A ^{13}C CP/MAS NMR Study of a Double *tert*-Butyl Group Rotation in the Solid State Using $T_{1\rho}$ and Line Shape Measurements

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Abstract: A combination of solid state ^{13}C CP/MAS NMR techniques has been used to study the rates of rotation of the *tert*-butyl groups in *cis*-4-*tert*-butyl-1-(*tert*-butylsulfonyl)cyclohexane. The methods employed include line shape analysis and $T_{1\rho}$ measurements with rates between 6×10^3 and 2×10^7 s^{-1} over the temperature range 202–320 K. It is demonstrated that ^{13}C $T_{1\rho}$ measurements from CP/MAS spectra can give quantitative information on intramolecular motions that agree with that from line shape analysis. The 1-*tert*-butylsulfonyl group shows $\Delta H^{\ddagger} = 38.2 \pm 1.5$ kJ·mol^{-1} and $\Delta S^{\ddagger} = +9.4 \pm 5.9$ J·K^{-1}·mol^{-1}. The 4-*tert*-butyl group shows $\Delta H^{\ddagger} = 33.5 \pm 3.2$ kJ·mol^{-1} and $\Delta S^{\ddagger} = +10.3 \pm 13.5$ J·K^{-1}·mol^{-1}. The rates of *tert*-butyl group rotation in the solid are considerably slower than those in solution. The anisotropic displacement parameters determined by X-ray diffraction for this compound are consistent with the dynamic information derived from the NMR measurements.

Introduction

NMR has long been the principal method for the investigation of conformations and conformational rate processes in solution.[1,2] An impressive amount of data in this area has been gathered and molecular mechanics calculations now give good agreement with experiment. Less has been done in the gas phase, but again NMR has contributed greatly to our understanding of conformational processes in gaseous molecules.[3] The advent of high resolution solid state NMR techniques, in particular ^{13}C cross polarization magic angle spinning (CP/MAS) NMR, has now enabled the power of NMR to be applied to conformational processes in the solid state.

X-ray diffraction gives the structure of a molecule in the solid state, provided that suitable crystals are available. Even though, as we shall discuss below, anisotropic displacement parameters derived from crystallographic measurements can, under appropriate circumstances, give dynamic information on molecular motions inside solids, solid state NMR is much better at giving this information. Kinetic information on conformational processes in solution state NMR is essentially limited to rate measurements derived from line shape analyses. Line shape changes occur in the region where the rate of exchange is comparable to the difference in spectral frequency between the sites involved in the chemical exchange. In solid state NMR spectroscopy many more interactions are available to be modulated by conformational exchange rates, which greatly extends the range over which dynamic information can be gathered. Previous CP/MAS work by Twyman and Dobson has shown how a combination of line shape analysis, magnetization transfer, and maximum dipolar broadening can provide dynamic information on conformational processes in solids[4] over a wide range of rates. The current paper shows how ^{13}C $T_{1\rho}$ measurements from CP/MAS spectra in particular can give valuable dynamic information. When combined with line shape analysis such measurements mean that a rate range of over three orders of magnitude can be made available.

In considering those molecules most likely to be amenable to showing conformational effects in their solid state NMR spectra, the "principle of least distress" is a significant guiding factor.[5] The environment surrounding a molecule in a crystalline solid is generally more robust than the solution environment. It is harder to deform the environment surrounding a molecule in a solid than a surrounding sheath of solvent molecules. We would, therefore, expect that in solids conformational processes that show only small

volumes of activation or only small overall volume changes are more likely to be observed. That is to say those changes which cause the "least distress" to the crystal structure should be the most readily observable by NMR methods. This principle has guided our search for conformational processes in solids and has led to our observing rotations of *tert*-butyl,[5,6] *tert*-amyl, and isopropyl[6] groups with the *tert*-butyl groups showing the lowest barriers to rotation. We have also observed what is probably the freezing out of the pseudorotation of a cyclopentane ring.[6] Others have observed restricted rotations of phenyl[4] and methoxy[7] groups. The principle of least distress also predicts that tightly bound solids with strong directional intermolecular interactions should show higher barriers to conformational change than more loosely bound solids.

In our observations of restricted rotations of *tert*-butyl groups using CP/MAS techniques[5,6] we have repeatedly noticed that at temperatures 60–80 K above coalescence there is a minimum in the intensity of the signals arising from the *tert*-butyl group. This was found to arise from a minimum in the value of $T_{1\rho}$ for the relevant ^{13}C signals leading to poor cross polarization efficiency. $T_{1\rho}$ is sensitive to molecular motions occurring at rates comparable to the spin locking radio frequency field. In our case simple extrapolation showed that the rates of rotation of the *tert*-butyl groups in the temperature range in question would be comparable to the precession frequency of the 80–90 kHz spin-lock field employed during the Hartman–Hahn condition. The literature on the matter, however, is contradictory with some authors, indicating that this relaxation process under CP/MAS conditions could be to the ^{1}H dipolar reservoir (for a discussion see refs 8–10). An analysis of the regions of which $T_{1\rho}$ can provide useful dynamic information has been given by VanderHart and Garroway.[11] This

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(3) Ross, B. D.; True, N. B. *J. Am. Chem. Soc.* **1983**, *105*, 4871.

(4) Twyman, J. M.; Dobson, C. M. *J. Chem. Soc., Chem. Commun.* **1988**, 786.

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shows that under the correct conditions $T_{1\rho}$ can give useful information on intramolecular motions in solid samples. $T_{1\rho}$ measurements on some simple *tert*-butyl derivatives that exist in plastic crystalline forms have been reported using ^{1}H NMR by Hasebe and Strange.[12-14] Their work was mainly concerned with molecular reorientations and not with intramolecular motions. In addition ^{13}C $T_{1\rho}$ measurements from CP/MAS spectra have been used to extract information on intramolecular segmental motion of polymers in the glassy state.[8-10] Therefore, it seemed sensible to us to test whether the ^{13}C $T_{1\rho}$ relaxation changes that we observe in our crystalline *tert*-butyl-containing compounds are indeed modulated by the bond rotation process.

cis-4-*tert*-Butyl-1-(*tert*-butylsulfonyl)cyclohexane[15] (**1**) is an ideal substrate with which to test the above ideas. It contains two well-differentiated *tert*-butyl groups whose signals can be edited free of signals from CH and CH_2 groups by means of a dipolar dephasing (non quaternary suppression, NQS) sequence. In addition its crystal and molecular structure have been studied by X-ray diffraction.[15] The anisotropic displacement parameters of the atoms in the *tert*-butyl groups are the largest, suggesting that there is appreciable disorder in the positions of the atoms within these groups that could arise from molecular motion.

Experimental Section

cis-4-*tert*-Butyl-1-(*tert*-butylsulfonyl)cyclohexane (**1**) (150 mg) identical with the sample used for X-ray crystallography was obtained as a gift from Professor E. L. Eliel and used without any further purification.

All NMR spectra were obtained on a Bruker MSL500 spectrometer in either high resolution or high power mode. ^{1}H high resolution spectra were obtained at 500.13 MHz on a sample of 10 mg of **1** in 0.5 cm^3 of CD_2Cl_2. Solid state ^{13}C spectra were obtained at 125.758 MHz in the CP/MAS mode using 4 mm o.d. rotors spinning typically at 4–6 kHz. All solid state spectra (other than Figure 1 and the 2D CPEXSY spectra) reported in this paper including $T_{1\rho}$ determinations were obtained by the cross polarization pulse sequence incorporating a 50 μs dipolar dephasing (non-quaternary suppression (NQS)) delay, sufficient to dephase any non-mobile carbons directly bonded to one or two hydrogens. A cross polarization contact time of 1 ms was used throughout. Chemical shifts were referenced relative to the CH_2 group in adamantane at 38.56 ppm determined on a separate sample. The 2D CPEXSY spectra were obtained using a standard pulse sequence including a 1 ms contact time and a 100 ms mixing time.

The spin locking radio frequency fields for both carbon and hydrogen are identical during the Hartman–Hahn condition and were determined to be 89 kHz. The same radio frequency power was used for the spin lock period in the $T_{1\rho}$ determinations which were done using a standard pulse sequence modified to incorporate a 50 μs NQS dephasing delay.

The calibration of the temperature controller was checked by obtaining spectra from rotors containing samples with known phase changes (*d*-camphor 374 K, *d,l*-camphor 350 K, pivalic acid 280 K, *d*-camphor 244.5 K, and adamantane 209 K).[16] The temperature calibration spectra were obtained under conditions as similar as possible (gas flow, spinning speed, RF field, etc.) to those employed during the measurement of the spectra of **1**, thus minimizing the effects of heating arising from sample spinning and high power decoupling.[17] Temperatures for the high resolution ^{1}H spectra were uncorrected.

Line shape analyses for a three-site system were calculated using a computer program kindly supplied by Dr. J. E. Anderson. Matching of calculated and observed spectra was done by visual comparison.

Theory

For a dipolar interaction between unlike spins (in this case ^{13}C and ^{1}H) and provided that the *tert*-butyl group is rotating more slowly than the methyls (see Discussion section)[18]

$$\frac{1}{T_{1\rho}} = \frac{B^2\tau}{(1 + \omega_1^2\tau^2)}$$

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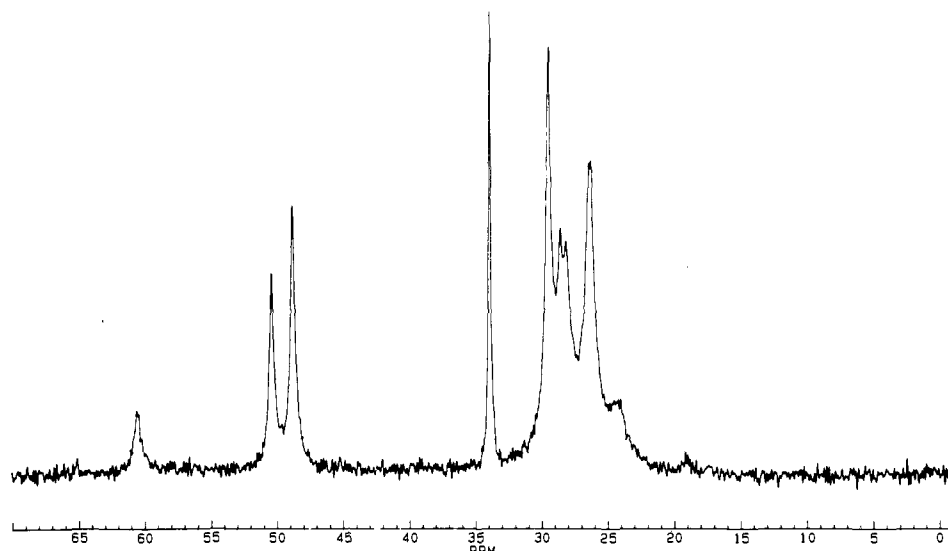(18) Hoodless, I. M.; Strange, J. H.; Wylde, L. E. *J. Phys. C* **1971**, *4*, 2742.

Table I. $T_{1\rho}$ Values for the *tert*-Butyl Carbons (ms)^a

T (K)	61 ppm	34 ppm	29 ppm	24 ppm
320	16.90			9.39
312	10.89			7.67
305	9.13			4.84
298	7.58			3.70
290	6.22	47.2	16.1	3.15
283	7.84	24.4	9.87	2.59
276	8.11	18.05	6.75	3.50
268	10.76	15.43	6.35	4.46
261	38.16	9.32	2.93	6.26
253	28.65	9.42	3.25	12.80
246		7.37	2.57	14.80
238		8.10	3.16	22.50
232		15.82	4.32	
224		27.25	7.28	

^{a} Errors in $T_{1\rho}$ values from least-squares plots are estimated as 5%.

where ω_1 is the frequency of ^{13}C in the spin lock field, τ is the correlation time for the molecular motion causing the relaxation (rotational correlation time), and B^2 is a measure of the ^{13}C–^{1}H dipolar interaction strength. Since the rotation rate of the *tert*-butyl group varies with temperature, τ and therefore $T_{1\rho}$ will also have a temperature dependence. This equation predicts that $T_{1\rho}$ will have a minimum at the temperature at which $\omega_1\tau = 1$.

Hence at the minimum value of $T_{1\rho}$

$$\omega_1\tau = 1$$

and

$$B^2 = \frac{2}{(T_{1\rho})_{min}\tau}$$

Thus the minimum value of $T_{1\rho}$ allows an experimental determination of B^2 and values of τ can then be derived from $T_{1\rho}$ measurements by solving the appropriate quadratic equation.

The value of τ used above refers to the correlation time for complete (360°) reorientation of the *tert*-butyl group. We assume that the *tert*-butyl group reorientates in a 3-fold potential energy well, therefore in order to derive the enthalpy and entropy of activation for surmounting the barrier in this potential energy profile the relevant rate constant (k) is that relating to a 120° reorientation of the *tert*-butyl group. Thus

$$k = 3/\tau$$

If the reductions in $T_{1\rho}$ arise from interactions involving the *tert*-butyl group rotation these equations, inter alia, predict four things that can be tested by experiment: (1) both the central and the methyl carbons in the same *tert*-butyl group should show $T_{1\rho}$ minima at the same temperature; (2) given a consistent geometry of the *tert*-butyl group the minimum values for $T_{1\rho}$ should be similar from one group to another; (3) rate constants determined from the $T_{1\rho}$ data should lie on the same Eyring or Arrhenius plot as rate constants determined from line shape analysis; and (4) experimentally determined B^2 values from the minima in the $T_{1\rho}$ should agree with values calculated for such internuclear interactions using the equation given by Abragam[19] and a model *tert*-butyl group geometry.

Discussion

Figure 1 shows the room temperature ^{13}C CP/MAS spectrum of **1** in which the *tert*-butyl resonances are partly obscured by resonances from the methine and methylene carbons. A 50-μs dipolar dephasing delay in an NQS pulse sequence edits out the methine and methylene carbons to allow observation of the *tert*-butyl carbons alone. Figure 2 shows the temperature dependent line shape changes in the CP/MAS NQS spectra of **1**. The high temperature limit peaks at 61 and 24 ppm are ascribed to the quaternary and methyl carbons respectively in the *S*-*tert*-butyl group. The corresponding peaks in the *C*-*tert*-butyl group are at 34 and 29 ppm, respectively. The low temperature limit methyl peaks are at 22, 24, and 25 ppm (*S*-*tert*-butyl) and 31 and 25 ppm (2:1) (*C*-*tert*-butyl). Exchange between these sites was confirmed by observation of cross peaks in a 2D CPEXSY spectrum at 173 K using a conventional pulse sequence and a 100 ms mixing time. At temperatures above the region where dynamic

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Figure 1. Room temperature ^{13}C CP/MAS spectrum of *cis*-4-*tert*-butyl-1-(*tert*-butylsulfonyl)cyclohexane (1).
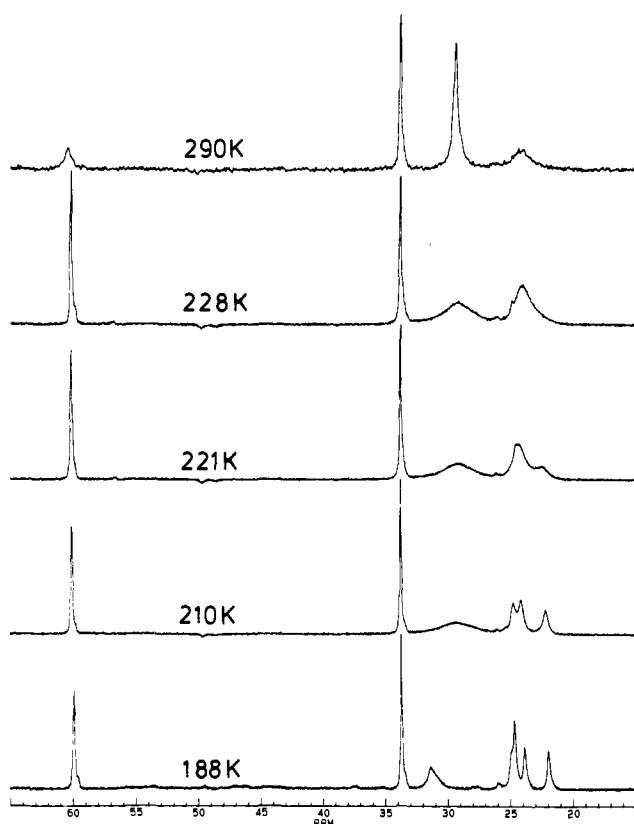

Figure 2. Temperature dependent line shape changes for the carbons in the *tert*-butyl groups obtained from NQS spectra incorporating a dipolar dephasing delay of 50 μs.

Figure 3. The variation of $T_{1\rho}$ with temperature for the carbon atoms of both *tert*-butyl groups.

line shape changes take place, reductions in intensity of the signals from the *tert*-butyl groups are observed. $T_{1\rho}$ measurements were performed for all four signals over the temperature range 209–333 K. The values obtained are reported in Table I and shown graphically in Figure 3. The values are seen to follow the inverted bell curve predicted by eq 1 with minima at ca 2.7 ms for the methyl carbons and ca 7.5 ms for the quaternary carbons. As predicted for behavior modulated by the bond rotation, both carbons from a given group show minima at the same temperature. Also, as predicted for a consistent *tert*-butyl geometry, the minimum values of $T_{1\rho}$ for a given type of carbon atom in the two different *tert*-butyl groups are comparable.

The modulated part of the dipolar interaction which is responsible for relaxation, B^2, was calculated from the apparent
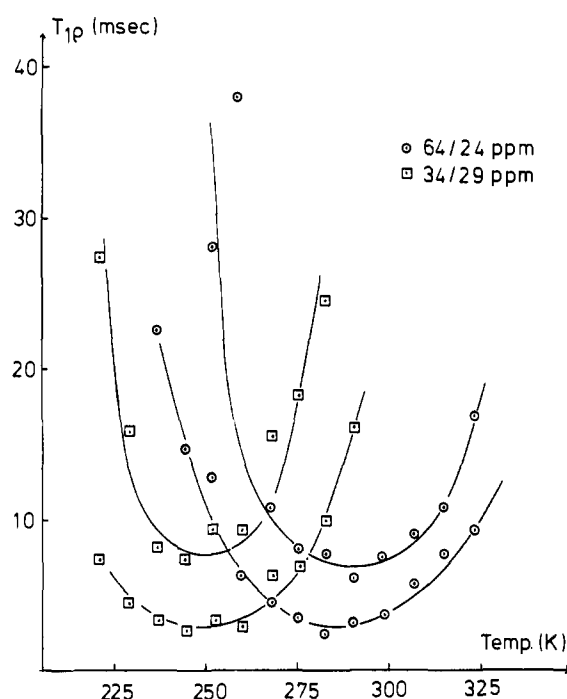
change in the theoretical second moment, M_2, of the natural ^{13}C absorption lines[20] brought about by the molecular motion. The method is described in detail in ref 12 and in outline here. The interaction between the carbons and the hydrogens was assumed to be averaged already by the rapid methyl group reorientation ($\tau_{Me} \ll \tau_{tBu}$). The additional reduction in M_2 due to the *tert*-butyl group rotation was then calculated assuming a spherical average of the lattice sums for all crystallite orientations (powder average). The mean methyl ^{13}C–^{1}H bond length was taken to be 110 pm and the mean methyl ^{1}H to central ^{13}C distance was taken to be 220 pm. The average bond angle C–C–H was taken to be 110°. These values are consistent with, but not identical to, the geometry given in ref 15. This reduction in M_2 gave B^2 (in frequency units) for both the central and the methyl carbons and the values are listed in Table II. The observed and calculated intramolecular interactions between the carbon atoms and the methyl hydrogens agree very satisfactorily within a factor of 2.

(20) Fukushima, E.; Roeder, S. B. W. *Experimental Pulse NMR A Nuts and Bolts Approach*; Addison-Wesley: Reading, MA, 1981; p 236.

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Table II. Observed and Calculated Values for the $^{13}C-^1H$ Dipolar Interaction Strength B^2 (s^{-2})[a]

resonance (ppm)	obsd value	calcd value
61	2.0×10^8	1.8×10^8
33	1.5×10^8	1.8×10^8
29	4.1×10^8	7.5×10^8
24	3.9×10^8	7.5×10^8

[a] Values of B^2 are calculated as described briefly in the text and in more detail in ref 12.
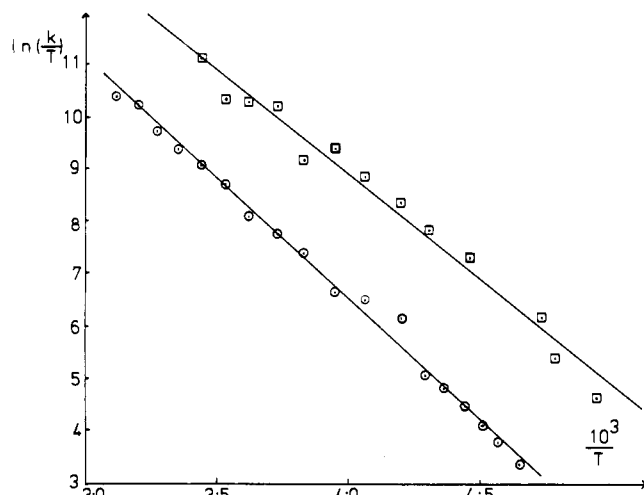
Figure 4. Eyring activation plot of $\ln(k/T)$ vs $10^3/T$ for the methyl carbon atoms in both *tert*-butyl groups. The points on the left-hand side of each line are from $T_{1\rho}$ measurements and are separated by a small gap from the points on the right which are from line shape analysis.

Table III shows the values of the rate constants obtained from both $T_{1\rho}$ measurements and from line shape analysis. These are presented in Eyring plots in Figure 4. The agreement between the independently derived, but complementary, rate data is very satisfactory with an almost perfect fit between the lines derived for both methods. Moreover, the agreement between the rates derived from $T_{1\rho}$ for both carbons in the same *tert*-butyl group is good although these rates are not plotted in Figure 4.

The agreement of all four criteria predicted by the theory with the experimental observations confirms that the $T_{1\rho}$ values are indeed being modulated by the rotations of the *tert*-butyl groups.

The theory employed assumes that the rotation of the individual methyl groups is more rapid than that of the *tert*-butyl group. Examples have been found where the reverse is the case. For example, this is found in *tert*-butyl chloride and bromide,[21] *tert*-butyl aldehyde,[22] *tert*-butyl cyanide,[23] and *tert*-butyl thiol.[24] In some of these examples it is the whole molecule that rotates more rapidly than the methyl groups. These are very different types of molecules from the one discussed here and in all of them one would expect a low barrier to *tert*-butyl rotation or molecular rotation in the solid. This is not the case with our compound where the *tert*-butyl groups are attached to an sp^3 hybridized carbon or sulfur carrying three other ligands that will serve to increase the barrier substantially. It is impossible to envisage the whole of our molecule rotating more rapidly than the methyls. In any case the rotation rates that we observe are smaller and the rotational barriers are substantially greater than the methyl rotation barriers found in the above quoted examples.

In the Eyring plots shown in Figure 4 both *tert*-butyl groups show lines that are not quite parallel indicating slightly different enthalpies of activation. In agreement with expectation the resonances with the $T_{1\rho}$ minima at higher temperature show the

Table III. Rate Constants for *tert*-Butyl Group Rotation (s^{-1})[a]

temp (K)	61 ppm	33 ppm	29 ppm	24 ppm
320	1.00×10^7			1.06×10^7
312	6.19×10^6			8.54×10^6
305	5.01×10^6			5.04×10^6
298	3.90×10^6			3.47×10^6
290	2.78×10^6	2.12×10^7	1.95×10^7	2.53×10^6
283	1.68×10^6	1.01×10^7	8.48×10^6	1.68×10^6
276	6.57×10^5	7.82×10^6	7.88×10^6	8.91×10^5
268	4.62×10^5	6.55×10^6	7.37×10^6	6.20×10^5
261	1.22×10^5	3.40×10^6	2.40×10^6	4.12×10^5
253	1.62×10^5	3.46×10^6	3.04×10^6	1.93×10^5
246		1.68×10^6	1.68×10^6	1.60×10^5
238		1.09×10^6	9.78×10^5	1.09×10^5
232		4.17×10^5	6.03×10^5	
224		2.32×10^5	3.29×10^5	
233				3.6×10^4
229				2.8×10^4
225				1.9×10^4
222				1.3×10^4
219				9.0×10^3
215				6.0×10^3
211			1.0×10^5	
209			4.5×10^4	
202			2.0×10^4	

[a] The upper set of values (224–320 K) are from $T_{1\rho}$ measurements. The lower set (202–233 K) are from line shape analysis. The combined data for the 29 and 24 ppm resonances, as plotted in Figure 4, give the following activation parameters: 29 ppm, $\Delta H^* = 33.5 \pm 3.2$ kJ·mol^{-1}, $\Delta S^* = +10.3 \pm 13.5$ J·K^{-1}·mol^{-1}; 24 ppm, $\Delta H^* = 38.2 \pm 1.5$ kJ·mol^{-1}, $\Delta S^* = +9.4 \pm 5.9$ J·K^{-1}·mol^{-1}. Errors quoted are 95% confidence limits (twice standard deviations from least-squares fitting).

larger values for ΔH^*. The enthalpies of activation (38.2 and 33.5 kJ·mol^{-1}) are lower than we have observed before in systems such as *tert*-butyl ammonium ions[6] and *tert*-butyl alcohols.[5] The current molecule does not possess the strong directional ionic or hydrogen bonding forces present in these other materials and it is likely that non-directional van der Waals forces predominate. This is in keeping with the generalized prediction by the principle of least distress that molecules in solids that are tightly bound by directional forces should show greater barriers to intramolecular motions.

Lii and Allinger performed molecular mechanics calculations on hydrocarbons that suggested that hindered systems such as *tert*-butyl groups should have significantly negative entropies of activation.[25] For example, they calculated the entropy of activation for the rotation of the central bond in 2,2,3,3-tetramethylbutane (di-*tert*-butyl) to be -36 J·K^{-1}·mol^{-1} in the gas phase. The current work suggests that in our systems, which should be more hindered than the gas phase, the entropies of activation are small and positive.

Twyman and Dobson, studying the rotation of a phenyl group in the solid using ^{13}C CP/MAS spectra, observed appreciable line broadening at temperatures well above coalescence.[4] This so called "maximum dipolar broadening" arises because the incoherent averaging caused by the intramolecular motion interferes with the coherent averaging of the decoupling field.[26] Although slight line broadening was observed in our studies (Figure 2, 290 K spectra) there was no dramatic line broadening of the type observed by Twyman and Dobson.

In order to assess whether, as in our previous observations,[5] the rotation rates are slower in the solid than in solution we recorded solution state ^1H spectra in CD$_2$Cl$_2$ solution down to 173 K. No line broadening other than that normally associated with viscosity changes was observed. The solution state coalescence temperatures are, therefore, at least 30 K lower than in the solid. In addition solution state $T_{1\rho}$ measurements on the ^1H spectra were made. $T_{1\rho}$ decreases as the temperature is lowered from ambient to 173 K but no minimum was observed in this temperature range. The

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Table IV. Principal Components (U_i; i = 1, 2, 3) of Mean Squared Atomic Displacement for Methyl Carbon Atoms in the *tert*-Butyl Groups and the Angle (θ) between Each Principal Axis and the Tangential Direction of the Carbon Atom (As Defined in the Text)[a]

atom	$U_i/\text{Å}^2$	$\theta/\deg$	atom	$U_i/\text{Å}^2$	$\theta/\deg$
C71	0.092	53	C81	0.086	63
	0.043	90		0.050	87
	0.067	37		0.075	56
C72	0.091	20	C82	0.091	9
	0.040	79		0.038	83
	0.077	73		0.075	84
C73	0.091	34	C83	0.105	17
	0.050	87		0.051	86
	0.066	56		0.066	73

[a] Anisotropic displacement parameters and atomic labeling are taken from ref 15 (Figure 4).

spin-locking ¹H radio frequency field was 38 kHz. These results indicate that the rate of rotation in solution at 173 K is probably at least two orders of magnitude greater than in the solid state.

We now make an assessment of whether the anisotropic displacement parameters (ADPs; alternatively referred to as thermal parameters) determined from the single-crystal X-ray diffraction data are consistent with the presence of disorder in this system due to the rotation of the *tert*-butyl groups. First, however, it is important to stress that ADPs reflect disorder arising both from molecular motion (dynamic disorder) and also from static positional disorder (because structure determination from diffraction-based methods gives a structural representation that is averaged over all the unit cells in the crystal). Measurement of ADPs at a single temperature, therefore, does not allow the source of structural disorder to be partitioned between these two possibilities. To differentiate between them accurate measurements of ADPs as a function of temperature is needed. Dunitz et al.[27,28] have shown that it is indeed possible to derive information relating to dynamic properties of crystalline solids, including an assessment of energy barriers for rotation of groups[29,30] such as the *tert*-butyl groups under consideration here, from careful consideration of the temperature dependence of ADPs.

It is also relevant to note that the components of the atomic displacement tensors $\{U_{ij}\}$ for different atoms are generally refined independently even when the molecule can, to a good approximation, be treated as a rigid body. By making use of this fact, Cruickshank[31-33] developed a method, later refined by Schomaker and Trueblood,[34-36] for using such data, recorded at a single temperature, to deduce tensors which describe the translational and librational motions of the rigid molecule as a whole or internal librational motions of groups within a molecule.

Figure 5. The structure and partial numbering used for *cis*-4-*tert*-butyl-1-(*tert*-butylsulfonyl)cyclohexane (**1**).

In the present work we have adopted a more qualitative approach for the interpretation of ADPs based on the plausible assumption, arising from our NMR measurements, that the main source of disorder for each *tert*-butyl group arises from libration about its local 3-fold axis. This essentially represents the motion of the *tert*-butyl group as being a libration inside a 3-fold potential energy well. In such a case, the major component of atomic displacement for the carbon atoms of the methyl groups in the *tert*-butyl group should be tangential to the circle which can be considered to pass through these three methyl carbons.

In order to assess whether this is indeed the case for the present compound, the measured ADP tensors for each of the methyl carbons were transformed from the crystallographic reference frame to their respective principal axis systems and the principal components of the tensors in this reference frame were determined using the methodology discussed in ref 37. These principal components represent the mean squared atomic displacements along the principal axes. The results are summarized in Table IV in which the principal components for each methyl carbon are given together with the angle between the relevant principal axis and the tangential direction at that carbon atom. This tangential direction is defined here as the vector product between (i) the normal to the plane containing the three methyl carbon atoms and (ii) the vector from the methyl carbon of interest to the centroid of the three methyl carbon atoms of the *tert*-butyl group.

As shown in Table IV the large values of the principal components of the mean squared atomic displacement suggest that there is appreciable disorder (static and/or dynamic) concerning the orientation of the *tert*-butyl groups about their 3-fold axes. Furthermore, for most of the methyl carbons the largest principal component of the ADP tensor derived from the X-ray diffraction study of this compound[15] corresponds to displacement in a direction close to the tangential direction for the carbon atom of interest. The nature of the observed anisotropy is, therefore, consistent with the idea that disorder arises primarily from reorientation about the local 3-fold axis of each *tert*-butyl group.

Conclusions

We conclude that $T_{1\rho}$ measurements in ¹³C CP/MAS NMR spectroscopy can be used to measure rates of internal molecular motions and that in our system the combination of rates derived from $T_{1\rho}$ and line shape analysis gives reliable values for the activation parameters. Allinger's proposal that for bond rotations in congested systems the entropy of activation should be substantial and negative would appear to require further appraisal. The large anisotropic displacement parameters observed for the *tert*-butyl carbons in **1** arise from the rotation of the *tert*-butyl groups.

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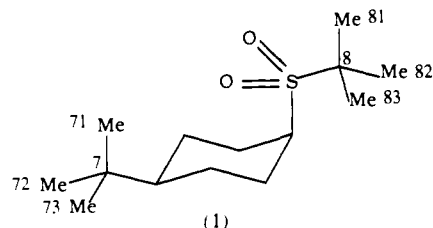(31) Cruickshank, D. W. J. *Acta Crystallogr.* **1956**, *9*, 754.

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