What we have learned from the study of solid *p-tert*-butylcalix[4]arene compounds

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The study of solid *p-tert*-butylcalix[4]arene and its compounds with a variety of techniques has provided a good understanding of the versatility of this host molecule, how to induce a number of distinct host–guest motifs, its molecular recognition properties, the complex phase relationships and unique properties such as gas adsorption without having obvious channels.

Introduction

The capture, storage, stabilization, transformation and transport of guest species in a range of host materials for a variety of possible applications has been a very active area of research for some time. The volumes on *Comprehensive Supramolecular Chemistry*[1] give an excellent summary of the state of affairs in the mid-1990s. Since then, there have been major advances. Several very different approaches can be distinguished, one dealing with the synthesis of molecular receptors in solution, another with the development of novel solid phases with guest–host properties. Sometimes the molecular concepts used in solutions are transferred to the solid state, a practice that often leads to quite inappropriate models: molecular recognition in solution may well be describable in terms of one or two key interactions, whereas in the solid state, even if it is a molecular lattice, this is seldom true as lattice stability will depend on the sum of many interactions.

Hof and Rebek[2] have recounted the development of solution-based receptors, from initial work on carcerands and cavitands, binding guests irreversibly[3,4] to assembled capsules where reversible binding and exchange was possible.[5] The size of such assembled capsules has grown considerably.[6,7] Although the emphasis has been on increasing size,[8] there are outstanding problems, including the characterization of the capsular content,[6–8] which often is highly disordered and accessible only by indirect methods. In order to be useful, capsules also need to be stable with respect to guest removal and exchange, something that has not been demonstrated for many large capsules. On the other hand, soluble capsules tend to be able to bind and exchange guest species, but detailed

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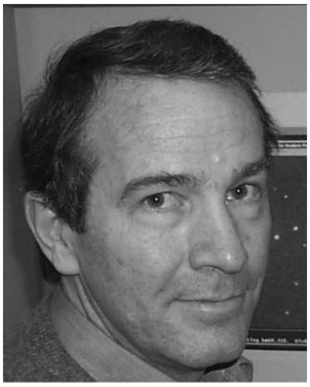
John Ripmeester

John Ripmeester was born in Voorburg, the Netherlands, in 1944. He received BSc (Hons. Chem.) and PhD (Phys. Chem.) degrees from the University of British Columbia, the latter in 1970 under guidance of Basil Dunell. He then took up a position as research associate at the University of Illinois (Urbana-Champaign) with Herbert Gutowsky, followed by a post-doctoral fellowship in the Division of Chemistry at the National Research Council with Don Davidson. He became a staff member at NRC in 1974, first with the Division of Chemistry where he became head of the Colloid and Clathrate Chemistry Section, then with the Steacie Institute for Molecular Sciences upon its establishment in 1991. Currently he is a Principal Research Officer and leads the Materials and Structure and Function Group. His research interests include the chemical applications of solid-state NMR spectroscopy, the development of multi-technique approaches to the characterization of materials, supramolecular chemistry, porous materials, clathrates, gas hydrates, and other guest–host materials. He has received a number of awards for his scientific contributions, including the Barringer Award in Spectroscopy, a Fellowship of the Royal Society of Canada, and Her Majesty the Queen's Golden Jubilee Medal.



Gary Enright

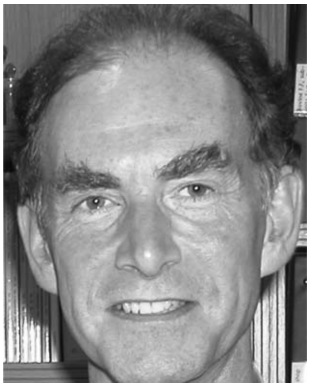
Gary Enright was born in 1946 in Vancouver (Canada). He received his BSc degree in Mathematics and Physics from the University of British Columbia (1968) and his PhD in Molecular Physics (1974) from the University of Toronto. In 1975 he joined the staff at the National Research Council of Canada where he is presently a Senior Research Officer. From 1975 until 1985 Dr. Enright's research was concentrated on X-ray diagnostics of laser-produced plasmas. From 1986 until 1992 his research was focused on the physics of X-ray lasers. In 1992 he joined the Steacie Institute for Molecular Sciences where he is an X-ray crystallographer with the Materials Structure and Function Group. His primary research interest is the study of structure and dynamics in guest–host materials.

structural information cannot be obtained and recourse has to be taken to modeling.[9]

The other approach to the capture, storage and transport of guest molecules is the development of novel solid frameworks. Here, the progression has been from frameworks only stable in the presence of guests (clathration – involving the transformation of a dense crystal form to an open structure containing the guest) to those that are able to take up guest species reversibly, thus exhibiting zeolite-like properties (sorption – the relatively free transport of guests into a framework with permanent void space). The latter has been demonstrated well by the numerous metal–organic frameworks which combine inorganic building blocks with organic linkers.[10] The emphasis in this area has been on building "robust" frameworks – thus mimicking zeolites. A still emerging concept is the construction of frameworks where the function of the framework might be controllable by some external stimulus, and such materials, known as dynamic, soft or flexible sorbents,[11] tend to show more complex behaviour that is neither pure clathration nor simple sorption often involving structural changes both at the molecular and crystal lattice levels as well as dynamics.[12–14] Key questions that still require further investigation include how crystalline materials respond to adsorption–desorption cycles if structural changes are involved, and how large structural changes can be accommodated by crystalline frameworks. Although dynamic aspects need to be studied by spectroscopic and thermal methods, an important aspect is the survival of single crystals during adsorption–desorption cycles so that the structural aspects of the processes also become accessible. The simple calixarene discussed below has played a major role furthering our understanding, in that it has provided a platform for systematic evaluation of its physicochemical properties.

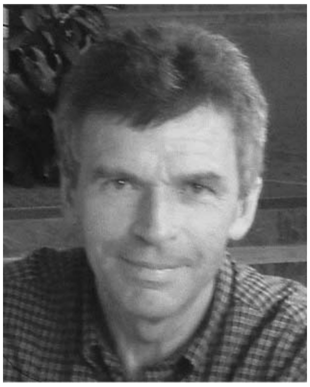
Results

This article will look at the past 10 years or so, a period during which our work on calixarenes developed. It started with a very simple question about the initial structural work on inclusion compounds of *p-tert*-butylcalix[4]arene (tBC): Why do the structural models for tBC compounds refine so



Christopher Ian Ratcliffe

Christopher Ian Ratcliffe was born in 1951 in Huddersfield, UK. He attended Durham University where he received his BSc (Honours) in Chemistry in 1972 and his PhD, under the supervision of Professor Tom Waddington, in 1975. He was a postdoctoral fellow with Professor Basil Dunell at the University of British Columbia and held Research Associate positions with Professsor George Wilkinson at King's College London and Professor Don Irish at the University of Waterloo before joining the National Research Council of Canada in 1982, where he is a Senior Research Officer with the Materials Structure and Function Group, Steacie Institute for Molecular Sciences. His current research interests include solid-state NMR spectroscopy, molecular dynamics, host–guest materials, gas hydrates, nanoparticles and nanoconfinement.



Konstantin A Udachin

Konstantin A Udachin was born in 1951 in Novorossiisk (Russia). He attended Donetsk State University (Ukraine), where he received his BSc (Honours) in Chemistry in 1973. He completed has PhD program in Physical Chemistry under the supervision of Dr V. I. Belevantsev at the Institute of Inorganic Chemistry, Russian Academy of Sciences (Novosibirsk), in 1980. In 1985 he started postdoctoral work under the supervision of Dr Yu. A. Dyadin at the same Institute, and his research there focused on the investigation of clathrate hydrates and other inclusion compounds. He first came to NRC on a NATO Fellowship and currently is an X-ray crystallographer with the Materials Structure and Function Group, Steacie Institute for Molecular Sciences. His recent accomplishments include the analysis of extremely complex disordered host–guest structures and the synthesis and structural characterization of clathrate hydrates at low temperatures by single-crystal X-ray diffraction.

Igor Moudrakovski

Igor Moudrakovski received his MSc in 1982 from Novosibirsk State University (Russia). This was followed by a PhD degree in 1987 from the Institute of Catalysis, Russian Academy of Sciences (Novosibirsk) under the supervision of Pof. Viacheslav Mastikhin, specializing in applications of solid-state NMR spectroscopy to heterogeneous catalysis. Igor first came to the National Research Council in 1992 on a fellowship where he continued his work on NMR spectroscopic investigations of solids. Since then he has joined the staff of the Steacie Institute for Molecular Sciences, NRC, where he is a Senior Research Officer with the Materials Structure and Function Group. Recently he has developed novel approaches for the characterization of porous solids and dynamic processes that occur in these materials using hyperpolarized Xe NMR spectroscopy and microimaging. With the arrival of the 900 MHz solid state NMR spectrometer at NRC he is pioneering the use of low gamma nuclei for a variety of materials applications. When he is not in the lab, you will find him fly fishing in local trout lakes.

poorly?[15] In answering this question, a variety of quite fundamental concepts had to be tackled. As a result, tBC, first characterized in the 1970s[16] and used mainly as a platform for synthetic modification,[17] has come into its own as an interesting material, arguably much more interesting than many of the hundreds if not thousands of derivatives that have been synthesized on the basic calixarene platform. The evolution of the structural and conceptual model for tBC guest–host materials has been documented a number of times.[15]

After many years of work on clathrate hydrate inclusion compounds, we felt the need to broaden our horizons, and looked for another guest–host system that might provide both challenges and opportunities, and settled upon the calixarenes. Calixarene chemistry was introduced to the modern research community by C. D. Gutsche,[16] and the first single crystal structures were solved by Andreetti and the Parma group in 1979 (Fig. 1(a)).[18] Only a few guest materials based on simple calixarenes had been prepared at the time, with both 1 : 1 and 1 : 2 host–guest structures identified. Upon examining the data we found that the structural models after refinement had remarkably poor agreement factors for such a relatively simple, small-molecule system.[15] What is more, the initial structural reports seemed to have set a precedent, as almost all subsequent structures reported involving the tBC platform had residuals that were quite large.[15] Another point was that C–H···π interactions were implicated in the stability of the compounds, suggesting that the host system could be seen as a molecular receptor with specific interactions between guest and host.[16a,19] On the other hand, simple molecules, including aromatics, were not observed to bind to calixarenes in solution under ambient conditions.[20] This would suggest that multiple short-range interactions are responsible for the stability in the solid state, making these materials more like extended clathrate frameworks than molecular receptors.

Initial ^{13}C solid-state NMR work[21a,b] showed a room-temperature spectrum in agreement with the fourfold symmetric structural model inferred from diffraction, however, a temperature dependent NMR study showed that a symmetry-lowering transition took place below 250 K.[21b] We suggested to a crystallographer colleague that a look at the structure of the low-temperature form might be interesting, but the answer came back that there was apparently no change from the room temperature structure on cooling to ~200 K. There did not appear to be a solution to this inconsistency between crystallographic and NMR data, and the problem was shelved for a time.

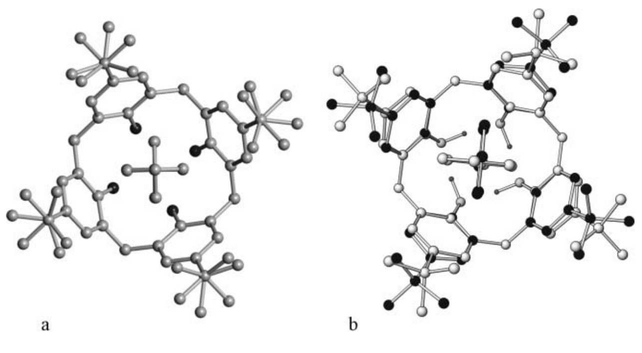


Fig. 1 The evolution of the tBC–toluene structure: (a) original room-temperature structure, note symmetrical calixarene, *tert*-butyl disorder, high residuals ($R1$ = 0.092); (b) the low temperature structure: note split positions of the aromatic rings and *tert*-butyls, good residual ($R1$ = 0.051). However, the symmetry is incorrect, as shown by NMR spectroscopy: there is a twofold distortion (see Fig. 3).

A reorganization at NRC brought both a single-crystal diffractometer and a crystallographer to our group. The old problem of the tBC structure resurfaced, and a PhD student was persuaded to look at tBC compounds in general, and the old inconsistency in structural information in particular. The molecular motion of the toluene guest was studied in detail with ^{2}H NMR spectroscopy. Below 250 K (and the calorimetric phase change) the number of symmetry-related sites of the guest was inferred to be lower than at room temperature: from fourfold rotation to twofold flips of the toluene ring (Fig. 2 (left), implying a distortion of the calixarene cavity from fourfold symmetry.[22] With a twofold distortion built into the structural model, the low-temperature structure could be refined. This improved the residuals, and it resolved the difficult-to-understand disorder of the *tert*-butyl groups (Fig. 1(b)). There was in fact a good correlation between the toluene guest orientation and a distortion of the tBC host molecule that locally broke the fourfold symmetry. So, the lower symmetry induced in the tBC molecule is accompanied by a reorientation of the *tert*-butyl groups (Fig. 1(b)). Another feature noted was that the upper end of the calixarenes was seen to be dynamic, as the ^{2}H NMR spectrum for the *tert*-butyl groups at room temperature showed considerable narrowing beyond that expected for the internal rotations of the *tert*-butyl group (Fig. 2 (right)). Likely, in the room-temperature phase the calixarene switches between twofold distorted forms at the same rate as the fourfold motion of the

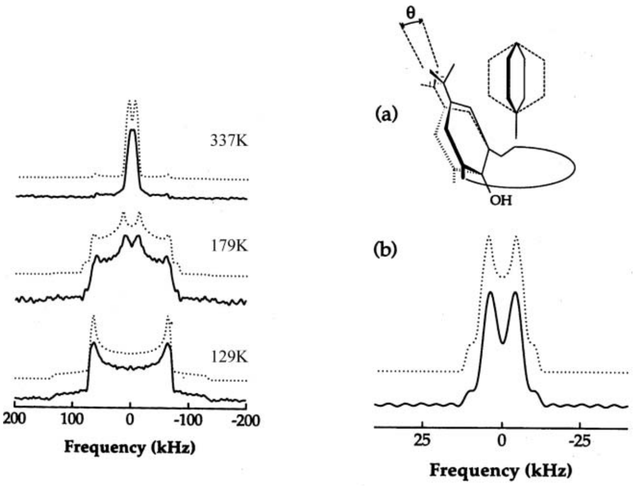


Fig. 2 (left) ^{2}H NMR lineshapes of toluene-d$_5$–tBC compound. The dashed lines are calculated for a static aromatic ring (129 K), twofold flips of the aromatic ring (179 K), and fourfold rotation (337 K); (right) ^{2}H NMR lineshapes of the toluene–tBC (*tert*-butyl-d$_9$) compound. The simulated lineshape is for *tert*-butyl groups performing C_3 rotation of the methyl groups, C_3' rotation of the *tert*-butyl groups, plus twofold jumps between the two positions indicated (15.4° apart).

toluene guest. As well, because ring current effects induce a large ^{13}C complexation induced shift (CIS) for a methyl group inserted in the cavity in the solid state,[21] it was possible to see that the majority of the methyl groups were deeply inserted in the cavity, but that some 5% or so were inserted the other way, and this was confirmed in the X-ray analysis. As well, toluene is not inserted exactly along the symmetry axis but at a tilt angle of $7 \pm 2°$, determined from both X-ray diffraction and NMR. At this stage one can conclude that the structure is far more complex than indicated initially and that it is a highly dynamic structure.

There remained an interesting dilemma: we had a good structural model from diffraction as judged by the residuals,[22] which was still inconsistent with the lower symmetry inferred from NMR for the low-temperature phase[21b] The NMR spectra suggested that the twofold distortions of the calixarenes were correlated in some way, but the diffraction data did not pick this up. This problem was resolved as a result of some surprising observations. During our initial low-temperature (173 K) X-ray data collections with Cu radiation (1.54 Å) additional reflections, indexed as half-integral with respect to the room-temperature lattice, were observed immediately upon cooling. These clearly indicated that some sort of superstructure was present.

Attempts to collect a data set based on the superlattice failed as these additional reflections disappeared again over a period of about 6 h. Meanwhile, a new CCD diffractometer had been purchased, and one of the first crystals studied was tBC–toluene. With Mo radiation, the extra reflections proved to be persistent! Now a structural model for the low-temperature phase could be constructed that was also consistent with the NMR data (Fig. 3).[23] We also had to conclude that the structural details inferred were in fact dependent on the wavelength of the radiation used, something that makes one think about fundamentals and the limitations imposed by the instrumentation that we use. The different results obtained using Cu *vs.* Mo radiation were ascribed to the fact that Cu radiation requires a crystal volume larger by about a factor of ten to produce coherent scattering. Clearly, the domains were of a size close to those required for coherent scattering with Cu radiation. With some mobility of domain boundaries the scattering using Cu radiation was averaged over domains, yielding the higher symmetry structure. NMR spectroscopy, being a local order technique, picked up the smaller crystalline domains, as did the Mo radiation.

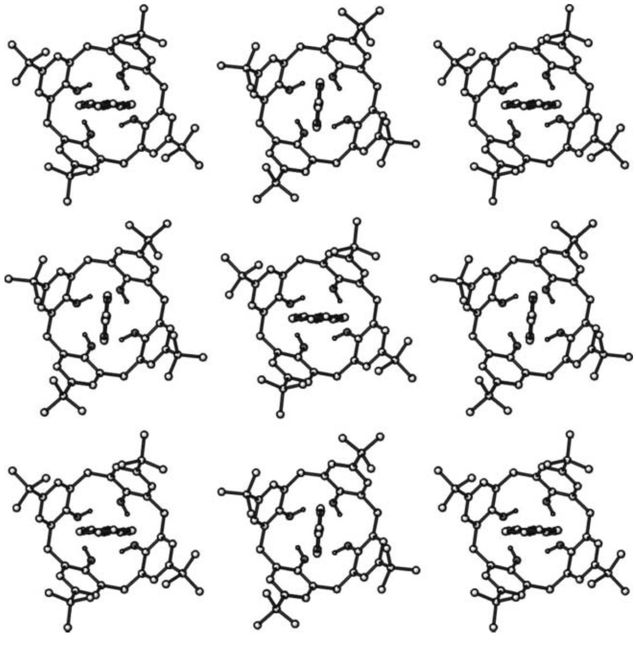


Fig. 3 The evolution of the tBC–toluene structure: the low-temperature twofold distorted ordered structure. The structural model now has a good residual ($R1 = 0.051$) and the symmetry is in agreement with the ^{13}C NMR spectrum.

Meanwhile other aspects of calixarene inclusion chemistry were being explored. Since tBC is relatively insoluble in most solvents, less conventional methods of compound formation were used.[24] In most instances prolonged heating of a suspension of the guest-free material at ~70 °C in the guest liquid eventually produced suitable single crystals of inclusion compounds. Several compounds were prepared with aliphatic and alicyclic compounds, suggesting that π–methyl interactions may in fact not be that important in contributing to the stability of the inclusion compounds.[24,25] Eventually it became clear that tBC was an extremely versatile host material forming a guest–host compound with just about any molecule of appropriate size, with multiple guest–host interactions responsible for stability.

Systematic investigation revealed a number of structural motifs, with recognizable trends as the size and shape of the guest molecules were varied (see, *e.g.* Fig. 4). A summary of the structures and trends is shown in Table 1, with some previously unreported structures (mesitylene, menthol, azobenzene) illustrated in Fig. 5 and 6.

Since the cavity in the 1 : 1 compound is quite asymmetric, it is possible to use it to identify features that are responsible for molecular recognition. Complexation-induced ^{13}C NMR shifts are of particular value for learning about which nuclei are in fact deeply inserted into the cavity, or, combined with X-ray

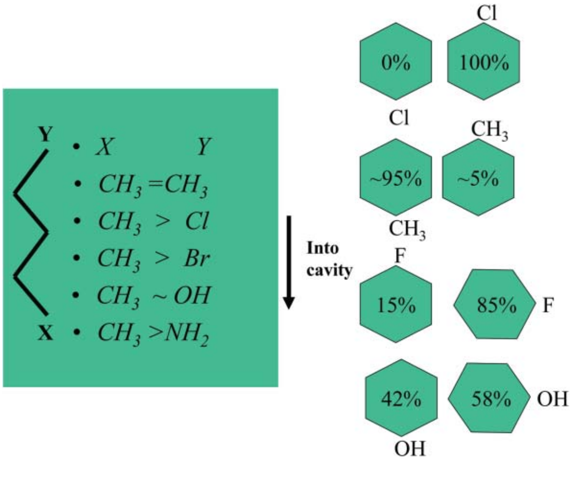


Fig. 4 Recognition inside the cavity; (left) in aliphatic compounds, with the preference for the depth of the cavity indicated; (right) aromatic compounds, showing the fractional occupancy of the two sites.

Table 1 *p-tert*-Butylcalixarene compound classification

Structural type or characteristic	Guest(s)
Dense guest-free (α)	—
Open guest-free (β_0') and guest–host	Xe, CO_2
Simple inclusion, 1 : 1 (β_1) axially symmetric, $P4/n$; $a = 12.55$, $c = 13.77$ Å	Pentane, benzene, pyridine, 1-chlorobutane, 1-bromobutane, 1-butanol, 1,3-dichloropropane, fluorobenzene, *n*-butylamine, phenol, 1,2,3,5-tetrafluorobenzene, acetone
Simple inclusion, 1 : 1 distorted	Mesitylene
$P2/c$; $a = 17.81$, $b = 13.9$, $c = 17.81$ Å, $\beta = 90.04^\circ$	Nitrobenzene
$Pna2_1$; $a = 29.4$, $b = 12.48$, $c = 12.72$ Å	1,3,5-Trifluorobenzene
$P2/c$; $a = 18.03$, $b = 27.11$, $c = 18.10$ Å, $\beta = 90.566^\circ$	Toluene (low temp.)
Simple inclusion, 1 : 2 (β_2), axially symmetric, $P4/nnc$, $a = 12.88$, $c = 25.10$ Å	Anisole, *n*-hexane, 1-octanol, dodecane, *p*-dichlorobenzene, toluene (high temp.), pentane (high temp.), *n*-butylamine (high temp.)
Simple inclusion, 1 : 2, distorted	Azobenzene, menthol
$P2_1/n$; $a = 12.70$, $b = 27.12$, $c = 12.79$ Å, $\beta = 90.649^\circ$	
$P\bar{1}$; $a = 12.66$, $b = 12.89$, $c = 14.59$ Å, $\alpha = 112.1$, $\beta = 103.3$, $\gamma = 90.492^\circ$	
Inclusion/intercalation	Tetradecane
Self inclusion and intercalation	1,2,4,5-Tetrafluorobenzene, dodecylamine
Self inclusion and π stacking	Hexafluorobenzene
Inclusion and H-bonding	*n*-Butylamine; *n*-butylamine and H_2O; diaminobutane
H-Bonding, secondary coordination	Isopropylamine, Ag^+; *n*-butylamine, H_2O

structural data one can draw conclusions about the presence of guest dynamics. For instance, halogens were seen to be excluded from the cavity (Fig. 4), and a general trend $CH_3 > CH_2 > CH \sim OH > Cl \sim Br$, was observed for the group most deeply included. Even though both chlorines in 1,3-dichloropropane were excluded from the depth of the cavity in favour of the methylene group, the chlorines of *para*-dichlorobenzene do reside in the depths of the double-sided cavity in the 1 : 2 guest–host compound – the net energy gained on inclusion still is more important than the less favourable interactions of Cl with the depth of the cavity. Recognition for substituted aromatics is also observed, although the behaviour is less clear cut (Fig. 6). The difference likely is that for the aliphatics the guest molecule can invert inside the cavity,[24,25] so that the observed guest orientation is the actual equilibrium state (which may be dynamically averaged, as for pentane). On the other hand, for the aromatics, the orientation likely is determined during crystallization as molecular motion that would invert the molecule in the cavity was not observed and the number of misaligned toluene molecules in tBC–toluene was seen to depend on the specific sample. Only competitive inclusion experiments, or the measurement of adsorption isotherms, will show whether there is any selectivity or potential for separations.

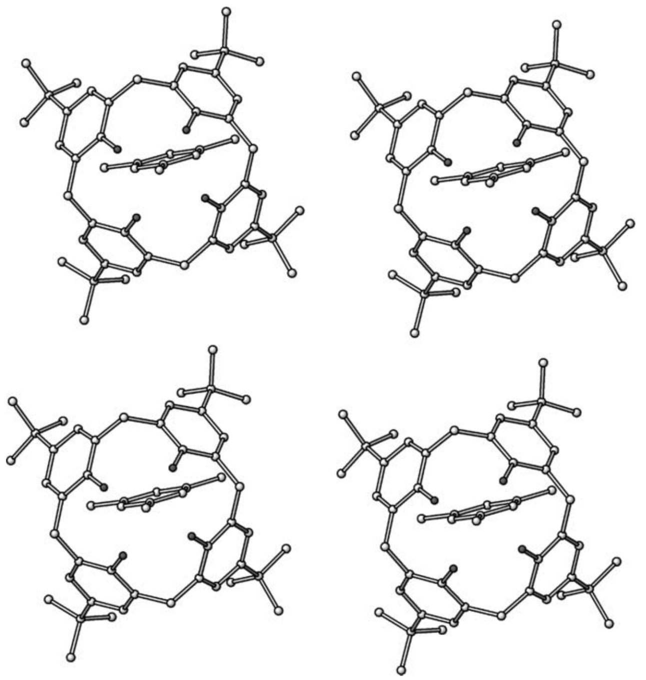


Fig. 5 Crystal structure of the 1 : 1 compound of tBC with mesitylene.

Given the general progress in understanding the common guest–host motifs, it then became of interest to try and modify the structural motifs by selecting appropriate guests. We note the versatility with which the calixarene framework can adapt to changing molecular sizes and shapes. The basic 1 : 1

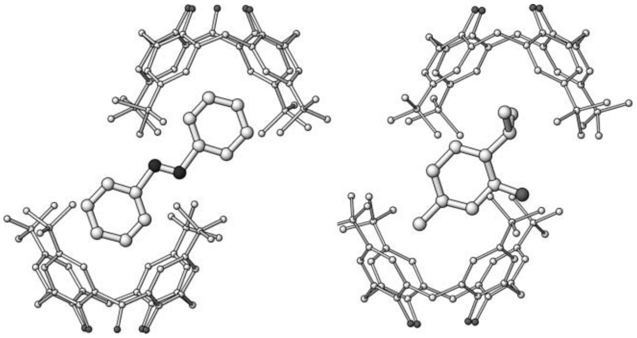


Fig. 6 Crystal structures of the 1 : 2 compounds of azobenzene and menthol with tBC.

compound is based on cylindrical symmetry of the guest, usually achieved by dynamic averaging. When cylindrical symmetry of the guest is no longer achievable a variety of twofold distorted frameworks arise (low-temperature form of the toluene compound, mesitylene – Fig. 3). The basic 1 : 2 guest host compound, with head-to-head calix capsules, is also based on cylindrical symmetry, this time for longer guests, and as molecules become even larger, the host molecule layers become offset to accommodate guests such as azobenzene and menthol (Fig. 4). Nitrobenzene introduced considerable asymmetry into the structure, with the nitrobenzene molecule inserted into the calixarene cavity at an angle to its symmetry plane, the nitro group protruding to one side, presumably because of guest–guest interactions.[26] When the nitrobenzene was diluted with another guest such as propane, the usual, more symmetrical guest insertion mode was observed for nitrobenzene.[27] It is interesting to note that the mesitylene inclusion, which is isostructural to the nitrobenzene structure, has methyl groups protruding to both sides. Other motifs observed were: a new, dense, guest-free form, and a clay-like intercalation compound, both obtained from tetradecane,[28] and guests such as tetradecane that spanned the offset bilayer of calixarene molecules. It also became clear that apparently very simple guest–host inclusions such as tBC–acetone could prove to be remarkable challenges for obtaining adequate structural models – with results from a single technique it is easy to postulate a model that is not correct because of a lack of constraints.[29a] A ^{2}H NMR study combined with high-quality X-ray structural data did lead to a good model that was consistent with both data sets.[29b] The motion of the acetone is quite complex, with the methyl groups exchanging with the ketone oxygen, but in such a manner that one methyl group is always in the cavity with the ketone function always pointing out of the cavity.

The introduction of an amine functionality into the guest showed that hydrogen bonding competes with non-specific interactions[30] to give a number of complex structures containing clusters of amine molecules. Other amine guests still followed the usual guest–host structural motif with 1 : 1 or 1 : 2 host–guest stoichiometry.

Since there was no correlation between the structural motif and the pK_a of the guest, we concluded that the molecular shape of the guest was important in addition to the amine functionality in directing structure. For instance, benzene and pyridine have the same orientation in the cavity[25d] Although the pyridine nitrogen points in specific directions there is no sign of any directional interactions between guest and host. For the 3 : 1 guest–host compound with *n*-butylamine, TGA measurements showed a multi-step decomposition, suggesting that several more distinct amine–tBC compounds were formed during guest loss.[30] Single crystals of these compounds, prepared at elevated temperature from the pure amine or from amine in tetradecane showed them to be the 1 : 1 and 1 : 2 guest–host compounds respectively, indicating that pseudopolymorphism is likely for many amine guests (Fig. 7).

Similarly, the introduction of π–π (electrostatic) interactions between guest and host was able to give yet other structural motifs. Polyfluorinated benzenes showed that with a high level of fluorine substitution, in some cases self-inclusion of the calixarene was preferred over guest inclusion, with the fluorinated benzenes now located either between the layers of tBC dimers, weakly π-coupled to the phenyl rings of the tBC molecules as in the 2,3,5,6-tetrafluorobenzene inclusion (Fig. 8(a)) or as π-stacked bridging ligands between tBC dimers as in the hexafluorobenzene inclusion (Fig. 8(b)).[31] It is entirely possible that pseudopolymorphism also will play a role here, as the structural motifs are likely to depend on guest concentration in solution as well as temperature.

The thermal decomposition of the various inclusion compounds shows quite distinct types of behaviour for different guests (Fig. 9): for some, such as toluene and pentane, there were two regions of guest weight loss. ^{13}C NMR spectroscopy showed that the first step corresponded to the loss of one guest along with conversion to a 1 : 2 guest–host compound, with additional guest loss leading to the dense α phase (Fig. 10). On the other hand, tBC–benzene lost most of its guest in one step. Attempts to study the crystal structure of the 1 : 2 toluene compound obtained by heating a single crystal of the 1 : 1 compound, surprisingly, were successful, as the phase change proved to be a single-crystal-to-single-crystal transformation (Fig. 11).[32] The reverse transition also occurs, as the 1 : 1 compound formed when the 1 : 2 form was exposed to toluene vapour at somewhat elevated temperature. What is more, a powder diffraction study of the intermediate forms showed that both the 1 : 1 and 1 : 2 phases were present simultaneously (Fig. 12). In addition we have shown that the structure of both crystal forms could be obtained from the same single crystal. The two forms differ mainly in the position

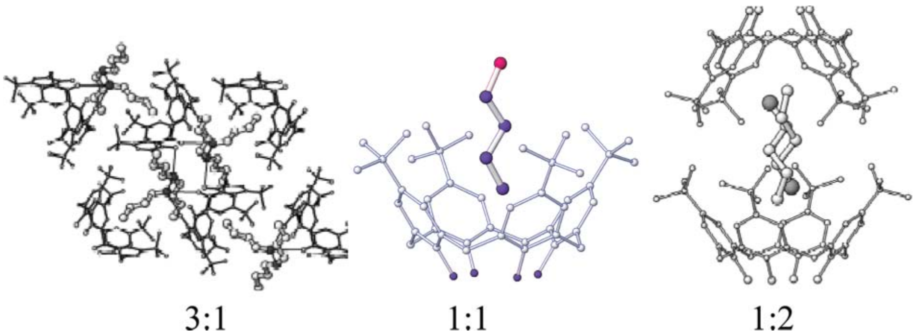


Fig. 7 Pseudopolymorphism of *n*-butylamine–tBC compounds: 3 : 1, 1 : 1 and 1 : 2 guest–host compounds. Hydrogen bonding competes with short-range intermolecular interactions to give a variety of compounds.

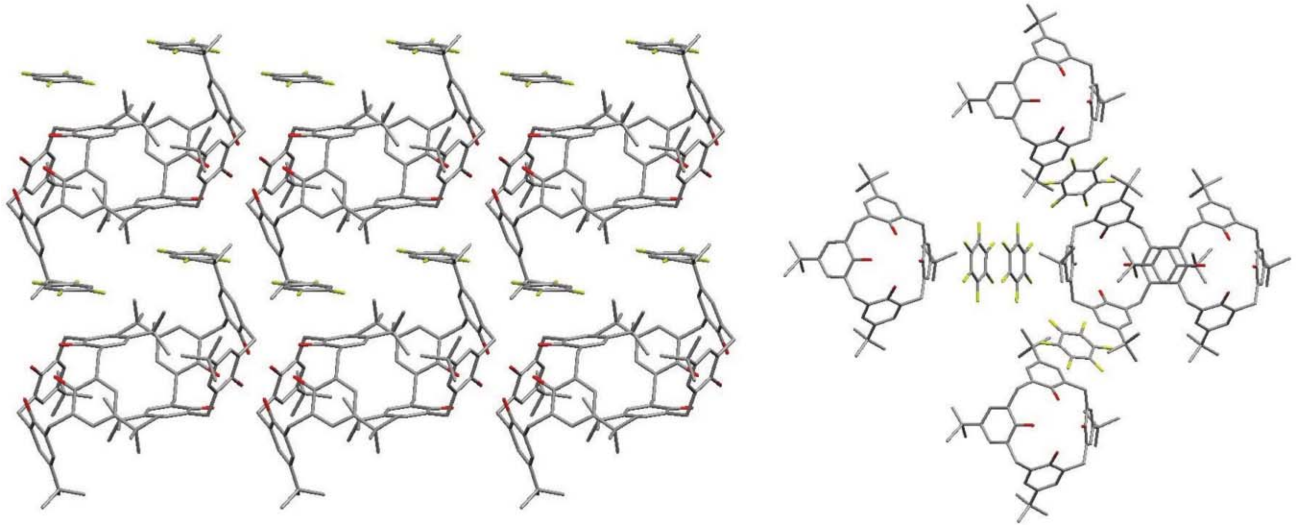


Fig. 8 The tBC inclusion with (a) 2,3,5,6-tetrafluorobenzene and (b) hexafluorobenzene; the tetrafluorobenzene weakly π-bonds with the tBC dimers, the hexafluorobenzenes form tilted π-stacked bridges between calixarenes dimers.

of the tBC molecules in the bilayers with respect to each other, so the single-crystal transition involves a ∼0.9 Å shift of molecules in adjacent bilayers. We can identify the intermediate form of the crystal with both structures present as a "hybrid" crystal. Such hybrid crystals were described by Ubbelohde in 1957,[33] but this is the first clear example of an organic hybrid crystal. One can see that when the 1 : 2 phase is included in the 1 : 1 single crystal at ∼125 °C, its unit cell volume is considerably larger than for the "free" 1 : 2 crystal at the same temperature. Since the difference in single-crystal volumes for the two coexisting forms still is quite large in spite of the expanded volume of the 1 : 2 crystal domains, there may well be less ordered "transition" regions at the domain boundaries which may serve to relieve strain.

At about this time the preparation of a remarkable low density form of the guest-free tBC was reported by ourselves[32] and Atwood *et al.*[34] Single crystals of this material could be converted to a 1 : 1 inclusion with vinyl chloride simply by dipping it into the liquid guest.[34b] Further work in our lab confirmed that the low-density form could also be filled with gaseous guests,[35] which were released again by programmed

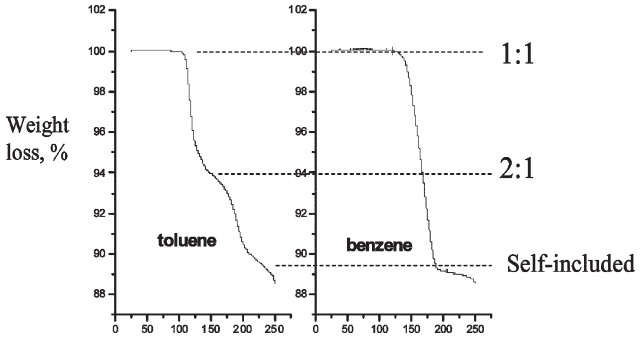


Fig. 9 Thermal decomposition of tBC compounds from TGA measurements. The 1 : 1 guest–host compound with toluene decomposes in a two-step process to give the 1 : 2 form, which then decomposes to the guest-free dense form. The 1 : 1 compound with benzene decomposes directly to the dense guest-free form. The tBC *n*-pentane and nitrobenzene compounds behave similarly to the toluene compound while tBC–methylene chloride and tBC–carbon tetrachloride behave similarly to the benzene compound.

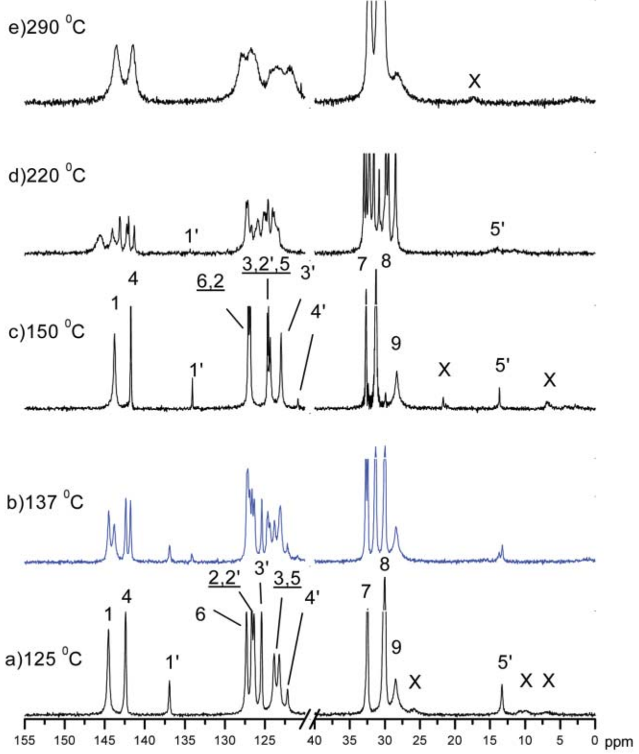


Fig. 10 Solid-state ^{13}C NMR spectra (RT) showing the thermal conversion of the 1 : 1 toluene–tBC compound; (a) after heating the sample to 125 °C, giving the tetragonal 1 : 1 form; (b) after heating the sample to 137 °C, leading to mixed 1 : 1 and 1 : 2 phases; (c) after heating to 150 °C, leading to the 1 : 2 form; (d) after heating to 220 °C, leading to the dense guest-free α form; (e) after heating to 290 °C, leading to the guest-free open β form.

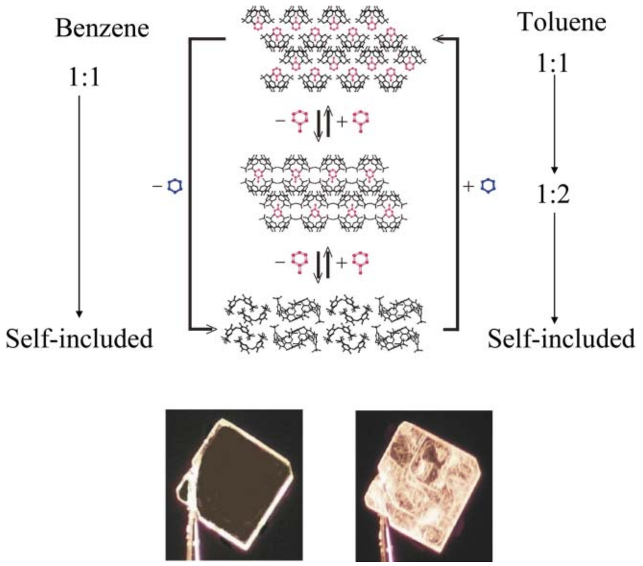


Fig. 11 (Top) Scheme illustrating the reversible single-crystal-to-single-crystal transition which occurs between the 1 : 1 and 1 : 2 toluene–tBC compounds. The conversion of either the 1 : 2 toluene or 1 : 1 benzene compound to the guest-free form does not preserve the single crystal state. (Bottom, right) Single crystal of 1 : 1 toluene –tBC (bottom left) after conversion to the 1 : 2 crystal.

heating, and that xenon atoms entered the lattice reasonably easily at higher temperatures. The loaded crystal in this case is identical to the low-density empty form, so the single crystal in fact behaved as an "organic zeolite" by adsorbing guests without changing structure.[36] Gas adsorption measurements showed Langmuir behaviour, indicating adsorption into pre-existing sites, but with temperature dependent and particle size dependent kinetic barriers.

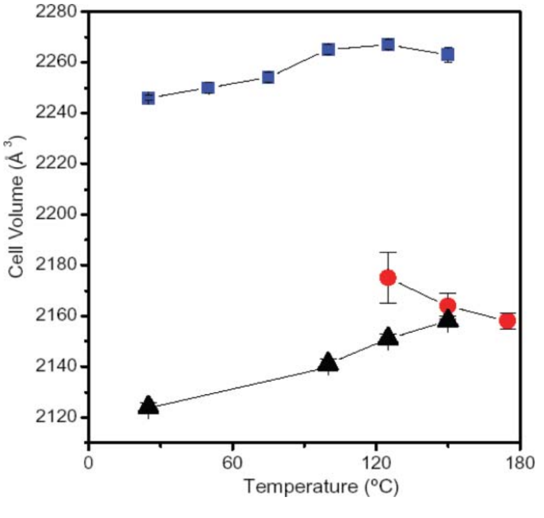


Fig. 12 Unit cell volumes as a function of temperature for the 1 : 1 toluene–tBC compound, (squares), half the unit cell volume for the 1 : 2 toluene–tBC compound (triangles) and half the unit cell volume for the 1 : 2 toluene–tBC compound included inside the 1 : 1 compound (circles). Note the large temperature region where both the 1 : 1 and 1 : 2 forms coexist.

In order to understand the inter-relationship of the major families of the guest–host compounds and the guest-free calixarenes, extensive work was done by DSC/TGA[37a] and NMR[37b] in order to follow guest loss, phase changes and the identification of the various phases. This proved to be rather difficult as a number of phase changes were irreversible, and guest loss from the 1 : 2 compound was quite slow after part of the sample had been converted to the dense, guest-free form. One of the thermal transitions is very dependent on compound purity, with the residual guest–host compound acting as an impurity in the guest-free form. Fig. 13 shows a scheme which accounts for the different phases and conditions of transformation, with Fig. 10 illustrating that the ^{13}C NMR spectrum is quite diagnostic of the different phases (note that the CIS for the 1 : 1 and 1 : 2 guest–host compounds with toluene is quite different).

Further elaboration of the chemistry of tBC is possible as well. The complex structures with amine clusters lend themselves well to attempts to build larger entities, for instance, using secondary coordination of the amine nitrogens.[38] It is relatively straightforward to include metal ions such as Ag$^+$, giving an amine–Ag cluster surrounded by tBC molecules (Fig. 14). This leaves the door open to the inclusion of other metallic ions, to further thermal treatment to remove the amines, thus leaving metallic species, or to involve either the metal or amine in further reactions.

Recent work suggests that there are quite a few interesting features left to discover in the simple calixarene systems. For instance the inability to obtain structural data and the very different results and conclusions regarding the capacity of tBC for CO$_2$ sorption suggest further degrees of complexity.[39]

Materials based on tBC are simple enough that good structures can be obtained, yet dynamics, sometimes involving both guest and host, allow the material to be active in processes. One remarkable feature is the ability of single crystals in several structural classes to undergo transitions accompanied by large-scale movement of both guest and host. Many of these can be associated with the bilayer structure of the host material where the host layers appear to move by distances of as much as 9 Å with respect to each other, and the ability of a single crystal to have domains of two distinct structures that coexist. The detailed understanding of such processes is still well beyond our means, as the transition not

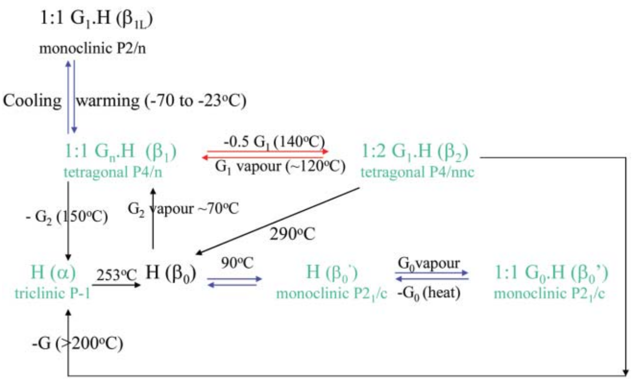


Fig. 13 Phase relationship of empty dense and open forms, 1 : 1 and 1 : 2 guest–host compounds (also see Table 1).

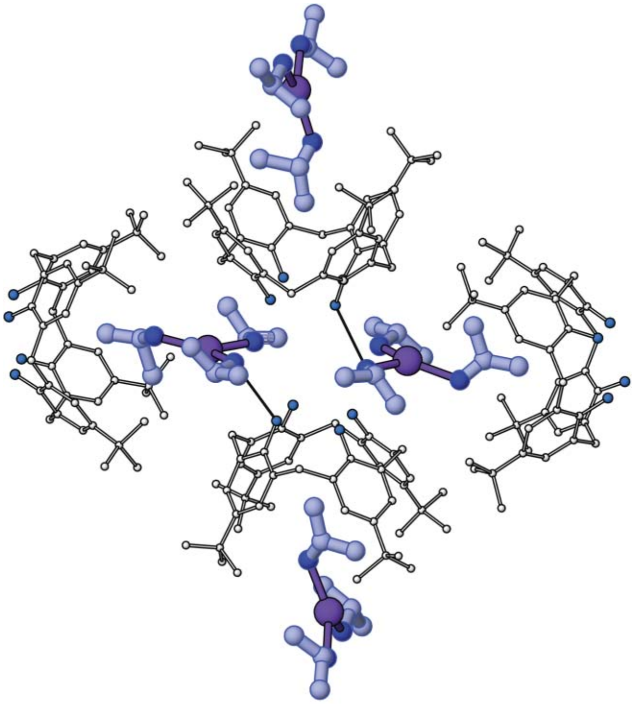


Fig. 14 tBC-amine–Ag cluster. View of the extended cavity formed by isopropylamine (iPA), Ag^+ and tBC in the *ab* plane. The iPA, Ag^+ and phenolic hydroxyls are depicted in blue (hydrogens omitted for clarity).

only involves sliding layers, but also guest transport into or out of the crystal – all this while maintaining the single crystal nature of the material.

It is also hoped that the high-quality structural data will provide some impetus to modelers to try and understand the structural motifs and recognition features of tBC. Whereas it is relatively straightforward to model 1 : 1 molecular guest–host interactions, carrying out calculations on extended frameworks is a far more complex matter.[40] If true materials design is to become possible, progress in this area is a necessity. Recent modeling work has already suggested that yet more structures are possible for small molecules.[41]

As the importance of flexibility of framework materials is becoming recognized as a desirable feature in the design of smart and responsive materials, appropriate methods to follow dynamic processes must quite naturally become part of the researchers' toolbox. We note that dynamics figures very strongly in a new set of slightly extended calixarenes (*n*-acyl (C_6, C_8) calix[4]arenes) that show some remarkable capabilities of guest exchange in single crystal form.[42]

It may be seen from this short discourse that the ultimate understanding and better refinement of the host–guest calixarene structures has relied heavily on the complementary use of single crystal X-ray diffraction and solid state NMR. This combination has been particularly effective in unraveling the complex effects of dynamic disorder and the ''apparent'' symmetries this may entail.

In summary our work has:

(a) Provided a good structural model, including the difficult to resolve disorder of the *tert*-butyl group for the tBC–guest structure.

(b) Shown that dynamics make it difficult to come up with good structural models for the guest from only solid-state NMR or single-crystal X-ray data – often both data sets are needed.

(c) Shown that tBC is a highly dynamic molecule (RT) in the solid state with rotation of the *tert*-butyl groups, the interconversion of twofold distorted forms to give fourfold average symmetry, and the reorientation of guest molecules, often over complex trajectories.

(d) Found mobile domain boundaries in tBC compound crystals at low temperatures that gave different structures for different X-ray radiation wavelengths used in collecting data.

(e) Established tBC as a versatile inclusion host that in the solid state behaves more like a clathrate than a molecular receptor, hence a variety of short-range interactions are involved in producing stable compounds.

(f) Worked out the phase relationship for various empty forms and the 1 : 1 and 1 : 2 guest–host compounds (Fig. 13).

(g) Shown that the asymmetric tBC cavity shows easily observable molecular recognition properties - quite suitable for molecular modeling and the determination of model potentials.

(h) Shown that the basic structural motifs can be modified by incorporating interactions such as H-bonding and π–π interactions.

(i) Shown that for small guest molecules the low-density phase of tBC behaves like an ''organic zeolite'' with pre-existing guest sites, with the filling describable by a Langmuir isotherm.

(j) Shown that some tBC phases are easily converted from one crystal form to another (with guest loss or gain) *via* a single-crystal-to-single crystal transition. The partially transformed crystal is a ''hybrid'' crystal that contains both crystal forms even though the unit cell volumes are quite different.

(k) Shown that tBC–amine compounds can be further elaborated with metallic species using secondary coordination.

Our work also promotes a different view of the way that supramolecular chemistry can be practised, especially when it concerns the solid state. The field has been dominated by the synthetic aspects – a need is seen for materials with specific functions which then are designed, synthesized and tested for those functions. The challenge is then seen to lie in the design and synthesis of the material, with the characterization a relatively routine aspect of the project. Experience has shown that often the designed functionality is not there at all, or present in some reduced form. However, much can be learned by studying the properties of simple materials. It is impossible to derive general conclusions from the limited amount of work done on each new material synthesized, and little can be taken forward to a next stage of design as every new covalent modification of a basic platform makes a new molecule as well as a new extended framework where the packing may change dramatically.

Crystal data

Diffractometer Bruker SMART CCD; Mo-Kα radiation (λ = 0.71073 Å); SHELXTL suite of programs was used to refine the structure.[43] All non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2, hydrogen atoms were placed in calculated positions and allowed to ride on the parent atoms.

tBC–menthol. Temperature of measurement, -100 °C; empirical formula: $C_{98}H_{132}O_9$; crystal size = 0.5 × 0.4 × 0.15 mm, triclinic crystal system, space group $P\bar{1}$, a = 12.661(1), b = 12.892(1), c = 14.587(1), α = 112.06(1), β = 103.32(1), γ = 90.49(1)°, V = 2135.3(3) Å^3, Z = 1, D_c = 1.131 Mg m^{-3}; $2\theta_{\max}$ = 57.5°, ω scan mode, absorption coefficient = 0.070 mm^{-1}, reflections collected: 25418, independent reflections: 10936 (R_{int} = 0.0311); data/restraints/parameters: 10936/71/551, goodness-of-fit on F^2 = 0.989, final R indices [$I > 2\sigma(I)$], R_1 = 0.076, wR_2 = 0.212, largest diff. peak and hole: 0.438 and -0.489 e Å^{-3}.

tBC–azobenzene. Temperature of measurement, -100 °C; empirical formula: $C_{50}H_{61}NO_4$; crystal size = 0.45 × 0.4 × 0.2 mm, monoclinic crystal system, space group $P2_1/n$, a = 12.701(2), b = 27.117(4), c = 12.794(2) Å, β = 90.65(1)°. V = 4406.0(11) Å^3, Z = 4, D_c = 1.116 Mg m^{-3}; $2\theta_{\max}$ = 45.0°, ω scan mode, absorption coefficient = 0.069 mm^{-1}, reflections collected: 31395, independent reflections: 5755 (R_{int} = 0.2015). data/restraints/parameters 5755/90/544, goodness-of-fit on F^2 = 0.851, final R indices [$I > 2\sigma(I)$], R_1 = 0.068, wR_2 = 0.102, largest diff. peak and hole: 0.242 and -0.190 e Å^{-3}.

tBC–mesitylene. Temperature of measurement, -100 °C; empirical formula: $C_{53}H_{68}O_4$; crystal size = 0.25 × 0.25 × 0.06 mm, orthorhombic crystal system, space group $Pna2_1$, a = 29.397(4), b = 12.4786(17), c = 12.7216(17) Å, V = 4666.7(11) Å^3, Z = 4, D_c = 1.095 Mg m^{-3}; $2\theta_{\max}$ = 45.0°, ω scan mode, absorption coefficient = 0.067 mm^{-1}, reflections collected: 31808, independent reflections: 6053 (R_{int} = 0.1453), data/restraints/parameters 6053/41/547, goodness-of-fit on F^2 = 1.064, final R indices [$I > 2\sigma(I)$] R_1 = 0.0704, wR_2 = 0.1593, largest diff. peak and hole: 0.245 and -0.255 e Å^{-3}.

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605275d

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