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Observation of solid-state phase changes in adamantanols using ^{13}C CP-MAS NMR

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Abstract

Molecular motion in the solid state in adamantan-1-ol and adamantan-2-ol has been investigated using high resolution ^{13}C NMR spectroscopy with the CP-MAS technique. Adamantan-1-ol is shown to undergo an ordered-disordered phase change at about 352 K, and adamantan-2-ol appears to have two phase changes characterised by an increasing gain of local molecular symmetry on the NMR timescale as the temperature is increased.

INTRODUCTION

Solid-state phase transitions in adamantane derivatives have been widely studied with, for example, a transition from an ordered to a disordered phase being observed in adamantan-1-ol at 353-369 K according to the technique used [1-4]. In addition, it has been shown previously that adamantan-2-ol has more than one phase change in the solid [5, 6]. It was demonstrated earlier that it is possible to detect solid-state phase transitions in organic materials using high resolution NMR techniques in solid state. A combination of magic-angle spinning (MAS), proton broadband decoupling and ^{13}C-^{1}H cross-polarisation (CP) has become a standard technique for obtaining high resolution ^{13}C NMR spectra from solid samples. Using adamantan-1-ol and adamantan-2-ol, the presence of such transitions was detected from small ^{13}C chemical shift changes with temperature [7]. The temperature variations across the NMR probe in that study had a disadvantage in that, at certain temperatures close to the transition point, two distinct sets of signals could be seen, corresponding to the two phases,

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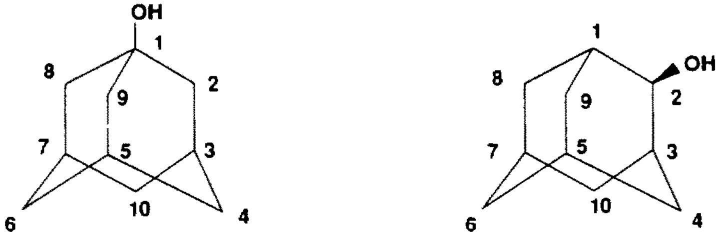
and the linewidth of the signals precluded a precise determination of the transition temperature. The study has now been repeated taking measurements at intervals of 2 K and allowing a substantial period of temperature stabilisation. The transition temperature can now be delineated more precisely and a significant linewidth change is also seen, which helps to define the transition point in adamantan-1-ol. For adamantan-2-ol, a more complicated phase behaviour can now be seen with the achieved higher spectral resolution.

EXPERIMENTAL

Adamantan-1-ol and adamantan-2-ol were purchased from Aldrich and used without further purification. The numbering system is shown in Scheme 1. NMR spectra were measured on a Bruker MSL-300 instrument operating at 300 MHz for ^{1}H and 75.4 MHz for ^{13}C. Typical acquistion parameters for the CP-MAS experiments using a 7 mm rotor were: spectral width 9000 Hz, recycle delay 5.0 s, 32 transients, time domain points 8192, no zero filling, no line-broadening factor, contact time 1 ms, rotation speed 2000 Hz. Some spectra were resolution enhanced by multiplying the NMR free induction decays (FIDs) by a weighting function known as Lorentzian–Gaussian transformation [8]. Typical parameters involved a Lorentzian sharpening of 6–7 Hz and a Gaussian broadening of 4–5 Hz. Spectra were measured at intervals of 10 K, allowing 10 minutes for equilibration for a coarse search for the transition. Close to the transition temperature, the temperature was raised in 2 K steps, allowing 45 minutes for equilibration prior to data acquistion. The magic angle was set by maximising the rotational sidebands of the^{79}Br resonance of KBr.



Scheme 1. The numbering system.

RESULTS

Adamantan-1-ol

Above the transition temperature, the CP-MAS ^{13}C NMR spectrum of adamantan-1-ol shows four sharp resonances, as expected. These have been previously assigned as C1: 67.9, C2, C8, C9: 45.3, C3, C5, C7: 30.9, and C4,

TABLE 1

^{13}C chemical shifts (ppm) as a function of temperature for adamantan-1-ol

Temperature/K	C1	C2	C4	C3
300	68.10	45.27	36.85	30.90
310	68.10	45.35	36.91	30.93
320	68.14	45.38	36.91	30.97
330	68.17	45.42	36.96	31.01
340	68.21	45.49	37.00	31.08
350	68.21	45.53	37.04	31.12
360	68.14	46.23	37.20	30.73
370	68.15	46.26	37.22	30.75

C6, C10: 36.8 ppm. The temperature dependence of the chemical shifts is given in Table 1. The discontinuity at the phase transition can clearly be seen in the plot of chemical shifts versus temperature shown in Fig. 1.

There is a distinct and uniform temperature dependence of all of the chemical shifts below the transition temperature and an abrupt change at the transition, which clearly lies somewhere between 350 and 360 K. In addition, the signal of C4 sharpens dramatically above the transition temperature, whereas the C1 resonance also sharpens with increasing

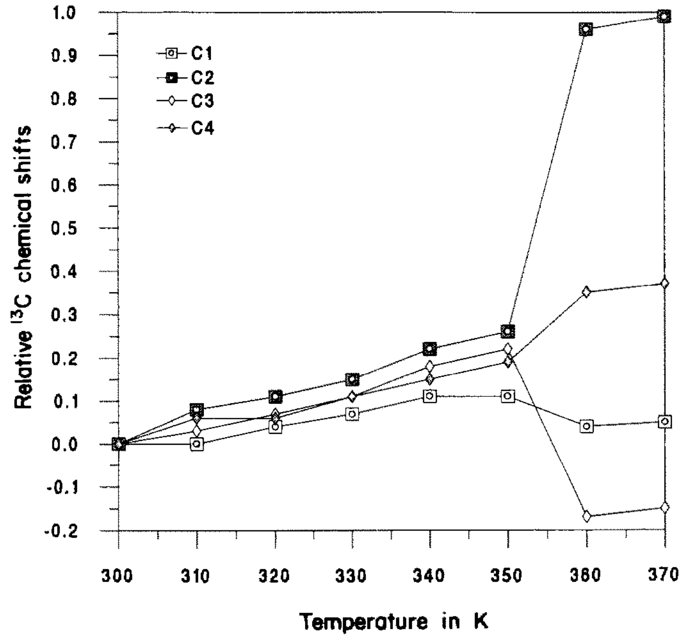


Fig. 1. ^{13}C chemical shifts of solid adamantan-1-ol relative to their values at 300 K as a function of temperature.

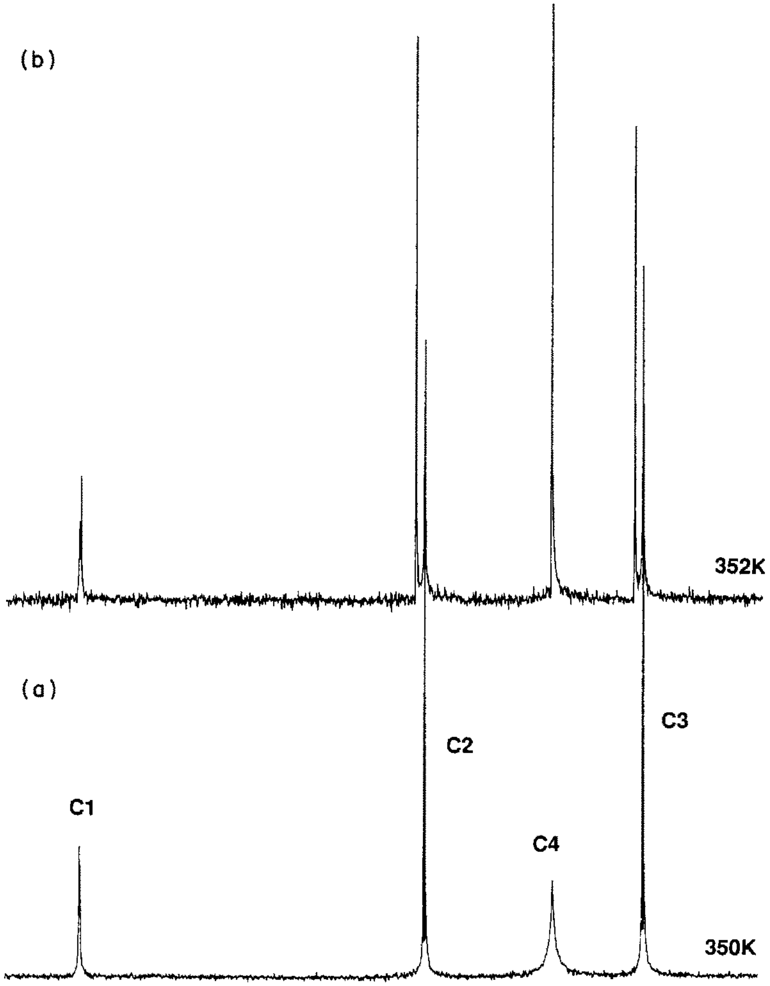


Fig. 2. ^{13}C NMR spectra of solid adamantan-1-ol at (a) 350 K and (b) 352 K. Chemical shifts are given in Table 1.

temperature but in a more gradual fashion. The transition has been pinpointed more precisely by observing the ^{13}C spectrum over the range 342–352 K. Figure 2 shows typical spectra, (a) taken at 350 K indicative of all of the spectra below the transition, with the C4 resonance broadened, and (b) measured at 352 K, which appears to be the transition point. Here there are two sets of signals, a minor component with shifts characteristic of the spectra below the transition with a broadened C4 resonance and a major component with a sharp C4 resonance and distinctly different shifts for the other carbons. The two sets of resonances presumably arise because of a small temperature gradient across the sample. The value observed here for the transition temperature agrees well with that determined by Amoureux et al. [1] and by Cuvelier [2].

Adamantan-2-ol

The temperature dependence of the ^{13}C CP-MAS spectrum of adamantan-2-ol is more complicated. At the highest temperature studied, 380 K (Fig. 3(a)), seven peaks are observed, and these have been assigned previously [1] with chemical shifts (ppm): C1, C3 (34.8), C2 (74.2), C4, C9 (31.4), C5 (28.7), C6 (38.5), C7 (28.2), C8, C10 (37.1). These seven peaks provide evidence for only one species in the solid state at 380 K, indicating a symmetrical environment for the pairs of carbons C1 and C3, C4 and C9 and C8 and C10, probably because of rapid rotation on the NMR timescale at the molecular lattice points.

At lower temperatures, in the range 375–330 K, the major change in the spectrum is observed for the resonance arising from C1 and C3, which splits, showing a non-symmetrical environment in the solid. This is shown clearly in Fig. 3(b). Resolution enhancement reveals similar if smaller splittings, with relative intensities of about 2:1, on the resonances from C2, C5 and C6. This phenomenon, shown in Fig. 4(a), cannot arise simply from a loss of molecular symmetry in the solid resulting in, for example, C1 and

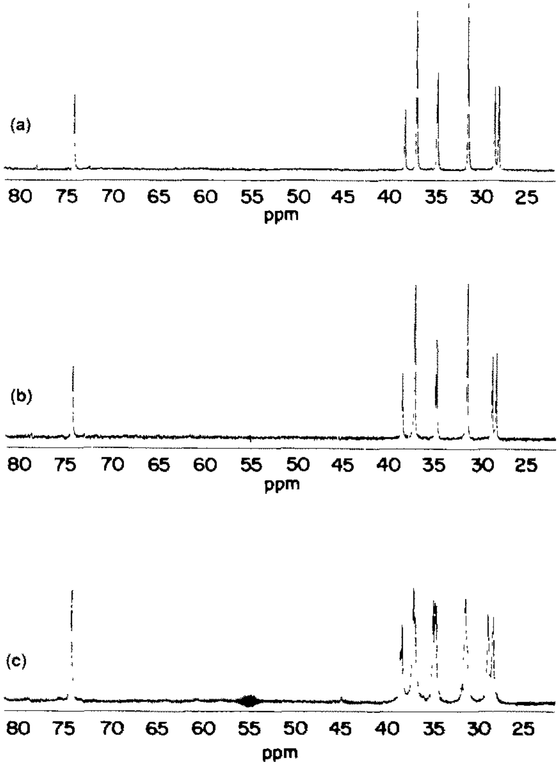


Fig. 3. ^{13}C NMR spectra of solid adamantan-2-ol at (a) 380 K, (b) 340 K, (c) 310 K after computer resolution enhancement.

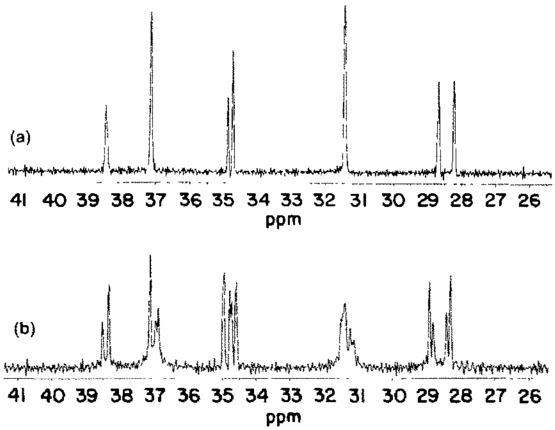


Fig. 4. ^{13}C NMR spectra of solid adamantan-2-ol at (a) 340 K, (b) 310 K after Lorentzian–Gaussian resolution enhancement. The resonance for C2 is not shown.

C3 no longer having the same chemical shifts, as the proportions would be 1:1. It is possible that, at 340 K, the OH group rotation is slow on the NMR timescale and two separate rotamers have been frozen out, each of which still has a plane of symmetry. Below 340 K, more extensive splitting of the resonances is observed (for example, Fig. 3(c), 310 K). This is not simply loss of symmetry for individual molecules, which would result only in separation of the resonances from C1 and C3, C4 and C9 and C8 and C10, because further extra splitting is observed. The effect is more clearly visible after resolution enhancement, Fig. 4(b), and may be caused by the presence of two or more nonequivalent unsymmetrical molecules in each unit, possibly different OH rotameric forms.

Thus, C1 and C3 now show four resonances consistent with two separate molecular forms in which the plane of symmetry has been lost. The signals for C8 and C10 show a similar pattern but not so well resolved. The resonances for C4 and C9 also have a complex form containing at least four components. As expected, the signals for C2, C5, C6 and C7 show splitting into two peaks.

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