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NOTE

The Double *tert*-Butyl Rotation in Solid *cis*-2-*tert*-Butyl-5-(*tert*-butylsulphonyl)-1,3-dioxane

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***cis*-2-*tert*-Butyl-5-(*tert*-butylsulphonyl)-1,3-dioxane displays a double *tert*-butyl coalescence at low temperatures in its ^{13}C CP/MAS NMR spectrum associated with slowing down of the rotation of both *tert*-butyl groups. The overlap of the resonances precluded the measurement of rates of rotation from lineshape analyses. However, ^{13}C $T_{1\rho}$ measurements above coalescence allowed rates of rotation and activation parameters for the rotations of both groups to be derived. The *C-tert*-butyl group has $\Delta H^\ddagger = 26.3 \pm 3.6$ kJ mol^{-1} and $\Delta S^\ddagger - 13 \pm 14$ J K^{-1} mol^{-1}. The *S-tert*-butyl group has $\Delta H^\ddagger = 31.8 \pm 2.2$ kJ mol^{-1} and $\Delta S^\ddagger - 9$ J K^{-1} mol^{-1}. © 1997 by John Wiley & Sons, Ltd.**

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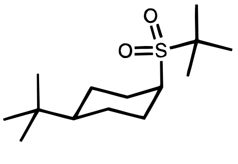
INTRODUCTION

We have previously reported the double *tert*-butyl group rotation in solid *cis*-1-*tert*-butyl-4-(*tert*-butylsulphonyl)cyclohexane (**1**).[1] In this compound the two *tert*-butyl groups displayed coalescences at different temperatures in their ^{13}C cross polarization magic angle spinning (CP/MAS) spectra from which rate constants for both *tert*-butyl group rotations could be extracted. We were also able to demonstrate that measurements of ^{13}C $T_{1\rho}$ values above the coalescence allowed rate constants for the rotations to be calculated and considerably extended the temperature range over which rates could be measured. We have since reported a wide range of molecular motions in the solid state including rotations of methyl, *tert*-butyl, *tert*-amyl and phenyl groups using these methods.[2–6] We have also observed rotations of trimethylammonium,[7] trimethylphosphonium[8] and trimethylsilyl groups.[9]

At the time of the original measurements on **1** we also studied the closely related compound *cis*-2-*tert*-butyl-5-(*tert*-butylsulphonyl)-1,3-dioxane (**2**). Compounds **1** and **2** were chosen for study for several reasons. First, the compounds have had their structures solved by single-crystal x-ray diffraction methods (**1**,[10] **2**[11]). An interesting feature of both structures is the eclipsing of the C-5—S bond with the *S-tert*-butyls pointing out of the ring. Second, they each present two *tert*-butyl groups on which the method of extracting rates of rotation from $T_{1\rho}$ values could be tested. Third, each compound should show different activation parameters for the rotations of its two *tert*-butyl groups. Finally, it is of interest to compare the rates and activation parameters for the group rotations in two very closely related structures.



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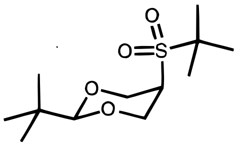

2

The spectral changes in **2** were less well delineated than those in **1** because of overlap of the methyl carbon resonances during the coalescence and a lower coalescence temperature, so our initial report only included the results from **1**.[1] We now report our observations on **2**. Details of the theory of the $T_{1\rho}$ method for evaluation of rate constants were given previously.[1] Other related work using ^{13}C CP/MAS NMR to study molecular dynamics in solids can be found elsewhere.[1–6]

RESULTS AND DISCUSSION

The ambient temperature ^{13}C CP/MAS NMR spectrum of **2** recorded at 125.758 MHz is displayed in Fig. 1(a). Dipolar dephased (NQS) spectra allow the identification of the lines from the *tert*-butyl groups as *S-tert*-butyl 61.8 and 25.1 ppm and *C-tert*-butyl 35.8 and 27.0 ppm. The other resonances are C-2 108.0 ppm, C-4,6 65.3 and 68.4 ppm and C-5 50.2 ppm. These chemical shifts are all with in a few ppm of the reported shifts in solution[11] apart from C-5, 56.8 ppm in solution *vs.* 50.2

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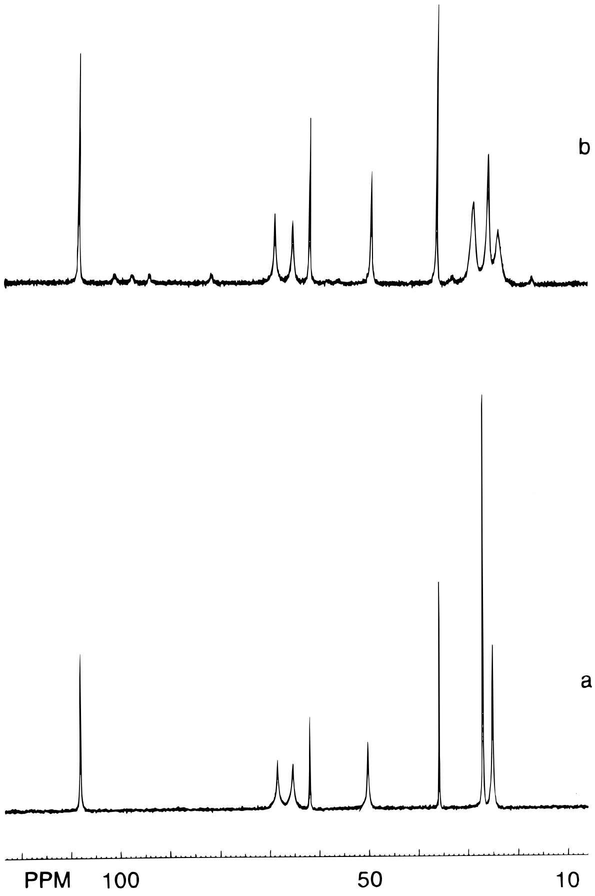

Figure 1. ^{13}C CP/MAS spectra of **2** recorded at 125.758 MHz and (a) 8.5 kHz and ambient temperature and (b) 4.1 kHz and 181 K.

ppm in the solid. This large change in chemical shift from solid to solution may mean that the eclipsed conformation about the C-5—S bond observed in the solid is no longer present in solution.

It is noticeable that the lines from the *S-tert*-butyl group are of lower intensity than those of the *C-tert*-butyl group. This is due to less efficient cross polarization because of shorter $T_{1\rho}$ values for these carbons. The reduction in $T_{1\rho}$ values arises because the rotation of the *S-tert*-butyl group is close to the precessional frequency of the ^{13}C nuclei in the spin lock field (*ca.* 63 kHz) during cross polarization.

As the temperature is lowered, the methyl resonances at 25 and 27 ppm decrease in intensity then regain some intensity, broaden and eventually give rise to a three-line pattern arising from the overlap of the decoalesced resonances [Fig. 1(b)]. Confirmation of chemical exchange between the low-temperature resonances at 23 and 28.5 ppm (coming almost certainly from the ambient line at 27 ppm) was obtained by means of a low-temperature CP/EXSY spectrum which displayed a cross peak between these two resonances consistent with the exchange process (Fig. 2). The overlap of the two coalescences precluded the measurement of rate constants for rotation from the lineshapes.

In order to study the kinetics of the rotation, $T_{1\rho}$ values were obtained for the two *tert*-butyl groups between 204 and 328 K (Table 1). The $T_{1\rho}$ values show the expected inverted bell-shaped curves. The minima for both carbons in each group occur as expected at approximately the same temperature whereas the minima for the two groups differ, occurring at *ca.* 260 K (*S-tert*-butyl) and *ca.* 230 K (*C-tert*-butyl) (Fig. 3). The minimum values for $T_{1\rho}$ for the quaternary and methyl carbons are similar and are close to the values measured and reported for **1**.[1]

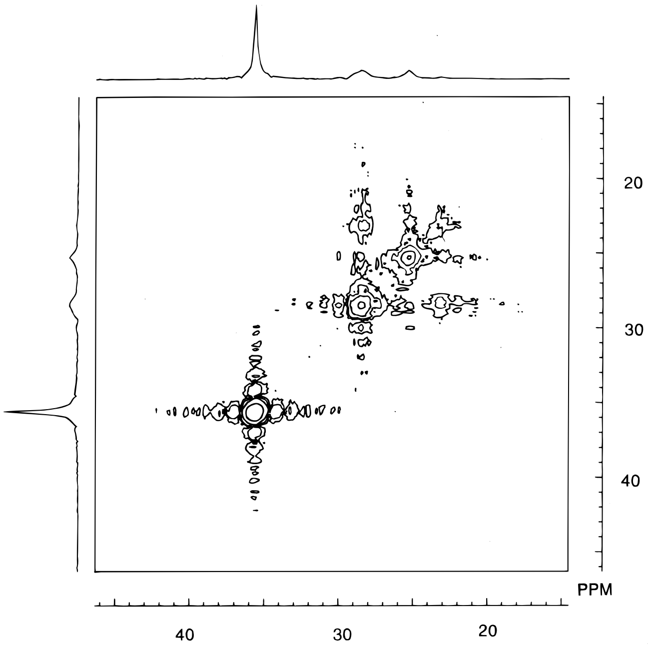

Figure 2. 2D ^{13}C CP/EXSY spectrum of **2** recorded at 125.758 MHz and 178 K with a mixing time of 200 ms.

Using the theory developed and the procedures outlined previously,[1] rate constants were derived from the $T_{1\rho}$ data and are given in Table 2. Activation plots from the combined rate constant data for both *tert*-butyl groups are linear and give the activation parameters shown in Table 3.

As with the previous compound studied (**1**), the *S-tert*-butyl group in **2** shows slower rates of rotation

Table 1. $T_{1\rho}$ **values (ms) for the *tert*-butyl carbons of 2 (ω_1 = 63 kHz)**

T (K)	62 ppm	36 ppm	27 ppm	25 ppm
328				37.0
321				25.6
313				23.8
306			50.0	18.5
299	47.6		41.7	14.3
292	31.3		45.5	12.2
284	22.7	47.6	22.2	8.5
277	13.0	22.7	9.4	4.2
270	6.9		14.5	4.6
262		20.8	8.2	3.8
255	7.0	13.7	5.9	2.4
248	8.3	10.0	4.2	3.0
241	8.9	8.6	2.8	4.0
233	25.6	5.3	3.9	5.8
226	38.5	6.3	4.2	9.2
219		8.2	3.3	11.6
212		9.4	4.1	15.6
204		13.2		

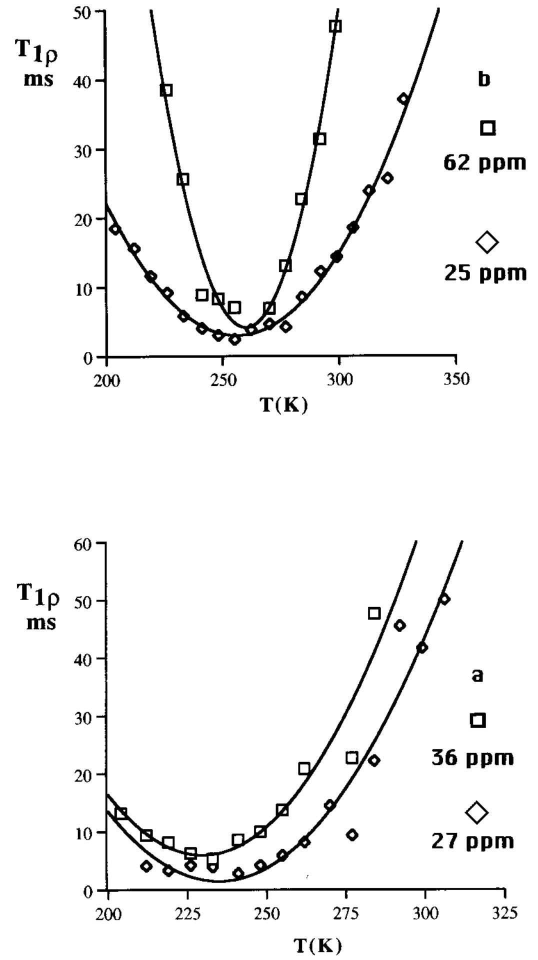

Figure 3. $T_{1\rho}$ measurements for the carbons of (a) the *C-tert*-butyl group and (b) the *S-tert*-butyl group in **1** at various temperatures ($\omega_1 = 63$ kHz). The lines are to guide the eye and are not best-fit curves.

for the same temperature and a larger enthalpy of activation. The enthalpies of activation for both groups are significantly lower than in **1**. The entropies of activation, although of low reliability, suggest a slightly negative value for both groups in **2**, whereas in **1** they suggest a slightly positive value. The entropies of activation for **1** and **2** do not agree with the gas-phase value calculated for the *tert*-butyl rotation in 2,2,3,3-tetramethylbutane (di-*tert*-butyl) by Lii and Allinger.[12] Lii and Allinger predicted a significantly negative entropy of activation from their molecular mechanics calculations on the isolated molecule (-36 J K^{-1} mol^{-1}). Our results suggest that this is not the case, at least in these solids.

Table 2. Rate constants (s^{-1}) for the *tert*-butyl group rotation in 2

T (K)	62 ppm	36 ppm	27 ppm	25 ppm
328				3.7×10^7
321				2.6×10^7
313				2.4×10^7
306			4.2×10^7	1.9×10^7
299	1.6×10^7		3.5×10^7	1.4×10^7
292	1.1×10^7		3.8×10^7	1.2×10^7
284	7.7×10^6	2.1×10^7	1.9×10^7	8.3×10^6
277	4.1×10^6	1.0×10^7	7.8×10^6	3.8×10^6
270	1.2×10^6		1.2×10^7	4.3×10^6
262		9.1×10^6	6.7×10^6	3.4×10^6
255	9.2×10^5	5.8×10^6	4.7×10^6	1.4×10^6
248	6.2×10^5	4.1×10^6	3.1×10^6	5.6×10^5
241	5.6×10^5	3.4×10^6	1.0×10^6	3.8×10^5
233	1.6×10^5	1.3×10^6	5.0×10^5	2.5×10^5
226	1.1×10^5	6.6×10^5	4.5×10^5	1.5×10^5
219		4.3×10^5	6.3×10^5	1.2×10^5
212		3.7×10^5	4.7×10^5	8.9×10^4
204		2.5×10^5		

Table 3. Activation parameters for compound 2

Parameter	27/36 ppm	25/62 ppm
$\Delta H^{\ddagger}$ (kJ mol^{-1})	26.3 ± 3.6	31.8 ± 2.2
$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	-13 ± 14	-3 ± 9
$\Delta G^{\ddagger}_{293}$ (kJ mol^{-1})[a]	30.2	32.6

[a] Calculated from the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values.

EXPERIMENTAL

Solid-state ^{13}C CP/MAS NMR spectra were obtained on a Bruker MSL 500 spectrometer at 125.758 MHz using 4 mm o.d. zirconia rotors. The following typical conditions were employed: contact time, 1 ms; spectral width, 30 000 Hz; acquisition time, 17.4 ms; spin locking field frequency, *ca.* 63 kHz; recycle delay, 5 s; and spinning speeds, 4–8 kHz. Chemical shifts were referenced to the CH_2 resonance in an external adamantane sample at 38.56 ppm. Dipolar dephased [non-quaternary suppressed (NQS)] spectra to aid spectral assignments were obtained by a standard sequence incorporating a 50 μs dipolar dephasing delay. $T_{1\rho}$ measurements were performed as described previously using a standard $T_{1\rho}$ sequence preceded by cross polarization.[1] Spin lock periods of up to 20 ms were employed with ^{13}C precessional frequencies (ω_1) of around 63 kHz. Temperatures in the MAS probe were calibrated using standard samples with known phase changes run under conditions as close as possible to those of the experimental observations.[13]

The 2D ^{13}C CP/EXSY spectra were obtained using a standard 2D NOESY sequence in which the initial excitation was provided by a cross polarization sequence. Spectra were obtained with a spectral width of 16 kHz in 1K data points zero filled to 2K (F_2 dimension) and 128 or 256 data points zero filled to 1K (F_1 dimension). Four FIDs were collected for each spectrum in the F_1 dimension. The final spectrum was presented in a 1K × 1K matrix with a digital resolution of *ca.* 16 Hz per point. Sine-bell apodization and symmetrization were employed to improve the presentation.

Activation parameters were derived from Eyring plots of the rate data. The theory and details of these methods are discussed elsewhere.[1,4] Errors in the activation parameters quoted in this paper are 95% confidence limits estimated as twice the standard deviation calculated from least-squares linear plots. Errors in the $T_{1\rho}$ values vary with the signal-to-noise ratio available from the sample in a reasonable time period. They would typically be around $\pm 5\%$.

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