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AN INVESTIGATION OF SOLID-STATE PHASE TRANSITIONS IN 1- AND 2-ADAMANTANOL BY ^{13}C CP–MAS NMR

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ABSTRACT

High-resolution ^{13}C NMR spectra have been recorded in the solid state at various temperatures for 1- and 2-adamantanol using the CP–MAS technique. The ^{13}C chemical shifts for these compounds have been assigned based upon literature precedents. Because different regions of the samples experienced slightly different temperatures, it was possible to observe more than one species at a given nominal temperature. These have been ascribed to the co-existence of different solid state phases and the results obtained have been compared with earlier NMR and DTA findings. Given accurate DTA measurements of the transition temperatures for a range of substituted adamantanes, this provides a precise way of calibrating variable temperature CP–MAS experiments, revealing the temperature and any temperature inhomogeneities actually at the sample.

INTRODUCTION

Adamantane has been shown to possess a solid-state phase transition from an ordered to a disordered structure, and several studies have been made of the thermodynamics of the process and of the molecular motion in the solid. The transition temperature has been measured as 208 K, with a corresponding entropy change of 16.2 J K^{-1} mol^{-1} [1]. This large entropy effect provides strong evidence of the order–disorder nature of the transition. Below 208 K, the molecules occupy a face-centred cubic structure and above 208 K there is much freer molecular motion and a reduction in ^{13}C–^{1}H dipolar coupling such that high-resolution spectra and resolution of

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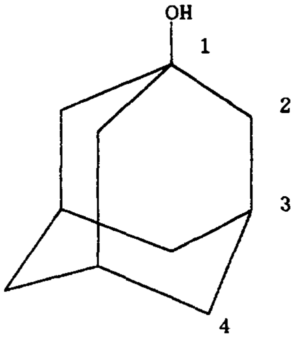

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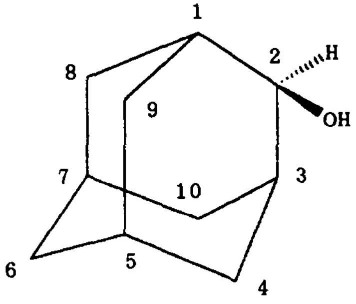

II

chemical shifts is possible in the solid without the use of magic-angle spinning [2]. 1-adamantanol (**I**) has also been studied and shown to have a similar transition which has been variously measured as 353 K with an entropy change at 40.6 J K^{-1} mol^{-1} [3,4], as 359 K on heating, with enthalpy and entropy of transition of 13 kJ mol^{-1} and 36 J K^{-1} mol^{-1}, respectively, and 342 K on cooling, with enthalpy and entropy changes of 12 kJ mol^{-1} and 34 J K^{-1} mol^{-1} [5], and as 369.16 K with the enthalpy and entropy of the transition being 9.63 kJ mol^{-1} and 18.25 J K^{-1} mol^{-1}, respectively [6]. We have also shown that for this molecule, it is possible to obtain high-resolution ^{13}C NMR spectra from the solid using a conventional instrument, again indicative of very extensive molecular motion, particularly above the transition temperature [7]. Interestingly, from FT–IR experiments, the activation energy for rotation about the O–H bond is higher in the high-temperature disordered phase than in the low-temperature ordered phase [5].

We have now studied this molecule by high-resolution ^{13}C NMR spectroscopy in the solid with the use of the cross-polarization/magic-angle spinning method (CP–MAS) to search for chemical shift effects reflecting the phase change. This well-established technique provides a means of removing the dipolar ^{13}C–^{1}H broadening and the ^{13}C chemical shift anisotropic effects, with enhancement of the sensitivity of the ^{13}C NMR detection [8]. In addition, we have studied 2-adamantanol (**II**) by this method because, previously, this molecule had also been investigated using differential thermal analysis (DTA) and NMR without CP–MAS and its phase behaviour evaluated [7,9]. Unlike 1-adamantanol, which has an axis of symmetry in the isolated molecule, 2-adamantanol has only a symmetry plane, and the earlier work showed at least two solid-state transitions. Of course this symmetry may not hold for the solid state where packing effects can effectively remove molecular symmetry.

EXPERIMENTAL

1- and 2-adamantanol were purchased commercially (Aldrich) and used without further purification. The CP–MAS ^{13}C NMR spectra were obtained on a Varian VXR 300 spectrometer operating at 75.43 MHz. A Doty Scientific MAS probe was used, with 7 mm outer diameter rotors spinning at modest speeds (~ 2 kHz). Cross-polarization was achieved with a contact time of 1 ms and recycle delay of 2 s. The number of transients acquired for each spectrum was 200. The variable-temperature spectra were obtained using sapphire rotors with macor end-caps. The inlet gas for bearing/spinning was heated by a coil before impinging on the rotor, and nominal temperatures were measured via a thermocouple sited in the gas stream some distance (ca. 2 cm) before the rotor.

RESULTS

The ^{13}C chemical shifts for 1-adamantanol (I) dissolved in $CDCl_3$ at 293 K have been assigned in the literature [10]. The shifts in the solid state are in close agreement so the assignment can be made by inspection. At 333 K (nominal probe temperature) four resonances are observed, as expected. At 366 and 370 K this is still the case, but the peaks arising from C2 and C3 have shifted by ca. 0.6 ppm, indicating that the phase change has occurred. The changes in the spectrum from 333–370 K are reversible. At 353 K, because of the temperature (and/or pressure) inhomogeneity across the sample, signals from two distinct species are observed (Fig. 1), with the chemical shifts of the major form corresponding to those seen at the higher temperatures. The two species are ascribed to two different solid-state phases in the region of the transition temperature (denoted A and B, see Table 1). The proportions based upon peak height are approximately 69 : 31. The transition temperature from DTA is known to be close to 353 K [3,4–6]. The peak arising from C4 is relatively broad at 333 K (and remains so down

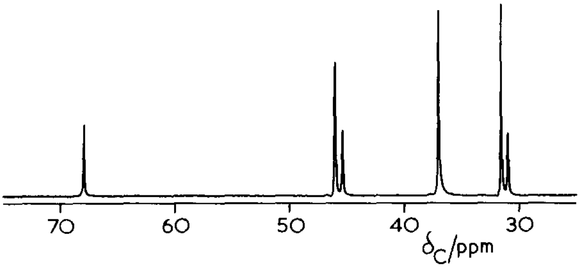

Fig. 1. Carbon-13 CP–MAS NMR spectrum of 1-adamantanol at 75.43 MHz and a nominal temperature of 353 K, showing signals from two phases. For spectrometer conditions and resonance assignment, see the text and Table 1.

TABLE 1

^{13}C Chemical shifts of 1-adamantanol

Carbon atom	Nominal temperature (K)				CDCl$_3$ [10]
	333	353	366	370	
C1	67.9	67.9	67.9	67.9	68.1
C2 (A)	45.3	45.4			45.2
C2 (B)		46.1	46.1	46.1	
C3 (A)	30.9	30.9			30.6
C3 (B)		31.5	31.5	31.5	
C4	36.8(br)	37.0	37.0	37.0	36.0

to at least 295 K), probably because of interference between molecular motion and either the decoupling rate or the MAS speed.

The ^{13}C chemical shifts for 2-adamantanol in CDCl$_3$ solution have also been published [10] with the ambiguity of the assignments of C5 and C7 being resolved later [11]. Again the solid-state shifts are in close agreement, and so assignment is possible by inspection. Only the resonances due to C1 and C2 show any evidence of the presence of more than one solid phase. For example, from the resonances observed for both C1 and C2, there appears to be a component which is in a minority and only appears (switching in frequency, see Table 2) at 373 and 393 K. If allowance is made for the inhomogeneity of the temperature across the sample, this situation might be

TABLE 2

^{13}C Chemical shifts of 2-adamantanol

Carbon atom	Nominal temperature (K)					CDCl$_3$ [11]
	318	328	353	373	393	
C1 (A)	34.7	34.7	34.9	35.0 [a]	35.0 [b]	34.6
C1 (B)	34.9	34.9	35.0	35.2 [b]	35.1 [b]	
C1 (C)					35.4 [a]	
C2 (A)	74.2	74.2	74.3	74.4 [a]	74.4 [b]	74.5
C2 (C)				74.6 [b]	74.6 [a]	
C4	31.4	31.4	31.5	31.6	31.7	31.0
C5	28.7	28.7	28.7	28.7	28.7	27.5
C6	38.5	38.5	38.5	38.5	38.5	37.6
C7	28.2	28.2	28.2	28.2	28.2	27.1
C8	37.1	37.1	37.2	37.3	37.3	36.5

[a] Major peak.

[b] Minor peak.

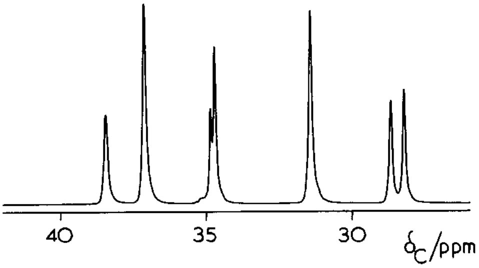

Fig. 2. Carbon-13 CP–MAS NMR spectrum of 2-adamantanol at 75.43 MHz and a nominal temperature of 318 K, showing the splitting of the signal from C1. The spectrum excludes the C2 resonance. For spectrometer conditions and resonance assignments, see the text and Table 2.

due to the presence of two solid-state forms given that the known transition is at 391 K [12]. In addition the resonance for C1 shows an additional minor-intensity peak at 393 K which may also be evidence for the highest temperature phase (denoted C in Table 2). A second solid-state transition has been observed using DTA at 352 K [12] and this might give rise to some very small differences observed between the spectrum at 353 K and spectra at lower temperatures. The spectra at 318, 328 and 353 K show a clear splitting of the C1 signal (Fig. 2), which presumably arises from lack of symmetry in the solid state (though the split peaks are surprisingly unequal in intensity). It is not possible to determine from NMR alone whether this is inter- or intra-molecular in origin.

In general, therefore, the ^{13}C CP–MAS NMR results are consistent with the earlier low resolution NMR and the DTA studies. In addition, given prior knowledge of solid state transition temperatures from DTA, the use of materials with transitions such as those described here allows the precise calibration of temperature at the sample for solid-state NMR studies, though the inevitable variations in pressure across the sample in a MAS spectrum must be borne in mind.

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