^{13}C and 2D WISE NMR Studies of the Host Mobility in Two Aromatic Complexes of *p*-Tert-Butyl-Calixarene

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Abstract

Solid-state NMR techniques are used to study the effect of the inclusion of toluene and benzene on the mobility of *p*-tert-butylcalixarene. We attribute the great increase in host mobility upon complexation to the lack of strong directional intermolecular interactions. The differences in the behaviour of the host in the two complexes are explained in terms of the steric effects of the guest methyl group.

Introduction

The complexation properties of non-derivatised calixarenes in the solid state, in particular, *p*-tert-butylcalixarene, C4 (Figure 1), have been extensively studied [1–9]. C4 easily forms complexes in the solid state with a variety of organic molecules. However, the nature and strength of the host–guest interaction have yet to be clarified. The presence of CH_3-π interactions between the methyl group of the host molecule and the aromatic group of the guest has been thought to explain the high affinity of *p*-tert-butylcalixarene for aromatic molecules [10]. Brouwer *et al.* suggested that weak dispersion interactions rather than specific directional interactions are involved in the complexation [8]. CH_3-π interactions have also been claimed to support the interpretation of NMR relaxometry measurements [11] and variable temperature crystallographic results [12].

We describe a detailed ^{13}C solid-state NMR study of C4 complexes with toluene and benzene, in the hope that a comparison of their spectroscopic properties will throw light on the presence or otherwise of specific intermolecular interactions. Both complexes have been previously described [8, 13]. In particular, the C4-toluene complex has been thoroughly studied, as it is easily prepared and is useful as a model for the study of host–guest interaction. Also, it was the first calixarene complex to be fully characterised: the crystal structure was first published in 1979 [14] and gave definitive proof of the conical structure of the calixarenes [10]. Other crystallographic studies [8, 12] help to understand the nature of the disorder of both host and guest molecules.

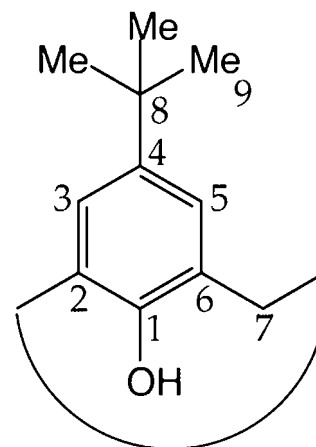Solid-state NMR is a powerful characterisation technique for these complexes, especially considering their high

Figure 1. Structure of *p*-tert-butylcalixarene.

degree of dynamic disorder. The first paper dealing with solid-state NMR studies on calixarenes discussed the ^{13}C CP/MAS spectrum of C4-toluene [5]. The authors attributed the upfield shift of the peak of the toluene methyl group to the complexation and to the interaction of CH_3 with the aromatic rings of the host.

In this work, we study the effect of complexation on the mobility of the host molecule in these C4-guest systems. Selectively deuterated guests were used to study the host molecule. The dynamics of pure C4 and its complexes were studied by solid-state NMR, using variable contact time (VCT) ^{1}H–^{13}C CP experiments [15], measurements of the spin-lattice relaxation times in the rotating frame ($T_{1\rho}$) [16] and two-dimensional ^{1}H <u>WI</u>de-line <u>SE</u>paration spectroscopy (2D WISE) [17].

This study provides a deeper insight into the complexation properties of this important class of compounds, helping to identify specific host–guest interactions. The complementary studies on the dynamics of the guests molecules [8,

13] showed that the guest rotates rapidly about the calix-arene symmetry axis. This motion is characteristic of C4 complexes [2, 4, 18, 19] and can be combined with other motions, such as in-plane rotation of benzene.

Theory

^{1}H–^{13}C CP/MAS is a solid-state NMR experiment designed to achieve a higher sensitivity for the rare nucleus through the transfer of polarization, driven by the heteronuclear dipolar interaction, from an abundant (^{1}H) to a dilute spin (^{13}C) [15]. A detailed examination of the cross-polarization dynamics yields information on the relative distances and mobility of the ^{1}H and ^{13}C nuclei. VCT experiments allow us to study the dynamics of the polarization transfer. In general, the intensity initially increases with contact time (t_m) but a decay is observed for longer t_m due to the relaxation of ^{1}H and ^{13}C in the rotating frame ($T_{1\rho}$). For an abundant-to-rare nuclei transfer the intensity of the polarized peak can be described by

$$I(t) = I_0(1 + T_{CP}/T_{1\rho C} - T_{CP}/T_{1\rho H})^{-1}\{\exp(-t_m/T_{1\rho H}) - \exp[-t_m(1/T_{CP} + 1/T_{1\rho C})]\}, \qquad (1)$$

where I_0 is the maximum intensity, T_{CP} is the cross polarization time constant and $T_{1\rho H}$ and $T_{1\rho C}$ are the relaxation times for ^{1}H and ^{13}C in the rotating frame. The cross-polarization rate ($1/T_{CP}$) depends on the square of the dipolar interaction while the relaxation time in the rotating frame provides important information on the mobility of the molecular fragments.

Variations in the relaxation rates of ^{1}H and ^{13}C magnetization can be associated with changes of mobility, where the term refers to all frequencies and amplitudes of the motions of molecular fragments in the solid. If the frequencies of such motions are of the same order of magnitude as the frequency of the rotating field **B**$_1$ during the spin-locking time, the relaxation rate reaches a minimum, and is larger for both higher and lower frequencies [20]. Since most of the solids have a relatively low motional frequency, an increase of the relaxation rates is often associated with an increased rate in the frequencies of the molecular motion.

As the ^{1}H linewidth is mainly determined by the homonuclear dipolar coupling and it is a function of the molecular dynamics, it decreases with increasing mobility. However, the inherent lack of resolution of single pulse ^{1}H solid-state NMR spectra does not allow us to distinguish different chemical sites. 2D WISE [17] combines the resolution of the CP/MAS along F2 with the ^{1}H linewidth analysis along F1, allowing one to compare the mobility of different fragments in the same molecule. Relaxation rates and ^{1}H linewidths can combine to give a qualitative picture of the effect of the inclusion of guests in the calixarene framework.

Experimental

Sample preparation

All chemicals were purchased from Aldrich and used without further purification. The complexes were prepared by adding 5.0 ml of deuterated toluene or benzene to 406 mg of C4. The suspensions were dried at ambient temperature.

X-ray diffraction

PXRD data were collected using a Stoe STADI-P high-resolution diffractometer, with Ge(111)-monochromated Cu Kα radiation (1.5406 Å) and a position-sensitive detector covering 6° ca. in 2θ. Data were collected in transmission geometry over the range $3 \leq 2\theta \leq 60°$ using an $\omega - 2\theta$ scan technique with a step size of 0.5° and 300 s counting time per step (total data collection time ca. 10 h).

Solid-state NMR

^{1}H–^{13}C CP/MAS spectra were acquired with a Chemagnetics CMX-400 spectrometer operating at 399.89 MHz For ^{1}H and 100.56 MHz for ^{13}C with a MAS probehead using zirconia rotors 4 mm in diameter. The spinning rate was 6.0 kHz, ^{1}H $\pi/2$ pulse length was 4.0 μs and the pulse delay 4.0 s. The Hartmann–Hahn condition was set with hexamethylbenzene. Spin-lattice relaxation times in the rotating frame were measured by inserting a delay during which a spin-locking field was applied to the proton channel either between the $\pi/2$ pulse and the cross polarization time ($T_{1\rho H}$) or immediately after the contact time ($T_{1\rho C}$) [16]. 12 delays in the 0.01–40.0 ms range were considered for the measurement of $T_{1\rho H}$, while 10 delays in the 0.01–19.0 ms range were taken for the measurement of $T_{1\rho C}$. In both cases the contact time was 5.0 ms. ^{13}C chemical shifts are quoted in ppm with respect to TMS.

2D WISE NMR spectra were acquired with ^{1}H $\pi/2$ of 3.80 μs at 4.0 kHz MAS rate. The pulse sequence was the standard CP-t_1-TOSS(t_2) [17], with 0.1 m s contact time. For C4, 800 scans (1024 points) were measured for 80 increments. The incremented delay was 12.0 μs. For C4-benzene 648 scans (2048 points) were measured for 48 increments. The incremented delay was 3.48 μs. For C4-toluene 572 scans (2048 points) were measured for 128 increments. The incremented delay was 15.7 μs. The pulse delay was 3.0 s in all 2D-WISE experiments.

^{1}H spectra were measured at 399.89 MHz, with 3.80 μs $\pi/2$ pulse and MAS at 11.0 kHz. ^{1}H chemical shifts are quoted in ppm with respect to TMS.

Results

Structure

The structure of C4 has been calculated from the powder X-ray diffraction pattern. The structure is in agreement with the single crystal analysis [21] and can be indexed considering a $P2_1/c$ space group with $a = 9.5878(5)$ Å, $b =$
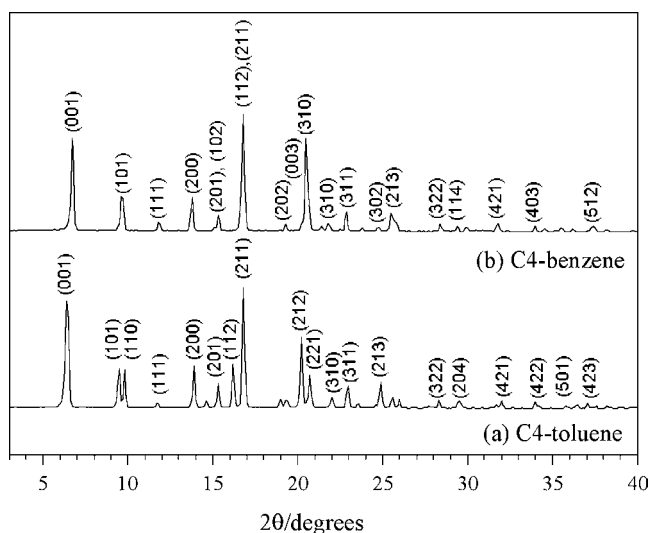
Figure 2. Powder X-ray patterns of (a) C4-toluene and (b) C4-benzene. Both have been indexed in the $P4/n$ space group.
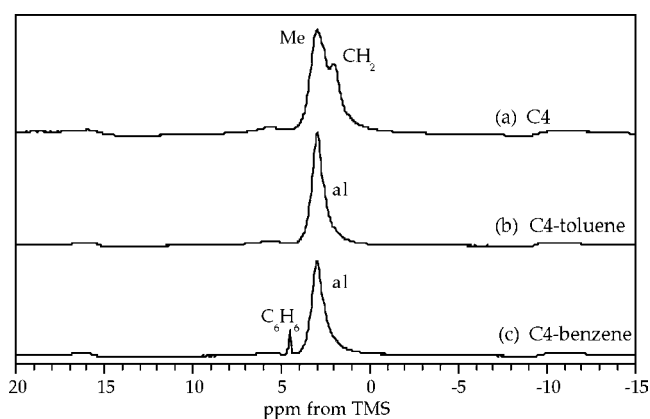

Figure 3. ^{1}H MAS NMR spectra of (a) *p*-tertbutylcalixarene; (b) C4-benzene; (c) C4-toluene acquired with MAS at 11 kHz 3.8 μs $\pi/2$ pulse, 4 s pulse delay and 16 scans. "ar" indicates the aromatic and "al" the aliphatic protons, "Me" the methyl group, "CH$_2$" methylene and "C$_6$H$_6$" benzene protons.

30.5003(17) Å, $c = 13.5412(8)$ Å and $\beta = 109.85(0)°$. The powder XRD pattern of C4-benzene (Figure 2b) has been indexed in the $P4/n$ space group with $a = 12.8872(21)$ Å and $c = 13.166(3)$ Å, in agreement with the structure of the 1:1 *p*-tert-butylcalixarene-benzene complex [8]. The PXRD pattern of C4-toluene (Figure 2a) has also been indexed considering a $P4/n$ space group with $a = 12.7833(18)$ Å and $c = 13.780(3)$ Å, consistent with the formation of the 1:1 *p*-tert-butylcalixarene-toluene complex [14].

The ^{1}H MAS NMR spectrum of C4 shows three components, attributable to the aromatic, methyl and methylene protons (Figure 3a). The larger linewidth of the peaks from aromatic protons compared to the aliphatic protons indicates a stronger dipolar interaction. This can be attributed to their relative immobility. The OH protons are not observable, most probably due to the strong intramolecular hydrogen bonding, which broadens the NMR peaks beyond detection.

The ^{1}H MAS NMR spectra of both C4-benzene and C4-toluene show only two broad components, attributable to the aromatic and aliphatic protons of the host (Figure 3b
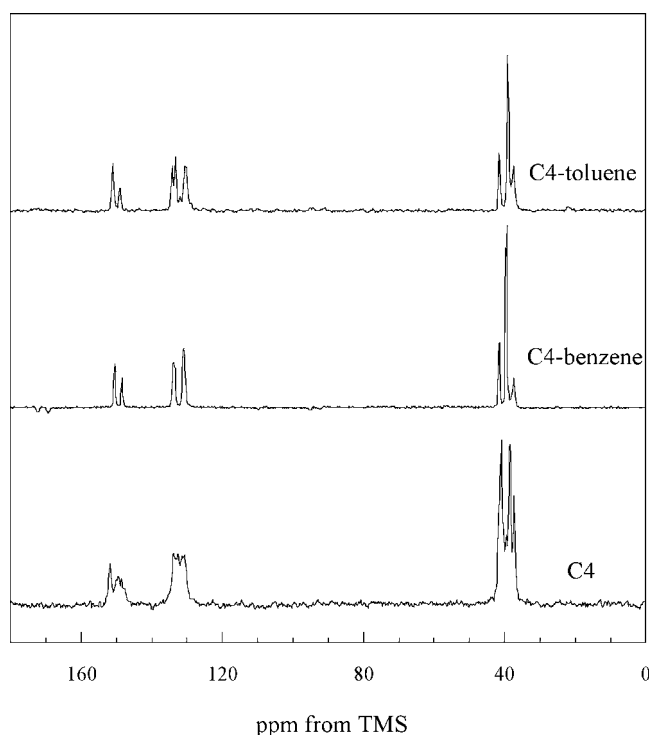

Figure 4. ^{13}C CP TOSS spectra of (a) *p*-tertbutylcalixarene; (b) C4-benzene; (c) C4-toluene acquired with 3.8 μs $\pi/2$ pulse, 5 s pulse delay, 4 ms contact time MAS at 4 kHz. 80, 652 and 128 scans were acquired for (a), (b) and (c) respectively.

and 3c). The lines from the methyl and methylene protons are superimposed. A third peak at 4.5 ppm in the spectrum of C4-benzene is attributed to the benzene protons of some non-deuterated sites. The very small linewidth and the long T_2 relaxation time (results not shown) of this peak indicates that the benzene is indeed very mobile. The chemical shift is moved significantly upfield from the value in solution (7.3 ppm), which is interpreted as an effect of the complexation [5]. We note that the difference between the chemical shifts of the benzene protons induced by complexation is the largest among those reported so far [22].

The chemical shift of C-7 in the calixarenes is known to be highly sensitive to the conformation, with changes of almost 7–8 ppm for the *syn* or *anti* orientations of the bridging aromatic rings [23]. The general similarity of the ^{13}C chemical shifts of the host in the pure C4 and in its complexes (Figure 4) shows that the conformation and the chemical environment of the calixarene hardly change upon complexation.

Dynamics

^{13}C TOSS (TOtal Suppression of Sidebands) NMR spectra provide some preliminary information on the relative mobility of the empty calixarene and the complexes. The spectra of the complexes are better resolved than that of C4, suggesting that the calixarene moieties are more ordered in the complexes than in the pure host. An increased ordering in the solid state can be achieved by dynamic averaging. Unlike for C4-benzene, the ^{13}C TOSS NMR spectrum of

Table 1. Full-widths-at-half-maximum of the lines of protons dipolarly coupled to the C4 carbon atoms. The numbering of the atoms is the same as in Figure 1. The FWHM's are calculated by the deconvolution of the extracted slices of the bidimensional experiment. When more that one peak is considered, the relative contribution is indicated in parenthesis

Site	FWHM (kHz)		
	C4	C4-benzene	C4-toluene
C-1	3.8 (57%)	65.0	100
	52.5 (43%)		
C-2,6	120	57.5	83.0
C-3,5	2.5 (2%)	62.5	73.0
	148 (98%)		
C-4	120	31.2	74.0
C-7	15.0 (13%)	12.0 (16%)	75.0
	100 (87%)	62.5 (84%)	
C-8	6.2 (12%)	35.0	92.0
C-9	100 (88%)	29.0	69.0

S 1. $^1H°-°^{13}C$ CP dynamics curves for pure C-4.

C4-toluene acquired under the same experimental conditions (contact time, MAS speed and r.f. power) shows peaks in the aromatic region attributable to the deuterated guest. This indicates that the molecular motion of benzene in the calixarene complex is faster than that of toluene. As a result, the averaging of the heteronuclear dipolar interaction responsible for the cross-polarization is more efficient and the corresponding signal is reduced.

The 2D WISE spectra correlate carbon sites with several motionally averaged protons (Table 1). At least three contributions can be distinguished from the ^1H slices of the 2D WISE spectrum of C4: a very broad component (FWHM > 100 kHz) attributable to rigid aromatic protons, a very narrow component (FWHM < 10 kHz) attributable to mobile methyl groups (undergoing fast rotation about both the methyl and the tert-butyl symmetry axes), and an intermediate component attributable to the CH_2-7 group. Although the contact time during 2D WISE experiments was short in order to minimize the effect of spin diffusion, non-protonated carbon atoms (C-1, C-4, C-8) correlate with ^1H lines. These correlations must arise from the presence of protons very close to the quaternary carbons. Surprisingly, the very narrow peak is dipolarly coupled with most of the ^{13}C peaks, with the exception of C-2,6 and C-4, which are very close to the aromatic protons H-3 and H-5. In particular, C-1 shows a significant contribution from the sharp peak, which is unexpected because the methyl groups are intramolecularly distant from C-1. Therefore, this must arise from intermolecular effect, in agreement with the crystal structure of the empty host, which shows partial self-inclusion in the solid state [21]. Different contributions to C-7, C-8 and C-9 in the 2D WISE spectra may be caused by the presence of two distinct tert-butyl groups in the structure. From the crystal structure it appears that some of them are intermolecularly included in the calixarene cavity while the others are located between calixarene cones [21].
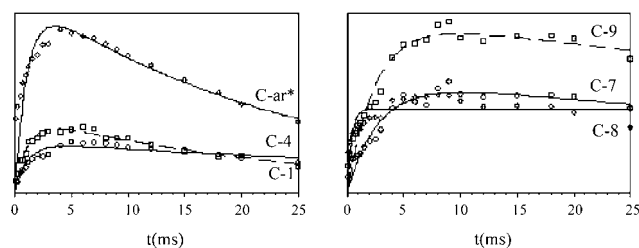
The 2D WISE spectrum of C4-benzene (Table 1) shows that, with the exception of C-4, the aromatic carbons are dipolarly coupled to the aromatic protons with FWHM = 62.5 kHz, which is smaller than that for C4 (Figure 5). On the other hand, C-4, C-8 and C-9 correlate with protons with FWHM = 30.0 kHz, attributable to the methyl groups. C-7 is coupled to the aromatic protons and to a narrower peak of the directly bonded protons. The relative contributions (16% and 84%) of these two components are similar to those for the C-7 in the empty calixarene (13% and 87%). Based on the linewidth of the peaks as measured from the slices of the WISE spectrum, the frequencies of the molecular motions decrease in the sequence: benzene > aliphatic > aromatic.

The 2D WISE spectrum (Table 1) also indicates that the protons in C4-toluene are more mobile than in C4, but less mobile than in C4-benzene. In C4-toluene all the carbon atoms correlate with protons with very similar linewidths. This may arise from an extremely rigid system, contradicting the observed sharpening of the ^{13}C NMR peak. The rates of motion of the different proton sites in this complex can also be very similar, implying that the presence of the methyl group in the guest molecule increases the mobility of the aromatic protons while reducing the mobility of the aliphatic protons, when compared to C4-benzene. The toluene appears to occupy a higher position within the cavity, due to the steric repulsion between the calixarene-cavity and the methyl group. As a result, the aromatic protons are less restrained, while the opposite applies to the aliphatic protons.

The spin-lattice relaxation times in the rotating frame and the cross-polarization time constants for the host carbon atoms of the empty calixarene and its complexes are given in Table 2 (typical $^1H-^{13}C$ CP dynamics curves are shown in Figure S1). The values of $T_{1\rho}$ are much longer for all the sites in the complexes, indicating a dramatic increase in the mobility of the host upon inclusion of the guest molecules.

^1H $T_{1\rho}$ relaxation times in the pure C4 are significantly shorter than in the complexes. Moreover, only a very small variation is observed for different C sites, indicating an efficient 1H spin-diffusion averaging out the differences in local mobility. This is most probably due to the closely packed self-included structure of C4 [21]. Unlike $T_{1\rho}H$, the measurement of $T_{1\rho}C$ spin diffusion is not a serious problem in view of the low natural abundance of ^{13}C, which ensures physical separation and thus a low spin diffusion rate [24]. The very long $T_{1\rho}C$ of C-8, 9 and C-4 are caused by the fast rotation of CH_3 and $C(CH_3)_3$ groups. C-7 methylene
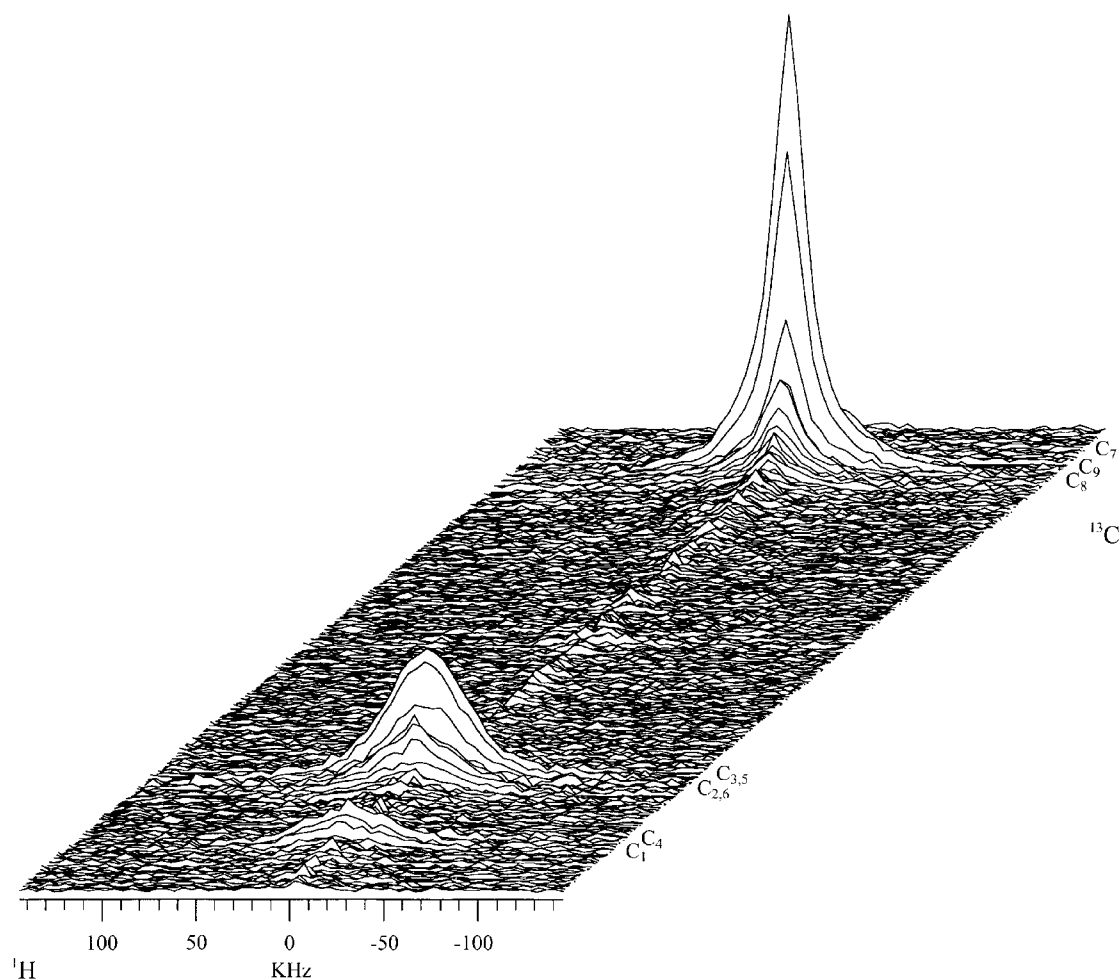
Figure 5. 2D-WISE spectrum of C4-benzene.

Table 2. Chemical shift, $T_{1\rho}H$, $T_{1\rho}C$ and T_{CP} of the host carbon atoms in host-free calixarene and in the benzene and toluene complexes

		C1	C-2,6	C-3,5	C-4	C-7	C-8	C-9
δ (ppm)	Empty	148.0	129.1	126.7	144.7	26.0		33.5
	Benzene	146.7	129.8	126.8	144.6	26.5	35.2	33.3
	Toluene	147.2	130.0	129.0	145.1	24.4	35.1	32.5
$T_{1\rho}H$ (R^2), ms	Empty	23 (0.99)	24 (0.99)	22 (0.99)	25 (0.99)	22 (0.99)		22 (0.99)
	Benzene	224 (0.98)	227 (0.98)	227 (0.98)	325 (0.78)	*	*	*
	Toluene	258 (0.97)	261 (0.99)	259 (0.95)	240 (0.94)	259 (0.80)	377 (0.78)	322 (0.78)
$T_{1\rho}C$ (R^2), ms	Empty	28 (0.99)	128 (0.96)	160 (0.90)	240 (0.80)	260 (0.89)		223 (0.97)
	Benzene	220 (0.98)	340 (0.96)	363 (0.96)	*	*	*	
	Toluene	464 (0.93)	433 (0.97)	*	4478 (0.75)	*	*	
T_{CP} (R^2), ms	Empty	0.65 (0.99)	0.56 (0.97)	0.38 (0.93)	1.75 (0.98)	3.40 (0.91)		2.80 (0.91)
	Benzene	0.78 (0.99)	0.78 (0.99)	0.78 (0.99)	1.73 (0.98)	1.20 (0.96)	3.12 (0.99)	3.79 (0.97)
	Toluene	0.82 (0.99)	0.79 (0.99)	0.79 (0.99)	1.58 (0.99)	1.01 (0.94)	3.35 (0.96)	3.13 (0.99)

* No decay is observed during the experiment.

carbons also appear to be very mobile. On the other hand the C-1, C-2,6 and C-3,5 show much faster $T_{1\rho C}$ relaxation. The very short $T_{1\rho C}$ for C-1 might be due to the formation of the rigid H-bonded network at the lower rim.

These observations are confirmed by analysis of the T_{CP} constants. A longer T_{CP} suggests a more efficient averaging of the heteronuclear dipolar interaction. Therefore very long T_{CP} times for C-4, C-7, C-8 and C-9 are due to their high mobility. While very long T_{CP} are typical for the CH_3 or $C(CH_3)_3$ carbon atoms, the CP for methylene carbons is usually thought to occur within the C—H bonds [25]. Very long T_{CP} for C-7 carbons, along with the long $T_{1\rho C}$, indicates very high mobility for this group, most probably related to the rotations around the axis connecting the benzene rings. On the other hand, much shorter T_{CP} for the C-3,5 indicates that the CP proceeds within the C—H bonds and is not affected by the fast molecular motion of either bonded or intercalated tert-butyl groups. The longer T_{CP} for C-1 and C-2,6 result from the larger C—H distances.

Inclusion of guests dramatically changes the source of the polarisation. Firstly, an at least ten-fold increase of $T_{1\rho H}$ is observed. For C-1, C-2,6 and C-3,5 carbons, $T_{1\rho H}$ increases in the order C4 < C4-benzene < C4-toluene. On the other hand for the C-4, C-7, C-8 and C-9 carbon atoms, where CP dynamics is mainly influenced by the aliphatic protons, the $T_{1\rho H}$ increase as C4 < C4-toluene < C4-benzene (Figure 6). A similar effect is found for the $T_{1\rho C}$ relaxation times. Secondly, compared with the pure C4, the $T_{1\rho H}$ values vary significantly for different C sites, probably due to the presence of different motions capable of promoting the relaxation. For C4-benzene this effect is most pronounced for the carbon atoms of the tert-butyl groups, while for C4-toluene it is also observed for C-3,5 atoms probably due to the fast rotation of the CH_3 group of the guest. Therefore, inclusion of toluene seems to enhance the mobility of the aromatic protons more than the inclusion of benzene, while inclusion of benzene mostly affects the aliphatic protons.

The values of T_{CP} are usually longer for corresponding sites in the complexes than in C4 alone, confirming that all protons, with the exception of the bridging methylene protons (CH_2-7), become more mobile upon complexation. We also note that the largest increase in the value of T_{CP} is found for the aromatic atoms, reflecting the general increase of the mobility of the host.

Discussion

In C4-toluene and C4-benzene [8, 14], the calixarene adopts the cone conformation as in C4 [21]. Crystallographic studies and ^2H NMR measurements show that the methyl group of the toluene molecule points towards the centre of the cavity while rotating about the calixarene four-fold axis. [9]. Benzene shows an additional kind of motion, rotation about its six-fold symmetry axis [8]. Benzene is located at the entrance of the cavity, close to the host methyl groups, though the crystallographic distance is larger than the sum of the atomic radii. As this value is only an average, the possibility of some weak intermolecular interactions cannot be ruled out.

The ^1H MAS NMR spectra did not allow us to compare the dynamics of the p-tert-butylcalixarene molecules in the pure host and in two of its complexes, as they cannot resolve all chemically inequivalent sites. On the other hand, ^1H–^{13}C VCT and 2D WISE experiments combine the information on the ^1H–^{13}C dipolar coupling and the ^1H–^1H dipolar interaction with the high resolution achieved by ^1H–^{13}C CP/MAS experiments.

2D WISE indeed shows that the mobility of the host increases upon inclusion of the guest, as the for ^1H lines are smaller for C4-benzene (65.0 kHz) and C4-toluene (100 kHz) than for C4 (120 kHz).

A more detailed and quantitative determination of the motion responsible for the reduction of the linewidth in ^1H spectra and of the increased relaxation time is beyond the scope of this paper. Here the main interest is to identify the effects of the complexation on these two spectroscopic features which can be used as an indication of the overall mobility. 2D WISE spectra of C4 and C4-benzene reveal several components in the ^1H lines but all the host protons in C4-toluene have comparable linewidths. The presence of the very narrow component in the 2D WISE spectrum of the empty host does not contradict the increased mobility upon complexation. It rather reflects that the solid state structure of C4 is different in the pure host from the one in the complexes. C4 molecules are closer to each other and show partial self-inclusion of tert-butyl groups leading to a much more compact structure of the empty C4 compared with the complexes with partial self inclusion in which some methyl groups can move more freely [21]. The differences between C4-benzene and C4-toluene are explained by considering the position of the guest molecules. Toluene's aromatic ring is located higher with respect to the cavity than benzene due to the presence of the methyl group. One should also consider that at room temperature these positions are only averages and the guest molecules can probably vibrate vertically in addition to rotating about the calixarene four-fold axis. This vibrational motion cannot be detected by ^2H lineshape simulation.

^1H–^{13}C CP/MAS experiments confirm an increase in the frequency of the motion of the host upon complexation, as $T_{1\rho H}$, $T_{1\rho C}$ and T_{CP} are, with one exception, longer. The increase is usually ten-fold for the spin lattice relaxation times, but increases up to forty-fold are found, for instance for the methyl carbon (C-9) upon inclusion of benzene. The only exception to this trend is the behaviour of the T_{CP} of the methylene (C-7) carbon. It was already found [9] that the dynamic disorder of the host molecules implies interconversion between two elliptical conformations with two-fold symmetry giving the averaged four-fold symmetrical cone. Such motion is coupled with rotation of the guest molecule within the host cavity and pivots about the C-7 atoms. The inclusion of the guests increases the mobility of the aromatic fragments at the expense of the local mobility of the C—H bond of CH_2-7. Comparison between the $T_{1\rho}$ of the same carbon atoms in the two complexes provides additional insight into
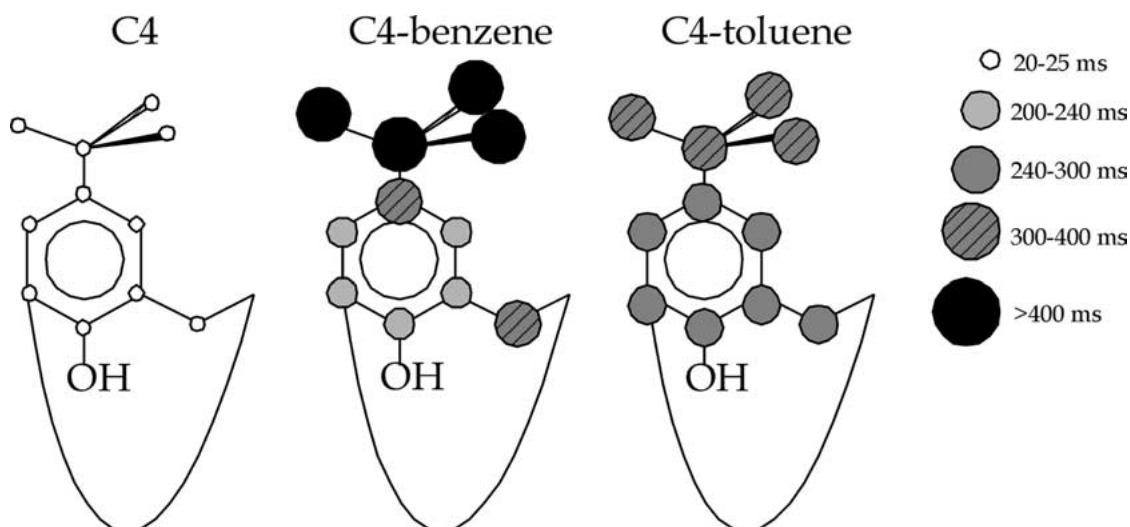
Figure 6. Schematic representation of the ^{1}H spin-lattice relaxation times in the rotating frame. Longer times are associated with higher mobility. The colour and size of the carbon atoms depend on the value of $T_{1\rho H}$.

the fundamental role of the steric features of the complex. The mobility of the aliphatic carbons is much higher for the benzene complex, while the opposite applies for the aromatic carbon atoms. As shown by the crystallographic data, in the C4-benzene the guest is located at the upper part of the host molecule, thus it can interact preferentially with the tert-butyl groups. The extremely long spin-lattice relaxation times for C-8 and C-9 in C4-benzene exclude the presence of a specific interaction which would have the effect of hindering the molecular motion. A comparison of C4-benzene and C4-toluene reveals that, although the 2D WISE spectra suggest that the host is more mobile in the benzene complex, the ^{1}H and ^{13}C spin-lattice relaxation times in the rotating frame indicate the opposite for the aromatic carbons. This discrepancy can be understood by considering that the ^{1}H lineshapes from the 2D WISE experiments depend on the strength of the homonuclear dipolar interaction, while the spin-lattice relaxation times depend on the fraction of the motion at the frequency of the spin-locking field. Therefore the results from the 2D WISE experiments reflect motion of the host only, as the guest is deuterated and does not contribute to the ^{1}H–^{1}H dipolar interaction. On the other hand the spin-lattice relaxation times are also affected by the motion of the guest. It can therefore be concluded that the mobility of the host aromatic framework is probably higher in C4-benzene than in C4-toluene. However, on average, the complex is more mobile in the C4-toluene. According to this interpretation, the methyl group in the toluene molecule weakens the complex rather than strengthening it.

We observe an increase of the mobility in the host upon complexation, suggesting that the host molecules are further apart as a result of accommodating a guest. This allows more free space per molecule and causes an increase in the motional frequencies. In general, we expect that directional non-covalent interactions have the effect of reducing the mobility of the groups bonded. Therefore, it is steric effects rather than specific interactions (i.e., the methyl-π interaction) which determine the inclusion of the guest.

Conclusions

The spontaneity of the formation of the C4-toluene and C4-benzene complexes indicates the presence of an attractive interaction between the host and guest molecules. On the other hand, as the same complexes are labile in solution, the host–guest attraction ought to be relatively weak. The host dynamics confirm that the force responsible for the complexation is weak, as the mobility of the host increases considerably upon complexation. We suggest that the driving force for the formation of these complexes is entropic, while the enthalpic contribution to the free energy is negligible.

A comparison of C4-toluene and C4-benzene shows that the methyl group of toluene makes the mobility of the host molecule more homogeneous, reducing the difference between the aromatic frameworks and the aliphatic groups in the C4-benzene complex. This has been attributed to the different position of the guest molecule inside the calix. The tert-butyl methyl groups in the C4-benzene and the host aromatic groups in C4-toluene are the area of closer contact between the host and the guest in the two complexes. Both are characterised by an increased mobility with respect to the other carbon atoms in the same host molecules. This suggests that no specific directional interaction comes into play during the formation of the complexes, and only weak dispersion forces are responsible for the complexation.

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