ K^{-1}$. The experimental points are obtained by substracting from the measured data the relaxation rate following from the data of Table 2. The solid curve is calculated using the data given in the Section 2.4.3.

maximal value of A_z for $10^3/T \simeq 23\ \text{K}^{-1}$ is approximately four times smaller than the relaxation maxima caused by the reorientations of a single methyl group. Similar results have been reported for other materials [11, 23, 24]. Several explanations are possible for the low temperature maximum:

(i) It is probable, that the influence of tunnelling of the methyl group 6 can no longer be neglected. Then a possible explanation of the maximum might be that the effective tunnelling splitting ω_T becomes comparable to ω_0 for $10^3/T \simeq 23\ \text{K}^{-1}$. However, this is unlikely because it can be calculated, that for a three-fold barrier with a height of 4.4 kJ/mol the tunnelling splitting is much larger than ω_0 for the whole temperature region $17 < 10^3/T < 34\ \text{K}^{-1}$ (this has been done using a formula for the temperature dependence of ω_T given in [7]). Therefore this possibility will not be further considered.

(ii) Because ω_T is so large (it is calculated that $\omega_\text{T} \simeq 3 \cdot 10^9\ \text{s}^{-1}$ for $10^3/T \simeq 23\ \text{K}^{-1}$) it may be assumed that $\omega_\text{T} \tau_\text{c} \gg 1$ for the low temperature region. It has been stated at the end of Sect. 2 that under this condition that part of the inter-methyl relaxation which is proportional to $J(n\omega_0)$, $n = 1, 2$, can be dominant for the relaxation. Then the relaxation maximum would be found for $\omega_0 \tau_\text{c} \simeq 1$ again, where τ_c now is caused by the random tunnelling of the methyl group through the barrier. In this way the fact that the maximum is too small can easily be understood, because it follows from the Tables 1, 2 and 3 that the inter-methyl relaxation is only 20 to 40% of the total relaxation.

(iii) Hubbard and Johnson [21] showed that for specific mixtures of three- and six-fold barriers two relaxation maxima can occur: one governed by the classical reorientations over the three-fold barrier, and a second governed by the classical reorientations over the six-fold barrier. The magnitudes of both maxima, which indeed are smaller than the value found for the case of a pure three- or six-fold barrier, depend on the type of mixing, and the activation energies correspond to the heights of the two barriers.

In both cases (ii) and (iii) the relaxation can be interpreted by a formula similar to Eq. (2), multiplied by some factor $x < 1$, and with $\omega_\text{T} = 0$. Table 4 gives the results, where the relaxation constant C is defined as $C = KSx$.

Table 4. The relaxation due to the reorientations of methyl group 6 with the activation energy of 4.4 kJ/mol at high temperatures. A = DMDMB; B = DMDMB-D4; C = DMDMB-D1; D = DMDMB-D1,4.

	p	E_a (kJ/mol)	$^{10}\log \tau_0$	C (s^{-2})
A	3/14	2.2 ± 0.3	-11.1 ± 0.2	$(4.4 \pm 0.6) \cdot 10^9$
B	3/11	2.3 ± 0.4	-11.1 ± 0.5	$(4.7 \pm 0.6) \cdot 10^9$
C	3/11	2.7 ± 0.3	-11.7 ± 0.4	$(4.8 \pm 0.6) \cdot 10^9$
D	3/8	2.6 ± 0.4	-11.5 ± 0.3	$(4.6 \pm 0.6) \cdot 10^9$

We observe that indeed the activation energy is much lower than the value obtained from the high temperature measurements. Now it follows from Table 4 that the value of τ_0 is at least one order of magnitude larger that the values found for the case of classical reorientations, see Tables 1, 2 and 3 (for $E_\text{a} = 2.5$ kJ/mol Eq. (6) predicts a value of $^{10}\log \tau_0 = -13.0$). It has already been stated in Sect. 2, that τ_0 is predicted to increase if the reorientations are caused by the random tunnelling process (if we insert $E_\text{a} = 2.5$ kJ/mol into Haupt's formula [11] for τ_0, derived for the case of random tunnelling, we obtain a value of $^{10}\log \tau_0 = -11.6$ which is in good agreement with the experimental values). Therefore we conclude that the relaxation in the temperature region $17 < 10^3/T < 34\ \text{K}^{-1}$ is caused by a random tunnelling process of methyl group 6 through the barrier, so that the apparent activation energy is related to energy differences between torsional levels within the barrier. Moreover, as it can be shown that for a three-fold barrier with a height of 4.4 kJ/mol indeed $\omega_\text{T} \tau_\text{c} \gg 1$, if the values of τ_0 and E_a of Table 4 are used, it is probable that the relaxation is caused by the inter-methyl interactions.

2.5. *Interpretation of the NMR Results*

A comprehensive discussion will be given in Section 4. Here we shall confine ourselves to the following remarks:

(i) The activation energy of the 6-methyl group corresponding to the classical reorientation is 4.4 kJ/mol. As the relaxation for $10^3/T > 17\ \text{K}^{-1}$ is caused by the random tunnelling of this group, the apparent activation energy of 2.5 kJ/mol corresponds to energy differences between torsional levels inside the potential well. These differences depend on the shape of the hindering potential. For instance, for a pure three-fold potential with a height of 5.2 kJ/mol the energy gaps between the ground torsional level and the higher levels are approximately given by: $E_{10} \simeq 1.6$ kJ/mol; $E_{20} \simeq 2.9$ kJ/mol and $E_{30} \simeq 4.4$ kJ/mol. For a pure six-fold barrier with a same height these numbers are: $E_{10} \simeq 2.8$ kJ/mol and $E_{20} \simeq 5.4$ kJ/mol. Hence if the barrier is three-fold the random tunnelling in the temperature region $17 < 10^3/T < 34$ K^{-1} would be mainly caused by non-magnetic transitions between the ground and second torsional level, whereas it would be caused by transitions between the ground and the first level for a pure six-fold barrier. Hence, the shape of the hindering potential from NMR data alone cannot be given without further knowledge of other energy differences between the various levels (this might be solved by measuring the relaxation also for $10^3/T > 34$ K^{-1}, but this is rather difficult because of the long relaxation times).

(ii) No experimental evidence has been found for the reorientations of the methoxy groups around the aryl oxygen bonds. This means that for the whole considered temperature range the correlation time characterizing this motion is larger than the correlation times characterizing the methyl reorientations.

3. INS Experiments

3.1. Introduction

In order to be able to differentiate between the various methyl groups in DMDMB, a series of inelastic neutron scattering experiments has been carried out applying

(i) selective deuteration of a methyl group;
(ii) variation of the temperature.

ad (i) The neutron scattering length of a deuterium nucleus is much smaller than its equivalent for hydrogen. Effectively a deuterated group becomes "invisible" in a neutron scattering experiment on a hydrogenous compound. So by comparing the spectrum of a partly deuterated sample with a non-deuterated one, the different methyl groups in principle can be identified.

ad (ii) At low temperatures only the excited torsional levels within a low barrier are sufficiently occupied to give rise to observable peaks in the neutron spectrum. Increase of the temperature will raise the population of higher levels, and then peaks of intermediate and high barriers become visible too. A rise in temperature will cause broadening of the excited levels so that the determination of the torsional transitions becomes less accurate.

In view of these considerations, and because of the limited time available on the spectrometer, only a non-deuterated sample and a sample having the 1-methoxy group deuterated were measured at four different temperatures.

3.2. Theory

In a neutron scattering experiment on an organic compound the dominant contribution is from the hydrogen atoms because of their large scattering length for incoherent scattering. The double differential scattering cross section for incoherent neutron scattering is given by

$$\frac{\mathrm{d}^2\sigma}{\mathrm{d}\Omega\,\mathrm{d}\omega} = b^2 \frac{k}{k_0} S_\mathrm{s}(\boldsymbol{\varkappa}, \omega)\,, \tag{8}$$

where b is the incoherent scattering length, k_0 and k are the magnitudes of the incident and the scattered neutron wave vectors respectively, and $S_\mathrm{s}(\boldsymbol{\varkappa}, \omega)$ is the self part of the scattering function at wave-vector transfer $\boldsymbol{\varkappa}$ and energy transfer $\hbar\omega$. The coherent scattering contribution in hydrocarbons does not exceed five percent of the total scattering and is mainly located at particular $\boldsymbol{\varkappa}$ values (Bragg scattering).

The dominant features in an inelastic neutron spectrum of a sample containing methyl groups are usually due to lattice vibrations and methyl torsions. This is caused by the fact that in first approximation the intensity of a peak is proportional to the mean squared amplitude of the corresponding vibration, which is large for these cases. It is not possible to assign these peaks a priori. The transitions between torsional levels of the methyl group in the hindering potential can be calculated from the Schrödinger equation in one dimension:

$$-\frac{\hbar^2}{2I}\frac{\mathrm{d}^2\Psi}{\mathrm{d}\alpha^2} + V(\alpha)\,\Psi = E\Psi\,, \tag{9}$$

where I is the moment of intertia of the methyl group, $V(\alpha)$ the angle dependent potential with rotation angle α, Ψ the eigenfunction and E the (energy) eigenvalue of the rotor. Eigenvalues in a 3-fold cosine potential with $V(\alpha) = \frac{1}{2} V_3(1 - \cos 3\alpha)$ are given by Herschbach [25]. The scattering function $S_\mathrm{s}(\boldsymbol{\varkappa}, \omega)$ in this case will show peaks at energy transfers corresponding with transitions between these energy levels. If 6-th and higher order terms are introduced in $V(\alpha)$ the level scheme will change correspondingly. So a unique determination of both height and shape of the potential is only possible if sufficient torsional transitions can be measured [1, 26, 27].

It should be noted that the former description with a static potential only applies at very low temperatures. At higher temperatures the hindering barrier will include a (small) fluctuating part due to the non-static environment of the methyl group. Effectively this results in a temperature broadening of the energy levels and hence the torsional transitions. This broadening will be small near the bottom of a deep potential well, but can be very large near the top of a well. As the energy levels near the top of the barrier are very sensitive to the shape of the potential, an accurate determination of this shape in the condensed phases at elevated temperatures is very difficult and often irrelevant.

3.3. Experiments and Data Handling

The neutron spectra were obtained with the rotating-crystal spectrometer RKS I at the HOR reactor in Delft. This spectrometer is described elsewhere [28]; it uses an incoming neutron-wavelength of 4.08 Å (energy 5 meV) and has an energy resolution of about 10%. ^{3}He-detectors were placed at 15 different scattering angles ranging from 8.5° till 91°. The spectra were recorded on a multichannel analyser, using 128 channels of 16 μs width for each scattering angle.

The sample chamber (flat plate geometry) was placed in a liquid-N_2 cryostat. The transmission of the samples under investigation was about 92%. The empty container was measured at 200 K. The uncertainty in the recorded temperatures was less than 2 K, including a temperature instability of about 1 K. An integrated number of counts per detector and measurement between $2 \cdot 10^5$ and $5 \cdot 10^5$ was reached. The measurements were performed on 1,4-dimethoxy-2,6-dimethylbenzene (DMDMB) and on 1-trideutero methoxy-4-methoxy-2,6-dimethylbenzene (DMDMB-D1) at 119, 200 and 264 K in the solid and at 294 K in the liquid phase. The glassy phase was observed for DMDMB only.

The obtained time-of-flight spectra were corrected for background and scattering from the aluminium sample-container. In order to improve the statistical accuracy of the inelastic data, the spectra for different scattering angles were added, using angles at 35° and higher only. The intensity of the inelastic spectra at angles below 35° was low, and therefore they would not have contributed to a higher precision. An example of the results of this procedure is given in Figure 4. It should be noted that the relative intensities of the peaks in each individual spectrum have to be considered with some caution as the heights are approximately proportional to $\varkappa^2$ and $\varkappa$ varies considerably with the energy transfer. Moreover, neutron spectra at different $\varkappa$ are added.

3.4. Analysis

The inelastic spectrum of both compounds under investigation shows three prominent peaks in the solid phase at 119 K (Figure 4). The difference in intensity between these spectra is in the first place due to the peak at 20 MeV, as can be seen in Fig. 5 where the direct difference of the two spectra is displayed with open circles. This suggests that this peak may be associated with the $1 \rightarrow 0$ torsional transition of methyl group 1 (the transition from the first excited to the ground torsional level). The peak at 4 meV probably is due to lattice vibrations for reasons to be given below. However, in the spectrum of DMDMB-D1 (Fig. 4) still an appreciable intensity is present at 20 meV, which leads to the conclusion that another methyl group with the same main torsional transition is present in the

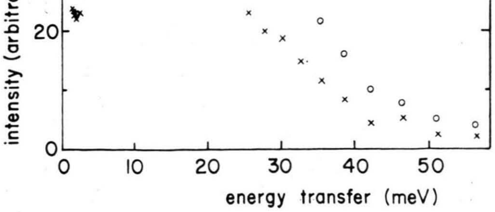

Fig. 4. Neutron-energy-gain spectra (summation of various scattering angles) at 119 K in the solid phase for DMDMB (circles) and DMDMB-D1 (crosses).

molecule. In view of the molecular geometry the most probable candidate is one of the adjacent methyl groups, so that coupled rotations must take place. Since it is irrelevant which of these two groups has this transition, group 2 is chosen. Apparently the deuteration of group 1 has little or no influence on the reorientational barrier of both groups 1 and 2. If one accepts that these two methyl groups have essentially the same neutron spectrum, it can easily be seen that by subtracting the measurement on DMDMB from twice the measurement on DMDMB-D1, a spectrum is left which shows features due to groups 4 and 6 and the two single hydrogen atoms on the benzene ring. This spectrum (with crosses in Fig. 5) shows peaks at 4 meV and 12 meV, while some intensity is present around 30 meV. Spectra at higher temperatures and in the liquid are given in Fig. 5 too.

The assignment of the peaks can be made as follows. The peak at 4 meV is visible in all spectra in the solid phase and disappears in the liquid. Furthermore, this peak is relatively sharp, even at high temperatures. It, therefore, is assigned to vibrations of the lattice. The peak at 20 meV, which has been assigned above, is substantially broadened at higher temperatures. This is to be expected for a strongly anharmonic methyl torsion [1, 29]. The strongly temperature dependent feature at 30 meV is associated with the 1 → 0 torsional transition of methyl group 4. This assignment is justified by the agreement with a neutron scattering study on para-azoxyanisole [27]. In the inelastic spectrum of this substance a peak was found at 31 meV for a methoxy group in a similar environment as group 4. The peak at 12 meV is assigned to the 1 → 0 torsional transition of group 6. Its temperature dependence indicates a methyl torsion [1, 29] and group 6 is the only remaining candidate.

From the torsional transitions, assuming a simple three-fold barrier, the potential heights can be determined. Because the position of the respective torsional peaks does not shift significantly with temperature in the solid and the liquid, it is concluded that the hindering barriers of the methyl groups are approximately constant. This is an indication that these barriers are intra-molecular in character. They are listed in Table 5.

From the deduced barriers, the transitions from the second excited level to the first excited level and to the ground state can be determined. These

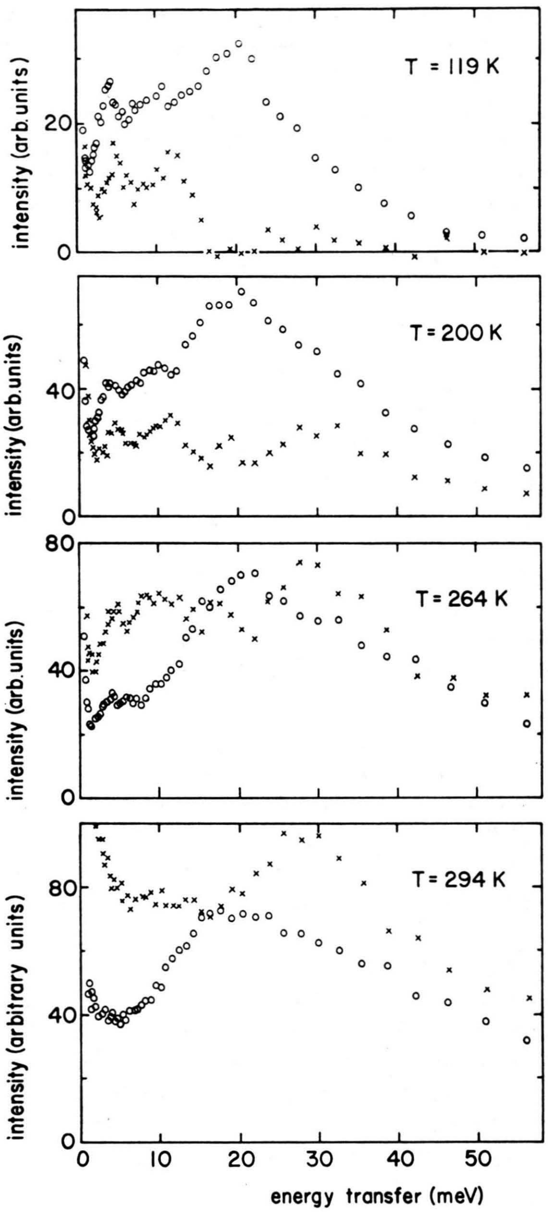

Fig. 5. Approximate spectra of methyl group 1 (circles) and of the groups 4 and 6 (crosses) at various temperatures, obtained from differences of spectra of partially deuterated and non-deuterated samples (see text).

Group	ΔE (meV)	V_3 (kJ/mol)
1 and 2	20 ± 1	7.5 ± 0.8
4	30 ± 2	16 ± 2
6	12 ± 1	3.1 ± 0.4

Table 5. Inelastic transitions ΔE and corresponding barrier heights V_3 of DMDMB(-D1) in the solid and liquid phase.

transitions may become important at higher temperatures. A close examination of the spectra of group 1 (Fig. 5) for instance reveals intensities at 18 meV and 38 meV with rising temperature, which correspond very well with the transitions in a three-fold cosine barrier from the second excited level. A corresponding tentative explanation can be given for the broadening of the feature at 12 meV (group 6).

4. Discussion

This section is dedicated to a comparison of the results on DMDMB as obtained with NMR and INS. Table 6 gives the activation energies E_a, frequency factors $^{10}\log \tau_0$ and barrier heights V_3 for the various methyl reorientations above 60 K as determined by liquid and solid state NMR and INS experiments (the liquid state NMR data are adopted from [3]). The barrier heights are calculated assuming a three-fold cosine-shaped hindering potential for the four methyl groups. The following can be observed:

(i) Except for CH_3 group 4 the agreement between the liquid state NMR and the other two techniques is poor, the resemblance for CH_3 group 6 being misleading as will be shown in Section 4.1. Limitations in the liquid state NMR method can give rise to this bad agreement, as will be discussed in the same section.

(ii) For the CH_3 groups 1, 2 and 4 the INS (solid and liquid state) and solid state NMR results compare well, justifying the assumption of a threefold potential barrier for these groups.

(iii) For CH_3 group 6 the INS and solid state NMR experiments lead to different values of V_3. This discrepancy can be solved if a mixture of a three- and six-fold potential is taken into account. This will be shown in Section 4.2.

(iv) The V_3 values of the various methyl groups provide information about the molecular geometry. This will be discussed in Section 4.3.

4.1. Discrepancy between the Liquid NMR and the Other Results

For methyl groups 2 and 6 very low E_a values are found via liquid state NMR. In order to compare these values with the solid state results it should be kept in mind that in the HR NMR spectrum of DMDMB in solution the methyl groups 2 and 6 are equivalent. Therefore the E_a value will be the slope of the plot of $\ln(\tau_c(2) + \tau_c(6))/2$ versus $1/T$. $\tau_c(2)$ and $\tau_c(6)$ are the τ_c values of CH_3 groups 2 and 6 respectively. Substituting the solid state NMR data one finds an E_a value of 5.7 kJ/mol in the temperature range where the liquid state NMR measurements were performed. This is distinctly much larger than the upper limit of 3.4 kJ/mol. The E_a values in the liquid and solid state need not be equal, as will be discussed later on, but such a large difference is not very likely. The most probable cause for this discrepancy will now be discussed. In liquids or solutions the methyl correlation time τ_c can only be determined if τ_c and the overall molecular correlation time τ_m are in the range $0.2 < \tau_m/\tau_c < 5$ [30]. Because this was the case for methyl group 4, its E_a value could be determined rather accurately. For the CH_3 groups 2 and 6 $\tau_m/\tau_c \simeq 5$. Therefore only an upper limit for E_a could be given. Immediately associated with this problem is a source of error which was not taken into account in the liquid state NMR data in Table 6, namely the uncertainties in the intermolecular distances. From the expressions for the relaxation times, given in Ref. [3], it can be deduced that a systematic error in r results in an error in τ_c which depends on the ratio τ_m/τ_c, and so on the temperature. This leads to a systematic error in E_a,

Table 6. Activation energies E_a, frequency factors $^{10}\log \tau_0$ and the threefold hindering potential V_3 for methyl reorientation in DMDMB above 60 K as determined by liquid and solid state NMR and INS experiments. The NMR V_3 value is given by $E_a + E_0$. E_0 is the energy difference between the ground torsional level and the bottom of the potential V_3.

Methyl group nr.	Liquid state NMR			Solid state NMR			INS
	E_a (kJ/mol)	V_3 (kJ/mol)	$^{10}\log \tau_0$	E_a (kJ/mol)	V_3 (kJ/mol)	$^{10}\log \tau_0$	V_3 (kJ/mol)
1	—	—	—	6.7 ± 0.5	7.7 ± 0.6	-12.5 ± 0.4	7.5 ± 0.8
2	$\leqq 3.4$	< 4.2	> -12.5	7.9 ± 0.4	9.0 ± 0.5	-13.3 ± 0.3	7.5 ± 0.8
4	11.8 ± 1.3	13.1 ± 1.5	-13.3 ± 0.2	13.6 ± 0.7	15.0 ± 0.8	-12.8 ± 0.3	16.0 ± 2.0
6	$\leqq 3.4$	< 4.2	> -12.5	4.4 ± 1.0	5.2 ± 1.1	-12.5 ± 0.4	3.1 ± 0.4

which can be large. For instance, in the liquid state expression for T_1 distances between ring protons and ortho methyl protons in their three equilibrium positions enter. Every deviation from the three equilibrium positions (chosen in the model to calculate expressions for the relaxation times [3]) makes the most relevant ring proton-methyl proton distance larger. It appears that a shift of the equilibrium positions over about 15 degrees raises the upper limit of 3.4 kJ/mol for E_a of CH_3 2 and 6 to 5.7 kJ/mol. This is the value one expects from the extrapolated solid state NMR data, as shown above. A shift of the equilibrium positions is very well possible, because there is evidence that the hindering potential for CH_3 group 6 is not pure threefold, as will be shown below. Finally, although it is likely that wrong internuclear distances are responsible for the different results of the liquid state NMR and the other two techniques, there may still be another cause, namely the different states of the samples. The INS experiments showed no significant differences between the liquid and solid phase. However, this experiment (as well as the solid NMR work) was performed on pure DMDMB, while the liquid state NMR measurements were done on very dilute solutions in $CDCl_3$. This might partly account for the fact that the liquid state NMR V_3 values of CH_3 groups 2, 6 and 4 (the value of the latter group being rather accurate) seem to be systematically lower than the solid state NMR and the INS results, since in a dilute solution of DMDMB in $CDCl_3$ the intermolecular contribution to the hindering potential may be less than in pure DMDMB. It is a pity that due to the bad accuracy of the liquid state NMR results for CH_3 groups 2 and 6 this statement cannot be made more quantitative and a significant comparison with the results of the solid state NMR and INS experiments is impossible.

4.2. *Discussion of the Solid State NMR and INS Results for Methyl Group 6*

From Table 6 it appear that a significant difference exists between the values of V_3 determined for group 6 by solid state NMR and INS, respectively. This is probably due to the assumption of a threefold cosine-shaped potential, since it is known [1, 24] that especially small potentials sometimes deviate appreciably from this shape. In the following we shall investigate if such a deviation can account for both neutron and NMR results.

The simplest way of changing the potential shape is the introduction of a six-fold term [1, 24]:

$$V(\alpha) = \tfrac{1}{2} V_3(1 - \cos 3\alpha) + \tfrac{1}{2} V_6(1 - \cos(6\alpha + \delta)), \qquad (10)$$

where α is the rotation angle and δ represents the phase shift of the six-fold term with respect to the threefold one. The minima and maxima of the three- and six-fold term coincide for $\delta = 0$ and $\delta = \pi$, respectively. Solutions for the energy levels in such a potential are given by Gloden [31] for these values.

In Fig. 6 a few potentials are given for different values of δ and V_6/V_3. These potentials have in common the torsional transition of 12 meV between the first excited level and the ground state, which was found in the neutron scattering experiments. Furthermore we have confined ourselves here to $V_6/V_3 \leq \frac{1}{4}$. For $V_6/V_3 > \frac{1}{4}$ the potential reveals six minima. This has a strong effect on the level scheme and leads to unrealistic results for the barrier height.

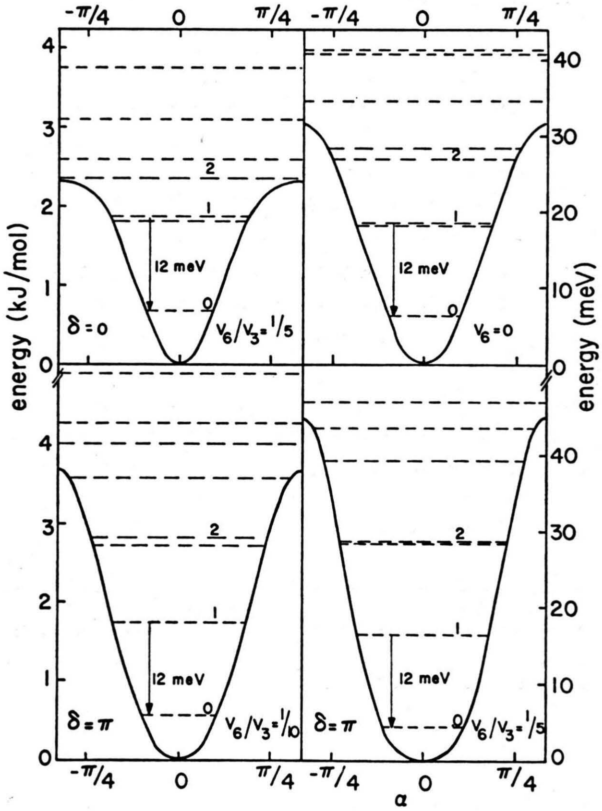

Fig. 6. Torsional levels (dashed lines) in various potentials $V(\alpha)$ (10 meV – 0.96 meV).

Table 7. Activation energies and differences between the second excited and ground level in various potentials.

Potential with $E_1 - E_0 = 12$ meV	E_a (barrier height $- E_0$) (kJ/mol)	$E_2 - E_0$ (kJ/mol)
$\delta = 0$, $V_6/V_3 = 1/5$	1.7 ± 0.5	1.8 ± 0.3
$V_6 = 0$	2.5 ± 0.4	2.1 ± 0.2
$\delta = \pi$, $V_6/V_3 = 1/10$	3.1 ± 0.6	2.2 ± 0.2
$\delta = \pi$, $V_6/V_3 = 1/5$	3.9 ± 0.4	2.3 ± 0.2

From Fig. 6 it can be concluded, that a deviation from the simple threefold cosine potential has a large influence on the barrier height derived from a torsional transition.

Interpretation of the activation energy as the energy difference between the torsional ground level and the top of the barrier yield E_a values for different potential shapes as given in Table 7. It is evident that for $\delta = \pi$ and $V_6/V_3 = \frac{1}{5}$ the correspondence with the value found in the solid-state NMR experiment at elevated temperatures, $E_a = 4.4 \pm 1.0$ kJ/mol, is best. Hence a solution to Eq. (10) with $\delta = \pi$ (broad potential minimum), $V_3 = 4.2 \pm 0.4$ kJ/mol and $V_6 = 0.8 \pm 0.4$ kJ/mol gives a consistent fit to the combined experimental data for group 6 of the solid state NMR and INS results. A mixture of a 3- and 6-fold potential for CH_3 group 6 with a phase shift of π radians can be very well understood if one realizes (neglecting effects of the chemical bonds) that CH_3 6 is sterically hindered at one side by methoxy group 1 and at the other side to a lesser extent by ring proton 5.

At temperatures between 30 K and 60 K the relaxation in the NMR experiments is dominated by tunnelling of group 6 with an activation energy $E_a' = 2.5 \pm 0.3$ kJ/mol. From Table 7 it can be seen that E_a' corresponds very well with $E_2 - E_0$ (the energy difference between the second excited level and the ground state in $V(\alpha)$) for $\delta = \pi$ and $V_6/V_3 = \frac{1}{5}$. This outcome is different from the literature [1, 32, 33] where E_a' is associated with $E_1 - E_0$. This is probably due to the fact that in Sect. 2 τ_c values were determined at higher temperatures than in the references stated.

4.3. Information About the Molecular Geometry

Now the comparison between the results of the different techniques has been made, it will be investigated whether conclusions about the molecular structure of DMDMB can be drawn from the experimental results, and whether the differences in potential barriers can be understood. First there is the remarkable fact that although CH_3 1 is sterically more hindered (by CH_3 2 and 6) than CH_3 4, its E_a value is smaller. This phenomenon was explained [34] in the following way: for a methoxy group like 1, surrounded by two ortho CH_3 groups, the C—O—C plane is perpendicular to the aromatic plane [35, 36] (it will be shown below that this is not quite true). In this position the CH_3 group in the methoxy group can reorient easier than a CH_3 group in an aromatic methoxy group (like CH_3 4) with none or only one ortho methyl substituent. For such a group the angle between the aromatic and the C—O—C plane is about 20° [35, 36]. This follows also from nuclear Overhauser effects and long range couplings in DMDMB in $CDCl_3$ solution [3]. In this near coplanar position the reorientation of CH_3 4 is strongly hindered by the ring protons. This explains the rather high experimental E_a value of CH_3 4. The latter is also in good agreement with the results of M.O. calculations [3], where a value of 16.8 kJ/mol was found for the barrier height.

Secondly there is the large difference in barrier heights for CH_3 2 and 6. As a consequence the hindering due to methoxy group 1 must be different for CH_3 2 and 6, which means that the angle θ between the aromatic- and C—O—C-plane is not 90°, as has been proposed elsewhere [35, 36], but less. This is supported by the fact that the activation energy of CH_3 1 is almost equal to that of CH_3 2. This suggests that CH_3 1 is very close to CH_3 2. However, from steric considerations on Courtauld's atomic models, and from the small nuclear Overhauser effect on CH_3 1 when CH_3 2 and 6 are saturated [3] it follows that θ can not be much less than 90°. This is still supported by relaxation measurements on solutions of DMDMB and on the same compound with CH_3 1 replaced by a CD_3 group [34]. It appears that CH_3 1 contributes only 3.5% to the relaxation of CH_3 2 and 6, so CH_3 1 cannot be too close to CH_3 2 and 6. Therefore, for θ a value of about 70° is estimated.

At the end it can be concluded that for the molecule investigated a combination of different experimental techniques, as presented in this paper appears to be very fruitful. More detailed and accurate information about methyl reorientations and the molecular geometry has been obtained than would have been possible with the separate techniques. Especially the combination of solid state NMR and INS gave information about the shape of the hindering potential of CH_3 group 6.

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