Self-inclusion and paraffin intercalation of the *p-tert*-butylcalix[4]arene host: a neutral organic clay mimic†

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Two newly identified structures arise upon the crystallisation of the *p-tert*-butylcalix[4]arene host molecule from tetradecane: the guest-free, self-included host structure, and a 1:1 host–guest structure in which the paraffin guest is anchored in the bowl-shaped host cavity and intercalates layers of host molecules in a lamellar structure reminiscent of clays.

The crystal structures of inclusion compounds formed between the *p-tert*-butylcalix[4]arene host and small organic guest molecules have been studied extensively in order to understand guest-induced structural motifs, inclusion propensities and molecular recognition capabilities.[1] The bowl-shaped cavity of this relatively small supramolecular host molecule provides an excellent test site for isolating and probing the weak non-covalent host–guest interactions that prevail in much more complex supramolecular materials.[2] Essentially, three structural motifs have been observed with *p-tert*-butylcalix[4]arene inclusions with neutral guests: 1:1 and 2:1 host:guest structures,[3,4] and more recently, hydrogen-bonded structures formed with amine guests.[5] Herein we report two additional structures involving *p-tert*-butylcalix[4]arene that demonstrate the versatility of this host molecule to form multiple structural motifs under only slightly different synthetic conditions.

The host:guest ratio of compounds formed between linear hydrocarbon guests and *p-tert*-butylcalix[4]arene changes from 1:1 to 2:1 when the guest contains chains longer than six skeletal atoms, *e.g. n*-hexane or 1-chloropentane.[4,6] The longest paraffinic guest to form a 2:1 compound appears to be dodecane, with the alkane folded into a compact isomer in the double-sided host cavity.[6] With the next paraffin in the series, tetradecane, 2:1 host:guest inclusions no longer form, but rather two quite distinct motifs become apparent.

In the first instance, heating of *p-tert*-butylcalix[4]arene in a solution of tetradecane at 70 °C for three days yields guest-free crystals **1**,‡ since the solid-state ^{13}C CP MAS (cross-polarisation, magic angle spinning) NMR spectrum [Fig. 1(a)] of this compound shows tetradecane resonances to be absent. The multiplicity pattern of the host resonances is consistent with low-symmetry environments for the host molecule in the asymmetric unit.

The X-ray crystal structure of **1** (Fig. 2) shows that the host cavities are occupied by Bu^t groups of host molecules in the adjacent layer to form a self-included structure, such as seen with *p-tert*-butylcalix[5]arene.[7] The included Bu^t group is disordered over two positions with a site occupancy of 0.22/0.78. The shortest distance between the carbon atom of the included Bu^t group and the calixarene cavity wall is 3.4 Å. To transform the 1:1 structural motif, as seen with the pentane guest,[4] to the self-included bilayer structure, each calix is rotated off the 4-fold symmetry axis by 28° and moved towards the facing layer by 4.1 Å.

In the second instance, heating of the host molecule in tetradecane at 70 °C for eight days gives a structure with tetradecane present as guest‡ as indicated by the tetradecane resonances in the ^{13}C CP MAS NMR spectrum [Fig. 1(b)]. Whereas the guest methylene resonances are coincident with the host resonances, the tetradecane methyl line is distinct at δ 12.

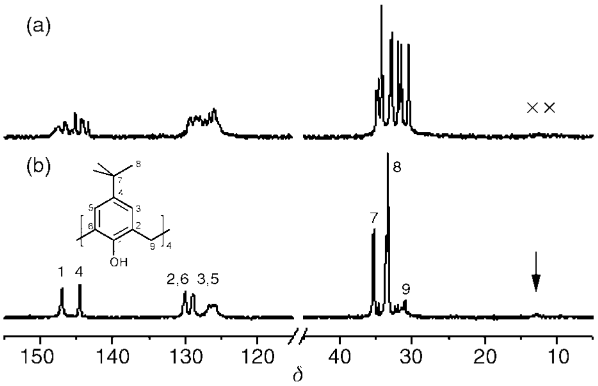

Fig. 1 Partial 50.3 MHz ^{13}C CP MAS NMR spectra: (a) self-included *p-tert*-butylcalix[4]arene **1**, (b) *p-tert*-butylcalix[4]arene–tetradecane inclusion/intercalation compound $\mathbf{1}\cdot C_{14}H_{30}$. Spinning sideband intensity is indicated by 'X'; the arrow indicates the tetradecane methyl resonance.

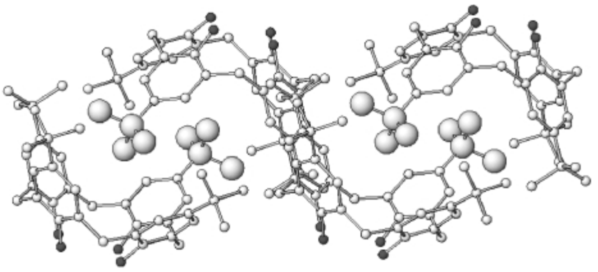

Fig. 2 Bilayer structure of the self-included *p-tert*-butylcalix[4]arene **1**. Hydrogen atoms are removed for clarity; oxygen atoms are black; cavity-filling *tert*-butyl carbons are shown at a larger radius for emphasis.

Like inclusions formed with short-chain hydrocarbon guests,[2,4] the X-ray crystal structure of the second compound $\mathbf{1}\cdot C_{14}H_{30}$ shows a host:guest ratio of 1:1. The packing of the host layer (*ab* plane, $a \approx b$ with $\gamma \approx 90°$) is only slightly distorted from the tetragonal motif commonly observed in other 1:1 compounds. In all other aspects, the structure of the second compound is quite distinct. The most notable feature is the pillaring of the host layers by the guest molecules. The structural model from diffraction refines to give two coexisting structural schemes that are consistent with this pillaring. In the first, one end of the guest is tethered in a host cavity, and at the point where the chain leaves the cavity it bends into the interlamellar space in a pillaring fashion [Fig. 3(a)]. The second scheme has two guest positions. One guest has both ends of the molecule tethered in host cavities of two adjacent bilayers and the second occupies vacant interlamellar space between pillaring guests [Fig. 3(b)]. In both schemes the host positions are

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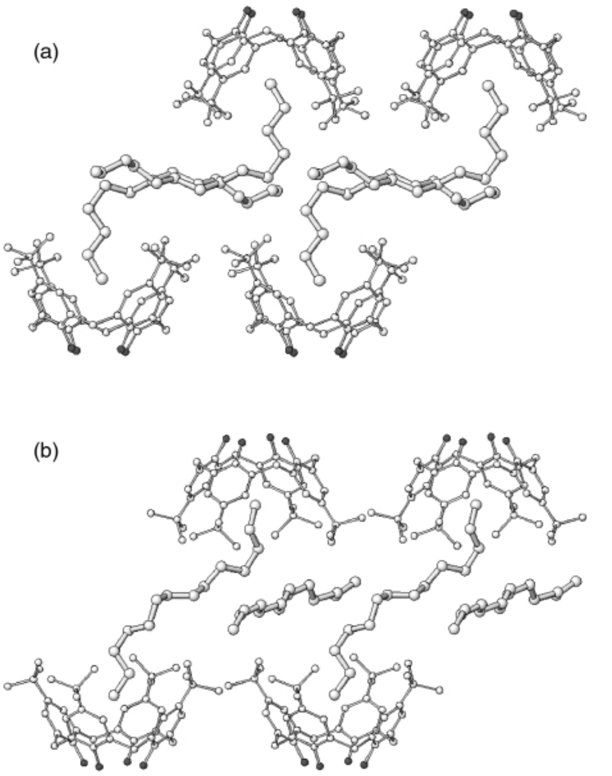

Fig. 3 Bilayer structure of the *p*-*tert*-butylcalix[4]arene–tetradecane inclusion/intercalation compound **1**·$C_{14}H_{30}$. (a) The end-to-interlayer spacing motif, (b) the end-to-end motif. Disordering in guest and host has been removed for clarity. Hydrogen atoms are removed for clarity; oxygen atoms are black.

identical, whereas the guest positions are disordered over two positions. The guest molecule in the interlayer space has a near all-*trans* conformation, but guest molecules that are included at either or both ends, are very different. All Bu^t groups in both structures are disordered over two positions with the site occupation *ca.* 0.5 , 0.4 to 0.6 and 0.3 to 0.7.

The bilayer structure of sodium calix[4]arenesulfonate, with the interlayer spacing occupied by water, has been compared to that of a clay.[8] The intercalated structure reported here shows a similar structure, although here it is a strictly neutral organic material, with lipophilic rather than hydrophilic regions. Examination of the bilayers of the 1 : 1 and 2 : 1 *p*-*tert*-butylcalix[4]arene–guest structural motifs suggests that the hydroxyl ends of the calixarenes are sufficiently polar to favour their mutual interaction in the bilayer, but allowing intercalation in the less polar interlamellar space. The present intercalated structure has well ordered layers separated by highly disordered interlayer regions giving a rather high diffraction *R*-value typical of clays. Clays also have the ability to tune the interlayer space by the intercalation of appropriate guests.[9] The *p*-*tert*-butylcalix[4]arene–tetradecane structure suggests that the distance between host bilayers may be tuned by intercalation of paraffins of appropriate length, and work to check this is currently in progress. Finally, noting that the self- and guest-included structures result from only slightly different crystallisation conditions, we anticipate that forming structures of *p*-*tert*-butylcalix[4]arene–tetradecane favouring only one of the two guest–host schemes (Fig. 3) may be possible by judicious choice of crystallisation conditions.

We have identified two new structural arrangements of supramolecular materials involving *p*-*tert*-butylcalix[4]arene. The self-included structure illustrates the collapsed lattice that likely occurs upon complete loss of guest from a *p*-*tert*-butylcalix[4]arene–guest inclusion compound. The structure formed with long paraffinic guests indicates synthetic access to a new class of calixarene-based lipophilic organic clay mimics. An upper limit to the length of the intercalating guests remains to be determined.

Notes and references

‡ *Crystal data*: **1**: $C_{44}H_{56}O_4$, $M = 648.89$, monoclinic, space group $P2_1/c$, $a = 9.5878(5)$, $b = 30.500(2)$, $c = 13.541(1)$ Å, $\beta = 109.852(1)°$, $U = 3724.5(4)$ Å^3, $T = 173$ K, $Z = 4$, $D_c = 1.157$ g cm^{-3}, μ(Mo-Kα) = 0.072 mm^{-1}, 43766 reflections measured, 9591 unique ($R_{int} = 0.0343$), $R = 0.0414$, $R_w = 0.0984$ [data $I > 2\sigma(I)$].

1·$C_{14}H_{30}$·$C_{44}H_{56}O_4$·$C_{14}H_{30}$, $M = 847.27$, triclinic, space group $P\bar{1}$, $a = 12.647(3)$, $b = 12.659(3)$, $c = 17.565(4)$ Å, $\alpha = 96.23(1)$, $\beta = 100.41(1)$, $\gamma = 90.12(1)°$, $U = 2748.8(11)$ Å^3, $T = 173$ K, $Z = 2$, $D_c = 1.024$ g cm^{-3}, μ(Mo-Kα) = 0.062 mm^{-1}, 17876 reflections measured, 6465 unique ($R_{int} = 0.125$), $R = 0.0889$, $R_w = 0.1975$ [data $I > 2\sigma(I)$].

Both structures were solved using direct methods and refined by full-matrix least-squares on F^2 using SHELXTL.[10] CCDC 158144 and 158145. See http://www.rsc.org/suppdata/cc/b0/b009133m/ for crystallographic data in .cif or other electronic format.

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