

## Experimental Section

<sup>13</sup>C{<sup>1</sup>H} ramped Cross Polarization Magic Angle Spinning (CP MAS) solid state experiments were performed at 14.1 T on a Bruker Avance Neo spectrometer with a commercial 3.2 mm MAS probehead at a frequency of 600.2 for <sup>1</sup>H and 150.9 MHz for <sup>13</sup>C, respectively. The <sup>1</sup>H resonance of 1 % TMS in CDCl<sub>3</sub> served as an external secondary reference using the  $\delta$  values for <sup>13</sup>C as reported by IUPAC.<sup>1,2</sup> The <sup>13</sup>C{<sup>1</sup>H} ramped CP MAS NMR was acquired at a low spinning frequency of 2.5 kHz. The contact time used was 1000 ms and the TPPM-15<sup>3</sup> sequence was used at a decoupling power of 82 kHz for <sup>1</sup>H decoupling. For deconvolution and fitting of spectra, the program deconv2Dxy<sup>4</sup> and SIMPSON package (version simpson-4.2.3)<sup>5,6</sup> were used. The isotropic chemical shift  $\delta_{iso}$ , the anisotropic chemical shift  $\delta_{aniso}$  and the asymmetry parameter  $\eta$  were extracted using the SIMPSON package in combination with home written fitting packages and follow the definitions as specified in the original simpson article<sup>6</sup>.

## Results and Discussion

To get a better understanding of whether the site disorder in the crystal structure is dynamic or static in nature, <sup>13</sup>C{<sup>1</sup>H} cross-polarization magic-angle-spinning NMR experiments were performed. In the crystal structure in total 9 carbon sites have been determined while for the aromatic carbon atoms split positions were required. In the <sup>13</sup>C NMR spectrum 8 peaks can be resolved and one more position in the aromatic regime is required to take account of the intensity ratios. Experiments at different spinning frequencies were conducted to determine the chemical shift tensors and achieve an assignment of the peaks to the crystallographic sites. The results of a non-linear least-square fit of the experiment NMR spectrum (Figure 1) are presented in Table 1. The peak assignment is based on well established isotropic chemical shift correlations<sup>7</sup>, line-broadening effects (vide infra) and peak area ratios. While a peak assignment based on the latter requires extra considerations for a cross-polarization experiment when comparing atoms with different number of H-atoms attached or different dynamics, it is straight forward for the carbon sites with different multiplicity of the CH<sub>2</sub> functions. All aromatic sites (C4/C4A to C9/C9A) have a multiplicity of 4, the CH<sub>2</sub> carbon atoms in the

adamantane cage C2 and C3 have a multiplicity of 4 and 2 respectively and the quaternary carbon C1 in the adamantane cage a multiplicity of 4. Peak A can unambiguously assigned to C4/C4A, while peaks B to F correspond to C5/C5a to C9/C9a. The peaks G, H and I of the carbon atoms in the adamantane cage can be assigned to C3, C2 and C1, respectively, because of peak areas and line-broadening effects through  $^1\text{H}$ - $^{13}\text{C}$  dipolar couplings in the  $\text{CH}_2$  functions (experiments not shown). Given that all peaks show a sharp peak line-shape and no additional splittings are observed, it can be concluded that the site disorder observed in the diffraction experiments is dynamic in nature.

Table 1: The experimental  $^{13}\text{C}$  chemical shift parameters for the  $\text{AdPh}_4$  structure. The isotropic chemical shift  $\delta_{\text{iso}}$ , the anisotropic chemical shift  $\delta_{\text{aniso}}$  and the asymmetry parameter  $\eta$  are shown in the table below; while the eigenvalues  $\bar{\delta}_{11}$ ,  $\bar{\delta}_{22}$ ,  $\bar{\delta}_{33}$  of the aromatic peaks carry errors of a few ppm, the errors of the atoms in the adamantane cage are bigger because fewer spinning side-bands were available in the experimental lineshape. Errors by a non-isotropic excitation profile of the cross-polarization experiment were neglected.

	Peak A	Peak B	Peak C	Peak D	Peak E	Peak F	Peak G	Peak H	Peak I
$\delta_{\text{iso}}$ / ppm	148.9	129.5	128.4	126.4	126.4	123.9	50.6	44.3	38.4
$\delta_{\text{aniso}}$ / ppm	-131	-117	-117	-106	-127	-115	13	-9	-9
$\eta$	0.29	0.79	0.74	0.73	0.74	0.70	0.73	0.54	0.85
$\bar{\delta}_{11}$ / ppm	233	234	230	218	237	221	64	52	47
$\bar{\delta}_{22}$ / ppm	195	142	143	141	143	141	49	47	39
$\bar{\delta}_{33}$ / ppm	18	12	12	20	-1	9	39	35	29
Peak area / a. u.	3.9	4.2	4.0	4.2	4.2	4.4	2.2	4.7	4.5

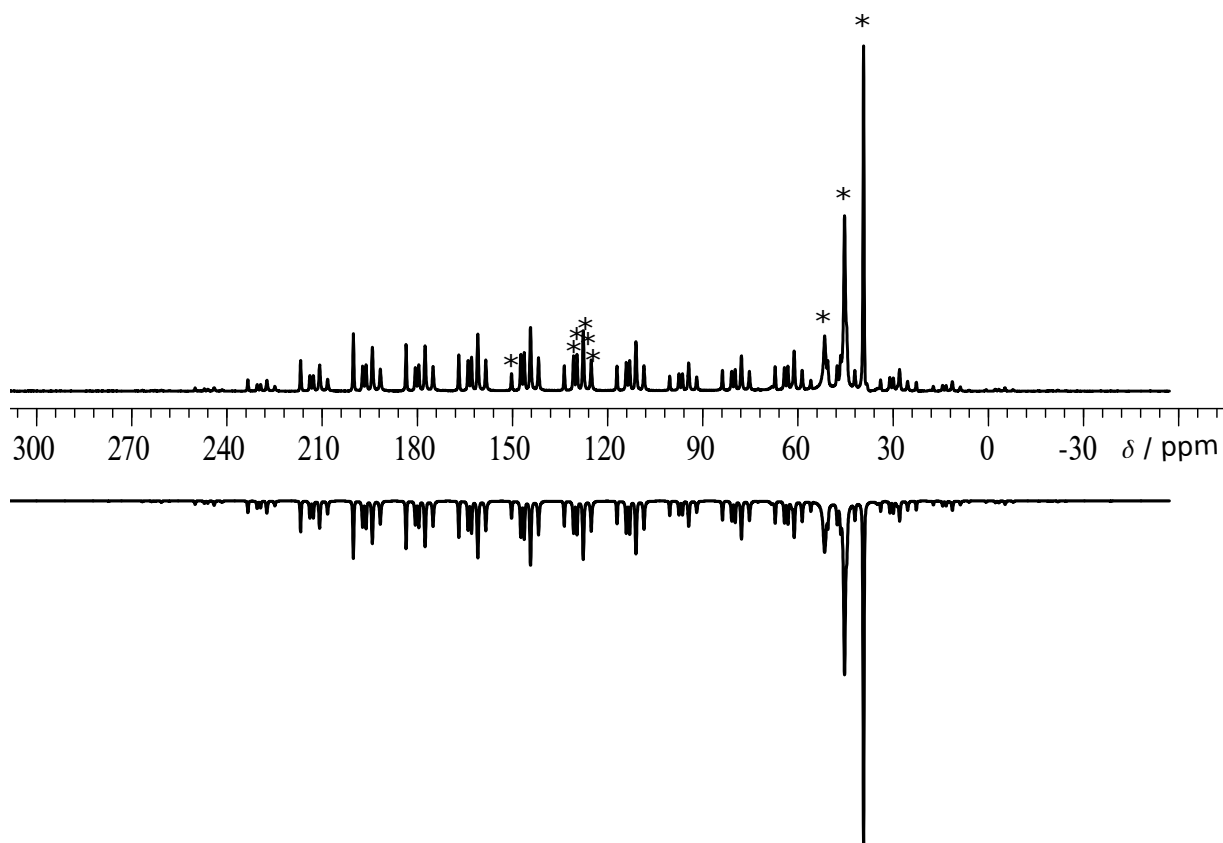


Figure 1: Experimental (top) and simulated (bottom)  $^{13}\text{C}\{^1\text{H}\}$  ramped CP MAS NMR spectrum obtained at a spinning frequency of 2.5 kHz; the fit achieved a mean square deviation of 0.14%.

## References

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