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Polymorphism of pure *p-tert*-butylcalix[4]arene: subtle thermally-induced modifications

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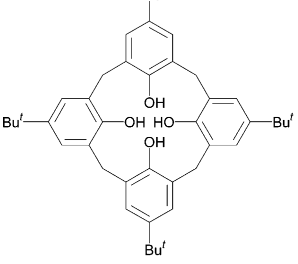
A low-density polymorph of the well-known host compound *p-tert*-butylcalix[4]arene undergoes subtle structural changes when heated and cooled.

As part of our ongoing studies[1] of the fascinating solid-state behaviour of the calix[*n*]arenes, we recently reported that the well-known host compound *p-tert*-butylcalix[4]arene (**1**, Scheme 1) can undergo dramatic single-crystal to single-crystal phase transitions.[2] We showed that the pure sublimed host material adopts a bilayer type of structure, **2**, featuring pairs of calixarenes facing one another in a slightly offset fashion. This motif results in the formation of isolated pockets of about 235 Å^3 per dimeric unit. Although there are no channels leading to these voids, the crystal is able to absorb vinyl bromide into its lattice with concomitant translation of adjacent bilayers by about 5.9 Å relative to one another. More recently, we revealed that **2** is also capable of absorbing volatile gases such as O_2, N_2 and CO_2, but without lateral shifting of the bilayers taking place.[3]

We have noted that a more efficiently packed polymorph, **3**, previously reported by Ripmeester,[4] does not appear to participate in guest sorption processes. In an effort to produce large quantities of polymorph **2** for further study, but without resorting to sublimation techniques, we investigated the possibility of obtaining the desired phase by desolvation of a toluene solvate of **1**. We determined that phase **2** can indeed be obtained by heating the solvate at 220 °C under reduced pressure for three hours.[5] Subsequently, Ripmeester showed that a complex relationship exists between the various polymorphic forms of pure **1** with regard to desolvation of its inclusion compounds.[6] In that report it was also revealed by differential scanning calorimetry (DSC) that the sublimed crystals undergo a slight, reversible phase change at about 92 °C whilst cooling to room temperature. Therefore, Ripmeester states that “the phase that Atwood *et al.* found upon sublimation is in fact not the same phase for which they determined the structure”. But, of course, one should bear in mind that we are interested in using the compound under ambient conditions. Thus, cooling of the material to room temperature should be taken as implied if not explicity stated when we consider the structure of the sublimed material. Nevertheless, we became intrigued by the various thermally-induced changes that **2** evidently undergoes.

Crystals were grown by sublimation as previously described.[2] A specimen suitable for single crystal X-ray diffraction analysis was selected and mounted on a SMART Apex diffractometer. A device had been constructed to bathe the crystal in a heated stream of nitrogen gas and intensity data were collected at 130 °C. We now compare the resulting structure (**2c**)† with those of two similarly prepared crystals, but determined at −100 °C (**2a**)[2] and 20 °C (**2b**)‡ (see Fig. 1).§



p-tert-butylcalix[4]arene (**1**)

Scheme 1

Each of the three structures **2a–2c** conforms to the space group $P2_1/n$, with the asymmetric unit comprising a complete calixarene molecule. The now familiar **abcd** bilayer structure[2] is evident in all three cases and layers of facing calixarenes are in van der Waals contact by virtue of their respective *tert*-butyl groups. Fig. 1a shows

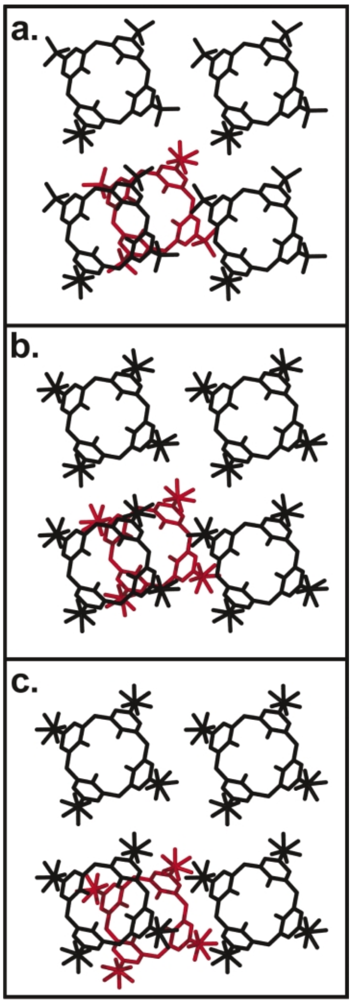


Fig. 1 Comparison between structures of sublimed **1** determined at (a) −100 °C, (b) 20 °C and (c) 130 °C (viewed along [010]). In each case, four calixarenes (black) belonging to the same layer are shown with their cavities facing away from the viewer. There is almost no variation in the relative positions of the molecules within each layer as the temperature is increased. One calixarene from the adjacent, facing layer is shown in red to highlight the subtle differences in the relative placement of neighbouring layers.

that only one of the *tert*-butyl groups is disordered over two positions at −100 °C. Each of the ordered *tert*-butyl groups is positioned between two proximal *tert*-butyl groups of a facing calixarene embedded in an adjacent layer. The disordered group is located in the midst of four *tert*-butyl groups, each belonging to a separate calixarene of the facing layer, and thus has more freedom of rotation about the Csp^2–Csp^3 single bond.

Fig. 1b shows that the packing mode of facing layers relative to one another is largely the same at 20 °C as at −100 °C. However, all four *tert*-butyl groups in **2b** are disordered over two positions at room temperature. This observation is easily rationalised since the bilayers are stacked along the crystallographic b axis, which elongates by 0.55 Å upon warming from −100 °C to 20 °C. Thus all of the *tert*-butyl groups are bestowed with more freedom of rotation.

The crystallographic b axis of **2c** is elongated by 0.50 Å in comparison to that of **2b**. Although the relative positions of the calixarenes within a layer remain seemingly unchanged upon heating to 130 °C, a lateral shift by 2.34 Å of one layer occurs with respect to its adjacent, facing layer (Figs. 1c and 2). This shift has a profound effect on the geometry of the lattice void between offset, facing calixarenes. In **2a** and **2b**, the approximately hourglass-shaped void has a diameter of *ca.* 2.42 Å at its narrowest point. In **2c**, a *tert*-butyl group of one of the calixarenes guards the opening of the other such that the diameter of the narrowest point of the void between the two molecules shrinks to 1.74 Å. On the atomic scale, the two calixarene cavities effectively become isolated from one another at higher temperatures (> *ca.* 92 °C) whereas they are merged at lower temperatures.

In conclusion, we have shown that the structure of sublimed **1** does not differ significantly when determined at either −100 °C or room temperature. Although the compound is vaporised at 280 °C, the crystals grow on the walls of the sublimation vessel where the temperature is approximately 150 °C. DSC studies reported by Ripmeester show that the structure of the sublimed material *before cooling to below 92 °C* is not identical to that at room temperature. We have now described the structure of this high temperature phase.

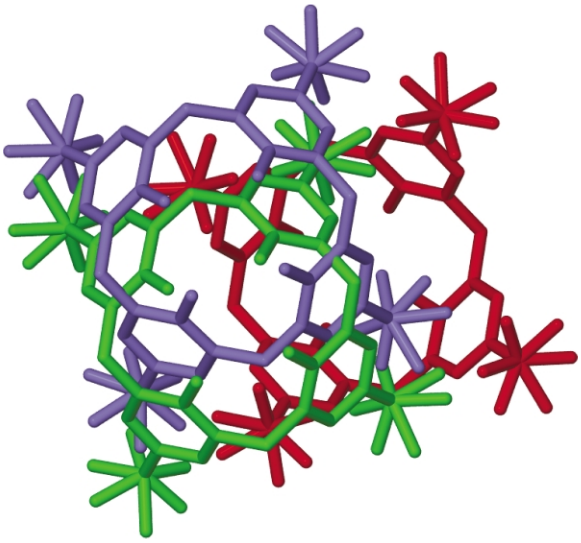


Fig. 2 X-Seed[7] overlay of the void-forming calixarene dimers of **2b** (red/green) and **2c** (red/blue). The molecule shown in red is common to both structures. The difference in location between the blue and green molecules represents a lateral shift of 2.34 Å upon heating the crystal from room temperature to 130 °C.

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Notes and references

† Crystal data for **2c**: $C_{44}H_{56}O_4$, M = 648.89, colorless prism, 0.40 × 0.30 × 0.15 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 12.804(3), b = 26.742(5), c = 12.799(3) Å, β = 90.13(3)°, V = 4382.5(15) Å^3, Z = 4, D_c = 0.983 g cm^{-3}, F_{000} = 1408, MoKα radiation, λ = 0.71073 Å, T = 403(2) K, $2\theta_{max}$ = 44.0°, 7552 reflections collected, 5188 unique (R_{int} = 0.3464). Final *GooF* = 1.090, $R1$ = 0.2373, $wR2$ = 0.5396, R indices based on 845 reflections with $I > 2\sigma(I)$ (refinement on F^2), 72 parameters, 0 restraints. Lp and absorption corrections applied, μ = 0.061 mm^{-1}. Most of the non-hydrogen atoms were located by direct methods. The remaining approximate atomic positions were derived from difference electron density maps. Owing to extensive thermal motion, as expected, all atoms were refined with isotropic thermal parameters. During early stages of refinement it was ascertained that all four *tert*-butyl groups were disordered over two positions each. Each of the four arene rings, together with its hydroxyl and disordered *p*-*tert*-butyl moieties, was refined as an idealized rigid group. Although the value of $R1$ is rather high, the structure is sufficiently well-resolved to allow direct comparison with previously reported structural modifications of **1**.

‡ Crystal data for **2b**: $C_{44}H_{56}O_4$, M = 648.89, colorless prism, 0.40 × 0.35 × 0.35 mm^3, monoclinic, space group $P2_1/n$ (No. 14), a = 12.581(2), b = 26.239(2), c = 12.718(2) Å, β = 90.34(2)°, V = 4198.2(10) Å^3, Z = 4, D_c = 1.027 g cm^{-3}, F_{000} = 1408, Enraf Nonius CAD4 diffractometer, CuKα radiation, λ = 1.54060 Å, T = 293(2) K, $2\theta_{max}$ = 119.9°, 12369 reflections collected, 5875 unique (R_{int} = 0.0315). Final *GooF* = 1.022, $R1$ = 0.0545, $wR2$ = 0.1345, R indices based on 3470 reflections with $I > 2\sigma(I)$ (refinement on F^2), 586 parameters, 28 restraints. Lp and absorption corrections applied, μ = 0.496 mm^{-1}. Most of the non-hydrogen atoms were located by direct methods and models for the disordered *tert*-butyl groups were completed by difference electron density synthesis. Each *tert*-butyl group was modeled over two positions with a total site occupancy of one. Hydroxyl hydrogen atoms were located in difference electron density maps and were refined with restraints. All non-hydrogen atoms were refined with anisotropic thermal parameters.

§ CCDC 231714–231715. See http://www.rsc.org/suppdata/cc/b4/b402452b/ for crystallographic data in .cif or other electronic format.

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