

Electrostatic and short-range interactions compete in directing the structure of *p*-*tert*-butylcalix[4]arene inclusion compounds of fluorinated benzenes†

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p-*tert*-Butylcalix[4]arene guest-host compounds with fluorinated benzenes show several structural motifs, thus indicating that the guest-host structure can be tuned to produce either a form with included guests or a form where the host self-includes with the guests outside the cavity.

The calixarenes are versatile materials that have been studied extensively, both as host materials and as platforms for the synthesis of designed, specific receptors.¹ *p*-*tert*-butylcalix[4]arene (tBC), one of the smaller, simpler members of this subgroup, is a versatile host that forms inclusion compounds with a variety of guest molecules.^{2,3} The most common structural themes encountered are based on bilayer structures of 1 : 1 and 2 : 1 host-guest stoichiometry where the guest either lies in a single cavity roofed by *tert*-butyl groups in the next layer, or in a capsule consisting of two opposed calixarene molecules.²⁻⁶ Other forms include an intercalation system with long-chain guests extending from inside the cavity to the interlayer space,⁴ and those where supramolecular stabilization gives rise to amine clusters by interacting with the calix *via* weak interactions and H-bonding.⁵ As well, there are dense⁴ and open guest-free polymorphs,⁶ the latter of which retains the bilayer motif and has been shown to take up small guests without changing structure.⁷

Recently, calculations⁸ have shown that the various solid-state tBC structures can be understood in terms of short-range intermolecular interactions. In seeking to extend the range of interactions that can be used to tune the guest-host structural motifs, we have used fluorine-substituted benzenes, as previous theoretical⁹ and experimental¹⁰ studies have indicated that the hexafluorobenzene molecule may well interact *via* electrostatic interactions in a supramolecular environment. The strategy employed was to study a number of tBC compounds incorporating fluorinated benzenes C₆F_{*n*}H_{6-*n*}, with *n* = 1, 3 (symmetric form), 4 (two isomers, 4a (1,2,4,5), and 4s (1,2,3,5)), 5, 6. All the crystals were grown from excess tBC in the fluorinated guest as solvent in a sealed vial at 70 °C.

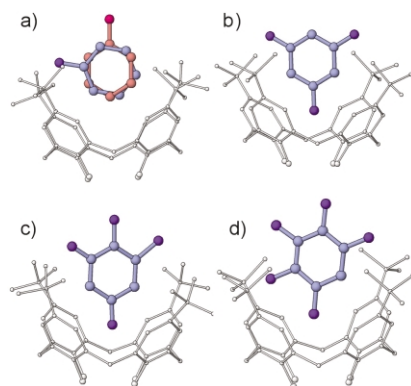


Fig. 1 The host-guest geometry for **1**(a), **2**(b), **3**(c) and **5**(d). Only one of the symmetry-equivalent positions of the guest is shown.

† Electronic supplementary information (ESI) available: X-ray details. See <http://www.rsc.org/suppdata/cc/b4/b401269k/>

The structures with *n* = 1 (**1**), *n* = 3 (**2**), *n* = 4s (**3**), and *n* = 5 (**5**) all have a standard 1 : 1 structural motif, as observed for toluene^{11,12} (Fig. 1).‡ For **1**, as for the toluene inclusion, the crystal is tetragonal, *P4/n* at 21 °C; here, we correct a structure reported earlier (ref. 13) regarding the orientation of the guest in the cavity: the C-F bond points outside the cavity, but is disordered over two inequivalent positions: one guest position, with a total fractional occupancy of 0.315 has the C-F bonds point approximately along the 4-fold axis of the cavity, the others taking up 4-fold disordered positions with the C-F bond at an angle of 78.3° to the 4-fold axis. For **1** (at -100 °C), and **2** and **5** at both -100 and 21 °C the structure shows the monoclinic distortion (*P2/c*) that was observed for toluene at low temperatures where the cavity has only two-fold symmetry. Although **3** appears to be isostructural to the room

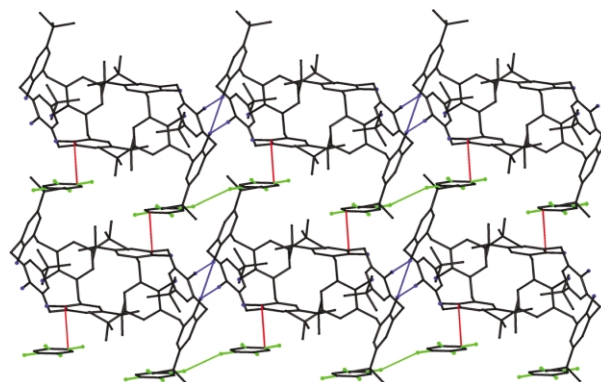


Fig. 2 Structure of **4** showing the layers of self-included host molecules and intercalated guests.

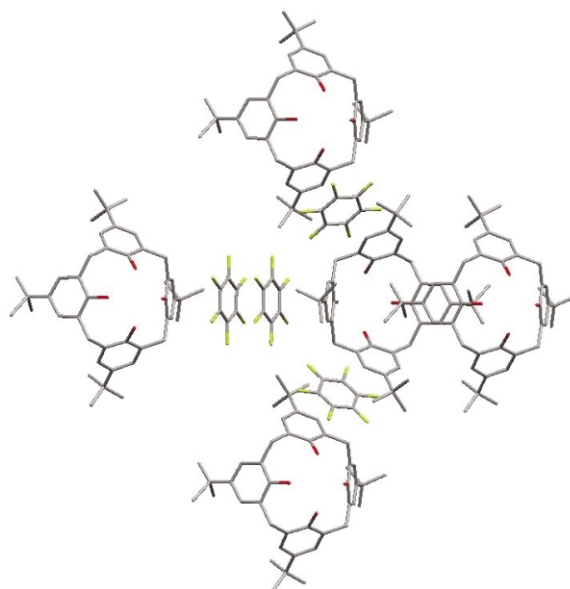


Fig. 3 Structure of **6** viewed along the *c* axis showing π - π stacking of the *exo*-guest and self-included host dimers.

Table 1 Summary of X-ray structural data for structures 1–6

Compound	1	1	2	3	4	5	6
<i>T</i> (°C)	21	−100	−100	−100	−100	−100	−100
<i>a</i> (Å)	12.8581(2)	18.0102(8)	17.910(2)	12.6344(9)	12.9108(10)	17.9842(18)	23.310(4)
<i>b</i> (Å)	12.8581(2)	13.1981(6)	13.467(2)	13.5174(9)	13.4629(10)	13.6634(14)	22.415(4)
<i>c</i> (Å)	13.2833(3)	18.0381(8)	17.840(2)	12.6433(9)	14.8239(11)	17.9165(18)	9.8489(16)
α	90	90	90	90	67.479(15)	90	90
β	90	89.975(10)	90.17(1)	90.05(1)	84.212(15)	90.262(15)	100.22(2)
γ	90	90	90	90	67.906(15)	90	90
System	tetragonal	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
Space group	<i>P4/n</i>	<i>P2/c</i>	<i>P2/c</i>	<i>P2/n</i>	<i>P$\bar{1}$</i>	<i>P2/c</i>	<i>C2/m</i>
Ref/ <i>R</i> _{int}	2833/.019	11349/.056	12159/.050	5589/.051	8993/.040	7713/.1132	2774/.088
<i>R</i> ₁ (2 σ)	.0527	.0644	.0558	.0543	.0552	.0627	.0638
<i>R</i> _w (all)	.1629	.1894	.1507	.1417	.1480	.1681	.1759

temperature toluene inclusion even at −100 °C, it has been solved as a twinned monoclinic (*P2/n*) structure.

It is clear from present and previous studies that small aromatic guest molecules included in the tBC cavity are oriented such that the plane containing the guest lies approximately along the cavity axis. It is interesting to note that in general C–H is preferred to C–F inside the cavity, but when an inward directed C–F is unavoidable, as with **2**, **3** and **5**, a compound still forms in spite of the less favoured C–F orientation. Steric interactions appear to inhibit an inward directed C–F adjacent to the axial position (~60° off-axis). This may explain why **4s** is able to be included inside the tBC cavity and **4a** is not.

The other structure with *n* = 4a (**4**) is in fact quite different. In this case, the host molecules form a layered structure consisting of self-included dimers (Fig. 2), much as seen for the dense guest-free material. Unlike the guest-free case however, adjacent dimers interact *via* intermolecular hydrogen bonding (O–O distance of 2.92 and 3.02 Å). A single layer of guest molecules intercalates between the host layers with the guests weakly π -bonded with the inserted phenyl group of the tBC dimers (C–C distances of 3.32 and 3.38 Å, dihedral angle between phenyl planes 6.85°). A short F–F contact distance of 2.92 Å is observed for adjacent guest molecules.

With *n* = 6 (**6**) the structure has 1 : 2 host–guest stoichiometry with the host molecules again forming self-included dimers. Fig. 3 shows the structure viewed down the *c* axis. The *exo*-cavity guest molecules act as π stacked bridges between adjacent host dimers. In addition, the inserted phenyl groups of the tBC host π -stack with adjacent dimers along *c*. All of the π -interacting phenyl groups are separated by 3.60–3.72 Å. The dihedral angle between the plane containing the guest molecules and that of the tBC phenyl group is 5.77(14)° for dimers bridged by a single guest and 14.47(7)° for those linked by a pair of guest molecules. As all the host phenyl groups interact with adjacent dimers, the dimers can be described as having a coordination number of eight in a distorted cube arrangement.

Clearly, the issue is not one of steric interactions forcing the guest to be *exo* to the cavity, as pentafluorobenzene and hexafluorobenzene hardly differ in size. The π – π stacking is reminiscent of the hexafluorobenzene–aromatic structures, where alternating molecules form extended stacks. It appears that hexafluorobenzene can be used as a synthon to direct structures away from those where short-range interactions dominate the packing by introducing electrostatic interactions that compete.

The densities of the compounds vary from 1.15 g cm^{−3} for **1** to 1.34 g cm^{−3} for **6** with the rest between 1.21 and 1.23 g cm^{−3}. The low density for **1** is not surprising since the guest is seen to be disordered and highly dynamic even at low temperature, suggesting excess free space is available within the cavity. The increased density for **6** is also not unexpected as the stoichiometry is different and the observed π -stacking may improve the packing efficiency.

We note that the irregularities in structural motifs on going from *n* = 1–6 may be indicative of a number of factors. In the first instance, we do not know enough about the electronic structure of the fluorobenzenes to see if there is a regular trend of molecular

quadrupole moments with the degree of fluorine substitution. Second, the directing effects are likely to be subtle, so that it may well be possible to find more than one structural motif with the same guest, as was indeed observed in the case of amine guests where H-bonding and short-range interactions compete,⁵ and where the structures can be tuned by controlling temperature and concentration.

Notes and references

‡ Crystal data for **1** to **6**: All data were collected on a Bruker SMART diffractometer with Mo K α radiation. In each case a full sphere of data was collected up to theta of 28° (25° for **5**, 21° for **6**). The data are summarised in Table 1. CCDC 237575–237581. See <http://www.rsc.org/suppdata/cc/b4/b401269k/> for crystallographic data in .cif or other electronic format.

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