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# Proton spin-lattice relaxation and methyl group rotation

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## Abstract

Proton spin-lattice relaxation times have been measured at 16, 31, and 59 MHz in 4-methyl-2,6-ditertiarybutyl phenol between 80 K and its melting point, 340 K. The variation of  $T_1$  with temperature shows two distinct minima. The lower-temperature minimum has been analyzed in terms of relaxation by reorientation of four of the six t-butyl methyl groups with an average apparent activation energy of about 2.4 kcal mole<sup>-1</sup> (104 meV molecule<sup>-1</sup>). The higher-temperature minimum has been analyzed in terms of relaxation by reorientation of the t-butyl groups about their  $C_3$  axes with four of the six t-butyl methyl groups reorienting very rapidly, and the remaining two reorienting with correlation time similar to that of the t-butyl group. The activation energy for the higher-temperature minimum is 5.76 kcal mole<sup>-1</sup> (250 meV molecule<sup>-1</sup>). Steric potential calculations are used to add weight to these assignments, and a number of peculiarities displayed by the lower-temperature minimum are discussed.

## Introduction

Magnetic resonance provides a powerful tool for the investigation of the dynamics associated with the classical reorientation and the quantum mechanical tunneling of methyl groups. 4-Methyl-2,6-ditertiarybutyl phenol (MDBP) provides an opportunity to investigate both these phenomena. The tunneling of the 4-methyl group at low temperatures has been studied extensively by both NMR (1-4) and ESR (5-8): Whereas the reorientation of the 4-methyl group dominates the nuclear spin relaxation below about 50 K (1), this mechanism is completely ineffective above about 80 K. At the higher temperatures, the relaxation is dominated by the reorientation of methyl groups within the t-butyl groups and by the reorientation of the t-butyl groups themselves.

Spin-lattice relaxation times ( $T_1$ ) have been measured previously between 80 and 135 K at 21 MHz (4) and a  $T_1$  minimum was observed at about 120 K. Here we present a more detailed study of  $T_1$  between 80 K and the melting point of 340 K. Minima in  $T_1$  are observed at 125 and 300 K, and we are able to interpret the data in terms of the dynamics of the t-butyl groups and their constituent methyl groups.

## Experimental

A commercial sample of MDBP was recrystallized several times from isopropyl alcohol. This was then powdered and sealed in a sample tube in an argon atmosphere, after degassing for about 12 hr.

Proton spin-lattice relaxation times ( $T_1$ ) were initially measured at 31 MHz using a  $\pi$ — $\tau$ — $\pi/2$  pulse sequence on a Bruker B-KR 322s spectrometer as described elsewhere (9). Temperatures were measured using a thermocouple placed very close to the sample. Certain aspects of the minimum at about 125 K then caused us to perform some measurements for this

minimum at 59 and 16 MHz. The relaxation was found to be exponential within experimental error under all conditions. The results are shown in Fig. 1.

### Results and Analysis

The Bloembergen-Purcell-Pound (BPP) theory (10, 11) forms the basis for the interpretation of  $T_1$  results in this temperature regime. Relaxation can be described by the general equation

$$T_1^{-1} = A \frac{\gamma^4 \hbar^2}{\omega_0} f(\omega_0 \tau_c), \quad [1]$$

where  $\gamma$  = magnetogyric ratio for protons,  $\hbar = h/2\pi$ ,  $\omega_0$  = Larmor frequency, and

$$f(\omega_0 \tau_c) = \left\{ \frac{\omega_0 \tau_c}{(1 + (\omega_0 \tau_c)^2)} + \frac{4\omega_0 \tau_c}{(1 + 4(\omega_0 \tau_c)^2)} \right\},$$

where  $\tau_c$  is the correlation time for reorientational jumps. The quantity  $\tau_c$  is generally assumed to have an Arrhenius dependence on temperature,  $T$ , and activation energy,  $E_a$ , namely,

$$\tau_c = \tau_c^0 \exp(E_a/RT).$$

The factor  $A$  has an  $r^{-6}$  dependence on the interproton distances and also depends on the particular kind of motion giving rise to the relaxation

The results show two distinct minima in  $T_1$ ; at 31 MHz there is a minimum of 29 msec just below the melting point and a second of 36 msec at about 125 K. When we tried to fit this  $T_1$  curve to a combination of two BPP functions (i.e., the sum of two functions of the form given in Eq. [1]) it became quite clear that although the higher-temperature minimum could be fitted reasonably the lower-temperature minimum gave an unsatisfactory fit. Whereas a normal BPP function is symmetric about the minimum the results for the lower-temperature minimum are not.

Further peculiarities of this minimum emerge from the frequency dependence of  $T_1$ . At the lowest temperatures, in the long correlation time limit where  $\omega_0 \tau_c \gg 1$ , Eq. [1] predicts that  $T_1 \propto \omega_0^{-2}$ . Comparison of the experimental results at 16, 31, and 59 MHz shows this not to be the case. This is discussed quantitatively later in this paper. The minimum value of  $T_1$  predicted by Eq. [1] occurs when  $\omega_0 \tau_c = 0.616$  and gives  $(T_1)_{min} \propto \omega_0$ . Comparison of the results at the three frequencies gives  $(T_1)_{min} \propto \omega_0^{0.85}$ . This departure from linearity is well outside the limits arising from experimental uncertainties. On the other hand, however, all the high-temperature slopes coalesce, as expected for BPP theory.

Below 100 K at all three frequencies the plotted results are linear with roughly equal slopes which are effectively the same as the slope on the high-temperature side of the minimum. Extrapolation of single BPP curves from these slopes, with a minimum equal to the observed value, leads to calculated higher-temperature slopes which are displaced to lower temperatures than the observed slope. Likewise, if the observed high-temperature slope is extrapolated in a similar manner, then the calculated low temperature slopes are displaced to higher temperatures than the observed slopes. The temperatures of the calculated minima for the two extrapolations at each frequency are also significantly separated. This clearly demonstrates that the low temperature minimum is broadened to some degree.

The extrapolations from the high-temperature slope fit the observed results down to the minimum more closely than the extrapolations from the low-temperature slope down to the minimum. This emphasizes the asymmetry of the minimum. The results of Carolan *et al.* (4)

show a pronounced bend in the  $T_1$  curve at  $\sim 100$  K. While our results do not show any drastic change at this point, the discussion above leads us to suspect that there may be some anomaly in the temperature region below the minimum down to about 100 K.

### Assignment of the $T_1$ Minima

As a first step in understanding the results it is useful to try to calculate minimum values of  $T_1$  for various possible relaxation mechanisms. This step essentially involves calculating values for the parameter  $A$  in Eq. [1]. The methods of Woessner (12) are particularly useful in this exercise.

In the temperature range with which we are concerned the 4-methyl group will be ineffective in relaxation, since its correlation time is extremely short. (In fact its  $T_1$  minimum appears at about 14 K at 21 MHz (1).) We must therefore look to the motions of the other methyl groups and the t-butyl groups themselves, and possibly the hydroxy proton, to explain minima at higher temperatures. We can probably neglect the effect of the hydroxy proton, however, since it is 1 proton out of a total of 24 and is close to only a few of the other protons. Hence it could only be responsible for a small degree of relaxation. The two t-butyl groups, on the other hand, contain 18 of the 24 protons in the molecule.

In the calculations we have assumed an idealized structure for the t-butyl group as follows: C-C = 1.54 Å, C-H = 1.10 Å, and all angles tetrahedral (values we have used previously (9)). The crystal structure (13, 14) shows only small deviations from these parameters for the carbon atoms.

We may adapt the equations of Dunn and McDowell (15) to encompass the contributions to  $T_1$  of the intramethyl proton-proton vectors for methyl groups performing  $C_3$  reorientation about their own axes while the t-butyl group as a whole performs  $C'_3$  reorientations about its principal axis. For an isolated t-butyl group with all angles tetrahedral

$$\left(\frac{1}{T_1}\right)_{\text{intramethyl}} = \frac{9}{80} \frac{\gamma^4 \hbar^2}{\omega_0 r^6} \left\{ \frac{32}{27} f(\omega_0 \tau_{c3}) + \frac{32}{27} f(\omega_0 \tau_{c2}) + \frac{76}{27} f(\omega_0 \tau_{c3}) \right\}, \quad [2]$$

where  $\tau \frac{-1}{\omega_3} = \tau \frac{-1}{\omega} + \tau \frac{-1}{\omega_2}$ ,  $r$  = interproton distance within a methyl group,  $\tau_0$  = correlation time for  $C_3$  reorientation of the methyl group, and  $\tau_{c2}$  = correlation time for  $C'_3$  reorientation of the t-butyl group. The contribution to  $C'_3$  relaxation due to intermethyl vectors can be estimated by the method of Albert et al (16), where the three spins of the protons in each methyl group are condensed onto their  $C_3$  center of rotation:

$$\left(\frac{1}{T_1}\right)_{\text{inter}} = \frac{27}{20} \frac{\gamma^4 \hbar^2}{\omega_0 r_*^6} f(\omega_0 \tau_{c2}). \quad [3]$$

For the structure assume,  $r = 1.797$  Å and  $r_* = 3.115$  Å.

There is no simple way of obtaining a value for intermethyl contributions to relaxation caused by methyl reorientations, nor for contributions due to interactions of the t-butyl protons with adjacent ring or hydroxy protons. We think it reasonable, however, to assume that these will be fairly small in comparison with the total intramethyl contributions, but bear in mind that such contributions will tend to reduce the calculated values to some small extent.

Since the X-ray results (13, 14) do not show any drastic differences in the structure or environment of the two t-butyl groups on each molecule, we assume that the two behave

essentially identically. Furthermore, if the two were different one suspects the NMR results would be much more complicated. We also assume that all of the protons of the molecule are relaxed via spin diffusion by whichever groups are most effectively relaxing at a particular temperature.

Using Eqs. [I]-[3] and the above-mentioned assumptions concerning interatomic parameters, we can calculate minimum values of  $T_1$  for various combinations of the  $C_3$  motions of the individual methyl groups within the two t-butyl groups and the  $C'_3$  motions of the t-butyl groups. When  $\omega\tau$  for a particular motion approaches 0 or  $\infty$ , that motion is ineffective in contributing to relaxation. Because of the mutual dependence of  $C_3$  and  $C'_3$  relaxations, as given in the third term on the right-hand side of Eq. [2], the value of the minimum in  $T_1$  produced by a particular motion depends on whether  $\omega\tau$  for the other motion approaches infinity (motion very "slow") or zero (motion very "fast"). Table 1 lists a series of values of calculated  $T_1$  minima at 31 MHz for MDBP. Our observed minima are 29 msec at 300 K and 35 msec at 125 K at 31 MHz. For convenience we label these A and B, respectively, and for the present, peculiarities of minimum B are ignored.

It is not inconceivable, without prior knowledge at this stage, that the t-butyl groups may have a lower barrier to reorientation than the methyl groups, and hence  $\tau_{o2}$  could be shorter than  $\tau_o$  at a given temperature. We consider, therefore, cases 10-12 in Table 1. If we suppose that  $C'_3$  motion is responsible in whole or in part for minimum B, minimum A must be explained by one of cases 10-12, all of which, however, require a  $T_1$  minimum that is much higher than the observed value of 29 msec for A. We therefore exclude  $C'_3$  motion from the assignment of minimum B and seek an explanation for B in terms of motion of methyl groups only, i.e., as one of cases 1-3 in Table 1. The observed value of 35 msec for minimum B agrees with case 2 in which relaxation is caused by reorientation of four of the six methyl groups in the t-butyl groups, with the remaining two methyls reorienting too slowly to contribute to relaxation. The possibility that B should be assigned to reorientation of all six methyls (case 1) is excluded not only on the basis of poor agreement between observed and predicted values of the  $T_1$  minimum but also because this would require an explanation of the depth of minimum A in terms of  $C'_3$  motion with all the methyls reorienting too fast to contribute (case 5).

Possible assignments of minimum A are now considered under the assumption that the principal contribution to relaxation is  $C'_3$  motion of the t-butyl groups with modification for the various possible simultaneous rates of methyl motions (cases 4-9). In view of the assignment made for B, only cases 6 and 8 are reasonable assignments for A. When a t-butyl group is in any one equilibrium position, at the temperature of minimum A, four methyl groups reorient very fast and two very slowly with respect to  $\omega_0$ . All six methyl groups probably reorient whenever the t-butyl group makes a  $C'_3$  jump, so that, on the average, four methyl groups reorient very fast, and the other two probably reorient with a correlation time equal to that of  $C'_3$  motion. The value of the minimum for such an assumption (case 8), viz., 33 msec, is close to the observed value of 29 msec for A.

The assignment of the minima can also be approached, empirically, since there is now quite a collection in the literature (9, 17-19) of  $T_1$ , information on t-butyl groups where assignments of minima seem unambiguous. By averaging the values of  $T_1$  minima observed, corrected to 31 MHz, and allowing for spin diffusion, one finds that the expected value for  $C'_3$  t-butyl reorientation with fast methyl motions in MDBP should be about 67 msec. The expected minimum value for  $C_3$  reorientation of all six methyls (with t-butyl very slow) is about 26 msec, and hence, for four or two methyls causing relaxation, the minimum value should be about 39 or

78 msec, respectively. Since these are derived from experimental values they will already include intermethyl contributions. Now from these figures we can see that  $C'_3$  with fast  $C_3$  motion for all methyls is much too high to fit the observed minima, and similarly for relaxation by only two of the methyl groups. The value for relaxation by four methyls is quite close to the value for minimum B, and we can exclude relaxation by six methyls using the same arguments as before. We must therefore arrive at the same assignments as those we obtained from theoretical arguments.

Having come to these conclusions, we must point out that the higher-temperature minimum A is rather unusual in that such a mechanism, where one methyl in each t-butyl group reorients more slowly than or at a rate equal to that of the t-butyl, has not been observed before for a t-butyl group. The explanation for this behavior must surely be made in terms of the structure of the molecule, and with this in mind we decided to take a closer look at the molecular configuration and dimensions of an isolated MDBP molecule.

### *Structural Considerations*

The X-ray crystal structure has been reported twice (13, 14), but only the heavy atoms have been located with certainty. These determinations show that each t-butyl group takes up a configuration where two methyl carbons sit on either side of the plane of the ring close to the oxygen atom, with the third methyl carbon in the plane of the ring and close to a ring proton.

One can immediately see a basis for differentiation of the t-butyl methyl groups into three types: (a) two methyls whose C atom lie in the plane of the ring, (b) two methyls close to the hydroxy proton, and (c) two methyls away from the hydroxyl proton. It would seem reasonable from the symmetry that the equilibrium position of the O-H bond should be either (i) in the plane of the ring, or (ii) in a plane at  $90^\circ$  to the ring. In either case (i) or (ii), (b) and (c) above still apply, although the t-butyls would be identical only in case (ii). We suspect case (ii) is more likely, since in this position interatomic repulsions are minimized. It now remains to be seen why one of the three types of methyl group has a much higher barrier than the other two.

To simplify calculations of interatomic distances and steric potentials we assumed a model in which some of the slight distortions indicated by the X-ray structural information were smoothed out as follows:

- (a) The ring and all atoms bonded directly to it were taken as strictly planar.
- (b) Bond lengths and angles which are approximately reflected in the plane perpendicular to the ring through  $C_1$  and  $C_4$  were averaged.
- (c) The t-butyl groups were again taken to be  $C_3$  symmetric about their C-C(CH<sub>3</sub>)<sub>3</sub> axes with all bond angles tetrahedral. Using the bond parameters from the more recent structure report (14), we find that this averaging leads to the parameters: O-C<sub>1</sub> = 1.38 Å, C<sub>1</sub>-C<sub>2</sub> = 1.40 Å, C<sub>2</sub>-C<sub>3</sub> = 1.39 Å, C<sub>1</sub>-C<sub>butyl</sub> = 1.55 Å,  $\angle C_2-C_1-O = 119^\circ$ ,  $\angle C_2-C_3-H_3 = 118.5^\circ$ ,  $\angle C_1-C_2-C_{butyl} = 122^\circ$ , and  $\angle C_1-C_2-C_3 = 117^\circ$ . In addition we took the following: Cs-Hg = 1.08 Å, O-H = 1.07 Å, and  $\angle C_1-O-H = 116^\circ$  (see examples in Ref. (20)) and bond parameters within the t-butyl groups the same as those used earlier to calculate  $T_1$ .

In most X-ray structural studies of compounds containing t-butyl groups, where attempts have been made to locate the protons, it has been found that the protons of each methyl group are staggered with respect to the C atom framework to which the group is attached. (See, for example, Refs. 21-25.) We were able to find only one neutron diffraction study of a compound with a t-butyl group (26), but this confirms that the "all-staggered" configuration is preferred. We

also know from a large amount of experimental evidence that the barrier to methyl rotation in a t-butyl group is usually of the order of 4 kcal/mole (180 meV/molecule) (27).

If one now considers the interaction of a methyl group in the ring plane with the adjacent ring proton, contacts are minimized when two of the methyl protons sit on either side of the ring proton. This gives a configuration which is the same as for the all-staggered model. In this position the closest proton-proton contact is 2.08 Å (using all the relevant bond parameters given above), whereas when the methyl is rotated by 60°, where it will be at the top of its internal barrier, the closest contact drops to 1.38 Å, which is extremely short and is therefore very repulsive. The van der Waals radius of H is 1.1 to 1.3 Å (28), which indicates that there will be significant interaction if two protons approach within 2.2 Å. (By internal barrier we refer to the barrier to rotation of the methyl group against the C atom frame to which it is attached.) Consequently, if the t-butyl framework is fixed, the barrier to rotation of this particular methyl should be considerably increased above values usually found for more isolated t-butyl groups.

With no hydroxy proton present, the remaining four methyl groups surrounding the oxygen would have equivalent barriers to rotation. The closest proton-oxygen contact is 2.19 Å when any one of these methyls is rotated with the t-butyl framework fixed. The van der Waals radius of oxygen is 1.4 Å (28), so in the case of O ··· H contacts there may be significant interaction if the approach is within 2.5 Å. Introduction of the hydroxy proton will then significantly affect two of these methyls. We find that the closest C-H ··· H-O approach is 1.54 Å when the hydroxyl group is in the plane of the ring and 1.82 Å when it is in the plane perpendicular to the ring; for some positions of the hydroxy proton between these planes the contact will drop below 1.54 Å. An interesting feature of these closest contacts is that they occur at methyl rotation angles not too far displaced from the all-staggered configuration. Since the interactions are repulsive their net effect will most probably be to counteract the internal barrier to some extent.

We found it quite instructive to perform some crude calculations of the barriers to rotation for the various groups using empirical exponential  $-6/12 \sim 6$ -type steric potentials. While we do not necessarily put much faith in the exact figures which these produced, the general qualitative features are likely to be quite reasonable.

To make the calculations as uncomplicated as possible we restricted them to one t-butyl group of an isolated molecule (ignoring intermolecular potentials) and calculated the potentials for rotation of one group at a time, keeping all the rest fixed. We included in the calculations all the t-butyl group atoms, the hydroxy group, a ring proton, and the three ring carbons to which these are attached. The potential used was of the form  $V(r) = a \exp(-br)/r^d - c/r^6$ , and we tried two sets of parameters  $a, b, c, d$ , as given in Table 2. Parameter set 1 has been used by Shmueli and Goldberg (29) and includes some parameters derived by Williams (30) for hydrocarbons which appear with regularity in the literature.

Initially the atoms of the t-butyl group were set in an all-staggered configuration and the hydroxyl group in the plane at 90° to the ring plane. The methyl group in the plane of the ring (methyl (1)) was then rotated. As expected, the potential for both parameter sets was dominated by interaction with the ring proton, and the position of the minimum was definitely in the all-staggered configuration. Next the methyl group closest to the hydroxy proton (methyl (2)) was rotated with the other two methyl groups all staggered. This time the minimum was found to be at a position away from the all-staggered configuration. A similar pattern emerged when methyl (3) was rotated. Consequently the second or third methyl was set at various positions while the third or second methyl was rotated, to find the approximate equilibrium positions for both. The

potential for methyl (I) was then recalculated for the new equilibrium positions, and also the potential for the hydroxy proton. For the hydroxyl proton the minimum was indeed found to be definitely in the plane at 90° to the ring. We then calculated the potential for rotation of the t-butyl as a unit, both in the all-staggered configuration and with methyls (2) and (3) in the angular positions indicated by the calculations.

The barrier values obtained from these calculations are given in Table 3. The differences in the magnitudes of the barriers between parameter sets 1 and 2, and the incredibly large barrier for t-butyl rotation for set 1 with methyls (2) and (3) in their calculated equilibrium positions were at first rather alarming. This can be explained, however, in terms of the "hardness" of the various atom-atom potentials used. "Hard" refers to a potential which increases rather rapidly at close contacts, whereas a "soft" potential increases more gradually. As mentioned earlier, we would not wish to place much emphasis on the actual values; it can be seen that the two sets of parameters give substantially different magnitudes for the potentials, and the calculations are essentially very crude. However, the general pattern is the same in that methyls (2) and (3) have relatively similar barriers which are significantly lower than those of methyl (1) and the t-butyl group. All this tends to lend weight to the proposed assignment of the  $T_1$  minima.

### Analysis of Results

Returning now to the experimental results, BPP parameters which fit the observed  $\ln T_1$  vs  $T^{-1}$  plots were obtained as follows:

(a) The slopes of the plots at temperatures below 100 K were obtained from linear least-squares fits for all three frequencies. In this region,  $\omega_0\tau_0 \gg 1$  and Eq. [1] can be reduced to  $T_1 = \text{constants} \times \exp(E_a/RT)$ . Hence  $\ln T_1$  vs  $T^{-1}$  has a slope  $E_a/RT$ .

(b) The 31 MHz results from the lower-temperature minimum at 125 K to the melting point were fitted by two BPP functions with the aid of a nonlinear least-squares computer program. Analysis of the data in this manner allows us to extract reasonable parameters for minimum A, while taking into account its overlap with minimum B. Since minimum B shows a number of peculiarities, however, the parameters obtained from the fit for this should not be treated as definitive, although the apparent activation energy is likely to be valid.

The derived parameters are given in Table 4, and the fits are shown in Fig. 1 as solid lines. The reasons for treating minimum B in this manner arise because of the peculiarities which were remarked upon earlier after our discovery that a single BPP function will not fit minimum B satisfactorily. The structural analysis indicates that four methyls responsible for the relaxation at minimum B may be differentiated into two sets of two. This suggests that the broadening might arise because there are two closely overlapping minima. Once again, however, we were unable to obtain a reasonable fit to minimum B when we used two BPP functions.

The linear fits below 100 K enable us to indicate the departures from  $\omega_0^{-2}$  dependence of  $T_1$  in the long correlation time limit. Specifically at  $1000/\tau = 11$  we find an  $\omega_0^{-2.1}$  dependence between 31 and 59 MHz and an  $\omega_0^{-1.6}$  dependence between 16 and 31 MHz.

At present our explanations of the anomalous behavior are purely speculative. It may perhaps be due to a phase transition of some kind (although none has previously been reported as far as we are aware). This possibility seems unlikely in that, to the low-temperature side of the anomaly,  $\tau_0$ , would appear to be shorter than expected if the high-temperature side of the minimum were extrapolated. Generally speaking, one expects a phase

change to lengthen  $\tau_0$  on cooling through the transition. Furthermore, since the activation energy on the low-temperature side of the anomaly is the same as that obtained from the high-temperature slope, an explanation in terms of a decreased  $\tau_0$  parameter would be required. It is difficult to visualize a phase transition which might do this.

Another explanation might possibly be that, although the minimum has been assigned assuming that four methyls are relaxing, with the possibility of differentiation into the two types suggested by the structural analysis, the slight crystallographic differences between the two t-butyl groups may introduce further differentiation. The minimum may in fact be due to overlap of four very slightly different minima, one for each methyl. This, however, would not necessarily explain the similarity of the activation energies above and below the minimum and the anomaly.

One further possibility would be superposition of the relaxation minimum caused by reorientation of the hydroxy proton. Since the contribution to the overall relaxation caused by this superposition would be very small, it would produce only a slight perturbation in the results. However, the steric potential calculations would indicate that this motion should have a considerably higher barrier than either Me(2) or Me(3) and therefore would not be expected to cause relaxation in the same temperature region.

The activation energies for the two mechanisms both fall within the ranges of values observed in other t-butyl compounds. For instance, the nonunique methyls in the t-butylammonium halides (9) on the average have  $E_a = 2.6$  kcal mole<sup>-1</sup> (113 meV molecule<sup>-1</sup>); the methyl groups in the t-butylammonium tropolone salt (17) have  $E_a = 3.0$  kcal mole<sup>-1</sup> (130 meV molecule<sup>-1</sup>); in a clathrate of t-butylamine (18)  $E_a = 3.2$  kcal mole<sup>-1</sup> (139 meV molecule<sup>-1</sup>); and in trimethylacetic acid (19),  $E_a = 2.35$  kcal mole<sup>-1</sup> (102 meV molecule<sup>-1</sup>). The average apparent activation energy from the lower-temperature mechanism for MDBP of about 2.4 kcal mole<sup>-1</sup> (104 meV molecule<sup>-1</sup>) compares favorably with these. The known values for C<sub>3</sub> reorientation of t-butyl groups (9, 17, 19, 32) vary between 10.25 and 3.1 kcal mole<sup>-1</sup> (445 and 135 meV molecule<sup>-1</sup>). The value of 5.76 kcal mol<sup>-1</sup> (250 meV molecule<sup>-1</sup>) obtained for C<sub>3</sub> motion complicated by a "slow" methyl in MDBP falls well within this range.

## Summary

The present work, together with previous studies forms an extensive analysis of methyl group dynamics in MDBP from 6 to 340 K. At 14 K there is a  $T_1$  minimum corresponding to the maximum contribution to the relaxation by the reorientation of the 4-methyl group (1), and the observed activation energy in the range from 6 to about 15 K is probably related to the coupling between the 4-methyl group rotation and the short-wavelength lattice phonons (1). At 29 K there is another  $T_1$  minimum (which becomes more apparent if all but the 4-methyl protons are replaced by deuterons) corresponding to the maximum contribution to the relaxation from nuclear spin symmetry conversion tunneling transitions (1). The activation energy in the range from about 20 to 50 K is determined by the 4-methyl group torsional splitting (1). The barrier to rotation of the 4-methyl group has been calculated (55) and compared with the experimentally determined value (3, 34). There is a third  $T_1$  minimum at 125 K corresponding to the maximum contribution to the relaxation by the reorientation of four of the six t-butyl methyl groups, and the activation energy determined from the observations in the range from about 80 to 100 K gives the barrier for this motion. Finally, there is a fourth  $T_1$  minimum at 300 K corresponding to the maximum contribution to the relaxation from the motion of the other two t-butyl methyl groups and the entire t-butyl groups. The observed activation energy from 140 to 340 K gives the

barrier for this motion. It is suspected that any motion associated with the phenol proton is negligible, but this is being investigated by NMR studies with selectively deuterated samples.

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Figures

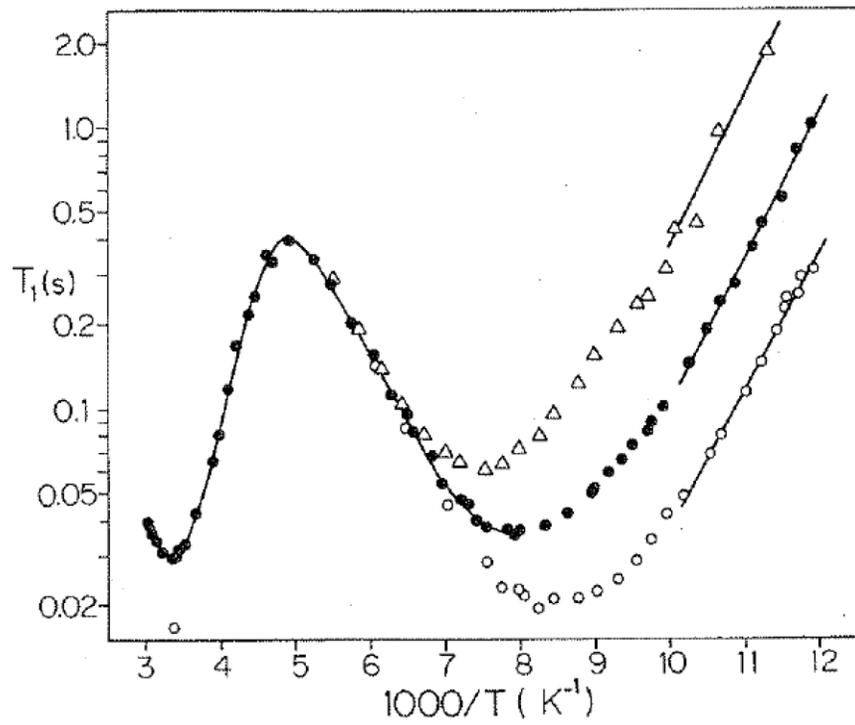


FIG. 1. Spin-lattice relaxation time  $T_1$  as a function of temperature. The observed values are indicated by open circles (16 MHz), closed circles (31 MHz), and open triangles (59 MHz), and the fitted curves are discussed in the text. The  $T_1$  minima at  $10^3/T = 3.3 \text{ K}^{-1}$  ( $T = 300 \text{ K}$ ) and  $8.0 \text{ K}^{-1}$  ( $T = 125 \text{ K}$ ) are referred to in the text by A and B, respectively.

## Tables

TABLE 1  
CALCULATED VALUES OF  $T_1$  MINIMA AT 31 MHz FOR MDBP

Motions		$T_1$ minimum (msec)	Case
$C'_3$ t-butyl	$C_3$ Methyls		
$\omega_0\tau_{c2} \gg 1$	6 with $\omega_0\tau_c \sim 1$	24	1
	4 with $\omega_0\tau_c \sim 1$ , 2 with $\omega_0\tau_c \gg 1$	36	2
	2 with $\omega_0\tau_c \sim 1$ , 4 with $\omega_0\tau_c \gg 1$	72	3
$\omega_0\tau_{c2} \sim 1$	6 with $\omega_0\tau_c \gg 1$	22	4
	6 with $\omega_0\tau_c \ll 1$	59	5
	4 with $\omega_0\tau_c \ll 1$ , 2 with $\omega_0\tau_c \gg 1$	37	6
	2 with $\omega_0\tau_c \ll 1$ , 4 with $\omega_0\tau_c \gg 1$	27	7
	4 with $\omega_0\tau_c \ll 1$ , 2 with $\omega_0\tau_c \sim \omega_0\tau_{c2}$	33	8
	2 with $\omega_0\tau_c \ll 1$ , 4 with $\omega_0\tau_c \sim \omega_0\tau_{c2}$	23	9
$\omega_0\tau_{c2} \ll 1$	6 with $\omega_0\tau_c \sim 1$	81	10
	4 with $\omega_0\tau_c \sim 1$ , 2 with $\omega_0\tau_c \gg 1$ or $\omega_0\tau_c \ll 1$	121	11
	2 with $\omega_0\tau_c \sim 1$ , 4 with $\omega_0\tau_c \gg 1$ or $\omega_0\tau_c \ll 1$	242	12

TABLE 2  
PARAMETER SETS USED IN THE STERIC POTENTIAL CALCULATIONS<sup>a</sup>

Interaction	Set 1 (29)				Set 2 (31)			
	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>
H---H	2171	3.74	24.39	0	3700	3.071	89.5	0
H---C	8503	3.67	111.82	0	33500	1.535	589.0	6
C---C	71782	3.60	512.69	0	301200	0	327.2	12
O---H	23707	1.87	93.5	0	19800	3.840	497.6	0
O---C	136350	1.80	428.7	6	178500	2.304	202.2	6

<sup>a</sup> Answers are in kilocalories per mole if distances are in angstroms.

TABLE 3  
BARRIERS TO ROTATION OBTAINED FROM STERIC POTENTIAL  
CALCULATIONS (kcal/mole<sup>-1</sup>)<sup>a</sup>

Group rotating	Methyls (2) and (3) at balanced equilibrium positions		Groups in "all staggered" configuration	
	Set 1	Set 2	Set 1	Set 2
Me(1)	11.2	43.2	10.5	41.3
Me(2)	2.7(35°) <sup>b</sup>	7.9(30°) <sup>b</sup>	3.1	7.9
Me(3)	1.3(25°) <sup>b</sup>	5.6(0°) <sup>b</sup>	1.6	3.6
OH	9.5	56.1	12.5	45.6
t-Butyl	232.1	46.2	24.2	12.9

<sup>a</sup> 1 kcal mole<sup>-1</sup> = 43.4 meV molecule<sup>-1</sup>.

<sup>b</sup> Position of balanced equilibrium, given as the angle of rotation from the all-staggered configuration. Clockwise rotation for methyl (2), anti-clockwise for methyl (3) when looking down the C-C axis. In set 1 a very "hard" oxygen potential dominates both the barrier height for the t-butyl group and the displacement of both Me(2) and Me(3) from the all-staggered configuration. In set 2 the potential of the hydroxy proton governs the displacement of Me(2) from the all-staggered configuration, and, with a softer potential, the oxygen atom is of minor significance.

TABLE 4  
RELAXATION PARAMETERS

	$\omega_0$ (MHz)	$A(\gamma^4 \hbar^2 / \omega_0)$ (sec <sup>-1</sup> )	Activation energy $E_a$ (kcal mole <sup>-1</sup> ) <sup>a</sup>	Correlation time $\tau_0^0$ (sec)
Minimum B slope	59		2.48 ± 0.42	
below 100 K	31		2.36 ± 0.07	
	16		2.25 ± 0.08	
Minimum B slope				
above 125 K	31	19.48 ± 0.44	2.38 ± 0.04	(2.57 ± 0.34) × 10 <sup>-13</sup>
Minimum A	31	23.55 ± 0.34	5.76 ± 0.09	(2.12 ± 0.35) × 10 <sup>-13</sup>

<sup>a</sup> 1 kcal mole<sup>-1</sup> = 43.4 meV molecule<sup>-1</sup>.