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Pseudopolymorphism of Aliphatic Amine/4-*tert*-Butylcalix[4]arene Inclusion Compounds: Supramolecular Stabilization as a Route to Polar Clusters and Layers

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Abstract: 4-*tert*-Butylcalix[4]arene (4tBC4A) is a versatile host capable of forming a variety of 1:1 and 2:1 inclusion compounds typically stabilized through van der Waals interactions. Preliminary studies in our group have demonstrated that inclusion of *n*-butylamine in 4tBC4A results in a series of pseudopolymorphic inclusion compounds, including a new 3:1 inclusion motif. Using a combination of SCXRD, TGA, solid state NMR, and PXRD, we now elaborate upon the relationship between these pseudopolymorphs. We also demonstrate that larger amines demonstrate a similar degree of pseudopolymorphism, allowing for the production of customized materials using self-assembly guided by competing weak forces. Finally, we comment on the structural implications of the relative dominance such forces in the formation of calixarene-based supramolecular frameworks.

Keywords: aliphatic amine · calixarene · host–guest systems · hydrogen bonds · supramolecular chemistry

Introduction

Supramolecular chemistry has developed into an extremely diverse field of research, with broad a range of organic, inorganic and hybrid metal-organic frameworks currently under investigation.[1–10] This research ultimately is driven by a desire to develop functional materials for various applications, such as gas adsorption[1,11,12] and catalysis.[13] The vast majority of such studies revolve around the synthesis of increasingly complex host molecules, so that insight into the weak forces guiding the self-assembly of such systems in the solid state is of secondary importance.

In the area of organic frameworks, the calixarenes and resorcinarenes are particularly attractive host compounds for the production of supramolecular receptors.[14–16] In particular, 4-*tert*-butylcalix[4]arene (4tBC4A) has been used extensively as a synthetic precursor because of the relative ease of synthesizing the compound. The parent compound itself has proven to be an excellent host for investigating the forces guiding self-assembly, with a range of 1:1 and 2:1 inclusion compounds having been reported.[17–22] Inclusion of alkanes follow this trend quite well, forming a series of 1:1 and 2:1 inclusion compounds with four-fold symmetry matching that of the host.[22,23]

As a host for use in producing molecular receptors with potential materials applications, 4tBC4A has generally been overlooked due to its relatively low solubility in common organic solvents (and insolubility in aqueous systems) and the relative simplicity of the inclusion motifs it exhibits. However, more recent studies have begun to demonstrate that 4tBC4A has considerable potential as a building block for producing functional materials. A family of interrelated polymorphs and pseudopolymorphs of 4tBC4A and its simple inclusion compounds have been characterized, including a low-density form which has shown potential as a gas adsorbent.[11,12,24–26] In light of some of the elaborate covalently modified calixarene receptors previously reported,[16,27,28] self-assembly of 4tBC4A frameworks with guest molecules

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containing different moieties presents an interesting alternative approach to producing more complex functional materials while avoiding complex organic synthetic pathways.

The potential of the self-assembly approach was initially demonstrated with the discovery of a 3.5(1,4-butanediamine):2(4tBC4A) inclusion compound.[29] The competition between directional interactions such as hydrogen bonding and dipole–dipole interactions, and non-specific van der Waals interactions with the calix cavity gives rise to a series of amine clusters within a calixarene lattice. Given the strong preference of alkylcalix[4]arenes, and 4tBC4A in particular, for including guests in such a way that the four-fold symmetry of the host is maintained,[17,21–23,30,31] this inefficient packing scheme strongly suggested such combinations of forces could be exploited to produce larger 4tBC4A assemblies containing polar clusters. Amine-containing frameworks could have a variety of applications, including serving as supports for metal centres with potential catalytic activity,[13,32] isolated pockets of solvent for reactions,[33,34] or as gas adsorbents.[35]

Our preliminary studies of the inclusion compounds formed by *n*-butylamine with 4tBC4A confirmed the potential of using aliphatic amines to produce complex hydrogen-bonded networks or metal-coordinated species, revealing the existence of a series of pseudopolymorphs.[36,37] We now report in detail on the synthesis of polar clusters and layers in 4tBC4A lattices, and the pseudopolymorphism that arises out of the competitive forces that guide the formation of such networks. We have made use of the complementary strengths of solid-state NMR (SSNMR) and X-ray diffraction (XRD) to probe the local and long range ordering of these crystalline solids, and to demonstrate in detail the relationship among the various pseudopolymorphs observed. In doing so, we illustrate how subtle changes in the guest can be used to control the nature of the clusters and layers initially formed, and thereby guide the subsequent transformations to other pseudopolymorphs, as well as guest free forms of the host compound.

Results and Discussion

Polar Clusters—*n*-butylamine and amylamine: Recrystallization of 4tBC4A from *n*-butylamine readily yields large, block-like crystals of compound **1** which are suitable for structural characterization by SSNMR and single crystal XRD. Considerable diagnostic information can be derived from analysis of the ^{13}C CP/MAS spectra of **1**. The ^{13}C CP/MAS spectrum (see Figure 1a) shows complex splitting patterns in both the aromatic and aliphatic regions. The majority of these resonances are readily assigned based on previous studies of 4tBC4A inclusion compounds, the information derived from dipolar dephasing experiments to suppress the signals of CH and CH_2 carbons experiencing significant dipolar coupling, and the solution ^{13}C spectrum of *n*-butylamine.[23,24,29]

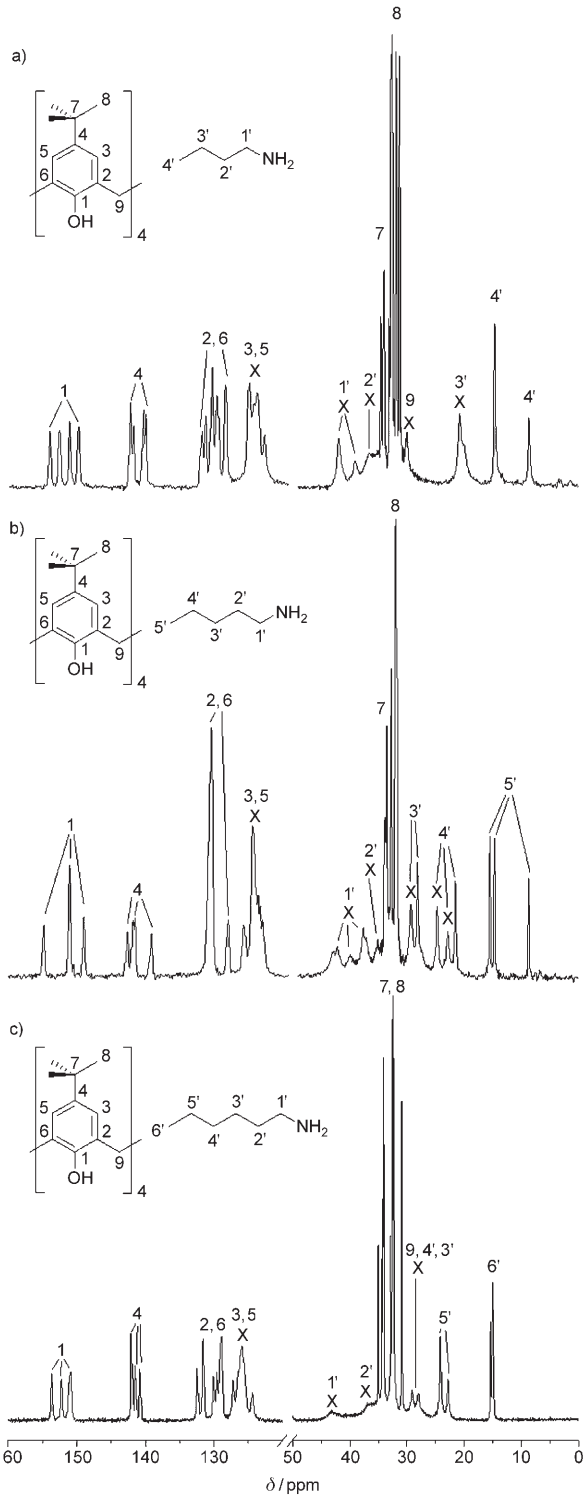

Figure 1. ^{13}C CP/MAS NMR spectra of a) clathrate **1**; b) clathrate **2**; and c) clathrate **3**. Spectra of clathrate **1** and **2** were collected on a Bruker AMX-300 spectrometer, while the spectrum of clathrate **3** was collected on a TecMag Apollo 200. X indicates a peak that is absent in the corresponding dipolar dephased spectrum.

The resonances attributed to C1 (δ 154–150 ppm) and C4 (δ 143–140 ppm) in the aromatic ring are of particular diagnostic value. Both carbons show a four-fold splitting, similar

to that observed for inclusions of 1,4-butanediamine[29] or nitrobenzene.[19] In both of these compounds, the included guest molecules induce a distortion of the host lattice away from the usual tetragonal symmetry. Given this, a similar guest-induced reduction in calixarene symmetry is expected for clathrate **1**.

In the upfield region, the resonances due to the methine bridge and *tert*-butyl methyl groups (35–31 ppm) also show considerable splitting, and they partially overlap each other, while the intensity of the peak due to the quaternary carbon in the *tert*-butyl is too low to make splittings easily observable. In contrast with the spectrum of 1,4-butanediamine:4tBC4A, the guest resonances are well resolved, with the multiplicity suggesting two distinct types of guest. The resonances due to C1′, C3′ and C4′ are clearly split, while the resonances due to C2′ partially overlap. Upon dipolar dephasing, all but the C4′ resonances disappear, supporting this assignment scheme as well as indicating an absence of dynamic motion in the aliphatic chains (which would result in the C–H dipolar coupling being averaged away such that the CH_2 resonances may be observed).

Further information regarding the structural arrangement of the guest becomes apparent through a comparison of the chemical shifts observed in clathrate **1** with those observed in solution for *n*-butylamine (see Table 1). The chemical shifts of the stronger signals correspond closely to the reported solution spectrum but with a slight downfield shift. The weaker signals generally exhibit upfield shifts, with the C4′ exhibiting the most dramatic complexation induced shift. This suggests that the primary amine site is an *exo* site, thereby experiencing a small degree of deshielding due to edge-on interactions with the aromatic rings of the calixarene. The secondary site is therefore an *endo* site, with the amine positioned such that the methyl is deeply inserted into the cavity, experiencing increased shielding. The relative intensities of the peaks (2:1) also support this.

Given this information, we expected that the packing scheme of clathrate **1** would consist of at least two distinct types of amine for each host molecule along with a reduction in lattice symmetry. The X-ray diffraction structure of **1** corresponds well to the predictions based on the SSNMR evidence (see Figure 2 and Table 4). Clathrate **1** crystallizes in the monoclinic spacegroup $P2_1/c$, with the inclusion of two *exo* amines and a single *endo* amine giving rise to an overall guest to host ratio of 3:1. This agrees well with the solid-state NMR spectra, as the arrangement of the *endo* amine with the methyl group deeply inserted corresponding

Table 1. ^{13}C CP/MAS NMR spectral data for clathrates **1**, **2** and **3**.[a]

Guest	Carbon	δ 4tBC4A[b]	δ Solution[c]	CIS[d]
n-butylamine (**1**)	C1′	42.84	41.96	+0.88
		39.86		−2.10
	C2′	36 (br)	36.07	n.a.[e]
	C3′	21.29	20.08	+1.21
		20.45		+0.37
	C4′	14.95	13.94	+1.01
		8.87		−5.07
amylamine (**2**)	C1′	43.00	42.41	+0.59
		40.83		−1.58
		38.44		−3.97
	C2′	35.98 (br)	33.78	n.a.
	C3′	29.96	29.27	+0.69
		28.73		+0.54
	C4′	25.24	22.68	+2.56
		23.30		+0.62
		21.94		−0.74
	C5′	15.79	14.11	+1.68
		15.02		+0.91
		8.94		-5.17
n-hexylamine (**3**)	C1′	43.19	42.43	+0.76
	C2′	36.85	34.09	+2.76
	C3′, C4′	29.14, 28.04	26.72, 31.88	n.a.
	C5′	24.22	22.77	+1.45
		22.82		+0.05
	C6′	15.39	14.09	+1.30
		15.00		+0.91

[a] All values are in ppm. [b] Chemical shift observed in 4tBC4A clathrate; br indicates broad peak. [c] Chemical shift of amine in solution, from SDBSWeb.[42] [d] CIS = Complexation-induced shift = (δ 4tBC4A) − (δ solution). [e] Not applicable.

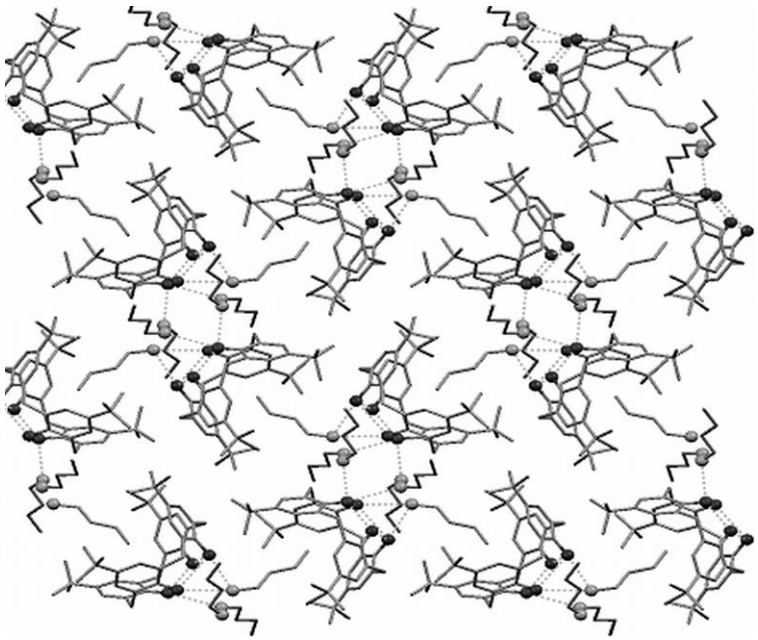

Figure 2. Structure of 4-*tert*-butylcalix[4]arene:3×(*n*-butylamine) (**1**) as viewed down the *a* axis. Dashed lines represent N···N and N···O hydrogen bonds. Hydrogens have been omitted for clarity, and only majority positions are depicted.

Table 2. TGA data for *n*-butylamine, amylamine and *n*-hexylamine clathrates with 4tBC4A.

Clathrate	T [°C][a]	% wt. lost[b]	Mol. guest lost[c]	n[d]
n-butylamine (**1**)	54.69–71.45	17.60	2.09	2.99
	129.76–156.58	7.597	0.90	
amylamine (**2**)	64.80-83.48	23.97	2.50	2.99
	151.90–191.81	4.735	0.49	
n-hexylamine (**3**)	55.39–67.49	25.82	2.43	2.99
	153.60–181.61	5.951	0.56	

[a] Temperatures are given for the onset and completion of transition. [b] Percentage of mass lost by sample. [c] Corresponding number of moles of guest lost by host. [d] Overall guest to host ratio = (total % wt. lost)/(1−total % wt. lost) × (mol. wt. of host)/(mol. wt. of guest).

well to the high degree of shielding observed for the weaker methyl resonance. The increased intensity of the unshielded resonances is the result of the combined contributions from two *exo* amines which are incidentally degenerate. CH and CH_2 resonances are not observed in the dipolar dephased spectrum, suggesting that the disorder observed for the solvent molecules is likely static.

This 3:1 motif arising from the inclusion of aliphatic amines contrasts dramatically with the simple inclusion compounds formed by the analogous alkanes.[23,38] This can be attributed to a reduction in host symmetry, leading to poor packing, and which is a consequence of proton transfer from one phenolic hydroxyl to one of the amines, in accord with calixarene pK_a values.[39–41] The X-ray data supports this, as only three of the phenolic oxygens are proton bearing, and excess electron density is found around one of the amino groups. The highly symmetrical and efficient packing schemes observed in 1:1 and 2:1 inclusion compounds are therefore not available in basic media.

The considerable stabilization offered by the formation of an ion-pair therefore directs the overall structural motifs to a lower symmetry. While the van der Waals stabilization that directs the inclusion motifs of neutral guests still plays a role in stabilizing the structure, the inclusion of *exo* amines within the structure indicates that hydrogen bonding also has a role to play in these structures. This raises the question as to how larger guests will be accommodated, as increased coiling similar to that observed for neutral guests should compete directly with such hydrogen bonding interactions. Variations in the inclusion motif arising from changes in the guest size should therefore provide insight as to the comparative strengths of these forces.

Recrystallization of 4tBC4A from amylamine gives rise to block-like crystals of clathrate **2**. As with clathrate **1**, the ^{13}C CP/MAS spectrum shows considerable splitting that is characteristic of reduced crystallographic symmetry (see Figure 1b). In the aromatic region, the C4 resonance (δ 139–143 ppm) shows four-fold splitting consistent with a loss of the four-fold symmetry of the calixarene. Interestingly, the C1 carbon only shows a three-fold splitting, with one peak with an intensity approximately twice that of the other two; this suggests that two of the four carbons are nearly identical. This is likely diagnostic of the pseudosymmetry of the calixarene arising from the hydrogen bonding scheme resulting from deprotonation of one of the phenolic hydroxyls. The remaining aromatic carbons give rise to relatively broad resonances that make assessing crystallographic splitting difficult.

In the upfield region (δ 8–45 ppm), the guest resonances show even more extensive splitting than with *n*-butylamine. Three-fold splitting of the resonances attributable to C1′, C4′ and C5′ can be clearly seen, indicating the presence of at least three crystallographically distinct amines in the asymmetric unit. Comparison of the chemical shifts to solution values indicate that two of these amines are found in the *exo* position, and one in the *endo* position. The intensities of these peaks suggest a similar number of amines in each position. This is most striking for C5′, with one peak showing a significant complexation induced shift upfield, indicating the insertion of the methyl group into the calix cavity (see Table 1). The minimal difference between the chemical shifts due to the other two amines suggests the *exo* sites are quite similar, as with *n*-butylamine.

Dipolar dephasing serves to further clarify the assignment of the spectrum. In addition to the methyl C5′ resonances, the most shielded resonances, attributed to C3′ and C4′, are retained upon dephasing. This suggests the presence of dynamic disorder in the *endo* amine. In contrast, the C1′ resonances disappear upon dephasing, suggesting the broadening of these peaks is likely due to coupling with the adjacent ^{14}N, as opposed to dynamic motion. Given the NMR data, we therefore expected a 3 × amine:1 × host inclusion compound similar to that observed for clathrate **1**.

Single crystal X-ray diffraction confirms this hypothesis, while demonstrating that the additional bulk of the amine results in subtle structural rearrangement. Clathrate **2** crystallizes in the monoclinic $P2_1/n$ space group, displaying essentially the same symmetry as clathrate **1**, with two amines in *exo* positions and one amine in an *endo* position (see Figure 3 and Table 4). The shift in the glide plane results in a more dramatic staggering of the amine pockets, with the capping 4tBC4A showing a 3.29 Å offset from layer to layer.

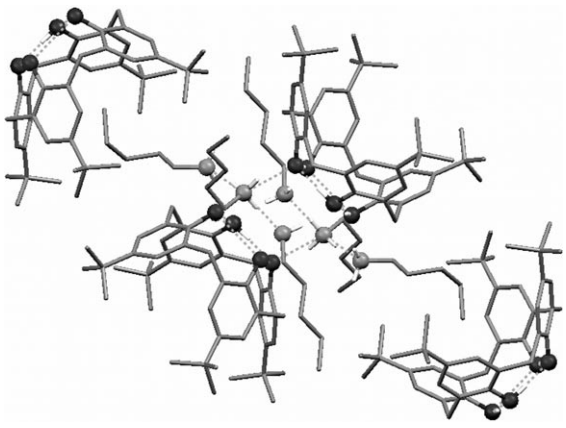

Figure 3. Capped cavity in 4-*tert*-butylcalix[4]arene:3 × (amylamine) (**2**) as viewed down the *a* axis. Hydrogen bonding is indicated by dashed lines. Protons on carbons are omitted for clarity, with only majority positions being shown.

In contrast with clathrate **1**, the *exo* amines do not display disorder. This explains the improved resolution of the SSNMR of clathrate **2**, with the inability to distinguish between the two sites in clathrate **1** attributable to broadening because of static disorder. As expected from the dipolar dephased spectrum, the *endo* amine displays a 60:40 disorder over two positions, with the disorder largely confined to an apparent rocking motion involving C3′ and C4′. Two *tert*-butyl groups exhibit unrelated two-fold disorder with occupancy ratios of 87:13 and 90:10.

The absence of disorder in the majority of the amines also leads to a more detailed structural model of clathrate **2** in comparison with clathrate **1**. The quality of the data allows us to determine from the difference map that one *exo* amine bears a proton abstracted from a phenol group of the calixarene. As a result, a series of hydrogen-bonded chains consisting of three amines is formed (N···N distances of 3.17, 2.93, and 2.80 Å), with the unprotonated amines hydrogen bonding (N···O distances of 3.17, 3.10, and 3.15 Å). Most significantly the protonated *exo* amines are separated from the O^- of the calixarenes by only 2.78 Å, providing us with direct structural evidence of the formation of an ion pair. The ordering induced in the remaining phenolic hydroxyl groups by this assembly results in two of the phenolic groups being pseudosymmetric, accounting for the threefold splitting observed in the NMR spectrum.

Furthermore, the lack of significant disorder in the structure makes the influence of guest size on the structural motif more readily apparent. The *endo* amine displays a distortion away from the all-*trans* conformation displayed by *n*-butylamine in clathrate **1**, presumably to accommodate the additional bulk of the guest, while maintaining a hydrogen bonded structure. A similar distortion is observed in one of the *exo* amines in order to facilitate the hydrogen-bonding scheme. This change in conformation is analogous to that observed for 2:1 inclusions of simple alkanes and haloalkanes,[22] where the energetic costs of assuming such conformations clearly are outweighed by the stabilization offered by the van der Waals interactions with the calixarene. The weakly-interacting alkyl guests show a structural shift from a 1:1 to a 2:1 guest:host inclusion ratio for *n*-hexane and longer alkanes.[22] Amylamine is approximately the same size as *n*-hexane, indicating that stabilization by hydrogen bonding is strong enough to overcome the influence of guest size in directing the packing motif.

Given the similarity in the conformational accommodation of the amine guest to fit within the calix cavity with that observed for the paraffins, it is reasonable to expect a structural shift due to guest bulk for inclusions of larger aliphatic amines. In addition to the simple 1:1 and 2:1 inclusions previously mentioned, very large paraffins give rise to pillared structures.[20] With the clusters formed by *n*-butylamine and amylamine clearly indicating that hydrogen bonding, such as the ion-pair interaction between the calixarene and amine, dominate the selection of the packing scheme, van der Waals interactions with the calixarene cavity and the steric bulk of the guest can be routes to fine tuning the structural motif.

Polar layers—hexylamine and dodecylamine: The influence of steric bulk in reduced symmetry systems of 4tBC4A is made apparent by moving to even larger guests. Crystallization of 4tBC4A from hexylamine yields clathrate **3**, with ^{13}C CP/MAS NMR spectroscopy demonstrating quite clearly that there is a significant shift in the structural motif when compared with both clathrates **1** and **2** as well as weakly interacting guests (see Figure 1c). While the aromatic region shows a similar degree of splitting to clathrates **1** and **2**, the lines are broadened. Unlike the previous two structures, the host resonances in the upfield aliphatic region are of considerably greater diagnostic utility.

Eight distinct lines attributable to C7 and C8 are clearly visible from δ 31–35 ppm, suggesting a further reduction in symmetry such that two crystallographically distinct host molecules are present in the asymmetric unit. For the hexylamine guests, only two crystallographically distinct positions of C5′ and C6′ can be resolved. Furthermore, the C5′ resonance is retained upon dephasing, indicating dynamic motion near the tail of the amine. The resonances due to C1′ and C2′ are quite broad, and C3′ and C4′ can not readily be distinguished because of broadening and overlap with the resonance due to the methine bridge in the host.

The chemical shifts observed for the guest provide the most significant information regarding the structure. No significant complexation induced shift is observed for any of the resonances, and in most cases, a slight degree of deshielding is observed (see Table 1). This provides strong evidence that all of the amines present are in *exo* positions, presenting a possible explanation for the presence of two calixarenes in the asymmetric unit. Several of the host aliphatic peaks are further upfield in comparison with the corresponding peaks in the spectra of clathrates **1** and **2**, with the resonance at δ 30.9 ppm exhibiting the most dramatic shielding. In the absence of any *endo* guest, the calixarene should self-include, giving rise to two crystallographically distinct calixarenes, with the *tert*-butyl carbons being shielded such that they exhibit a complexation induced upfield shift.

Despite the high quality of the data obtained, our initial attempts to solve and refine the structure of **3** in $P\bar{1}$ were unsatisfactory. Even after modelling the disorder of the host and guest molecules, *R* was 0.1628 with thermal ellipsoids remaining quite large. Furthermore, the resulting unit cell contained only one 4tBC4A molecule, disagreeing with the solid state NMR evidence. Solution in *P*1 gave rise to a much more satisfactory answer, which also shows much better agreement with the NMR spectra obtained.

While the overall 3:1 guest to host ratio observed in other aliphatic amine clathrates is maintained, the packing of the guest molecules is only pseudosymmetrical. The asymmetric unit therefore contains six independent hexylamines and two 4tBC4A units, arranged in alternating layers (see Figure 4 and Table 4). A single *tert*-butyl group on one of the calixarenes exhibits a 65:35 disorder, while C4′, C5′, and C6′ of three of the amine sites are disordered over two positions (with occupancy ratios of 65:35, 72:28, and 80:20).

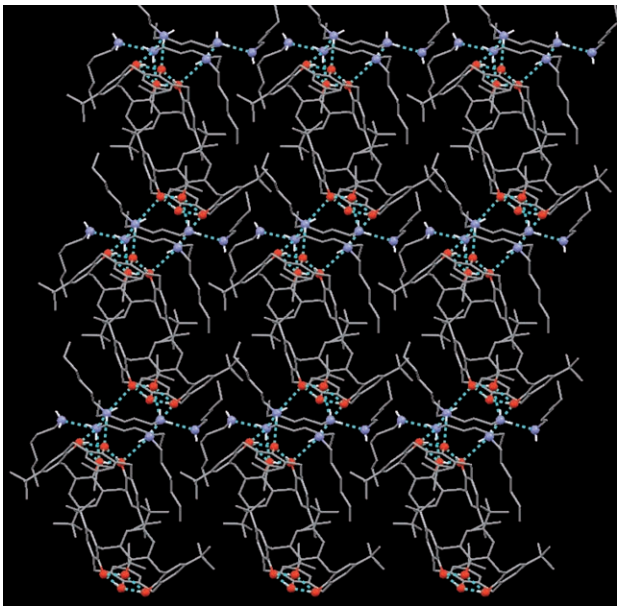

Figure 4. Structure of 4-*tert*-butylcalix[4]arene:3×(*n*-hexylamine) (**3**) as viewed down the *a* axis. Hydrogens on carbons are omitted for clarity, with only majority positions being shown.

Two of the amines reside entirely within the layer defined by the calixarenes, displaying minimal distortions away from the all *trans* conformation. The alkyl tails of the remaining four amines are intercalated between adjacent self-included pairs of 4tBC4A, with three of theses amines showing distortions away from an all *trans* conformation. Given this, the two types of amine observed by NMR are likely these two conformationally distinct sets of amines, with most of the splitting lost due to the pseudosymmetrical arrangement of the guest and broadening due to dynamic motion. As seen previously with weakly interacting guests,[23] this amine clathrate of 4tBC4A (as opposed to all others) shows a correlation of the disorder observed in a guest with that of a *tert*-butyl group. In this case, however, it arises from the packing requirements of an *exo* guest, suggesting the energies involved in the conformational shift of the guest and the *tert*-butyl rotation are similar.

This implies that stabilization by inclusion within the calixarene cavity, even with moderate conformational distortion, would interfere with the significant stabilization offered by directional bonding. The guest is now too large to allow for coiling while still maintaining the hydrogen bonding network. However, the improved packing arising from intercalation therefore indicates that these weak interactions with the calixarene are sufficient to compensate for the energetic penalty associated with moderately distorted conformations.

The intermolecular bonding is also more complex than that observed for clathrates **1** and **2** (see Figure 5). The guests are observed to organize into two distinct clusters of three amines, consisting of two neutral and one protonated amine (N···N distances of 2.84, 2.96, 2.79, 2.95 Å). In each case, one neutral and the protonated amine interact with a calixarene in the adjacent layers (N···O distances ranging from 2.79 to 3.16 Å). In contrast with the inclusions formed by the two smaller amines, the protonated amines each interact with two proton-bearing hydroxyls instead of the deprotonated phenol, suggesting that the influence of guest size is also sufficient to partially disrupt such an arrangement.

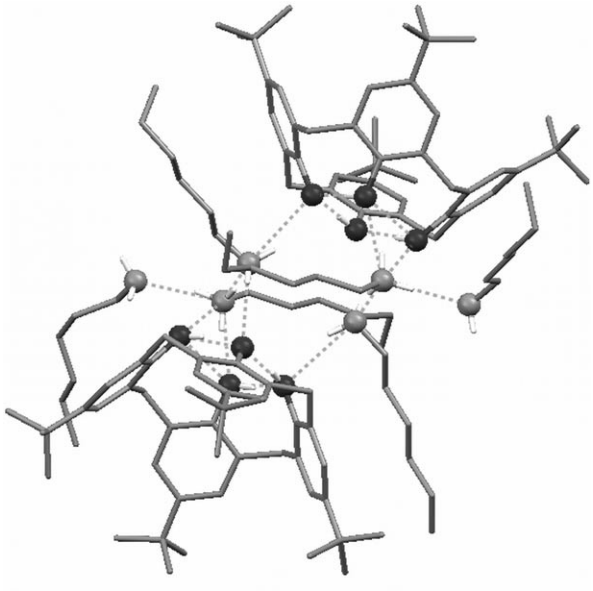

Figure 5. Diagram of the hydrogen bonding between host and guest in the 4-*tert*-butylcalix[4]arene:3×(*n*-hexylamine) clathrate **3**. View down the *a* axis, with hydrogen bonds indicated by dashed lines. Only majority positions are depicted, with hydrogens on carbons are omitted for clarity.

Given the balance of three interactions observed in clathrate **3**, further increases in guest size would be expected to further shift the inclusion motif away from the 3:1 guest to host cluster motif to increasingly distinct layered structures. Recrystallization of 4tBC4A from dodecylamine gives rise to a 2:1 guest to host layered structure without intercalation (clathrate **4**). The bulk of the guest is now too great for stabilization by intercalation to be effective when compared to non-specific interactions between the chains of adjacent amines. Like clathrate **3**, **4** exhibits triclinic symmetry, but the reduced guest content and lack of conformational variation to accommodate intercalation allows for a centre of inversion (see Figure 6 and Table 4). The guests are disordered over two positions (50:50 and 75:25 distributions), while three of the *t*-butyl groups are disordered (with 60:40, 82:18 and 92:8 distributions). As with clathrate **3**, the guests interact with adjacent phenolic hydroxyls through the amino groups, serving to bind adjacent calixarene layers together (N···O distances of 2.86 to 3.15 A).

Pseudopolymorphism arising from amine polar clusters and layers: The shift in motifs from clathrate **1** to clathrate **4**

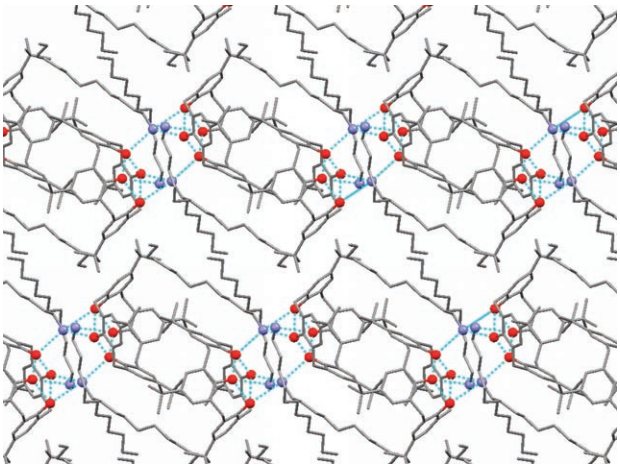

Figure 6. Structure of 4-*tert*-butylcalix[4]arene:2×(dodecylamine) (clathrate **4**) as viewed down the *a* axis. Hydrogen bonds are depicted as dashed blue lines. Hydrogens are omitted for clarity. Only majority positions are depicted.

clearly demonstrate that while the hydrogen bonding between the amino group and the calixarene phenolic group arising from the acid–base chemistry of the compounds dominates the structural motif, the ultimate structural arrangement depends heavily on the balance between stabilization through non-specific interactions and packing concerns arising from increases in guest size. Previous studies of simple 4tBC4A inclusion compounds have clearly demonstrated that by heating such inclusion compounds (as with toluene inclusions) or introduction of an alternative guest (as with nitrobenzene inclusions), the balance between these forces is altered, allowing for control of the structural motif.[24,29,36]

The inclusion of amines in different environments due to the competition of specific and non-specific interactions introduces an intriguing complication when compared with these previous studies. As discussed above, the competition between these forces gives rise to differing degrees of guest stabilization by the host. This raises the possibility of selectively removing guest amines from the host framework in a controlled fashion, producing related pseudopolymorphs. Given the relative volatility of short chain aliphatic amines, we suspected that modest increases in temperature should be sufficient to induce such a structural transformation.

Thermogravimetric analysis of clathrate **1** indicates that the material loses guest in two steps separated by about 80 °C (see Table 2). The first step, corresponding to the loss of two molecules of *n*-butylamine, occurs just below the boiling point of pure *n*-butylamine (78 °C). Given the structural data, such a loss likely corresponds to the loss of the two *exo* amines, which are only stabilized by hydrogen bonding and hydrophobic interactions not unlike those the molecules would experience in solution. The resulting 1:1 guest to host inclusion compound, clathrate **5**, would therefore consist of an *endo* stabilized amine which exhibits considerably greater thermal stability.

The nature of this structural transformation is clarified by the combination of NMR spectroscopy and XRD. Comparison of the ^{13}C CP/MAS NMR spectra of clathrate **1** before and after heating under conditions similar to that used for TGA indicates that the material remains crystalline, but undergoes a dramatic structural shift (see Figure 7). Heating clathrate **1** at approximately 60 °C gives rise to a complex spectrum that indicates that the original compound has been mostly consumed to give rise to a new phase. Further heating clarifies the interpretation (Figure 7b) of this new phase, clathrate **5**.

In this new compound, the aromatic resonances have collapsed to single peaks, suggesting that the four-fold symmetry of the calixarene has been restored. Only a single set of guest resonances are observed without significant differences from the solvent chemical shifts. The dipolar dephased spectrum suggests that the guest is now dynamic. The PXRD also shows a dramatic simplification consistent with increased symmetry (see Supporting Information and Table 3). In conjunction with the TGA data, this suggests that clathrate **5** is a 1:1 guest to host inclusion compound (similar to that observed for weakly interacting paraffins[22]) that arises directly from desolvation of clathrate **1**.

Table 3. Unit cell constants determined by indexing of PXRD patterns of clathrates **1**, **2** and **3**, and the products arising from removing amine by heating.[e]

Clathrate	**1**	**5**[a]	**2**	**6**[b]	**3**	**7**[c]	α *apo*[d]
a [Å]	12.91	12.95	12.85	12.90	13.24	12.89	9.60
b [Å]	20.01	12.95	25.07	12.90	13.98	12.89	30.42
c [Å]	20.68	12.94	18.61	26.05	16.06	26.13	13.44
α [°]	90	90	90	90	96.25	90	90
β [°]	90.92	90	107.9	90	104.5	90	109.7
γ [°]	90	90	90	90	98.01	90	90
V [Å^3]	5346.2	2171.5	5703.2	4334.9	2818.0	4342.8	3693.4

[a] Obtained by heating **1** at 100 °C. [b] Obtained by heating **2** at 100 °C. [c] Obtained by heating **3** at 70 °C. [d] Obtained by heating **3** at 185 °C. [e] Plots of PXRD patterns are available as Supporting Information.

Upon further heating to completely remove the remaining guest, the resulting guest free host is obtained. No crystallographic splitting is observed in the aromatic region of the ^{13}C CP/MAS spectrum, with only a two fold splitting observed for the peaks in the aliphatic region. This is quite similar to the spectra previously reported for the low-density guest free forms of 4tBC4A (β_0 and β_0') as obtained through sublimation[43] or desolvation of 4tBC4A:toluene inclusion compounds.[24] The PXRD pattern for this *apo* form is consistent with that of the β_0 forms,[43] but too few peaks are available to index the cell reliably.

The stability of clathrate **5** prompted us to attempt to obtain crystals of the material by recrystallization through slow evaporation at approximately 70 °C. Single crystal X-

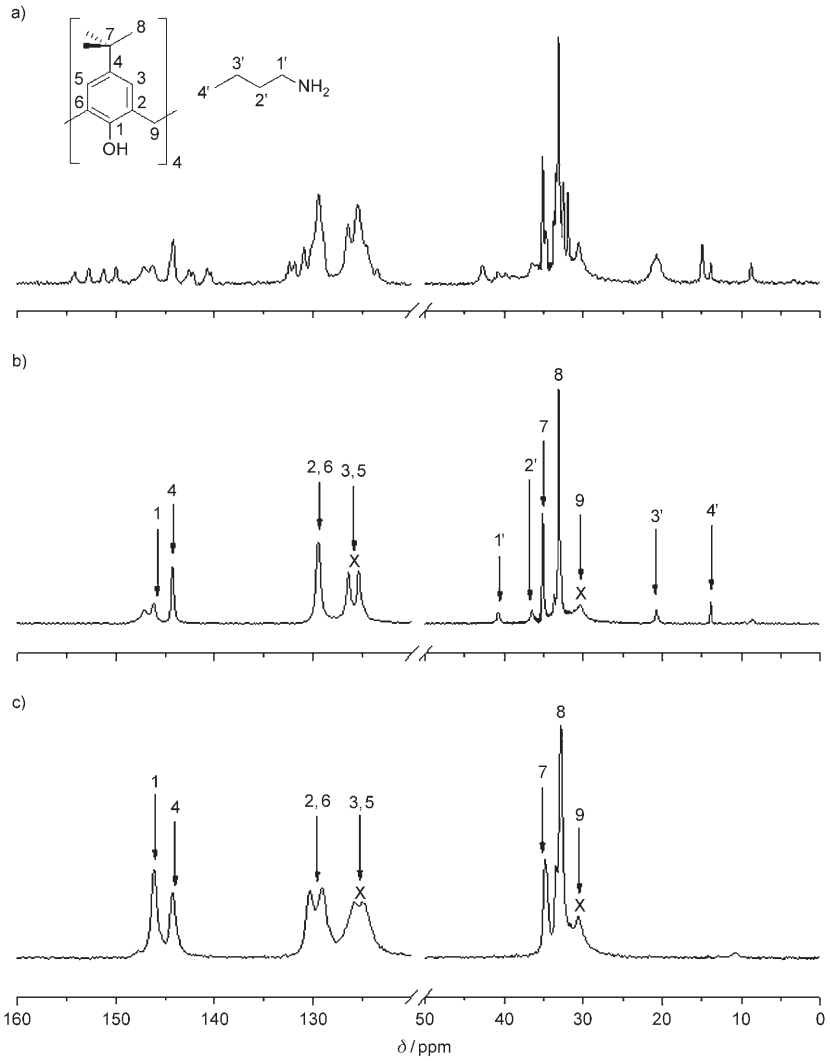

Figure 7. ^{13}C CP/MAS spectra of 4tBC4A:3×(*n*-butylamine) clathrate **1** after heating at: a) 60 °C for 30 min; b) 100 °C for 30 min (clathrate **5**); c) 200 °C for 30 min (β form). Peaks that are unobserved in the corresponding dipolar dephased spectrum are marked with an X.

ray diffraction confirms that the resulting material is a 1:1 inclusion compound with *P*4/*n* symmetry, with the amine guest disordered over four sites within the calixarene cavity, exhibiting no directional interactions. The PXRD pattern obtained for clathrate **5** can be indexed based on the predicted powder pattern from this data (see Table 2), indicating that the single crystal is representative of the bulk material obtained by heating clathrate **1**.

The related 2:1 guest to host inclusion compound of 4tBC4A and *n*-butylamine can also be isolated by recrystallization at elevated temperatures from a dilute solution of the amine in tetradecane.[36] The resulting family of three pseudopolymorphs suggests that the *n*-butylamine inclusions represent a convergence of steric hindrance and hydrogen bonding in determining structural motifs in amine–4tBC4A inclusion compounds. At high degrees of dilution, it is possible to force the inclusion motif to one that is apparently disfavoured, suggesting that the shift from the 1:1 compound to the 2:1 compound is disturbed by the hydrogen bonding arising from the presence of the amino functionality.

This is confirmed by the thermally induced collapse of clathrate **2** to give rise to the 2:1 4tBC4A:amylamine clathrate **6**. The TGA in this case shows the loss of 2.5 molecules of amine, followed by the loss of 0.5 molecules (see Table 2). There is a noticeable increase in the temperatures required to force the guest out of the host lattice, but the first transition is now well below the boiling point of the free solvent (104 °C). The increased bulk of an additional carbon, and the conformational shift away from all *trans* clearly contributes to this comparative increase in the destabilization of the *exo* amines. The increased temperature of the second step is representative of the increased energy required to open the host capsule containing the guest.

As before, the ^{13}C CP/MAS spectrum establishes the structural shift and gives rise to a highly symmetrical structure (see Figure 8). Once again, the splitting in both the aromatic and guest peaks is characteristic of four-fold symmetry, with the guest exhibiting dynamic motion. In addition, it is possible to determine that the transformation does not involve intermediate structures, as a spectrum taken at an intermediate temperature is only a combination of the spectra for **2** and **6**. The loss of amine is also apparent from the dramatic reduction in intensity observed for the guest reonances. It is not possible, however, to distinguish between the 2:1 and 1:1 compounds using NMR, as the two structural motifs have nearly identical asymmetric units.

The symmetry differences do give rise to distinct PXRD patterns. The additional glide planes give rise to subtle shifts in several indexable peaks (see Supporting Information and Table 3). Single crystals of **6** can be prepared in a fashion similar to that used for preparing the 2:1 clathrate of *n*-butylamine, with only a marginal increase in the length of the *c* axis to accommodate the slightly larger guest.[36] As expected from the absence of any significant complexation induced shift for the guest resonances in the NMR spectrum,

Table 4. SCXRD data for clathrates **1** to **7**.

Identification code	KU78 (**1**)	POB14 (**2**)	POB106 (**3**)	JR26 (**4**)	KU88 (**5**)	POB48 (**6**)	POB45 (**7**)
formula	$C_{56}H_{89}N_3O_4$	$C_{59}H_{95}N_3O_4$	$C_{62}H_{101}N_3O_4$	$C_{68}H_{110}N_2O_4$	$C_{48}H_{67}N_1O_4$	$C_{23.25}H_{31.25}N_{0.25}O_2$	$C_{23.50}H_{31.75}N_{0.25}O_2$
F_w	868.30	910.38	952.46	1019.58	722.03	346.24	349.74
T [K]	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
λ [Å]	0.71070	0.71070	0.71070	0.71073	0.71070	0.71073	0.71070
crystal system	monoclinic	monoclinic	triclinic	triclinic	tetragonal	tetragonal	tetragonal
space group	$P2_1/c$	$P2_1/n$	$P1$	$P\bar{1}$	$P4/n$	$P4/nnc$	$P4/nnc$
unit cell							
a [Å]	12.9405(6)	12.9164(8)	13.3420(15)	13.419(2)	12.9816(5)	12.8481(6)	12.8201(7)
b [Å]	20.0923(9)	24.9406(16)	14.0770(16)	15.599(2)	12.9816(5)	12.8481(6)	12.8201(7)
c [Å]	20.7519(9)	18.5354(12)	16.1519(18)	17.638(3)	12.6459(6)	25.2599(19)	25.617(2)
α [°]	90	90	96.248(2)	108.555(3)	90	90	90
β [°]	91.1220(1)	107.3670(1)	104.320(2)	107.354(3)	90	90	90
γ [°]	90	90	98.009(2)	101.963(3)	90	90	90
V [Å^3]	5394.6(4)	5698.8(6)	2878.0(6)	3149.0(8)	2131.11(15)	4169.7(4)	4210.3(5)
Z	4	4	2	2	2	8	8
ρ_{calcd} [Mg m^{-3}]	1.069	1.061	1.099	1.075	1.125	1.104	1.104
μ [mm^{-1}]	0.066	0.065	0.067	0.065	0.070	0.068	0.068
F(000)	1912	2582	1052	1128	788	1508	1524
crystal size [mm^3]	0.45×0.40×0.20	0.4×0.16×0.08	0.32×0.32×0.16	0.40×0.40×0.25	0.40×0.40×0.15	0.32×0.24×0.16	0.16×0.16×0.16
θ range [°]	1.57 to 28.75	1.41 to 29.62	1.48 to 29.58	1.32 to 27.50	1.61 to 28.69	1.61 to 29.62	1.78 to 29.64
index ranges	$-17\le h\le 17$	$-17\le h\le 17$	$-18\le h\le 18$	$-17\le h\le 17$	$-17\le h\le 17$	$-17\le h\le 17$	$-17\le h\le 17$
	$-27\le k\le 27$	$-34\le k\le 34$	$-19\le k\le 19$	$-20\le k\le 19$	$-17\le k\le 17$	$-17\le k\le 17$	$-17\le k\le 16$
	$-28\le l\le 28$	$-25\le l\le 25$	$-22\le l\le 22$	$-22\le l\le 22$	$-17\le l\le 17$	$-35\le l\le 34$	$-35\le l\le 35$
reflns collected	63744	71636	36360	34741	24796	48778	48776
ind. reflections	13978	16005	15865	14408	2759	2959	2976
R(int)	0.0554	0.0364	0.0248	0.0595	0.0296	0.0582	0.0532
completeness to θ_{max} [%]	99.7	99.7	98.1	99.5	99.5	99.9	99.5
abs. corr.	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan	multi-scan
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	13978/85/699	16005/58/857	15865/53/1736	14408/109/989	2759/37/211	2959/9/159	2976/11/143
GoF on F^2	0.943	1.011	1.040	1.065	1.011	1.041	1.057
final R indices [$I>2\sigma(I)$]							
$R1$	0.0564	0.0509	0.0418	0.0759	0.0470	0.0524	0.0613
$wR2$	0.1382	0.1279	0.1065	0.1959	0.1350	0.1405	0.1746
R indices (all data)							
$R1$	0.1249	0.0815	0.0484	0.1222	0.0608	0.0763	0.0888
$wR2$	0.1565	0.1456	0.1122	0.2163	0.1447	0.1547	0.1919
largest diff. peak and hole [e Å^{-3}]	0.423 and −0.324	0.447 and −0.324	0.354 and −0.216	0.422 and −0.261	0.318 and −0.310	0.333 and −0.185	0.335 and −0.254

the carbons are not deeply included within the calixarene cavity (see Figure 9). The guest is positioned in such a fashion in order to minimize contact between the amino group and the cavity across for the eight guest positions arising from the disorder across the four-fold axis and inversion centre of the structure.

The powder pattern can be indexed in the space group obtained from the SCXRD data set, with slight increases in the unit cell parameters because of expansion of the cell at room temperature. The elevated temperature disrupts the stabilization from hydrogen bonding, such that the bulk of the guest now guides the structural motif, following the pattern established for paraffins. However, the NMR and PXRD evidence indicate that complete desolvation still results in the formation of the low-density guest free form of4tBC4A. Even given the increased difficulty in removing the guest from the capsule formed by the two host molecules should, it is still more favourable for the compound to remain in an open form than to collapse into a dense form following desolvation.

Interestingly, the TGA of clathrate **3** is quite similar to that observed for clathrate **2**. The overall trend is identical, with 2.5 equivalents of hexylamine followed by 0.5 equivalents lost with heating. However, the temperature required to eliminate amines in the first transition is less than that observed for clathrate **2** (see Table 2), and is dramatically less than the boiling point of hexylamine (132 °C). As with the conformational distortion of the guests observed in the crystal structure clathrate **3**, this is reflective of the fact that the hydrogen bonding and ion–ion interactions are only able to partially compensate for the absence of guest stabilization through van der Waals interactions with the calixarene cavity.

As before, the combination of SCXRD, ^{13}C CP/MAS NMR and PXRD make it apparent that the 2:1 compound has been isolated. The ^{13}C CP/MAS NMR shows the expect-

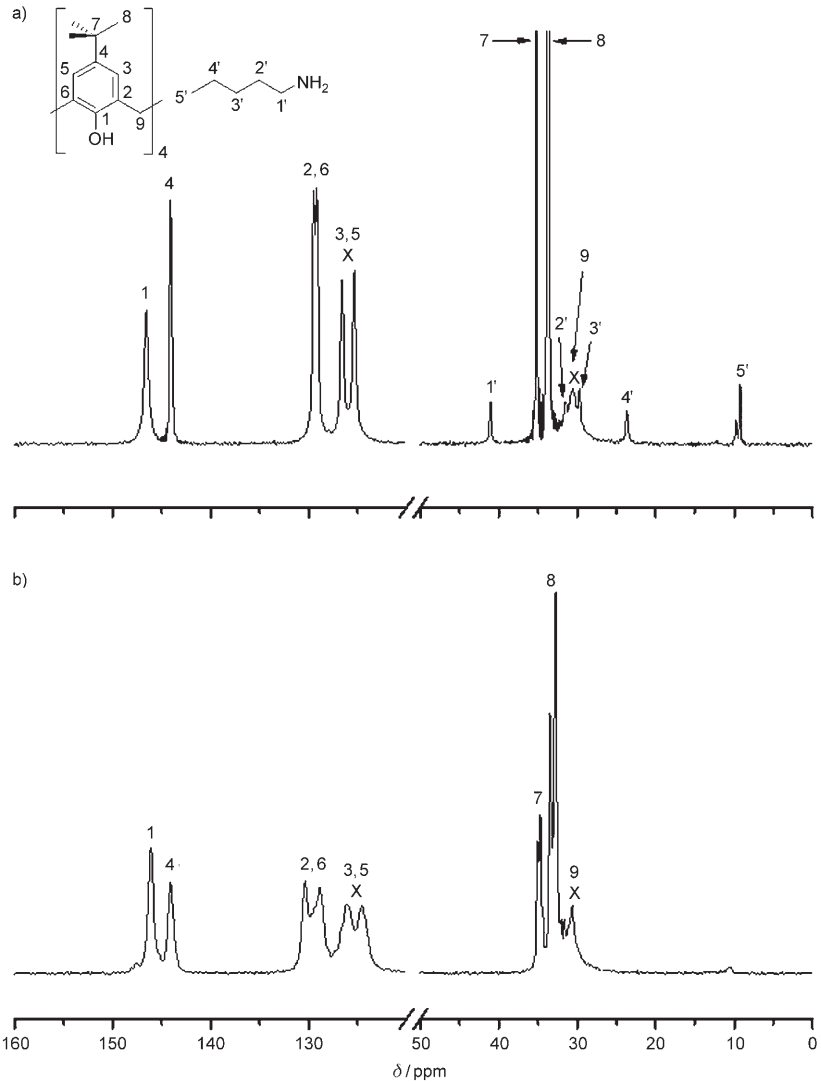

Figure 8. ^{13}C CP/MAS spectra of 4tBC4A:3×(amylamine) clathrate **2** after heating at: a) 100 °C for 30 min (clathrate **6**); b) 200 °C for 30 min (β form). Peaks that are unobserved in the corresponding dipolar dephased spectrum are marked with an X.

ed decrease in splitting multiplicity from a restoration of four-fold symmetry (see Figure 10), but in this case the guest methyl exhibits a complexation induced shift of approximately 5 ppm. As expected, the single crystal structure indicates that the increased bulk of the guest causes the methyl now to be deeply inserted into the calix cavity (see Figure 11). The PXRD (see Supporting Information and Table 3) pattern agrees well with that based on the predictions from this single crystal structure. This makes it clear that it is not selective removal of *exo* amines from the initial clathrates that guides the formation of the subsequent pseudopolymorphs. Instead, the heat induced disruption of hydrogen bonding results in the van der Waals interactions with the host and guest bulk becoming the primary directors of the structural motif.

Complete desolvation also leads to the formation of a different *apo* host than observed for clathrates **1** and **2**. The ^{13}C CP/MAS spectrum clearly shows an increase in splitting in both the aromatic and aliphatic regions consistent with the densely packed guest free form of 4tBC4A (α), while the PXRD pattern is indexible based on the available single crystal data for this form.[24] Given the lack of *endo* guests in the structure of clathrate **3**, this suggests that the guest free form obtained by desolvation at low temperatures is actually guided by the initial inclusion motif observed, altogether avoiding the balancing of temperature and heating rate dictated by the balance of forces in the toluene inclusion system.[24] Judicious choice of guest size allows one not only to dictate the structure of the inclusion compounds that result, but also that of the empty guest form obtained after desolvation.

Conclusion

The introduction of a strong directional interaction has a considerable impact on the structural motifs observed in 4tBC4A:amine inclusions. By disrupting the molecular symmetry of the calix through deprotonation, the ensuing ion–ion interactions and hydrogen bonding dominate the structural motifs. As such, all of the fully aminated compounds exhibit complex hydrogen bonding schemes. The van der Waals interactions with the calix cavity and the size of the guest are involved in the fine tuning of the structure. Small guests are stabilized by inclusion, favouring the formation of capped cavities, while larger guests will form layers as self-inclusion of the calix becomes more favourable.

The delicate balance between these forces is most apparent in the desolvation behaviour of these clathrates. Modest heating allows one to disrupt the directional non-covalent interactions, such that non-directional interactions with the calixarene dominate the motif. As a result, the resulting dependence of the inclusion ratio on the guest size mirrors that seen in other paraffins.[38] More intriguingly, while temperature previously has been shown to play a major role in determining the guest free form obtained,[24] it

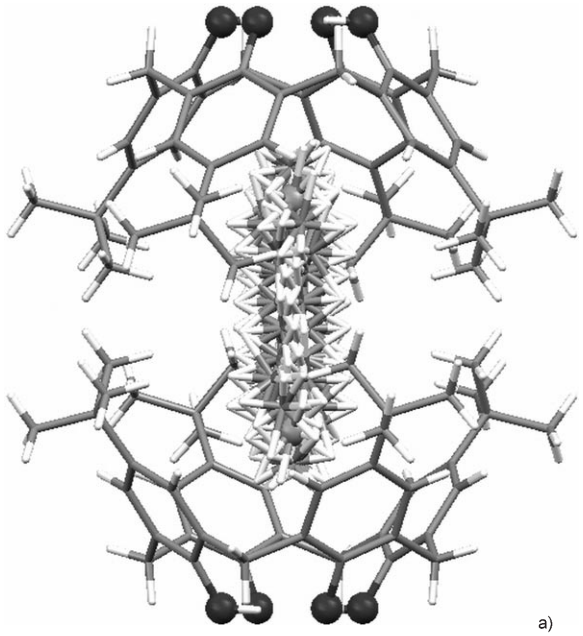

Figure 9. View of the 2:1 host to guest clathrate **6** along the *a* axis. The amylamine guest is disordered over eight positions, with the methyl group just above the cavity of the calixarene.

is now clear that the guest size also influences which of the two guest free forms can be obtained upon total desolvation, with increased size evidently favouring formation of the dense form.

While supramolecular chemistry is chiefly concerned with non-covalent interactions, a surprising amount of effort is focused on covalent modification of host molecules in attempts to direct structural motifs. The diversity of inclusion motifs arising from the inclusion of simple aliphatic amines in 4tBC4A clearly demonstrates that self-assembly guided by competing non-covalent interactions is an excellent alternative to covalent modification in producing a diverse range of structures in a controlled manner. It is hoped that continued study will further clarify the roles of the various forces involved in guiding the formation of such structures, as well as the potential material applications of such amine-containing supramolecular frameworks.

Experimental Section

Crystals of 4tBC4A:3×(*n*-butylamine) (clathrate **1**), 4tBC4A:3×(amylamine) (clathrate **2**), 4tBC4A:3×(*n*-hexylamine) (clathrate **3**), and 4tBC4A:3×(dodecylamine) (clathrate **4**) were all prepared in a similar manner. In a typical synthesis, 0.500 to 1.000 g (7.72×10^{-4} to 1.54×10^{-3} mol) of 4tBC4A was placed in a vial along with 6 mL of amine. The resulting mixture was heated to approximately 70 °C, and stirred for approximately 15 min to dissolve all of the 4tBC4A. The vials were then loosely capped and set aside to allow slow evaporation of the amine. In most cases, after approximately five days, clear crystals were observed to have formed.

Crystals of (4tBC4A):(*n*-butylamine) (clathrate **5**), 2-(4tBC4A):(amylamine) (clathrate **6**), and 2(4tBC4A):(hexylamine) (clathrate **7**) were prepared by alternative methods. Typically, 0.5 to 1.5 g of 4tBC4A (7.72×10^{-4} to 2.31×10^{-3} mol) was placed in a vial along with

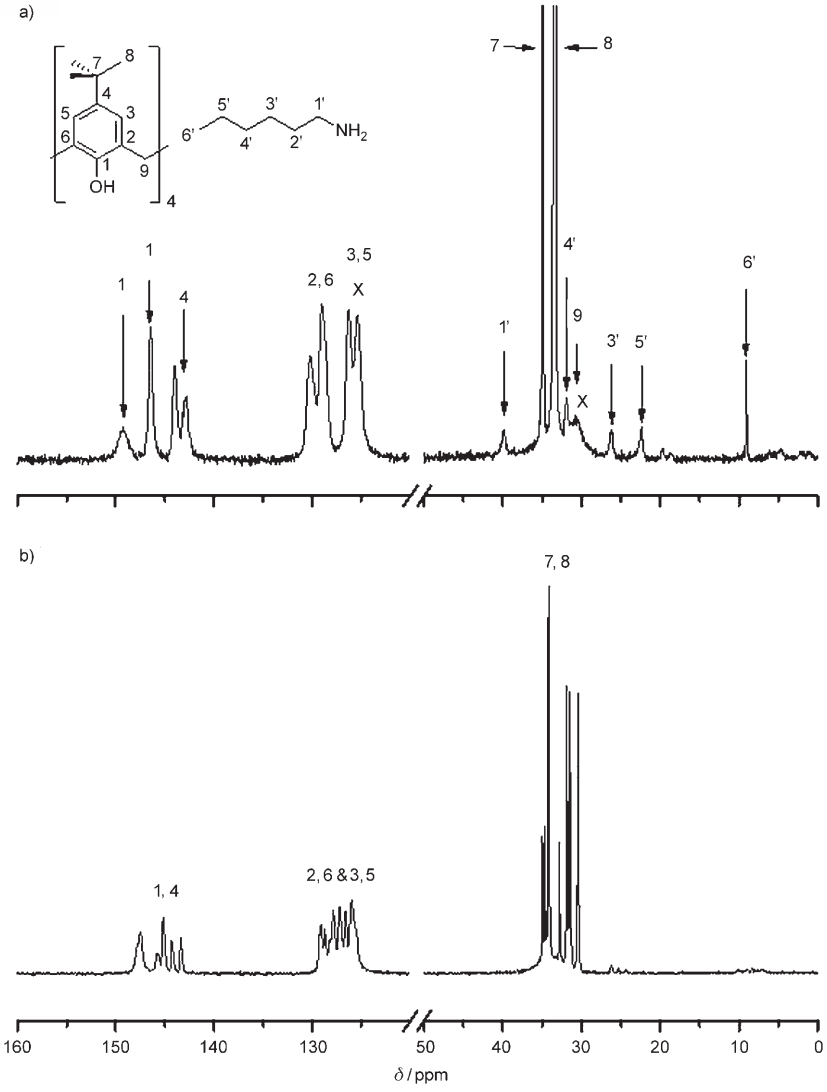

Figure 10. ^{13}C CP/MAS spectra of 4tBC4A:3×(hexylamine) clathrate **3** after heating at: a) 700 °C for 30 min (clathrate **7**); b) 185 °C for 30 min (α form). Peaks that are unobserved in the corresponding dipolar dephased spectrum are marked with an X.

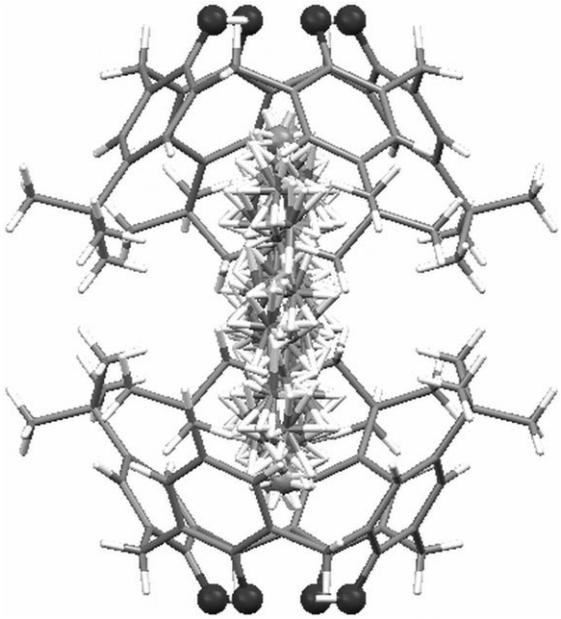

Figure 11. View of the 2:1 host to guest clathrate **7** along the *a* axis. The hexylamine guest is disordered over eight positions, with the methyl group of the guest now inserted into the cavity of the calixarene.

3 mL of amine and 6 mL of tetradecane. The vial was sealed and placed in an oven at 70 °C for in order to induce a slow process of dissolution followed by recrystallization. After one to two weeks, crystals of the appropriate clathrate were observed to have formed, and the vials were removed from the oven.

Single crystal X-ray diffraction data (see Table 4) were collected on a Bruker SMART 1 K CCD diffractometer ($Mo_{K\alpha}$ $\lambda = 0.71073$ Å) equipped with a graphite monochromator. Data were collected at 173 K for clathrates **1**, **2**, and **4–6**, and at 125 K for clathrate **3**. In each case, an empirical adsorption correction was applied using the SADABS program. Structures were solved using direct methods and refined using full-matrix least squares on F^2 using the SHELXTL suite of programs.[44] For clathrates **2** and **3**, the hydrogen atoms on the disordered groups were placed in calculated positions and refined as riding atoms, with all other hydrogen atoms found from the difference map. For all other clathrates, hydrogen atoms on fully ordered heteroatoms were found from the difference map, with all other hydrogen atoms placed in calculated positions and refined as riding atoms.

CCDC-181 105, -603 068, -603 069, -603 070, -603 071, and -603 072 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Thermogravimetric analysis was carried out using a TA Instruments TGA 2050 instrument, with samples heated from room temperature to 400 °C at a rate of 5 °C per minute. TGA data were interpreted using TA Instruments Universal Analysis for Windows 95/NT suite (version 2.3C). The overall host to guest ratio *n* was calculated based on the weight loss prior to decomposition of the host at ~300 °C. Based on this, the molar mass of the inclusion compound was calculated, and the proportion of amine lost in each step calculated.

Thermal desorption studies of clathrates **1**, **2**, and **3** were carried out in a stepwise fashion using a vacuum oven to heat bulk samples. In each case, crystals of the clathrate were removed from the mother liquor, blotted dry using filter paper, and gently ground using a mortar and pestle. Samples were heated for 30 min at each temperature, and then allowed to cool to room temperature. At each temperature, the samples were analyzed using PXRD and ^{13}C CP/MAS solid state NMR.

Powder X-ray diffraction data were collected at 293 K on a Scintag X-2 Advanced diffractometer ($Cu_{K\alpha} = 1.54178$ Å) equipped with a graphite monochromator, using the θ–θ scan mode. Samples were scanned over a 2θ range of 5 to 60°, using a scan rate of 0.02°/sec and a count time of 1 s. The resulting diffraction patterns were manually indexed using the predicted pattern from the SCXRD structures (corrected for appropriate wavelength) as a guide, along with the program Crystal Cracker[45] and the Powder 4.0 program suite.[46] Unit cell parameters were then obtained by fitting the calculated 2θ values to the observed peaks.

^{13}C CP/MAS spectra for clathrates **1**, **2**, **5**, **6**, and the β *apo* form of 4tBC4A were collected using a Bruker AMX-300 spectrometer (^1H = 300.145 MHz, ^{13}C = 75.483 MHz) using a Doty 5 mm high speed MAS probe. A pulse delay of 3 s and a contact time of 2 ms were used, with samples being spun at approximately 5 kHz. Dipolar dephased spectra were obtained by inserting a 40 μs delay between cross polarization and acquistion, during which time the decoupler was switched off. ^{13}C CP/MAS Solid State NMR spectra for clathrates **3**, **7** and the α *apo* form of 4tBC4A were collected using a Tecmag Apollo 200 spectrometer (^1H = 200.1357 MHz, ^{13}C = 50.331 MHz) using a Doty 7 mm high speed MAS probe. A pulse delay of 3 s and a contact time of 3 ms were used, with samples being spun at approximately 3 kHz.

Acknowledgements

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