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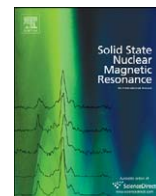


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Spin-lattice relaxation study of the methyl proton dynamics in solid 9,10-dimethyltritycene (DMT)

N. Piślewski^{a,*}, J. Tritt-Goc^a, M. Bielejewski^a, A. Rachocki^a, T. Ratajczyk^b, S. Szymański^{b,*}

^a Institute of Molecular Physics, Polish Academy of Sciences, Smoluchowskiego 17, 60-179 Poznań, Poland

^b Institute of Organic Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

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ABSTRACT

Proton spin-lattice relaxation studies are performed for powder samples of 9,10-dimethyltritycene (DMT) and its isotopomer DMT-*d*₁₂ in which all the non-methyl protons in the molecule are replaced by deuterons. The relaxation data are interpreted in terms of the conventional relaxation theory based on the random jump model in which the Pauli correlations between the relevant spin and torsional states are discarded. The Arrhenius activation energies, obtained from the relaxation data, 25.3 and 24.8 kJ mol^{−1} for DMT and DMT-*d*₁₂, respectively, are very high as for the methyl groups. The validity of the jump model in the present case is considered from the perspective of Haupt theory in which the Pauli principle is explicitly invoked. To this purpose, the dynamic quantities entering the Haupt model are reinterpreted in the spirit of the damped quantum rotation (DQR) approach introduced recently for the purpose of NMR lineshape studies of hindered molecular rotators. Theoretical modelling of the relevant methyl group dynamics, based on the DQR theory, was performed. From these calculations it is inferred that direct assessments of the torsional barrier heights, based on the Arrhenius activation energies extracted from relaxation data, should be treated with caution.

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1. Introduction

In 9-methyltritycene (MT) derivatives substituted in the peri positions, the torsional potential barriers of the methyl group can be extremely high. Even when only one of the three peri-hydrogen atoms (see Fig. 1) is replaced with a bulkier moiety, the barrier can exceed 40 kJ mol^{−1} such that the freezing of the stochastic dynamics of the methyl group can be observed in liquid-phase NMR spectra at temperatures above 170 K [1–4]. Unfortunately, for the parent compound, the unsubstituted MT, experimental estimates of the barrier height for the methyl group are nonexistent. In solution, neither the lineshape nor nuclear spin relaxation studies of MT could provide such data. From one side, in MT the methyl protons form magnetically equivalent group A₃, whose resonance signal is insensitive to the reorientational dynamics of the methyl group. From the other, for the anticipated barrier height, the intramolecular motion in MT is presumably orders of magnitude slower than the overall molecular tumbling and, therefore, it would hardly contribute to relaxation. Hence an insight into the relevant dynamics can only be gained from solid phase studies. In this paper we present our preliminary results for

the methyl group dynamics in solid 9,10-dimethyltritycene (DMT, see Fig. 1) in which the two methyl groups are structurally equivalent and each of them has the same immediate environment as the single group in MT. To this end, we employ proton spin-lattice relaxation measurements for powdered samples. In order to get the possibly unbiased results, we use a selectively deuterated isotopomer, DMT-*d*₁₂, in which all of the (12) non-methyl protons are replaced by deuterons. For the sake of comparison, results for the perprotio species are also reported. At variance with DMT, for the parent MT, there is no facile route to completely deuterate all non-methyl protons in the molecule.

Apart from that already specified, there has been one more reason to pursue this research. The methyl group in the peri-substituted 9-methyl derivatives investigated in solution presents a strange dynamic behaviour, which fact was for the first time recognized not long ago. Even at relatively high temperatures, above 170 K, the incoherent motion of the methyl group, evidenced in resonance lineshapes, can be nonclassical [5–8], in accord with predictions of the quantum mechanical model, called damped quantum rotation (DQR) approach [9]. The DQR effects can be expected to occur also in DMT. It seemed therefore interesting to check whether the conventional treatment of the relaxation data for DMT is sufficiently adequate here. The affirmative answer arrived at in our study will be commented upon extensively in the Results and discussion section. For that purpose, Haupt's theory of spin-lattice relaxation for the methyl

* Corresponding authors. Fax: +48618684524 (N. Piślewski); fax: +48226326681 (S. Szymański).

E-mail addresses: narczyzp@ifmpan.poznan.pl (N. Piślewski), sszym@icho.edu.pl (S. Szymański).

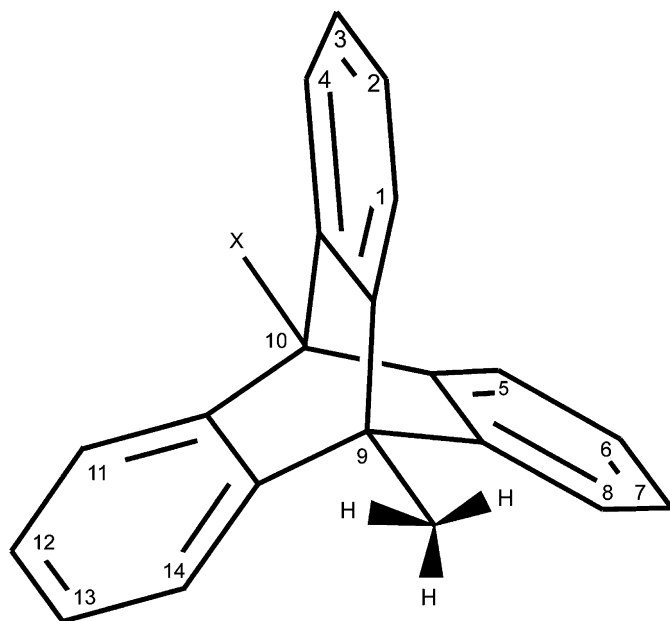


Fig. 1. Molecular structure of MT ($X = H$, symmetry C_{3v}) and DMT ($X = CH_3$, symmetry D_{3d}). In MT, the positions 1, 8, and 14 are peri positions; in DMT, also positions 4, 5, and 11 are peri positions.

group [10] is invoked, reinterpreted in the spirit of the DQR approach.

2. Materials and methods

The polycrystalline sample of DMT (see above), was prepared and purified according to a published procedure [2]. The selective deuteration yielding DMT- d_{12} was carried out by repetitive heating at about 300 °C of a suspension of the compound in D_2O with traces of D_2SO_4 , sealed in a thick-wall glass ampoule. After three cycles of about 24 h each more than 95% of the non-methyl protons were replaced by deuterons, as found from integration of the 1H spectrum of the raw product in $CDCl_3$. The peri positions (see Fig. 1) and the remaining aromatic positions have proven similarly susceptible to deuteration. The samples of both DMT and DMT- d_{12} for T_1 NMR study, placed in glass tubes, were evacuated at room temperature at 6×10^{-6} Pa for 24 h to remove oxygen and then sealed under vacuum. The NMR proton spin-lattice relaxation times T_1 were measured using a SXP 4/100 Bruker pulse spectrometer operating at 90 MHz, corresponding to the magnetic field B_0 of 2.1 T. Spin-lattice relaxation times were determined by an inverse recovery method in the temperature range of 96–470 K. The temperature of the sample was controlled by means of a continuous nitrogen gas-flow system and determined to the accuracy of 1 K. For both the samples, the recovery of the magnetization was found to be exponential at all temperatures. The errors in the measurements of T_1 were estimated to be about 5–10% (at the lowest temperatures).

Differential scanning calorimetry measurements were performed for a powdered sample of DMT put in aluminium pans with pin hold lids, over a temperature range of 300–500 K, using a Netzsch DSC 200 calorimeter, with scanning rate of 5 K min^{-1} . The DSC experiment was performed both by heating and cooling.

Quantum chemical calculations of the molecular geometry of DMT and theoretical modelling of the torsional barrier for the methyl groups in DMT were performed at the B3LYP/6-31G+(2d,p) level of theory using the Gaussian 03 package [11].

3. Results and discussion

The temperature dependences (96–470 K for DMT and 120–445 K for DMT- d_{12}) of the proton spin-lattice relaxation times T_1 in the isotopomers of DMT are presented in Fig. 2. In each case, the course of the T_1 values shows one minimum localized at a very high temperature, 365 K, and forms a plateau at temperatures below 220 K, with rather long values of T_1 exceeding 100 s. Below that temperature, the reorientational dynamics of the methyl groups are presumably too slow to contribute to the observed relaxation process. Over the whole temperature range investigated, the relaxation times for DMT are consistently longer than for DMT- d_{12} . From our calorimetric study of DMT above room temperature there is no evidence of a phase transition in the range where the reorientational dynamics are the main source of relaxation.

Disregarding cumbersome nuances of the processes underlying the apparent uniform, single-exponential character of the observed relaxation behaviour [12], the differences in the relaxation rates for DMT and DMT- d_{12} can to a rough approximation be interpreted in terms of a phenomenological weighting of contributions from different sub-ensembles of protons present in the sample of DMT:

$$1/T_1 = (n/N)(1/T_1^{\text{methyl}}) + [1 - (n/N)](1/T_1^{\text{non-methyl}}), \quad (1)$$

where $N = 18$ is the total number of protons in one molecule of DMT and $n = 6$ is the number of protons belonging to the two CH_3 groups; for DMT- d_{12} , where $N = n = 6$, Eq. (1) is a mere identity. Provided that in both materials T_1^{methyl} is nearly the same, the overall relaxation in DMT will be slower than in DMT- d_{12} if in the former $T_1^{\text{non-methyl}}$ happens to be longer than T_1^{methyl} . According to Eq. (1), in the hypothetical instance where contribution to relaxation of the non-methyl protons in DMT were negligible, the ratio of $T_1(\text{DMT})/T_1(\text{DMT-}d_{12})$ would be about three. Actually, above 220 K the relaxation in DMT- d_{12} is only about twice as fast as in DMT. The additional relaxation mechanism in DMT is presumably due mostly to the dipole-dipole (DD) interactions between the methyl protons and the most proximate to them aromatic protons at the peri positions, modulated by the stochastic dynamics of the methyl groups. However, a quantitative description of such cross-relaxation effects does not appear to be an easy task and is out of scope of the present work. In the rest of this paper the discussion will be concentrated mainly on the relaxation behaviour of the methyl groups in DMT- d_{12} . The isolated group model will be used and arguments validating its applicability to this system will be presented. Various cross-relaxation effects that may be expected to occur in that material will be evaluated assuming that contributions thereof to the overall relaxation rate are approximately additive.

If the Pauli correlations between the spin and torsional states of the methyl group are disregarded, the spin-lattice relaxation of the three-proton system of the methyl group can be explained as a result of mechanical random jumps of the group around its three-fold axis. For isolated methyl groups, O'Reilly and Tsang [13] reported the following formula:

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

where

$$C = \frac{9}{20} \left(\frac{\mu_0 \gamma_H^2 \hbar}{4\pi r^3} \right)^2. \quad (3)$$

In Eq. (2), r is the interproton distance and τ_c the correlation time of the jump process. The validity of such an interpretation of τ_c will be discussed later on. Application of Eq. (2) in practice is

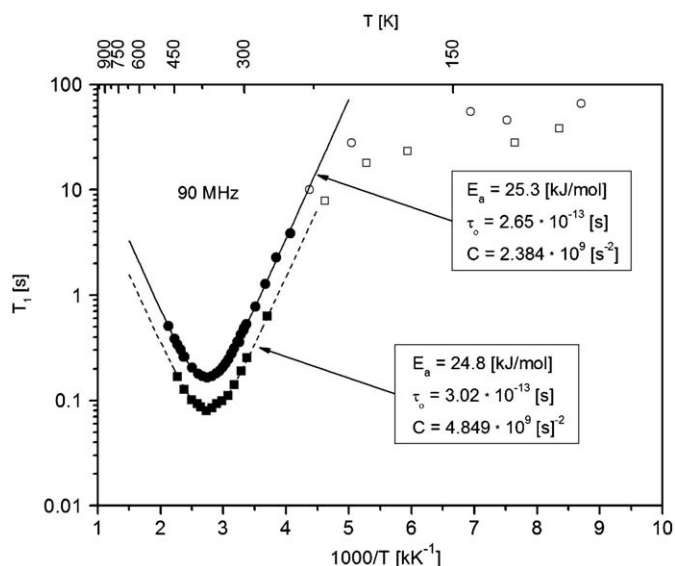


Fig. 2. Fits of Eq. (2) to the relaxation data for DMT (circles) and DMT- d_{12} (squares).

usually combined with the assumption that the relevant dynamics obey the Arrhenius law:

$$\tau_c = \tau_0 \exp(E_a/RT), \quad (4)$$

where E_a is the energy of activation of the jumps and τ_0 is the pertinent preexponential factor.

We performed multi-parameter fits of Eq. (2) to the T_1 data obtained for DMT and DMT- d_{12} at temperatures above 220 K, making use of Eq. (4) to describe temperature dependence of τ_c . The fitted parameters included C , τ_0 , and E_a . The solid lines in Fig. 2 represent the results of the fits. In the temperature range taken into account in the data analysis, the assumed theoretical model afforded perfect reproduction of the observed temperature trends of T_1 for both, DMT and DMT- d_{12} . The optimized values of C , τ_0 , and E_a are given in the figure. With such a high quality of the fits, the fitted parameters, and especially C , come with very low standard errors, involving in each case the last digit displayed.

Before proceeding to further discussion of the fit results, we consider the validity of the assumption that in DMT- d_{12} the methyl groups are isolated. Unfortunately, the crystal structure of DMT is not known. According to the theoretical geometry of DMT, calculated using the Gaussian 03 package [11], the shortest distance between the methyl and non-methyl protons is that of 0.24 nm between an aromatic peri proton (deuteron in the case of DMT- d_{12}) and each of the two methyl protons disposed syn to it. For any imaginable packing of the molecules of DMT- d_{12} in a crystal lattice, occurrence of still shorter proton-proton contacts between different molecules can be safely excluded. The relative contribution to relaxation of the largest proton-deuteron DD couplings, those across the distance r_{DH} of 0.24 nm, modulated by the methyl group dynamics, can be roughly estimated by the ratio $r_D^6/r_{DH}^6 \approx 0.003$, where $r = 0.179$ nm is the calculated distance between protons on the same methyl group. This is far below the experimental error in the T_1 measurements. Therefore, the contribution to the observed relaxation in DMT- d_{12} of the proton-deuteron interactions can be neglected. The same involves DD interactions between protons on different methyl groups in the same molecule, since they are distant by more than 0.6 nm. Even without knowledge of the crystal structure of DMT, a rough assessment of the possible relevance of DD interactions between protons on the methyl groups in different molecules is also

possible. We consider a hypothetical arrangement of the crystal lattice where such groups would be most proximate. Because of the peculiar molecular structure of DMT, such an arrangement would involve stacking of the molecules of DMT along the molecular C_3 axes, with two subsequent molecules rotated about these axes by 60° (the eclipsed conformation appears to be highly unfavourable because of interferences between the aromatic rings from neighbouring molecules). Then the closest head-to-head (or head-to-tail, because head and tail are symmetry-related) contacts between the methyl groups from subsequent molecules should not fall below the sum of the Van der Waals radii of the methyl carbon atoms, about 0.34 nm. Thus the limiting distances $r_{HH'}$ between a fixed proton on one methyl group and the individual protons on the other would range from 0.29 to 0.33 nm. The relative contribution of the intergroup interactions, calculated per pair of the interacting nuclei, to the observed relaxation in DMT- d_{12} can be roughly evaluated by a weighted average of the ratios $(r_{HH'}/r)^6$ which range from 0.025 to 0.055. Thus, for DMT- d_{12} , the neglect of intermolecular DD interactions between the (methyl) protons may involve some bias on the model adopted in the data interpretation, unless in reality the intergroup distances are longer than it was assumed in the above analysis. In the further discussion, further arguments in favour of the isolated group assumption will be provided.

For DMT, the situation is different because of the occurrence of the already discussed additional relaxation mechanisms. In view of the high quality of the fit with Eq. (2), this additional mechanism must follow a similar temperature dependence as does the dominating mechanisms due to the DD interactions within isolated methyl groups.

The estimated values of E_a , of about 25 kJ mol^{-1} , fall in a rather high range as for methyl groups. Except for the peri-substituted MTs studied in solution, we are aware of only one example, namely alanine in both the solid phase [14] and in solution [15], where the methyl group suffers similarly strong hindrance.

The differences between the values of E_a for DMT and DMT- d_{12} (see Fig. 2) are small enough to be interpreted in terms of some subtle structural consequences of the isotopic substitution. This can also be a reasonable explanation of the moderate difference between the optimized values of τ_0 . The entire difference between the two systems is reflected in the values of C the ratio of which is about 2. As such, it deviates substantially from 3, the value corresponding to the hypothetical instance where DD interactions between the methyl and non-methyl protons are too weak to give rise to an effective relaxation mechanism but strong enough to ensure fast transfer of the Zeeman polarization between protons of different groupings.

For DMT- d_{12} , the value of C should give, according to Eq. (3), a correct estimate of r , the distance between protons on the same methyl group. Actually, the value of $r = 0.193$ nm, calculated in this way (coming with unbelievably low standard error, propagated from that of C) falls far above the theoretical value of 0.179 nm. However, the quantity r^{-6} in Eq. (3) should not be directly referred to the interproton distance. It should be understood as the squared quantum mechanical average of the inverse cube of that distance, $\langle r^{-3} \rangle^2$, over the vibrational ladder. In the temperature range of our present interest, the average $\langle r^{-3} \rangle$ involves no longer the sole zero point vibrations but growing with temperature contributions of the excited states, especially of the bending vibrations of the $C_9-C_{\text{methyl}}-H$ and $H-C_{\text{methyl}}-H$ fragments, of relatively low energies. From liquid-phase studies it is well known that, even for such seemingly rigid moiety as the $C-H$ bond, the $C-H$ distance calculated from the dipolar ^{13}C relaxation rates can exceed the crystallographic distance by 4% [16–18]. The vibrational correction of about 8% obtained presently for DMT- d_{12} appears thus to be quite reasonable, considering both the

temperature range to which it pertains, and the greater number, as compared to one C–H bond, of vibrational degrees of freedom involved in the averaging. The distance of 0.193 nm obtained for high temperatures can be compared with that of 0.182 nm, calculated from the DD coupling constant in the methyl group, 19.93 kHz, measured at 70 K in NMR spectrum of a single crystal of methylmalonic acid [19]. It should be emphasized that any bias on the estimate of r resulting from neglect of the possible occurrence of additional relaxation mechanisms, would push the value of r down. Since the occurrence of such additional (although inefficient) mechanisms is almost certain, the unbiased value of r may be even higher than 0.193 nm.

With the vibrational correction to the proton-proton distance within the same methyl group exceeding 8% of the nominal value, much greater such correction can be expected to occur for protons located at different molecules, since in the latter case large-amplitude and low-energy lattice vibrations must also contribute to the averaging. This is one more argument validating the isolated group model adopted for DMT- d_{12} .

If there had been no observations of a peculiar dynamical behaviour of the methyl group in other methyl-bearing materials, after having reaffirmed consistency of the results obtained for DMT- d_{12} , the present discussion would have to be closed. As was already mentioned, in a series of peri-substituted 9-methyl derivatives, the stochastic dynamics of the methyl group evidenced in NMR lineshapes of liquid (i.e., dissolved) samples cannot be interpreted in terms of the conventional jump picture. On the other hand, the observed spectra can be reproduced using the DQR model [9]. The same involves other materials, containing protonated and deuterated methyl groups, studied in the solid state [19,20]. Because the DQR model is not widely known, its key points will be briefly exposed below.

In that approach, instead of a single rate constant of the mechanical jumps of the methyl group, the relevant dynamics are described in terms of two quantum mechanical rate constants which measure damping rates of two specific, long-lived coherences engaging pairs of sublevels at the subsequent torsional levels of the methyl group. Their lifetimes are long on the time scale of vibrational relaxation processes within the torsional ladder, induced by impact of the condensed environment. Such a resistance of these peculiar coherences to dissipation is a consequence of the spin-space correlations imposed on the quantum states of the methyl group by the Pauli principle. One of these coherences, whose leading component is Boltzmann average over the torsional ladder of the coherences between the perfectly degenerate Kramers sublevels, is dubbed “Kramers coherence”. The other, called “tunnelling coherence”, is similar to the latter, but instead of one of the Kramers sublevels, it engages the third sublevel, shifted up or down in energy from the Kramers pair by the “tunnelling” quantum. The tunnelling coherence evolves in time as damped oscillation, with damping-rate constants k_t and oscillation frequency Δ . The behaviour of the Kramers coherence involves pure damping with rate constant k_K because, due to the perfect degeneracy of the individual Kramers pairs entering it, its oscillation frequency is identically zero. In the DQR approach, the long-known tunnelling effect, leading to the Heisenberg couplings between the methyl protons [21,22], is measured by the oscillation frequency of the tunnelling coherence. If it happens that k_t and k_K are equal, the stochastic term in the DQR lineshape equation is automatically converted into the classical jump term entering the familiar Alexander–Binsch equation [23,24]. The ratio $c = k_t/k_K$ can thus serve as a quick measure of departure of a given methyl-like system from the jump model. It must be stressed in this point that even when $k_t = k_K$, neither of the two, when taken separately, can be interpreted as the classical constant describing the jumps. Conversely, within the

DQR approach the jump process appears as a composite phenomenon comprising two synchronized quantum rate processes.

For the 9 MT derivatives investigated in solutions, evident flaws of the line shape fits with the jump model are visible for the values of c above 1.10, whereas the DQR fits are virtually perfect [5–8]. In solution studies, the maximum value of c found hitherto is about 1.30 [8]. Such extent of deviations from the jump model does not appear to be large, although the fact that it was spotted in a liquid solution at temperatures above 170 K is remarkable. For other materials bearing weakly hindered methyl groups, which can be studied at lower temperatures in the solid state, the situation is probably different. Actually, for the methyl group in an oriented single crystal of methylmalonic acid investigated in the range 70–100 K using the lineshape method, the values of c , exceeding 5, do depart substantially from the “classical” value of 1 [19].

In relaxation theories for the methyl group, the essential role of the Pauli spin-space correlations was recognized by Haupt [10] long ago. He focused on the instance of DD relaxation in isolated methyl groups. The relevant stochastic dynamics he described in terms of multiple correlation times which from the perspective of the DQR theory are recognized to be the inverse damping rate constants of the individual coherences entering the “tunnelling” coherence. The single, effective correlation time introduced finally by him in a somewhat imprecise manner is nothing other than the inverse of the damping-rate constant k_t invoked above. It was also recognized by Haupt that, in absence of interactions of the methyl protons with “foreign” nuclei, including those belonging to other methyl groups, the process which in the DQR approach is dubbed the Kramers process is irrelevant to relaxation. More recently, an independent treatment of the relaxation behaviour of the methyl group, in a way closely resembling the DQR (lineshape) theory, was reported by Diezemann [25]. In that paper, working expressions were derived for a deuterated methyl group whose relaxation is due to quadrupolar interactions of the methyl deuterons. Unlike for the isolated protonated group, in that instance both k_t and the “Kramers” constant k_K are needed to describe the relaxation behaviour. Both these constants are to be employed, too, when DD relaxation of the ^{13}C nucleus in a protonated methyl group is concerned. The latter problem was treated lately in detail, with the basic idea of the DQR approach, i.e., the description of the relevant dynamics in terms of k_t and k_K , implemented in an ad hoc manner [26]. In summary, for an isolated methyl group the central Haupt equation for spin lattice relaxation of the methyl protons (in its version reported by Mueller-Warmuth et al. [27]) should be rewritten in the form:

$$\frac{1}{T_1^{\text{methyl}}} = \frac{C}{2} \sum_{m=2}^{-2} \frac{m^2 k_t}{k_t^2 + (\Delta - m\omega)^2}, \quad (5)$$

where as was already mentioned, Δ is the oscillation frequency of the tunnelling coherence decaying with rate constant k_t . For $|\Delta| \ll \omega$, Eq. (5) is turned into Eq. (2) with $\tau_c = 1/k_t$. As can easily be seen, rather than by the above inequality, the range of validity of Eq. (2) is traced out by the strong inequality

$$|\Delta|/k_t \ll 1. \quad (6)$$

The use of Eq. (2) for the interpretation of the relaxation data for DMT- d_{12} appears to be fully legitimate: Considering the magnitude of the activation energy obtained from the fit, total neglect of the tunnelling frequency in the data analysis seems to be well-justified.

Nevertheless, in order to verify further the validity of that simplifying assumption, we decided to perform theoretical simulations of the relevant DQR quantities, using our parameterized

model [9] described in detail in Ref. [28]. In its basic version, it employs four adjustable parameters: (i) the height of the relevant $V(1-\cos 3\phi)/2$ -shaped torsional potential; (ii) and (iii) the parameters f_c and f_s describing perturbations of the methyl rotor by its condensed environment acting as a quantum mechanical thermal bath and (iv) the “cut-off” frequency ω_c of the bath, above which the density of the bath oscillators decays rapidly. The constants f_c and f_s (of the dimension of angular frequency) measure the displacements of the bath oscillators that result in the “breathing” (cosine-type) and “shaking” (sine-type) perturbations, respectively, of the torsional potential [9,28,29]. In the model, for fixed values of V , f_c , f_s , and ω_c , the values of k_t , k_K and Δ are calculated in a consistent manner in any requested temperature range. Recently, the model was extended such that the torsional potential can be optionally augmented by the six-fold term of $V_6(1-\cos 6\phi)/2$.

Earlier that model afforded a fair reproduction of the experimental temperature dependences of k_t , k_K and Δ for the methyl group in a single crystal of methylmalonic acid [19], obtained from lineshape studies. Presently, the model parameters were adjusted (in a trial-and-error manner) in such a way that the experimental Arrhenius curve for the values of $k_t = 1/\tau_c$ be reproduced by the theoretical values in the range 220–450 K. In view of the fact that, for given V , the output data remains practically unchanged when the values of f_c and f_s are varied in such a way that the ratios f_c/ω_c and f_s/ω_c are kept constant, the value of $\omega_c/2\pi c_L$ (c_L is the speed of light) was fixed at 600 cm^{-1} . This is the value used in the simulations for methylmalonic acid [18]. Since in the latter case the optimized values of f_c and f_s happened to be nearly equal (120 and 125 , respectively, when expressed in cm^{-1}), in the present simulations it was assumed that $f_c = f_s \equiv f$. Therefore, with the standard value of the rotational constant, 5.28 cm^{-1} , and fixed ω_c , only two parameters, V and f , had to be adjusted. A plot of the discrete theoretical values of k_t , calculated for $V = 2370\text{ cm}^{-1}$ and $f/2\pi c_L = 150\text{ cm}^{-1}$, with the experimental Arrhenius curve for DMT- d_{12} superposed on them, is shown in Fig. 3. As can be seen from the plot, the theoretical values fairly reproduce the experimental curve, i.e. the straight line in Arrhenius coordinates, although their temperature trend shows a slight curvature at the highest temperatures. This is not surprising, because the Arrhenius law is a phenomenological relationship.

According to the standard interpretation, for a hindered rotator the Arrhenius activation energy is the difference between the potential energy maximum and the zero point torsional energy. For the methyl group in DMT- d_{12} , the experimental value of $E_a = 24.8\text{ kJ mol}^{-1}$ corresponds to 2074 cm^{-1} , whereas the above difference, calculated for the optimum value of $V = 2370\text{ cm}^{-1}$ obtained from the DQR simulations, amounts to 2205 cm^{-1} . This appears to be a substantial discrepancy. It seemed thus reasonable to confront these two estimates of the torsional barrier with the assessments based on quantum chemical calculations using the Gaussian 03 program [11]. The calculations involved only intramolecular contributions to the barrier. The theoretical profile of the barrier was calculated for fixed values of the torsional angle ϕ . The latter was defined as the dihedral angle between the plane of one of the benzene rings and the plane intersecting C-9, C-methyl, and the methyl hydrogen which in the minimum energy structure (see Fig. 1) is oriented trans to that benzene ring. With this definition, $\phi = 0^\circ$ for the structure at the minimum energy. The values of ϕ were increased from 0° to 60° by 15° increments; for each value, the remaining (internal) atomic coordinates were optimized until a conditional energy minimum was achieved. The height of the barrier (the energy difference between the structures of $\phi = 60^\circ$ and 0°), of 2312 cm^{-1} , calculated in this way, proved to be quite close to the estimate of 2370 cm^{-1} obtained from the DQR simulations. The difference of about

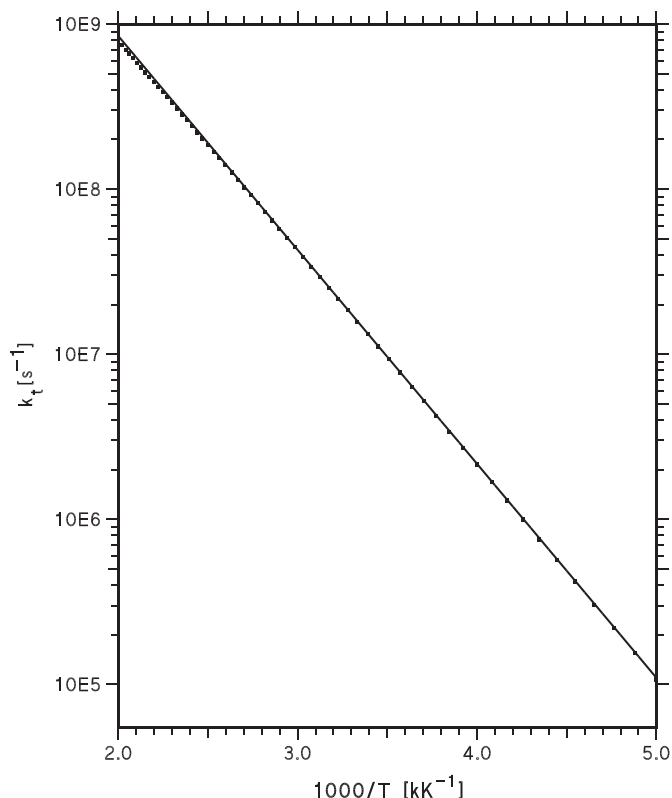


Fig. 3. Theoretical values of k_t (squares) and the Arrhenius plot (continuous line) for the experimental values of $1/\tau_c$ for DMT- d_{12} ($k_{t0} = 1/\tau_0 = 3.31 \times 10^{12}\text{ s}^{-1}$ and $E_a = 24.8\text{ kJ mol}^{-1}$, see Fig. 2). The k_t values were calculated for the following model parameters: $V = 2370\text{ cm}^{-1}$, $f/2\pi c_L = 150\text{ cm}^{-1}$ ($f \equiv f_c = f_s$), and $\omega_c/2\pi c_L = 600\text{ cm}^{-1}$, assuming the purely three-fold potential (see text).

60 cm^{-1} can probably be ascribed to intermolecular contributions to the barrier.

With the calculated values of the potential energy for the incremented values of ϕ , we could evaluate the possible role of the theoretical profile of the torsional barrier for the validity of the conclusions derived from the DQR simulations. The shape of the (intramolecular) torsional barrier could be fairly reproduced by fitting the following expression:

$$V_{\text{intra}}(\phi) = V_{3\text{intra}}(1 - \cos 3\phi)/2 + V_{6\text{intra}}(1 - \cos 6\phi)/2 \quad (7)$$

to the calculated (five) values, with the rms error of 13 cm^{-1} and the optimized values of $V_{3\text{intra}} = 2304 \pm 6\text{ cm}^{-1}$ and $V_{6\text{intra}} = -157 \pm 7\text{ cm}^{-1}$. It seemed interesting to check to what extent an admixture of the six-fold component, of the magnitude of $V_{6\text{intra}}/V_{3\text{intra}} = -0.07$ estimated from the quantum chemical calculations, to the profile of the torsional barrier could alter the results of the DQR simulations. The DQR simulations were repeated for the potential of

$$V(\phi) = V[(1 - \cos 3\phi) - 0.07(1 - \cos 6\phi)]/2, \quad (8)$$

where again, the adjustable parameters included V and f . This time, the experimental Arrhenius curve (see Fig. 3) was reproduced for a slightly modified value of $f/2\pi c_L = 157\text{ cm}^{-1}$ and the same value of V , 2370 cm^{-1} , as in the simulations for $V(\phi) = V(1 - \cos 3\phi)/2$, described above. Now, for the potential of Eq. (8) with $V = 2370\text{ cm}^{-1}$, the zero-point torsional energy is by about 20 cm^{-1} lower than for the simple three-fold potential with the same value of V . Accordingly, the discrepancy between the experimental Arrhenius activation energy, 2074 cm^{-1} , and the energy difference of 2225 cm^{-1} between the potential maximum and the lowest torsional state is even higher than in the case of

the simple three-fold potential. We have too little substance to unequivocally resolve which of the two models of the torsional potential is closer to reality. Nevertheless, we can conclude that, for protonated methyl groups, a simple assessment of the barrier height on the basis of the Arrhenius activation energies derived from relaxation data may be highly inaccurate.

Now, the applicability of Eq. (2) for the interpretation of the data for DMT- d_{12} will be discussed. Its validity will be confirmed if the strong inequality in Eq. (6) does hold in the relevant temperature range. For the values of Δ and k_t obtained in the DQR simulations for the pure three-fold potential a plot of the ratio Δ/k_t against temperature is shown in Fig. 4, where also the values of $c = k_t/k_K$ (to be commented later on) are displayed. The plots are extended down to 150 K, to include the region where the rate processes could be studied by the lineshape method. As can be seen in Fig. 4, in the range of 220–450 K which is of interest in the relaxation studies the ratio Δ/k_t varies smoothly in the limits of -0.055 to 0.017 , such that the critical inequality in Eq. (6) is essentially fulfilled. Hence, the validity of the conventional approach to handle the experimental data is rather unquestionable, provided only that the correlation time in Eq. (2) is identified with $1/k_t$. The sole fact that the theoretical curve in Fig. 2 perfectly reproduces the experimental T_1 values is an insufficient proof of the accuracy of the model. For DMT, the fit is equally perfect, despite of the evident bias of the model in that case.

At temperatures below 150 K (the range not shown in Fig. 4), the calculated values of Δ show the typical behaviour known from inelastic neutron scattering studies on weakly hindered methyl groups [29], although they are orders of magnitude smaller than in the systems of interest for such studies. Below 60 K they stay close to the value of $\Delta/2\pi = -73$ Hz, equal to the tunnelling splitting of the ground torsional state, and above 60 K they monotonically tend to 0, which value is reached at about 125 K. The simulations presented in the literature (where different sign convention is adopted for Δ), assuming various models of temperature dependence of Δ , usually stop at the “critical” temperature at which Δ crosses zero for the first time. This is probably the reason why the view about a quick and inevitable decay of tunnelling with increasing temperature has become so popular, despite of the fact that it has never been substantiated theoretically. At a first glance, our calculations based on the DQR approach may seem to contradict this view radically: The simulated temperature behaviour of Δ above that “critical” temperature proves to be complicated and strongly divergent with increasing temperature. As can be seen from the plot of Δ/k_t

in Fig. 4, above 300 K the tunnelling frequency actually increases with temperature at nearly the same rate as does k_t . As a matter of fact, the simulations discussed do confirm that common-sense view, although not in its literal formulation. In the DQR model, both Δ and k_t are associated with the same quantum mechanical entity: a coherence engaging both spin and space coordinates of the system, entangled by the Pauli principle. If, as in the present case, the inequality $|\Delta|/k_t \ll 1$ holds true at high temperatures, any effort to detect the oscillatory evolution of such coherence must fail since it will be completely erased during a small fraction of its oscillation period.

The values of c displayed in Fig. 4 show a monotonical decrease with temperature, from about 2.5 at 150 K, to about 1.1 at 450 K. Over the interval of 160–225 K, where the calculated values of k_t and k_K are commensurate with the DD interactions between the methyl protons, and as such are potentially extractable from the line shape fits, there are realistic perspectives of detecting deviations from the jump model. The lineshape studies should be carried out for a single crystal of DMT- d_{12} . Efforts to obtain such a crystal of suitably big size are underway.

4. Conclusions

Proton spin-lattice relaxation studies were performed for powder samples of DMT and its selectively deuterated isotopomer DMT- d_{12} . The relaxation data were first interpreted in terms of the conventional relaxation theory based on the random jump model in which the Pauli correlations between the spin and torsional states of the methyl proton system are discarded. The Arrhenius activation energies, obtained from the relaxation data, 25.3 and 24.8 kJ mol⁻¹ for DMT and DMT- d_{12} , respectively, are very high as for the methyl groups, although they are lower than in the analogous methyltritycene derivatives where the peri-hydrogen atoms are replaced by bulky substituents.

The applicability of the jump model to the relaxation data for DMT- d_{12} was considered from the perspective of the Haupt theory in which the Pauli principle is explicitly invoked. To this purpose, the correlation time entering the Haupt theory was reinterpreted in the spirit of the DQR approach as being identical with the inverse rate constant k_t defined in that approach. Such a cautiousness towards the conventional approach was found natural in view of the fact that methyl groups suffering even stronger hindrance can behave according to the predictions of the DQR theory. Theoretical modelling of the relevant dynamics of the methyl group, based on the latter theory, confirms that the conventional approach in its suitably reinterpreted version is valid in the case considered presently. However, these calculations have revealed that the usual inferences regarding the height of the torsional barrier for methyl groups, based on the Arrhenius activation energies extracted from the relaxation data, should be treated with caution.

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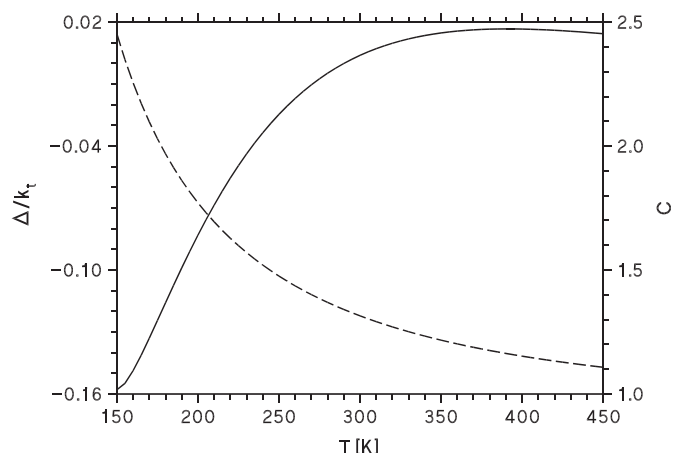


Fig. 4. Plots of theoretical values of Δ/k_t (left axis, solid line) and $c = k_t/k_K$ (right axis, dashed line) for DMT- d_{12} as functions of temperature, for the model parameters given in the caption for Fig. 3.

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