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Polymorphism of pure *p-tert*-butylcalix[4]arene: conclusive identification of the phase obtained by desolvation

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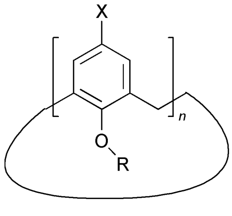
In its pure form, the well-known host compound *p-tert*-butylcalix[4]arene forms at least two polymorphs; one of these phases is now identified as that formed upon guest removal.

The calix[*n*]arenes (Scheme 1) comprise an extensive family of cyclic, polyphenolic compounds that can be tailored synthetically by altering X, R and *n*. Despite the obvious potential for constructing diverse and exotic molecules, we have generally found that the relatively simple calixarenes (X = H, Bu^t, SO_3^-; R = H; *n* = 4, 6, 8) exhibit the most interesting behaviour in the solid state.[1,2]

More than two decades ago, Andreetti and coworkers reported the X-ray structural analysis of a 1 : 1 complex, **1a**, of *p-tert*-butylcalix[4]arene, **1**, with toluene.[3] This pioneering study unambiguously confirmed the cone conformation of the host molecule, and showed that its cavity is capable of accommodating small aromatic species. Subsequent studies[4] have revealed that inclusion compounds involving **1** most often crystallize with the host molecules packed as bilayers. Furthermore, the bilayer packing mode can be subdivided into two major categories (Fig. 1): **A**, space group *P*4/*n*, host:guest ratio 1 : 1 and the guest is partially inserted into the calixarene cavity; **B**, space group *P*4/*nnc*, host : guest ratio 2 : 1 and two calixarene molecules face one another to form a dimeric capsule which can completely enclose the guest.

Thermogravimetric analysis of **1a** (Fig. 2) yields two distinct weight-loss events, each accounting for half of the total amount of toluene originally present in the material. The first weight-loss occurs with an onset temperature† of 108 °C. We have recently shown[2] that this corresponds to a transition from a structure of type **A** to one of type **B** as adjacent bilayers shift laterally by *ca.* 9 Å relative to one another. This process occurs as a single-crystal-to-single-crystal phase transformation and is triggered by relatively weak van der Waals interactions between host and guest molecules. Loss of the remaining toluene occurs with an onset temperature of 120 °C, yielding the host material in its pure, unsolvated form.

There has been some speculation with regard to the structure of **1** after guest removal. To date, desolvation of adducts of **1** has yielded only polycrystalline material, thus precluding unambiguous X-ray structural analysis. However, Ripmeester recently reported the crystal structure of pure **1** grown over a period of three days at 70 °C from a tetradecane solution of the compound.[5] In this phase, **1b**, the host molecules associate with one another as mutually self-included dimers in which each molecule inserts one its Bu^t groups into the other's cavity. This



Scheme 1

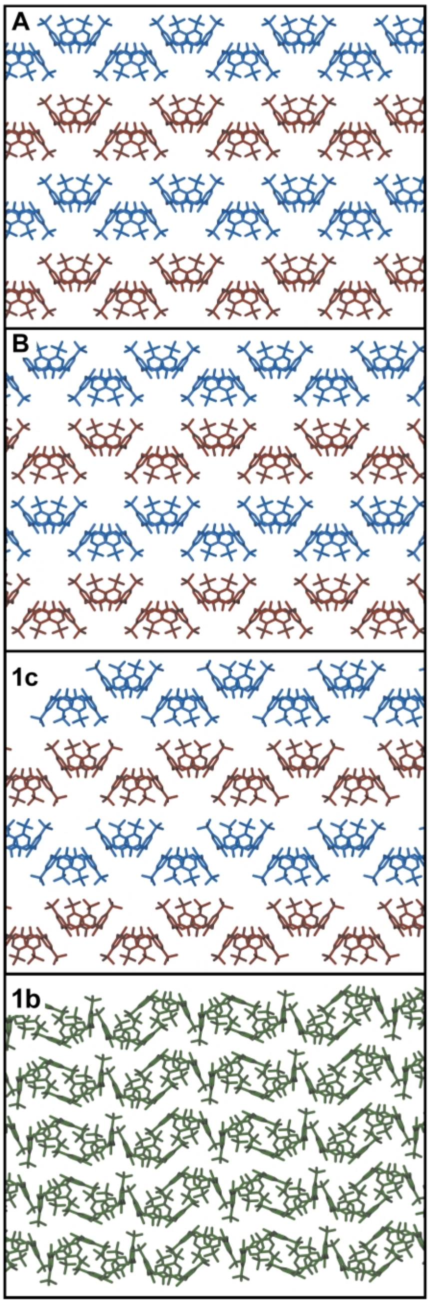


Fig. 1 X-Seed[7] projections contrasting **1c** with the two most commonly observed bilayer packing arrangements (**A** and **B**) of **1**. Adjacent bilayers are shown in alternating red and blue, respectively. In **A**, facing calixarenes are offset with respect to one another and the guest molecules (not shown) are partially inserted into their cavities. Adjacent bilayers of **B** are translated laterally relative to those of **A** such that facing calixarenes form dimeric capsules. In **1c**, facing calixarenes are slightly offset and form skewed, unoccupied capsules. The self-included dimer structure, **1b**, obtained from a tetradecane solution of **1** is also shown.

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arrangement is relatively well packed with an efficiency of 0.67. In the absence of any known polymorphic structures of pure **1**, it was reasonable to speculate that **1b** might be the phase that obtains upon guest removal. Indeed, this assumption was endorsed in a subsequent report[6] dealing with solid–vapor guest inclusion/decomposition processes involving **1** and a related compound. Therefore, in light of the recent interest in solid–solid phase transitions of **1**, it is relevant to finally address this issue conclusively.

We obtained diffraction-quality single crystals of **1** by sublimation of the compound at 280 °C under reduced pressure. The structure of this sublimed phase, **1c**, has already been described in detail.[2] Phase **1c** proves to be a polymorphic form of pure **1** and, in contrast to **1b**, has a relatively low packing efficiency of 0.59. The molecules pack in the familiar bilayer motif with facing calixarenes slightly offset relative to one another (Fig. 1). This arrangement results in the formation of skewed capsules, each with an estimated free volume of 235 Å^3. Furthermore, these capsules are unoccupied, thus accounting for the rather low efficiency of packing.

Following previously reported procedures,[3,5] we also prepared crystals of **1a** and **1b**. The former were heated at 220 °C under reduced pressure for three hours in order to remove all of the toluene guest molecules. X-Ray powder diffraction patterns of the various materials were recorded and are shown together in Fig. 3. It can clearly be seen that, upon removal of toluene by heating, **1a** undergoes a phase transition to eventually yield **1c**.

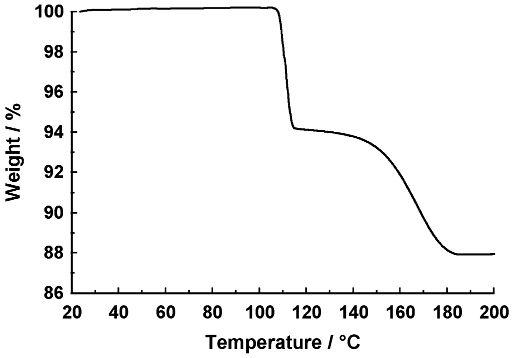

Fig. 2 Thermogravimetric analysis of **1a**, the 1 : 1 host : guest complex of **1** and toluene. The sample was heated at a rate of 0.1 °C/min and purged with nitrogen gas flowing at 40 ml min^{-1}.

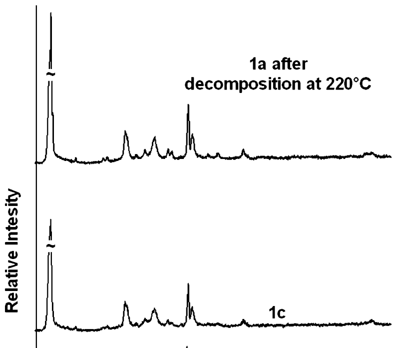

Fig. 3 X-Ray powder diffraction patterns showing that, upon removal of toluene, the host molecules of **1a** revert to phase **1c** rather than **1b**.

We have similarly investigated 1 : 1 host : guest adducts of **1** with *p*-chlorotoluene, *p*-fluorotoluene, chlorobenzene and fluorobenzene. In each case, we found that guest removal results in phase **1c**. Although we concede that it may still be possible to form phase **1b** by means of guest removal, we have not yet observed this to be the case for the limited series of inclusion compounds considered here.

It is important to note that, with regard to the arrangement of the calixarene molecules, the fundamental difference between **1c** and the structures of types **A** and **B** is that adjacent bilayers are shifted laterally relative to one another (Fig. 1). In all three structural types, the molecular spacing, both within and between the bilayers, is practically identical. The surfaces of the bilayers are composed of bulky Bu^t groups, interspersed with calixarene cavities and the crevices between adjacent Bu^t moieties. Thus it is not difficult to envision how adjacent bilayers are able to slide over one another in order to facilitate guest uptake or release as a solid/liquid or solid/vapor inclusion reaction. As yet, the influence of weak van der Waals interactions on both the stability as well as the dynamics of molecules in the solid state has been largely overlooked. However, we have shown that studies of simple, yet elegant model systems provide valuable insight into the organic solid state, and that a high degree of cooperativity exists between molecules during phase transitions.

Notes and references

† The onset temperatures given here do not comport with those reported previously by us (see ref. 2). It is well-known[8] that guest-loss onset temperatures are highly dependent on factors such as heating rates and particle size distribution. In the present study, a relatively low heating rate was used in order to clearly distinguish the two weight-loss events.

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