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# Solid State NMR Spectroscopy of Calix[4]arene-based Carceplexes

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**$^{13}$C CP/MAS spectroscopy of calix[4]arene-based carceplexes shows that in the solid state the cavity walls of the carcerand are rigid, whereas the pendant groups of the resorcin[4]arene as well as the ends of the propyl goups of the calix[4]arene moiety exhibit some flexibility. Temperature dependent $^2$H measurements of the DMSO-$d_6$ carceplex reveal that two different sites are present for the DMSO guest with an energy difference of 1.7 kcal mol$^{-1}$.**

*Keywords:* Caraplex, calix[4]arene, $^{13}$C CP/MAS spectroscopy, $^2$H NMR spectroscopy

## INTRODUCTION

Calix[4]arene-based carcerands (**1, 2**) comprise an interesting approach towards a molecular switch, since different orientations of incarcerated guests lead to different diastereoisomers due to the non-symmetric cavity of the host molecule [1]. Recently we described the synthesis of a variety of different carceplexes and their properties in solution. Moreover, it has been demonstrated that calix[4]arene-based carcerands can be organized on a molecular level using self-assembled monolayers on a gold surface [2]. Since it is anticipated that the behavior of incarcerated guests may differ between solution and the self-assembled monolayers we explored the properties of calix[4]arene-based carcerands using $^{13}$C CP/MAS and $^2$H solid state NMR spectroscopy [3, 4]. The $^{13}$C CP/MAS experiments were used to determine the rigidity of the cavity in the solid state, whereas temperature dependent $^2$H NMR measurements were used to study the dynamic behavior of DMSO-$d_6$ inside the calix[4]arene-based carcerand.

Previously, $^2$H solid state NMR spectroscopy measurements have been reported for the crystalline benzene-$d_6$ and acetonitrile-$d_3$ resorcin[4]arene-based carceplexes[5]. From the data, which were only obtained over a limited temperature range from 310 - 400 K, the authors concluded that benzene rotates rapidly around

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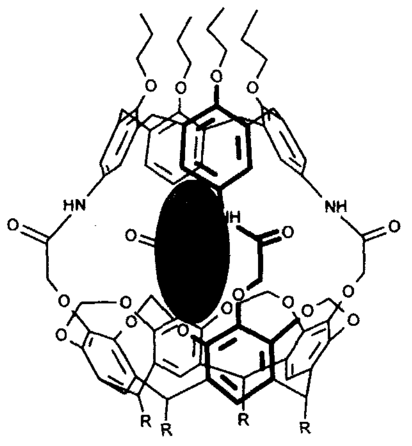
*Corresponding author.



**1** G = *N*,*N*,-dimethylacetamide (DMA)

**2** G = DMSO-$d_6$

R = $C_{11}H_{23}$

CHART I

its $C_6$-axis, with additional reorientation around the $C_4$-axis of the carcerand. For acetonitrile this reorientation was rapid ($\gg 10^5\ s^{-1}$).

## $^{13}$C CP/MAS SPECTROSCOPY

$^{13}$C CP/MAS spectra were recorded for the *N*, *N*-dimethylacetamide (DMA) and DMSO-$d_6$ carceplexes **1** and **2**, respectively. The observed spectra show large similarities with the solution spectra (see Fig. 1). Unfortunately, the guest signals are too weak to be observed or are obscured by the carcerand signals. The fact that the absorptions for the calix[4]arene-based carcerand are broad, indicates that the molecules do not all have the same environment or the same averaged $C_{4v}$ symmetry. Whereas in solution all carceplexes show $C_{4v}$ symmetry as indicated by single resonances for the aromatic hydrogen and carbon atoms, the spectra for the solid correspond to a material without lange range order.

In order to investigate molecular motion, a dipolar dephasing experiment was carried out. In this experiment carbon nuclei with directly attached hydrogen atoms that are rigidly held in the lattice disappear in the spectrum (see Fig. 2) [6]. This phenomenon is especially clear for some of the aromatic carbon atoms. Furthermore, the lines for the carbons corresponding to the $OCH_2O$ of the resorcin[4]arene moiety at ca. 100 ppm, the $ArCH_2Ar$ and the $OCH_2$ of the calix[4]arene moiety at ca. 35 and ca. 70 ppm, respectively, disappear in the dipolar diphased spectrum. The signal at ca. 70 ppm most likely also contains the absorption for the $OCH_2C(O)$ of the bridge between the calix[4]- and resorcin [4]arene, unfortunately due to the line broadening no decisive evidence is found. Nevertheless, the dipolar dephasing experiment shows that in the solid state the $OCH_2O$ bridges of the resorcin[4]arene, the $ArCH_2Ar$ bridges and the $OCH_2$ atoms of the calix[4]arene moiety, and probably the $OCH_2C(O)$ of the bridges, are rigidly held in the lattice which means that the

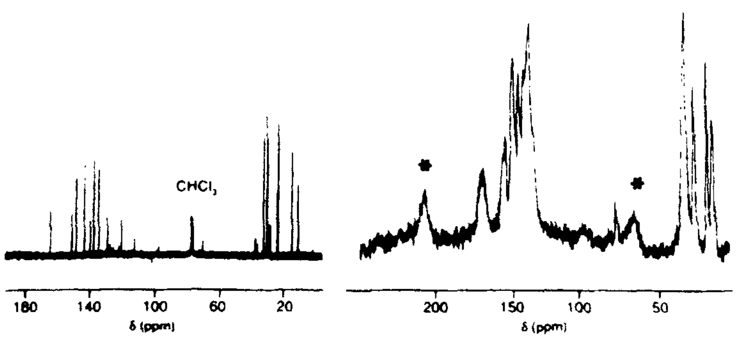


FIGURE 1 $^{13}$C Solution ($CDCl_3$, left) and CP/MAS (right) NMR spectrum of DMA carceplex **1**. Asterisks denote spinning side bands.

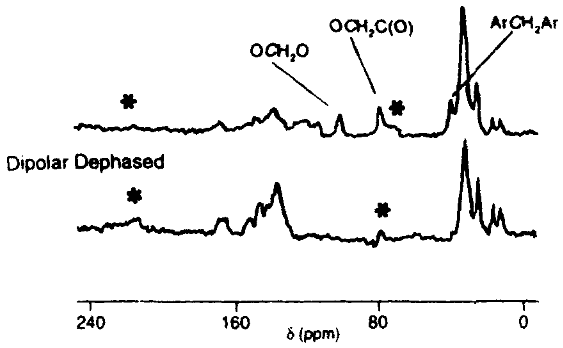


FIGURE 2 $^{13}C$ CP/MAS (top) and dipolar dephased NMR spectrum (bottom) of DMSO-$d_6$ carceplex 2. Asterisks denote spinning side bands.

cavity does not show much change in volume. The pendant groups of the resorcin[4]arene ($C_{11}H_{23}$) as well as the ends of the propyl groups of the calix[4]arene exhibit some motional freedom. The rigidity of the cavity of the calix[4]arene-based carcerand might lead to different rotational behavior of the incarcerated guests. Reduced flexibility may also be present in the self-assembled monolayers due to the presence of neighboring carcerands.

## $^2H$ NMR SPECTROSCOPY

In order to investigate the rotational behavior of DMSO-$d_6$ inside the calix[4]arene-based carcerand in the solid state, eight spectra were recorded over a temperature range from 193 to 343 K, some of which are represented in Figure 3. Since the methyl groups can be oriented either towards the calix[4]- or the resorcin[4]arene moiety the observed pattern is an averaged response. It should be noted, however, that the spectral response will be the same if the rotation of the methyl groups is faster than the correlation times, i.e., they will be dynamically equivalent.

A number of options are available for fitting the observed lineshapes depicted in Figure 3. The best fit was obtained by using two general powder patterns with a variable intensity ratio, $f_1$ and $f_2$ (= $1-f_1$). This indicates that the observed spectra arise from two different types, two sites, of incarcerated DMSO-$d_6$.

Fitting the data using two dynamically equivalent or non-equivalent methyl groups in a single DMSO guest, which corresponds to one non-axial powder pattern and two non-axial powder patterns in a 1:1 ratio, respectively, did not result in a good fit. The quadrupolar coupling constants and asymmetry parameters from the fits for both sites are presented as a function of the temperature in Figures 4 and 5, respectively.

Figures 4 and 5 show that for site 1, $\chi$ and $\eta$ are 50 kHz and ca. 0.05, respectively, whereas for site 2, $\chi$ and $\eta$ are 30 kHz and ca. 0.4, respectively. The quadrupolar coupling constant for site 1 decreases slightly with increasing temperature, whereas for site 2 it is temperature independent. The asymmetry parameters tend to increase slightly for both sites with increasing temperature. For a rigidly held DMSO molecule with only methyl rotation, $\chi$ would be 55 kHz and $\eta$ relatively small. This indicates that in site 1 only methyl rotation is present, whereas in site 2 an additional motion beside the methyl rotation is present. In the $^2H$ solution NMR spectrum only one resonance was observed which indicates that rotation of the incarcerated DMSO molecule is fast on the NMR timescale. This difference between the solution and solid state may be caused by a reduced flexibility of the cavity of the calix[4]arene-based carcerand as indicated by the CP/MAS experiment (*vide supra*).

Since the line shape parameters from the fitting procedure for sites 1 and 2 do not vary dramatically with temperature, the observed change in the $^2H$ powder patterns must result from a difference in population between the two sites. In Figure 6 the population ratios are plotted against the temperature. Despite some scattering, a reasonable straight line is observed ($r$ = 0.93). This indicates that, although interconversion between both sites is slow, they are

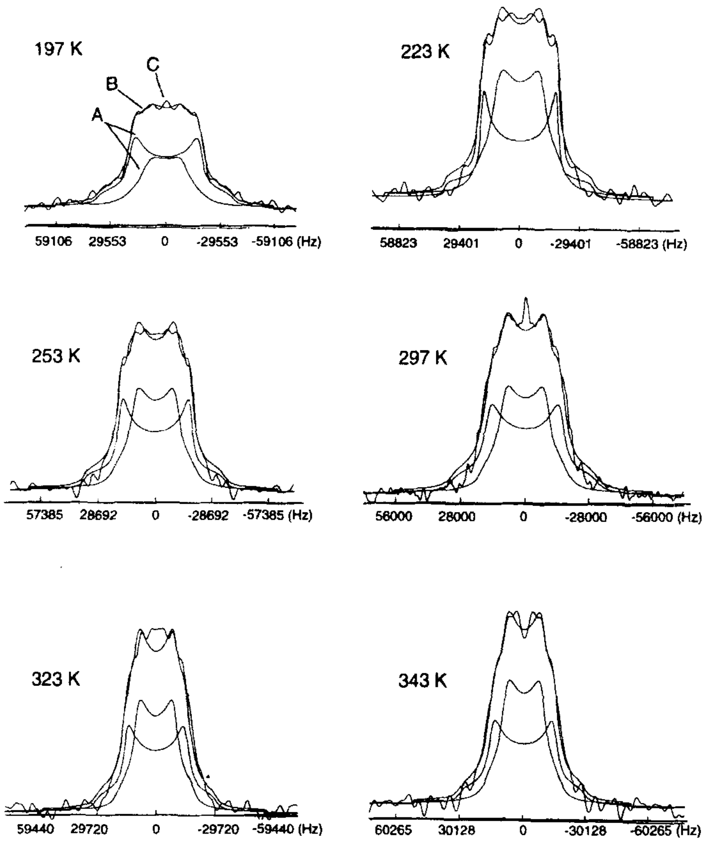


FIGURE 3 $^2$H NMR solid state powder patterns of DMSO-$d_6$ Carceplex 2. A = calculated patterns for sites 1 and 2. B = Pattern for site 1 plus site 2. C = experimental pattern.

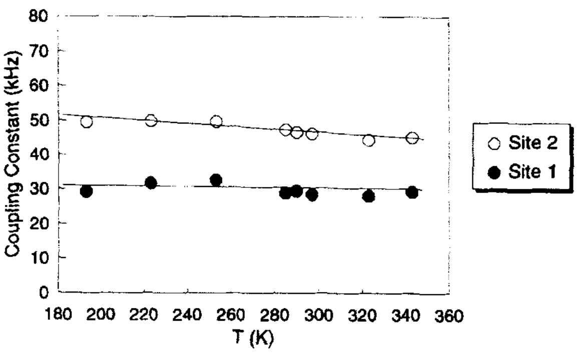


FIGURE 4 Calculated quadrupolar coupling constants, $\chi$, calculated from $^2$H solid state NMR lineshapes of DMSO-$d_6$ carceplex 2.

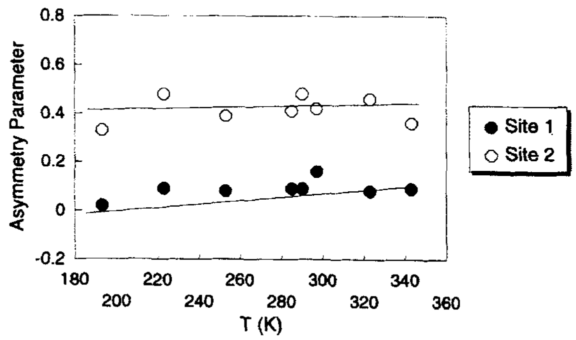


FIGURE 5 Asymmetry parameter, $\eta$, calculated from $^2$H solid state NMR lineshapes of DMSO-$d_6$ carceplex 2.

in equilibrium. Using a least squares fit and the Boltzman equation an energy difference of 1.7 kcal mol$^{-1}$ between the two sites is calculated.

The nature of the two sites in terms of orientation of the DMSO molecule inside the calix[4]arene-based carcerand can only be specu-

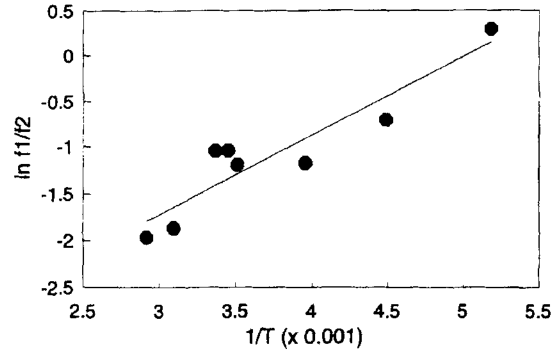


FIGURE 6 Ratio of occupied sites calculated from $^{2}$H NMR powder patterns of DMSO-$d_6$ carceplex **2** versus $1/T$.

lated on. With respect to a molecular modeling study [1d], the most likely explanation would be that site 1 corresponds to a DMSO molecule oriented along the long axis of the carcerand, whereas for site 2 the DMSO molecule is in the xy-plane of the cavity.

## CONCLUSIONS

It has been shown that solid state NMR can be useful for investigating the properties of calix[4]arene-based carceplexes. The results indicate that the behavior of incarcerated guests in the solid state may very well differ from that in solution. The $^{13}$C CP/MAS dipolar dephasing experiments revealed that the cavity of the calix[4]arene-based carcerand is probably not as flexible as in solution. Most likely this will increase the energy barriers for rotation between different stereoisomers with respect to values determined in solution. Furthermore, temperature dependent $^{2}$H NMR measurements showed that 2 different types of DMSO-$d_6$ are present in the corresponding carceplex in the solid state, whereas in solution only a time-averaged signal was observed. The results indicate that solid state NMR spectroscopy can be helpful for the development of calix[4]arene-based carceplexes as a molecular switch since currently self-assembled monolayers on gold are being investigated. The rotational properties of incarcerated guests in these monolayers will be in between the behavior in solution and in the solid state.

## EXPERIMENTAL

Carceplexes **1** and **2** were prepared according to literature procedures [1d]. $^{13}$C CP/MAS spectra were recorded on a Bruker AMX 300 and a Bruker MSL200 equipped with a Bruker 4 mm MAS probe and a Chemagnetics 7 mm pencil probe, respectively. Single cross polarization contacts were used with contact times between one and five ms. Dipolar dephased spectra were obtained by turning the decoupler off for 40 ms before data acquisition. 500 W Data sets were collected at sweep width settings of 20 and 30 kHz which were zero-filled to 4 K before Fourier transformation. Up to 100000 scans were recorded in order to obtain adequate signal to noise ratios.

The $^{2}$H NMR lineshapes were obtained on a Bruker MSL300 spectrometer equipped with a solids probe (5 mm solenoid coil). Quadrupole echoes were generated with a standard $90_x$-$\tau$-$90_y$ pulse sequence with a $\tau$ value of 35 ms. The 90° pulse length was between 2.5 and 3 ms, the delay time in the experiments was between 0.5 and 2 seconds. 256W Echoes were collected at a sweep width of 500 kHz, and zero-filled to 4K before Fourier transformation. Between 10000 and 50000 scans were collected to obtain sufficient signal to noise ratios. Temperature variation was achieved with cold nitrogen gas and a Bruker temperature controller. Lineshapes were fitted using the Bruker Winfit package.

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