A Dynamic NMR Study of Sterically Hindered Trialkylmethanols in the Solid Phase

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The temperature dependence of the ^{13}C CP/MAS NMR spectrum of solid tri-*tert*-butylmethanol and three similar trialkylmethanols is reported. That energy barriers are 20–30% higher than found in solution is attributed to constraints of the lattice which also seem to cause the rotation and libration processes for these molecules to merge into a single process. The complications that may be encountered when studying dynamic NMR behaviour in solids are also discussed.

Nuclear magnetic resonance spectroscopy is a technique widely used in the study of the internal dynamics of the molecules both in solution and in the solid phase. Most work in solution involves studying signal coalescence as the temperature is changed (dynamic NMR), and this allows rotational processes to be identified and the energy barriers to be measured.[1] In the solid state, a number of NMR interactions such as dipole–dipole coupling and relaxation are affected by molecular motion, and variations in the second moment of wideline proton spectra and proton relaxation times (T_1, $T_{1\rho}$ and T_{1D}) can all give measurements of rotational correlation times, from which barriers may be deduced, but they are not sufficient alone, except in simple cases, to determine precisely which rotational mode is involved.[2] Other information about low energy motions and rotational barriers in solids comes from variable temperature static ^2H NMR spectra, as the quadrupolar lineshape is critically dependent on any dynamic behaviour, but analysis of these lineshapes is time-consuming and depends critically on the assumed molecular motion.[3,4] There have so far been comparatively few solid state studies that observe peak coalescence phenomena due to dynamic behaviour on the chemical shift timescale.[5–10]

In this paper we report variable temperature ^{13}C CP/MAS NMR spectra of the sterically hindered alcohols $R^1R^2R^3COH$ (**1–4**), where R is *tert*-butyl or 1-adamantyl. These molecules have been established as having six (rather than three) equivalent skewed conformations in solution during a 360° rotation of a *tert*-alkyl group owing to the presence of long range steric interactions in the perfectly staggered conformation.[11,12] The staggered conformation is not an energy minimum for these molecules, so in the NMR spectrum there are two separate sets of changes with temperature, corresponding to rotation through the eclipsed conformation and libration through the staggered conformation becoming slow on the NMR timescale. This is illustrated diagrammatically in Fig. 1 for tri-*tert*-butylmethanol (**1**) which in solution has a barrier of 9.2 kcal mol^{-1} for libration and of 10.0 kcal mol^{-1} for rotation,* and for which the singlet in the NMR spectrum at room temperature splits successively on cooling to a 2:1 doublet, and then to a 1:1:1 triplet. Similar considerations apply when some or all of the alkyl groups are adamantyl rather than *tert*-butyl, with progressively increasing barriers. In this paper we observe the classical dynamic coalescence behaviour for the resonances from the CH_3 and CH_2 signals in the solid state spectra of these materials, of the kind routinely observed in solution studies. We compare these results to those observed in solution, and comment on the difficulties in spectral interpretation that can occur when studying such phenomena in the solid phase.

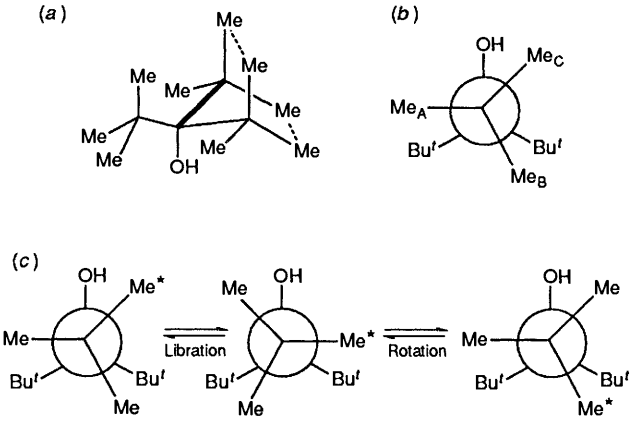

Fig. 1 (*a*) The completely staggered conformation of tri-*tert*-butylmethanol. The dashed lines indicate some of the long range steric interactions, which make this conformation unfavourable. (*b*) Newman representation of one of the six equivalent preferred conformations of tri-*tert*-butylmethanol, showing the three inequivalent methyl groups (labelled A, B and C). (*c*) Representation of the rotational and librational processes for tri-*tert*-butylmethanol.

Experimental

^{13}C CP/MAS spectra were recorded on a Bruker MSL-300 spectrometer equipped with a Bruker B-VT1000 variable temperature unit. A contact time of 1 ms was generally used, except at those temperatures when the proton $T_{1\rho}$ was very short when a 0.2 ms mixing time was applied. The proton 90° pulse was typically 5.0 μs. Recycle delays of 1–5 s were generally sufficient for tri-*tert*-butylmethanol, but some of the other alcohols studied required longer delays (up to 1 min) at certain temperatures. Some spectra were also recorded without cross-polarization (*i.e.* using only single pulse excitation with high-power proton decoupling). Chemical shifts are quoted from external TMS. The samples were cooled in 10 K steps and left for 5 min at each temperature to equilibrate. The temperature was measured by a thermocouple located close to the sample chamber. Temperatures are expected to be accurate within ±2 K, for temperatures above 200 K, and ±4 K for temperatures below 200 K. Spectra were repeated during a warming cycle after the cooling cycle to check that thermal equilibrium had been established. This was observed to be the case except in the one specific instance discussed below. Static wideline ^1H NMR spectra were also recorded on the tri-*tert*-butylmethanol

* 1 cal = 4.184 J.

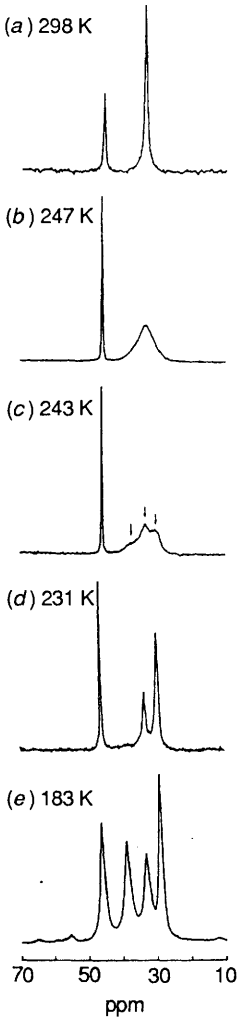

Fig. 2 ^{13}C CP/MAS spectra of tri-*tert*-butylmethanol at various temperatures

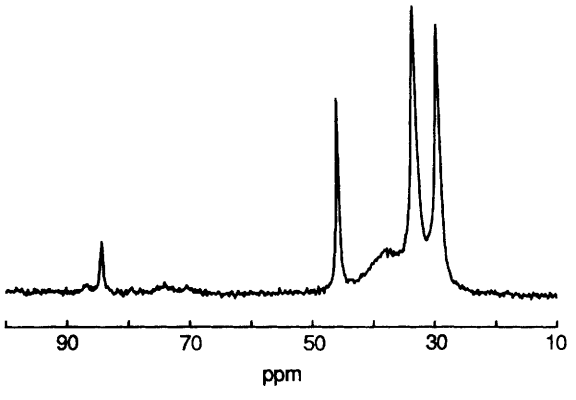

Fig. 3 ^{13}C MAS spectra of tri-*tert*-butylmethanol at 231 K recorded without cross-polarization. The spectrum should be compared with that in Fig. 2(*d*).

sample. Differential scanning calorimetry (DSC) experiments were recorded using a PE DSC 7 calorimeter in order to detect any solid state phase transitions that might be occurring.

Results and Discussion

The set of ^{13}C CP/MAS NMR spectra for tri-*tert*-butylmethanol (**1**) is shown in Fig. 2. Above *ca.* 298 K rotation is fast on the NMR timescale and a singlet is seen at 33.4 ppm for the methyl carbons. As the sample is cooled that singlet broadens and in a single set of changes splits to three components seen between 247 and 243 K (at 37.6, 33.3 and 29.5 ppm). These chemical shifts agree well with those observed in solution, and average close to the fast exchange value. However, the equivalent processes in solution are observed to occur at *ca.* 200 K, implying that the energy barriers in the solid state are about 2 kcal mol^{-1} greater than in solution. Furthermore, the two separate sets of spectra changes seen in solution (associated with rotation and libration) seem to be condensed into a single change in the solid phase which involves both processes becoming slow simultaneously.

Surprisingly, however, by 231 K only two of these three methyl peaks are still visible (at 33.2 and 29.3 ppm) in the cross-polarization spectrum. It is possible that the site corresponding to the third peak does not cross-polarize efficiently owing to a combination of a very short $T_{1\rho}$ value for neighbouring protons and the molecular motion partially reducing the dipole–dipole interaction through which cross-polarization takes place. To test this, the spectrum at 231 K was recorded without cross-polarization using only single pulse excitation with high-power proton decoupling. This showed the presence of the third methyl signal (*ca.* 37.6 ppm), though it is noticeably broader than the other resonances (see Fig. 3). Between 193 and 223 K only the two methyl signals at 33.0 and 29.1 ppm are detected, whether by cross-polarization or conventional single pulse excitation. The sudden broadening and eventual disappearance of the third methyl signal is attributed here to dipolar broadening due to the reduced decoupler efficiency that occurs in solids when the rate of reorientation matches the power of the proton decoupling field.[13] In fact, measurements of such linewidth changes are themselves another method of measuring rotational energy barriers in solids.[13] Below 183 K the third methyl signal reappears in the cross-polarization spectrum with peaks at 38.5, 32.8 and 28.8 ppm [Fig. 2(*e*)].

That just one of the methyl peaks broadens beyond detection in the temperature regime investigated is at first sight surprising, suggesting that one methyl group has an anomalously high rotational energy barrier. The maximum broadening of this methyl peak occurs at *ca.* 208 K when using a decoupler power that corresponds to 50 kHz, and this enables us to estimate the free energy of activation for rotation for this methyl group to be *ca.* 7.6 ($\pm$0.5) kcal mol^{-1}. Some confirmation of this interpretation comes from molecular mechanics calculations using Allinger's MM3 programme[14] which indicate that for an isolated tri-*tert*-butylmethanol molecule the energy barriers for the rotation of the three non-equivalent methyl groups [labelled A, B and C in Fig. 1(*b*)] are very different, namely 7.7, 3.4 and 0.7 kcal mol^{-1} respectively. The calculated value for the highest of these barriers happens to agree well with that derived from the maximum dipolar broadening in the solid state NMR spectra.

An interesting effect was observed in a sample of **1** which had been heated to temperatures above 303 K. As expected, narrow peaks resulted for all the signals with a singlet for the methyl groups. However, on recooling below 303 K the expected gradual broadening of the methyl signals did not occur until much lower temperatures than previously required. This suggests that there may be a solid phase transition around 303 K, which is only slowly reversed upon cooling. The barriers for rotation and libration are lower in this new phase, but any dynamic broadening for this phase could not be separated from the effects of the gradual reversal of the phase transition. The phase transition was confirmed by static wideline proton spectra of the compound, which showed a dramatic reduction in linewidth at about this temperature. Above *ca.* 303 K the static proton linewidth was less than 1000 Hz (exceptionally narrow for a solid) indicating that the molecules in the solid were extremely mobile, thus reducing the effects of proton–proton

Table 1 Range of rotational energy barriers for compounds **1**–**4** in the solid state estimated from the CP/MAS spectra as described in the text

Compound	Range of barriers/kcal mol^{-1}
1 $(Bu^t)_3COH$	11.0–13.0
2 $(Bu^t)_2AdCOH$	12.4–15.2
3 $Bu^t(Ad)_2COH$	13.9–18.7
4 $(Ad)_3COH$	16.8–20.0

dipolar coupling. This is perhaps unsurprising in view of the near spherical symmetry of this molecule. In keeping with this increased molecular mobility, the rotation and libration processes are less hindered by the lattice than in the low temperature phase.

Differential scanning calorimetry (DSC) on **1** was also performed to confirm the nature of the transition. There is a large transition at 302.6 K with an enthalpy change of $\Delta H = 6.9$ kJ mol^{-1}, which is only slowly reversed on cooling the sample from above the transition. Thus it is possible for this high temperature phase to persist at temperatures as low as 233 K unless a very slow cooling rate is used. It is interesting to note that this extremely mobile high temperature phase is formed at temperatures some way below the melting point of the solid (which is 393.4 K), and also that the enthalpy change on melting is only $\Delta H = 2.9$ kJ mol^{-1}.

In general solid state phase transitions hinder the interpretation of any dynamic NMR behaviour occurring, but fortunately the phase transition of **1** is some way above the coalescence temperature of the methyl peaks. DSC shows that the other trialkyl-substituted methanols (**2**–**4**) investigated do not show any phase transitions in the temperature range investigated (153–373 K). Significant dynamic NMR behaviour in these compounds is observed in their ^{13}C CP/MAS NMR spectra. Unlike the case of **1** discussed above there appears to be no unexpected 'loss' of a peak from the spectra at any temperature investigated. Line broadening (presumably due to the reorientation rate becoming comparable to the proton decoupling field) does occur at the lower temperatures, but has yet to reach a maximum by 153 K. This suggests that the highest energy barrier for CH_3 rotation must be less than *ca.* 5.3 kcal mol^{-1}. All four samples showed small splittings of peaks at the lowest temperatures studied (down to 153 K), suggestive of a crystallographic phase transition, though this was not corroborated by the DSC measurements.

One feature observed when recording the CP/MAS NMR spectra of these compounds is the significant variation in proton relaxation times with temperature. In the case of **1** there is a minimum in proton $T_{1\rho}$ around 203 K, resulting in a substantial reduction in overall CP signal intensity; this was partially compensated for by the use of a short contact time (0.2 ms) near this temperature. The proton T_1 relaxation time also varied with temperature for all samples, and reached up to *ca.* 15 s at some temperatures for compounds **2**–**4**, so care had to be taken over the choice of recycle delay between scans in each experiment at each temperature. A full analysis of the variation of ^1H relaxation times with temperature was not attempted since there are many simultaneous rotational modes in these compounds.

The spectral changes observed for the mixed alcohols di-*tert*-butyl-1-adamantylmethanol (**2**) and di-1-adamantyl-*tert*-butylmethanol (**3**) are complicated even in the high-resolution solution spectra, since various singlets split into two, three, or six peaks with much overlap. For both compounds in the solid state, changes take place at much higher temperature and are incomplete at the highest temperature studied (373 K).

For **2**, the separate processes of concerted libration, and rotation of *tert*-butyl and adamantyl groups with different barriers, cannot be distinguished in the mass of changes. For **3**, all processes are slow in the solid at room temperature and only above 353 K is there significant broadening of signals. The solid state spectrum at 373 K corresponds to the solution state one at about 293 K.

While it is tempting to suggest that **2** and **3** show all rotation and libration subsumed into a single exchange process dominated by the needs of the lattice such as is suggested above for **1**, the temperature dependence of the spectra of **2** and **3** can only be said to be not incompatible with such a suggestion. Spectral complexity allows no discrimination in this case between a concerted process and the discrete processes of the solution behaviour.

Tri-1-adamantylmethanol (**4**) shows little sign of any change in the ^{13}C CP/MAS NMR spectrum by 363 K, and rotation and libration are still slow on the NMR timescale at all the temperatures observed.

Very generally, since slow exchange chemical shifts are similar in solution and in the solid, and the temperatures of equivalent solid state and solution spectra are 20–30% higher in the solid, barriers are 20–30% higher than in solution, so results can be suggested as shown in Table 1. Either a single concerted process or separate processes are taking place with barriers falling within the ranges shown, but no aspect of the solid state spectral changes allows a distinction between the six-site calculation used in the solution phase studies[11] and the classical three-site treatment.[15] Using the latter for **1**, we computed spectra which match those recorded at intermediate rates of the dynamic process by trial and error variation of the rate constant and of the line width at each site. There is thus no unique rate constant calculated for any spectrum, but all matches for **1** led to barriers falling within the wide range quoted in Table 1.

The striking differences in the present results compared with solution are firstly that the barriers are noticeably higher (except perhaps in the high temperature mobile phase of **1**), and secondly that the rotational and librational processes are not seen separately, but are combined in a single set of spectral changes. In the solid either both processes become slow over the same temperature range or a single process interconverts the molecule between any one of the six equivalent minimum energy conformations.

These two differences between the solid and solution state may be related. The enhanced barrier suggests that the lattice adds to the encumbrance of the rotation process, quite in keeping with earlier experience.[9] It does not apparently affect the preferred conformation greatly, since the chemical shifts of the slow-exchange triplet in solution and in the solid are similar. It seems plausible that when a molecule moves towards the staggered or eclipsed conformation, the distortion necessary to overcome the additional restraint imposed by the lattice takes the molecule to a state that allows continuation to the next or next but one minimum.

The results in this paper also provide a striking example of the problems that may be encountered in using variable temperature CP/MAS to study dynamic behaviour in solids. Firstly the optimum conditions for recording CP spectra at each temperature may vary considerably depending on the proton relaxation behaviour. Furthermore, different peaks may cross-polarize with quite different efficiencies. Secondly peaks may be broadened considerably, owing not only to dynamic NMR coalescence behaviour but also to reduced decoupling efficiency at certain reorientation frequencies. This can make spectral interpretation particularly difficult. If these factors are taken into consideration, however, it is clear that dynamic NMR peak coalescence behaviour is a useful method for determining rotational barriers in the solid state.

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