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Supramolecular Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713649759>

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To cite this Article Brouwer, Eric B. , Enright, Gary D. , Ratcliffe, Christopher I. and Ripmeester, John A.(1996) 'Dynamic molecular recognition in solids: A synoptic approach to structure determination in p-tert-butylcalix[4]arene-toluene', *Supramolecular Chemistry*, 7: 1, 79 – 83

To link to this Article: DOI: 10.1080/10610279608054999

URL: <http://dx.doi.org/10.1080/10610279608054999>

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Dynamic molecular recognition in solids: A synoptic approach to structure determination in *p*-tert-butylcalix[4]arene- toluene¹

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(Received August 16, 1995)

Materials in which weak molecular recognition plays a part often are disordered to an extent that hampers the derivation of reliable structural data. Modelling the detailed structure then cannot be done in a critical fashion, so that in many cases the molecular recognition process itself is not understood very well. Using solid-state NMR methods along with newly obtained crystallographic data, we show that *p*-tert-butylcalix[4]arene-toluene is a fluxional guest-host material at room temperature. The new structural model refines down to an *R*-value of 0.046 instead of the 0.092 value obtained for a model based only on crystallographic data. Problems with a difficult-to-understand disorder involving the tert-butyl groups are resolved, and a number of previously unknown structural and dynamical features regarding the nature of the inserted toluene become apparent. Crystal data for C_{12.75}H₁₆O at 290 K: tetragonal *P4/n*, *a* = 12.7725(2), *c* = 13.8068(5) Å, *D*_c = 1.089 g cm⁻³, *Z* = 8, 1385 observed data *I* > 2.5σ(*I*), *R* = 0.046.

Increasingly complex materials are being designed and synthesized to function as receptors that employ various kinds of molecular recognition.² Materials that exhibit the desired properties need to be characterized thoroughly to link function to structure, as they serve as models for the rational design of new generations of receptors. Calixarenes, first reported about 15 years ago, have proved to be a particularly versatile family of new receptor materials.^{3,4} However, some of the simplest calixarene structures have been difficult to study because of problems with disorder.^{5–8} We show that a synoptic approach, where methods sensitive to long range and local order are used together, can be used very effectively to solve such difficult structures, and can put a proper

perspective on the dynamic nature of guest-host interactions. The problems encountered in understanding the relatively simple *p*-tert-butylcalix[4]arene-toluene compound will be characteristic of structural studies for many such “soft” solid assemblies as the *p*-tert-butylcalix[8]arene-fullerene.^{9–10}

In the initial diffraction study on the toluene compound,⁵ the structure was solved in terms of a unit cell where the calix has 4-fold symmetry. The toluene guest is inserted methyl group first into the calix along the 4-fold axis and satisfies the high symmetry requirements by showing 2-fold disorder. The tert-butyl groups also show a complex positional disorder with the methyl groups distributed over two sites occupied in a 77:23 ratio. The *R*-value for the RT structure was only 0.092, and many publications acknowledge that these calixarene structures are problematic.^{3–8} Most *p*-tert-butylcalix[4]arene-guest compounds (with the exception of *p*-tert-butylcalix[4]arene-nitrobenzene) form high symmetry structures at room temperature with evidence of dynamic disorder.¹¹ NMR studies in solution also are consistent with a calixarene in a cone conformation with 4-fold symmetry.¹² The early structural work^{5,6} and the solution NMR studies have provided the experimental input for comparison with the results of subsequent modelling studies^{13,14} which, in general, have shown agreement with the experimental symmetric cone model for the calix with the guest molecule on the symmetry axis. At best, one can say that the lack of good structural data does not allow critical testing of the modelling calculations.

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We have shown previously that at room temperature the toluene guest molecule reorients between equivalent orientations 90° apart with its long axis approximately along the 4-fold axis in the crystal.¹⁵ From a doubling of many lines in the ^{13}C NMR spectrum evidence was found for symmetry lowering below a phase transition observed at 248K. It was surprising therefore that a redetermination of the structure at temperatures below the phase transition showed that the overall lattice symmetry appeared to be unchanged, and the unit cell parameters had changed very little.¹⁶ Refinement of the X-ray data gave a structural model which initially appeared to have a similar disorder to that reported for the room temperature structure. On closer inspection, however, it was apparent that the disorder involved translation as well as rotation, and could be understood in terms of a 50:50 disorder that was correlated with the orientation of the guest.

In order to elucidate the matter, temperature dependent ^2H NMR measurements were made on the compound containing toluene- d_5 guest.¹⁷ Fig. 1 shows that toluene is held rigidly in the lattice at 129K, and that at 337K the toluene molecule undergoes rapid 4-fold reorientation, as described above.¹⁸ At 179K, the lineshape is characteristic of rapid 2-fold flips about the molecular long axis.

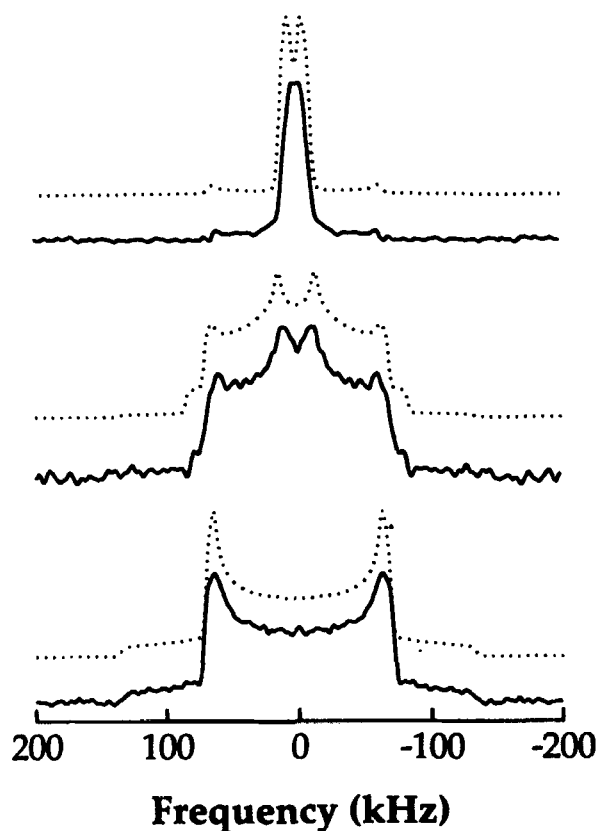


Figure 1 ^2H NMR lineshapes for *p*-*tert*-butylcalix[4]arene-toluene- d_5 at 129K (*bottom*), 179K (*middle*), 337K (*top*). Dashed lines are simulated lineshapes for the rigid lattice, rapid 2-fold flips and rapid 4-fold rotation, respectively.

This is a key observation, as it suggests that each individual guest-host unit has at most 2-fold symmetry, rather than the 4-fold symmetry suggested by diffraction results. When the structural data obtained at 150K were refined with a constraint that each guest-host unit has 2-fold symmetry and that there are two orientations 90° apart for each, an *R*-value of 0.054 was obtained (Fig. 2). By employing the same constraints we have refined the 290K structure to an *R*-value of 0.046.

It is clear that the apparent high symmetry of the calix at low temperature must be due to space-averaging over sites occupied by lower symmetry calixarene units. This is also confirmed by the ^{13}C CP/MAS NMR spectrum¹⁷ obtained at low temperatures, which shows that many resonances which were single lines at room temperature have split into multiplets (Fig. 3). Perhaps the most informative resonance is that of the toluene C-1 carbon centred at 139 ppm. The single line at 290K splits into at least seven components with slightly different chemical shifts and of different intensities at 115K. This confirms that there is no long-range ordering of individual calix units, and that the splitting arises from the different situations that arise when one calixarene unit is surrounded by nearest neighbours which are distorted from 4-fold symmetry in one of two ways. The diffraction results show that this low temperature disorder sets in gradually when the crystal is cooled. Initially, weak reflections at half-integral values of *h* and *k* are observed at 150K, and these disappear after a few hours. As explained above, a 90° rotational jump of the toluene guest is accompanied by significant motion of the flexible calix host molecule. In the low temperature phase

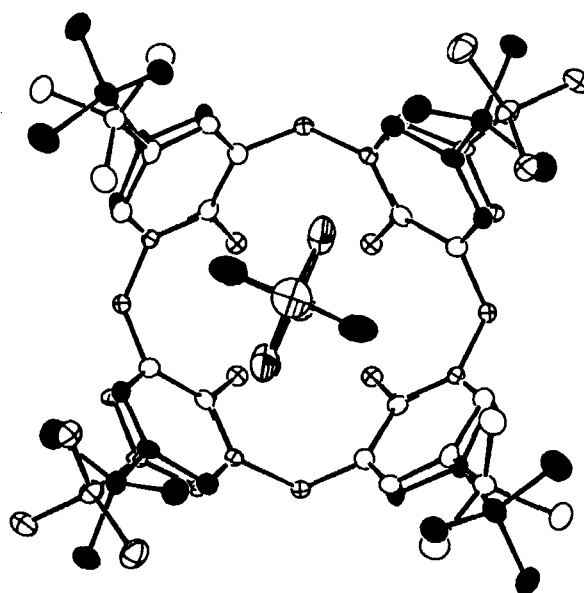


Figure 2 *p*-*tert*-butylcalix[4]arene-toluene structure at 150K from diffraction; the two 2-fold distorted forms are shown superimposed, with the distinguishable atoms for one of the two forms in solid black.

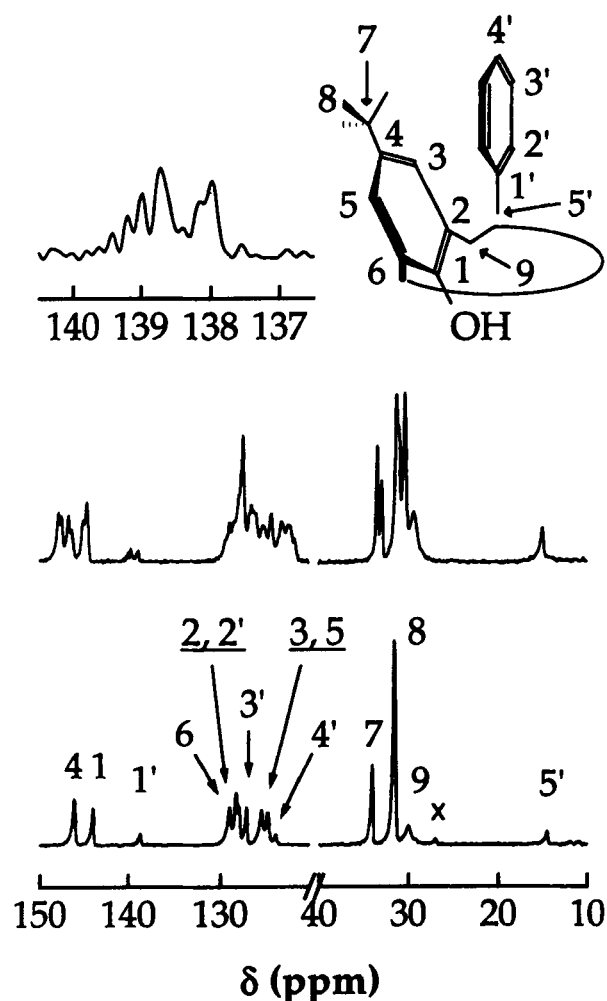


Figure 3 ^{13}C CP/MAS NMR spectrum of p-tert-butylcalix[4]arene-toluene at 290K (*bottom*) and 115K (*top*); inset shows detail of the toluene C-1 resonances at 115K; X marks a spinning sideband.

these jumps apparently still occur, but infrequently as the ^2H lineshape is not affected by the motion. Steric interactions between adjacent calixarene units (in a plane perpendicular to the four-fold axis, see also ref. 11) induce correlated orientational jumps, and, as a result there will be a short-lived correlation in the orientation of adjacent guest-host units which gives rise to the observed half-integral reflections (Fig. 4).

The structural model that now emerges shows that at room temperature there is dynamic recognition of the 2-fold symmetric guest. Two of the aromatic rings of the calixarene with attached tert-butyl groups tilt towards the plane of the toluene ring, and two of the calix rings with attached tert-butyl groups tilt away from the edges of the toluene ring. As the toluene ring rotates, the tert-butyl groups and phenol rings of the calixarene follow the toluene motion (Fig. 5a). This “breathing” motion of the calix unit pivots about the bridging tert-butylphenol-methylene bond. In addition, there is a

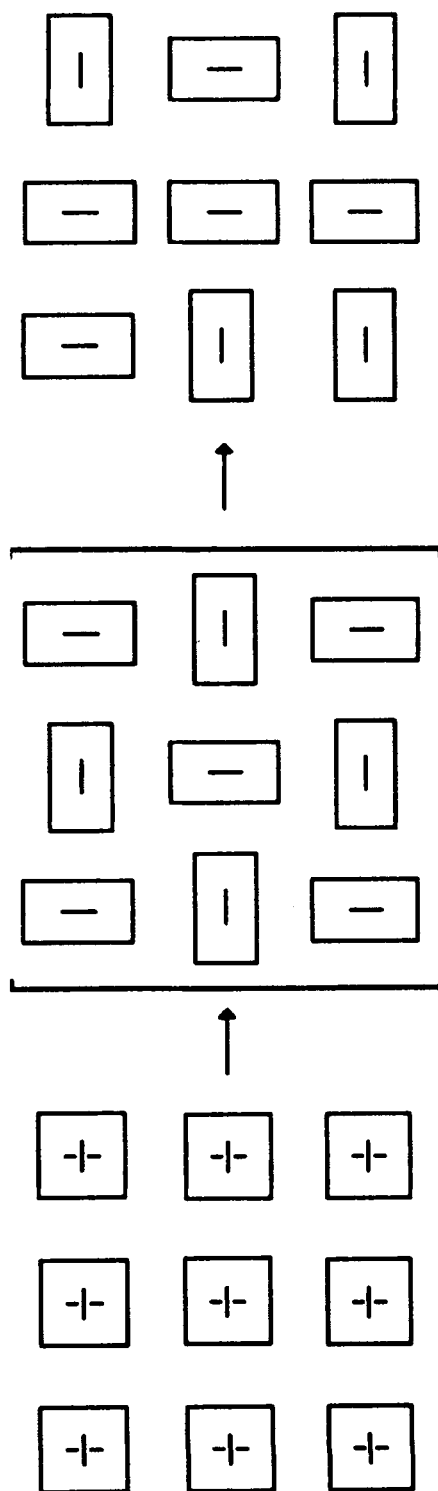


Figure 4 Schematic representation of the nature of disorder in the title compound: (*bottom*) dynamic disorder of guest-host units with 2-fold symmetry, which gives 4-fold symmetry on time average in the 290K structure; (*middle*) lattice of guest-host units with frozen-in distortion and some correlation between orientation of neighbouring units which gives rise to superlattice reflections in the low temperature phase; (*top*) as in (*middle*), but without correlation in orientation of neighbouring units; the apparent high crystal symmetry is due to space-averaging.

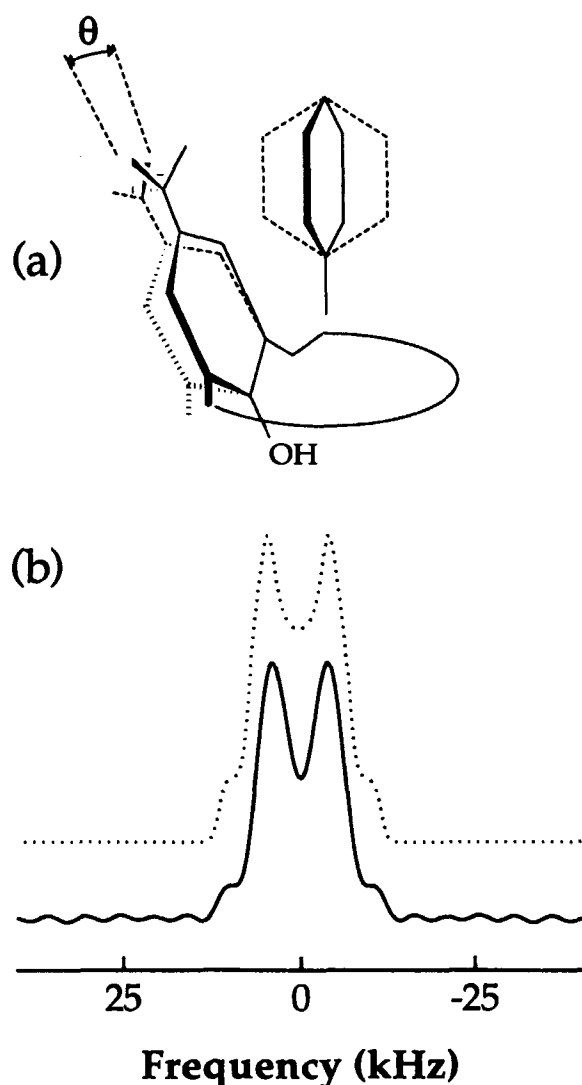


Figure 5 (a) Schematic representation of the coupling of the guest rotation to the 2-fold distortion of the calixarene; note the change in *tert*-butyl group conformation; (b) lineshape for *tert*-butyl- d_9 -calix[4] arene-toluene at room temperature. The simulated lineshape is for a *tert*-butyl group undergoing $C_3 + C_3'$ rotation as well as rapid 2-fold jumps between the orientations indicated.

change in conformation of the *tert*-butyl group. The dynamic nature of the 2-fold distortion was confirmed by examining the ^2H NMR spectrum of calixarene molecules in which the *tert*-butyl methyls had been deuterated. The effective ^2H quadrupole coupling constant χ ($= e^2qQ/h$) was reduced to 17.1 kHz with the asymmetry parameter $\eta = 0.123$ (Fig. 5b) from the value expected for C_3 and C_3' rotation of the *tert*-butyl methyls of 18.9 kHz, with $\eta = 0$. This small reduction is consistent with the presence of a motion between the two positions 15.4° apart for the $(\text{CD}_3)_3\text{C}-\text{C}$ bond. The X-ray refinement gives a value of 9.5° for this angular separation.

Further refinement of the X-ray structural data obtained at 150K showed some other significant structural

features. First of all, the inferred toluene bond distances along the 4-fold axis are somewhat shorter than the expected values, which indicates that the toluene molecule is actually tilted slightly off the 4-fold axis of the calix. The best results were obtained with a tilt angle of $7 \pm 2^\circ$. This is confirmed from the NMR experiments by the observation of a reduction of the quadrupole coupling constant of the ring deuteron in the para position to 173.33 kHz at 179K from the value of 183.3 kHz measured for the rigidly held molecule at 129K. This leads to a tilt angle of 8.0° in reasonable agreement with the diffraction results.

The presence of some unassigned residual electron density led to the suggestion that some of the toluene molecules were, in fact, inserted upside down in the calix. Again, it was possible to confirm this from the NMR spectrum. Since the resonance for normally inserted methyl carbons is shifted to high field from the position found in the liquid by 6 ppm due to ring current effects,¹⁹ the presence of a weak line near the normal resonance position should be indicative of reversed toluenes with protruding methyls. A line was indeed found at 21.9 ppm, and estimates are that about 5–10% of the toluene molecules are inverted. Such information is again critically important for the testing of modelling calculations.

In conclusion, we have shown that by using a combination of methods sensitive to both long- and short-range order it is possible to derive structural models which, because of dynamic disorder, are difficult to obtain with only diffraction methods. The results show a number of previously hidden structural features that are important for defining the nature of molecular recognition processes in the calixarenes, and should be of paramount importance in providing experimental data for modelling studies. The approach proposed should be of general applicability to calixarenes, supramolecular assemblies and other "soft" solids which show considerable disorder.

ACKNOWLEDGEMENTS

The authors thank E. Gabe for helpful discussions, J. Bennett for technical assistance, and NSERC for partial financial support of this work in the form of a Graduate Fellowship (EBB) and an Operating Grant (JAR).

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- 16 Crystals of the title compound were obtained by slow cooling from toluene. Crystal data at 150K: tetragonal, space group *P4/n*, $a = 12.5540(3) \text{ \AA}$, $c = 13.7665(17) \text{ \AA}$, $V = 2169.7(6) \text{ \AA}^3$, $Z = 8$, $D_c = 1.214 \text{ g cm}^{-3}$. The structure was solved and refined on the basis of 1727 observed reflections ($F < 2.5\sigma$). The final R and R_w values were 0.051 and 0.077 respectively. Crystal data at 290 K: tetragonal, space group *P4/n*, $a = 12.77259(23) \text{ \AA}$, $c = 13.8068(5) \text{ \AA}$, $V = 2252.43(9) \text{ \AA}^3$, $Z = 8$, $D_c = 1.089 \text{ g cm}^{-3}$. The final R and R_w values were 0.046 and 0.063 respectively. The structure was solved and refined on the basis of 1385 observed reflections ($F < 2.5\sigma$). The data were collected using a $\theta/2\theta$ scan mode on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromatized Cu K_α ($\lambda = 1.54056 \text{ \AA}$) radiation.
- 17 ^2H NMR lineshapes were recorded as a function of temperature at 46.1 or 30.7 MHz on Bruker AMX-300 or MSL-200 NMR spectrometers. ^{13}C CP/MAS NMR spectra were recorded at 50.3 MHz on a Bruker MSL-200 NMR spectrometer equipped with a Chemagnetics pencil probe for variable temperature work.
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