

## Note

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### SOLID STATE $^{13}\text{C}$ NMR AND PHASE TRANSITIONS IN HYDROXYADAMANTANES

SALMAN R. SALMAN \*

*Chemistry Department, College of Science, University of Baghdad, Jadiriya, Baghdad (Iraq)*

JOHN C. LINDON, R. DUNCAN FARRANT and MICHAEL J. SEDDON

*Department of Physical Sciences, Wellcome Research Laboratories, Langley Court, Beckenham, Kent BR3 3BS (Gt. Britain)*

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#### ABSTRACT

The phase transitions within solid 1-hydroxy- and 2-hydroxyadamantane have been studied using solid state  $^{13}\text{C}$  NMR spectroscopy at different temperatures. The values obtained for the phase transitions for the compounds were comparable but much less precise than those reported using differential thermal analysis (DTA) techniques. Disordered solids such as adamantane derivatives appear to be amenable to such solid state NMR analysis. It is most likely, however, that in general the additional use of cross polarization/magic angle spinning will be required.

#### INTRODUCTION

In recent years, solid state  $^{13}\text{C}$  NMR has received increasing attention. There have been a host of papers describing the application of solid state  $^{13}\text{C}$  NMR both with and without cross-polarization and magic angle spinning (CP/MAS) to structural problems in chemistry; the background to the techniques has been described many times [1]. However, there is much less work devoted to distinction of solid–solid phase changes. A number of publications have dealt with phase changes in phospholipid and related systems [2–4] and work has been reported on phase changes in solid polymers [5], solid lead acetate [6] and solid cycloalkanes [7]. Whilst these latter studies used the CP/MAS NMR technique, a number of other molecules have been studied using differential thermal analysis (DTA) [8,9].

For example, the DTA of several substituted adamantanes were recently reported [10]. It was found that the majority of these compounds gave one

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\* Author to whom all correspondence should be addressed.

sublimation peak but that 1-hydroxyadamantane (1-HA) gave an extra peak and 2-hydroxyadamantane (2-HA) gave two extra peaks. These extra peaks were proved to be due to solid–solid phase transitions. The aim of this work is to find out whether solid state  $^{13}\text{C}$  NMR could be used to support our previous findings.

## EXPERIMENTAL

1-Hydroxy- and 2-hydroxyadamantane (Aldrich) were used without further purification. Both compounds were run on a Bruker AM-200 spectrometer operating at 50.3 MHz for the  $^{13}\text{C}$  nucleus. The spectra were run using a 10 mm sample without spinning or broadband proton decoupling using a spectral width of 32 KHz and an acquisition time of 0.393 s. Some high temperature spectra were obtained with broadband proton decoupling to demonstrate the limits of resolution in the solid state in such dynamic solids.

## RESULTS AND DISCUSSION

The solid state  $^{13}\text{C}$  NMR spectra of both 1-HA and 2-HA consist of a single broad line without fine structure. On warming the solid in the NMR probe, the line width narrows progressively until it is possible to apply broadband proton noise decoupling at which point the various chemically shifted resonances are resolved. It can then be estimated that the chemical shift dispersion adds a fixed amount to the observed linewidth. This has been subtracted from the figures given later. The remainder of the linewidth is then made up from partially averaged anisotropic contributions such as dipolar couplings and chemical shift anisotropy. In an isotropically reorient-

TABLE 1

$^{13}\text{C}$  NMR linewidth as a function of temperature for 1-Hydroxy- and 2-Hydroxyadamantane

1-Hydroxyadamantane		2-Hydroxyadamantane	
Temp. (K)	Linewidth (Hz)	Temp. (K)	Linewidth (Hz)
303	4830	303	8180
353	1870	323	7080
383	890	343	2850
413	790	363	2510
423	660	383	1930
		403	530
		423	530

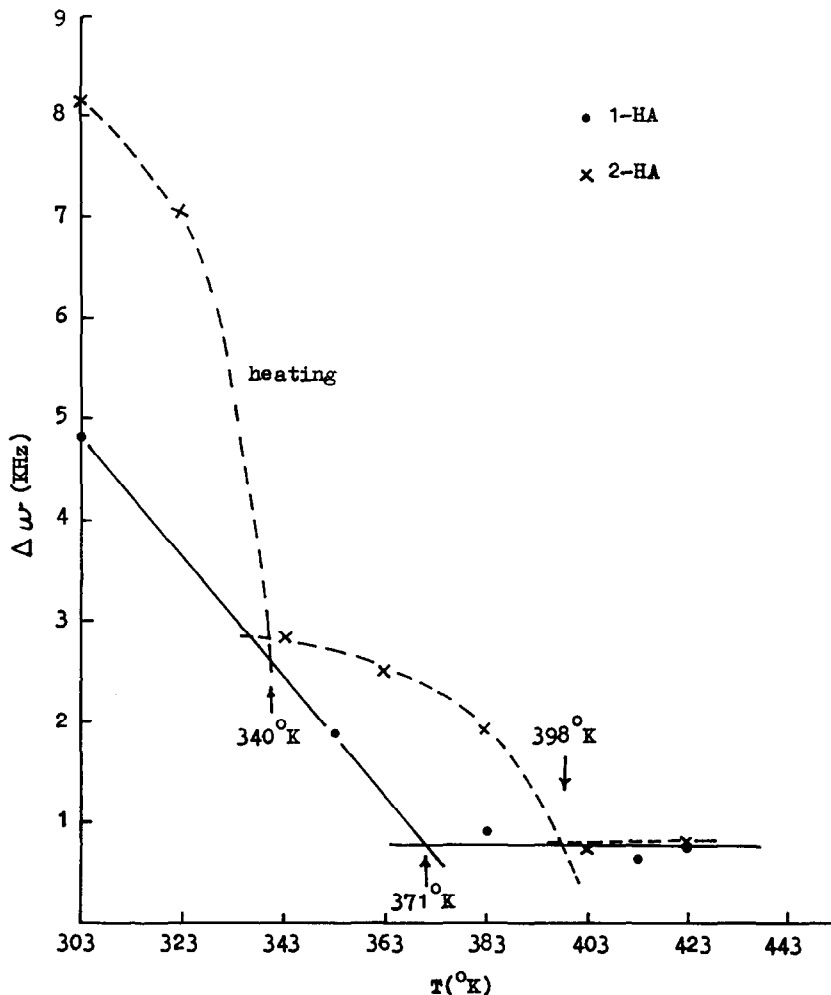


Fig. 1. Spectral linewidth (kHz) vs. temperature (K). ····, 1-Hydroxyadamantane; ×-×-×, 2-hydroxyadamantane.

ing sample, where the rate of reorientation is greater than these average values, they will disappear. Table 1 gives the linewidth of the spectra as a function of temperature. The values given in this table are also presented graphically in Fig. 1. From this figure it is possible to estimate the transition temperatures. The phase transition temperatures using solid state  $^{13}\text{C}$  NMR for 1-hydroxyadamantane is 371 K compared to 369.15 K obtained from DTA measurements [10]. For 2-hydroxyadamantane the solid  $^{13}\text{C}$  NMR measurement gave two transition temperatures (Fig. 1, Table 2). The first at a temperature slightly less than 343 K and the second at 398 K; while DTA gave the values 325.15 and 391.15 K respectively (Table 2). The extra peaks in 1-hydroxyadamantane and 2-hydroxyadamantane were assigned as an ordered-disordered solid-solid phase transition [10,11]. The DTA measure-

TABLE 2

Phase transition temperatures (K) for 1-hydroxy- and 2-hydroxyadamantane

Compound	DTA	NMR
1-Hydroxyadamantane	- 369.15 [10]	- 371
2-Hydroxyadamantane	325.15 [11] 391.15 [11]	< 343 398

ments indicated that these transitions are reversible. The solid state  $^{13}\text{C}$  NMR results supported these findings and also indicated that the transitions are reversible, because the NMR spectra retain their features after cooling.

## CONCLUSIONS

$^{13}\text{C}$  NMR of solid 1-hydroxy- and 2-hydroxyadamantane support the DTA findings reported previously that the extra peaks in the DTA scans of these two compounds are due to a phase transition and that this transition is reversible.

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