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π-Methyl interactions and p-tert-butylcalix[4]arene-guest stability: NMR and crystallographic studies of cyclohexane and *n*-pentane inclusion compounds[1]

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Despite the absence of π(guest)-methyl(host) interactions, p-tert-butylcalix[4]arene-cyclohexane [$C_{12.5}H_{17}O$, tetragonal, P 4n, a = 12.9446(4), c = 12.8156(4) Å, D_c = 1.134 g cm^{-3}, Z = 8, 1697 observed data $I > 2.5\sigma(I)$, R = 0.054] and p-tert-butylcalix[4]arene-*n*-pentane [$C_{12.25}H_{17}O$, tetragonal, P 4n, a = 13.0230(19), c = 12.6190(12) Å, D_c = 1.119 g cm^{-3}, Z = 8, 1641 observed data $I > 2.5\sigma(I)$, R = 0.048], characterized by NMR and X-ray diffraction, are stable and isoluble compounds.

The nature and strength of guest-host interactions are of great importance to molecular recognition processes in materials such as the calixarenes. One interaction that has been invoked numerous times to explain the stability of calixarene guest-host compounds is that between the host **tert**-butyl groups and the aromatic ring of the guest.[2–4] Early work on calixarenes showed that stable compounds form between aromatic guests and p-**tert**-butylcalix[4]arenes, and crystallographic results on several compounds formed the basis for the conjecture that the structures are stabilized by the interaction of the aromatic rings with the **tert**-butyl methyl groups.[4,5] In subsequent structural work on calixarene compounds, π-methyl interactions are thought to account for the stability of calix compounds,[3,6,7] including the recently reported calix-fullerene compounds.[8] Understanding the role of this interaction has been restricted by the disorder ubiquitous in diffraction studies on **tert**-butylcalixarene compounds which has led to structural models with large residuals,[2–7] which often obscure subtle host-guest interactions. In this communication we address the exigency of π-methyl interactions in the formation of stable calix-guest compounds.

Although several structures of modified p-**tert**-butylcalix[4]arene compounds with nonaromatic compounds are known,[9] no structures of p-**tert**-butylcalix[4]arene compounds with strictly aliphatic guests have been reported. In order to test the necessity of π-methyl interactions for stable compound formation, we set out to prepare p-**tert**-butylcalix[4]arene compounds with aliphatic guests, an effort hampered by the notorious poor solubility of p-**tert**-butylcalix[4]arene in aliphatic solvents.[3] Stable p-**tert**-butylcalix[4]arene inclusion compounds of cyclohexane **1** and *n*-pentane **2** were prepared successfully from vapour-diffusion of the hydrocarbons into a 3-nitrotoluene solution of p-**tert**-butylcalix[4]arene.[10] This synthetic technique offers a general route to the preparation of otherwise inaccessible p-**tert**-butylcalix[4]arene-hydrocarbon compounds.

Representation of the p-**tert**-butylcalix[4]arene-guest units of **1** and **2** are shown in Fig. 1.[11] In both structures, the guests are dynamically averaged along the 4-fold calix axis. In **1**, each calix **tert**-butyl group is disordered (88:12) over two positions. Remarkably, the **tert**-butyl groups show no disorder in **2**. The absence of significant disorder of the calix **tert**-butyl groups typically observed

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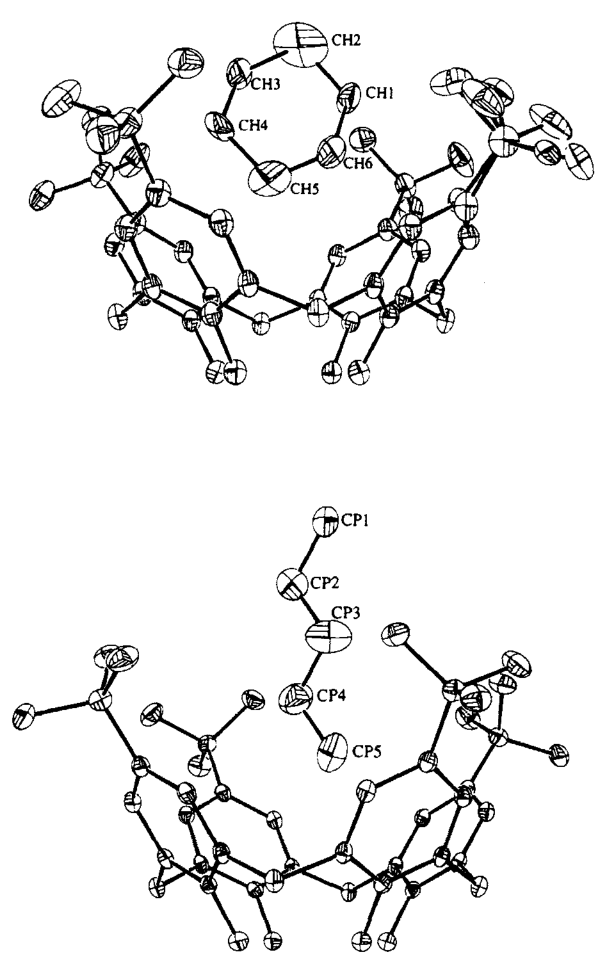

Figure 1 ORTEP plots of **1** (*top*) and **2** (*bottom*) with H atoms excluded for clarity. The thermal ellipsoids are drawn at the 30% probability level.

with calix structures suggests that structure-distorting interactions between guest and host are minimal. The high quality of structures **1** and **2** are reflected in the *R*-values (**1**: 0.054; **2**: 0.048) which are lower than those typically observed for this class of compounds.[6]

Cyclohexane was modelled as a rigid group (C-C bond length = 1.535 Å) in the chair conformation. The guest carbon atom (CH5) deepest inside the calix cavity is close to the axis of the calixarene, and the line between CH5 and the cyclohexane carbon atom directly across the ring (CH2) is 13.1° off the calix C_4 axis. The CH5 atom is 4.15 Å above the plane defined by the four phenolic oxygens and is located 3.54 Å from the plane of the nearest phenyl ring, approximately equidistant (3.80 Å) from the lower three phenyl ring carbons. Deeper penetration of the cyclohexane is prevented by steric interaction between the CH6 (labelled sequentially around the cyclohexane ring) atom and the adjacent phenyl carbons (CH6-C distances of 3.40, 3.49 and 3.52 Å). Other notable short contact distances occur between the cyclohexane carbon atoms CH1, CH3 and the **tert**-butyl carbons in the next layer (CH1, CH3-methyl distances are 3.58, 3.77 Å). Significantly, the cyclohexane CH5 hydrogens are not oriented towards the phenyl ring but rather point to the space in between two adjacent phenyl rings.

n-Pentane was also modelled as a rigid group (C-C bond length = 1.535 Å) in the all-*trans* conformation. The long axis (CP1–CP5) of the pentane molecule was within 2° of the calix 4-fold axis. The methyl group deepest inside the cavity is 4.05 Å above the plane defined by four phenolic oxygens and 3.52 Å from the plane of the nearest phenyl ring, approximately equidistant (3.70 Å) from the bottom three phenyl carbon atoms of the phenyl ring. Significantly short contacts occur between the protruding two pentane carbon atoms and the **tert**-butyl methyls of the next layer (CP2-C distance of 3.37 Å and CP1-C distances of 3.67, 3.75 and 3.98 Å).

What, then, are the stabilizing interactions between guest and host? Clearly, no π_{guest}-methyl$_{calix}$ interactions are possible, and reciprocal interactions between π_{calix}-methyl$_{guest}$ interactions[3,12] are excluded by the absence of methyl groups in cyclohexane. In both structures, there is no evidence for π-methyl interactions. If anything, the guest is positioned to *minimize* close contact with the calixarene aromatic group. A significant factor for the guest position seems to be the interaction of the guest in one calix-guest unit with similar units in the layer above it, which appears to "push down" the guest into its calix cavity.

^{2}H NMR spectra of the per-deuterated guest-calixarene (**1'**, **2'**; Fig. 2) indicate the dynamics of the guest, and are used interactively with diffraction data to refine structural models. The 243 K axial ^{2}H lineshape of **1'** reflects the sum of two motions: a 3-fold rotation of cyclohexane about its C_3 molecular axis[13] + rotation of the guest about the calix 4-fold axis. The lineshape is narrower than expected due to a tilt of 11° (XRD: 13.1°) between the axis defined by the cyclohexane C-1 and C-4 carbons and the calixarene C_4 axis.

The 240 K lineshape of **2'** consists of the methyl and methylene doublets, indicating an axially rotating *n*-pentane. Narrowing of the methyl lineshape from the expected (χ = 23.3 *vs* 28.0 kHz) suggests additional, low-amplitude motion.[14] Details of the guest dynamics will be reported later.

The stability of p-**tert**-butylcalix[4]arene-aliphatic compounds suggests that the prevalent concept of π-methyl interactions in calixarene compounds warrants further investigation. The π-CH interaction may certainly be one component involved in the formation and stability in p-**tert**-butylcalix[4]arene-guest compounds, but it may not be as significant as other interactions such as crystal packing. Finally, the minimal presence of

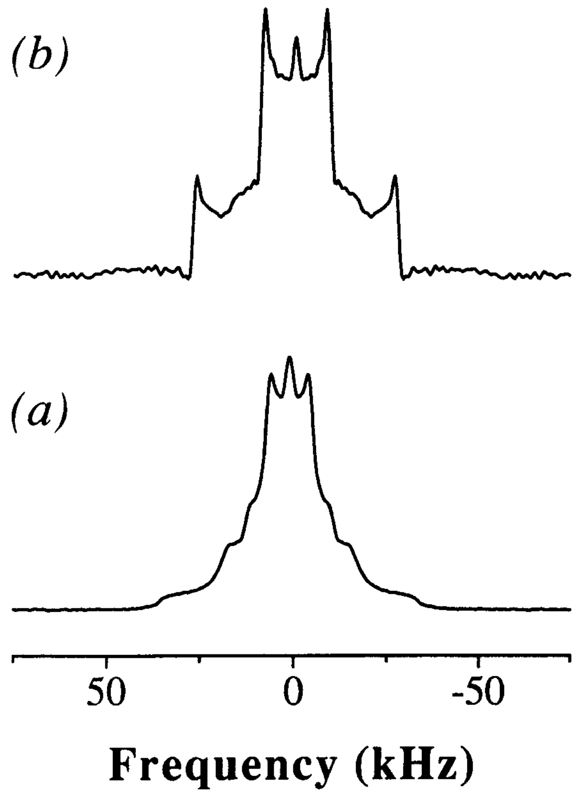

Figure 2 ^{2}H NMR spectra of 1' (*a*, T = 243 K; $\chi_{ax\text{-}D} = 46.0$ kHz; $\chi_{eq\text{-}D} = 15.3$ kHz; $\chi = e^2qQ/h$) and **2** (*b*, T = 240 K; CD_3: $\chi = 23.3$ kHz, $\eta = 0$, CD_2: $\chi = 69.3$ kHz, $\eta = 0$). The spectra were collected on Bruker AMX-300 (46.1 MHz) and MSL-200 (30.7 MHz) spectrometers utilizing a Bruker static probe with 5 mm (AMX-300) or 10 mm (MSL-200) coils and a quadrupolar echo sequence; echo spacings = 35 ms; delay time = 8 s; $\pi/2$ pulse = 2.5 μs (AMX-300), 4 μs (MSL-200).

tert-butyl positional disorder in **1** and **2** offers an opportunity to clarify and further develop the type and role of intermolecular interactions in calixarenes, a task we are currently pursuing.

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REFERENCES

1 Issued as NRCC No. 39076 (to be supplied in proof).

2 Andreetti, G. D.; Ugozzoli, F. in *Calixarenes*, Vicens, J. and Böhmer, V. (Eds.), Kluwer, Dordrecht, **1990**, p. 87.

3 Gutsche, C. D. *Calixarenes*, RSC, Cambridge and London, **1989**.

4 Andreetti, G. D.; Ori, O.; Ugozzoli, F.; Pochini, A.; Ungaro, R. *J. Incl. Phenom.* **1988**, *6*, 523.

5 Andreetti, G. D.; Ungaro, R.; Pochini, A. *J. Chem. Soc., Chem. Commun.* **1979**, 1005; Ungaro, R.; Pochini, A.; Andreetti, G. D.; Domiano, P. *J. Chem. Soc., Perkin Trans. 2*, **1985**, 197.

6 Perrin, M.; Oehler, D. in *Calixarenes*, Vicens, J. and Bohmer, V. (Eds.), Kluwer, Dordrecht, **1990**, p. 65.

7 Ungaro, R.; Arduini, A.; Casnati, A.; Ori, O.; Pochini, A.; Ugozzoli, F. in *Computational Approaches in Supramolecular Chemistry, NATO ASI Series C426* Wipff, G. (Ed.), Kluwer, Dordrecht, **1994**, p. 277.

8 Constable, E. C. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2269.

9 McKervey, M. A.; Seward, E. M.; Ferguson, G.; Ruhl, B. L. *J. Org. Chem.* **1986**, *51*, 3581; Arduini, A.; Ghidini, E.; Pochini, A.; Ungaro, R.; Andreetti, G. D.; Calestani, G.; Ugozzoli, F. *J. Incl. Phenom.* **1988**, *6*, 119; Harrowfield, J. M.; Ogden, M. I.; Richmond, W. R.; White, A. H. **1991**, 1159; Steed, J. W.; Juneja, R. K.; Burkhalter, R. S.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1994**, 2205.

10 p-**tert**-butylcalix[4]arene (238 mg, 0.366 mmol) was dissolved in 3-nitrotoluene (3 mL) in a small vial which was placed inside a larger, capped vial containing cyclohexane (3 mL) at room temperature. After 2 d, the crystal-containing solution in the inner vial was filtered yielding colourless crystals of **1** (179 mg, 0.244 mmol, 67% yield); **2** was prepared in a similar fashion. Microcrystalline powders of **1** and **2** may also be prepared by mixing p-**tert**-butylcalix[4]arene with the appropriate hydrocarbon at low heat for 1 h, followed by filtration. Both **1** and **2** are stable (with respect to loss of guest) for several weeks at room temperature.

11 *Crystal data* for **1**: $C_{12.5}H_{17}O$, Tetragonal, $P\,4n$, $a = 12.9446(4)$, $c = 12.815(2)$ Å, $V = 2147.4(4)$ Å^3, $Z = 8$. $D_c = 1.134$ g cm^{-3}, $\mu = 0.51$ mm^{-1}. The intensity data of **1** and **2** were collected at 150 K on an Enraf-Nonius CAD-4 diffractometer with monochromatized Cu-Kα using the $\theta/2\theta$ scan mode, $2\theta_{max} = 140°$. Of 2052 unique reflections measured, 1697 were observed $[I > 2.5\,\sigma(I)]$. $R = 0.054$, $R_w = 0.086$, GOF = 3.42. *Crystal data* for **2**: $C_{12.25}H_{17}O$, Tetragonal, $P\,4n$, $a = 13.023(2)$, $c = 12.619(1)$ Å, $V = 2140.2(4)$ Å^3, $Z = 8$. $D_c = 1.119$ g cm^{-3}, $\mu = 0.50$ mm^{-1}. Of 2045 unique reflections measured, 1641 were observed $[I > 2.5\,\sigma(I)]$. $R = 0.048$, $R_w = 0.070$, GOF = 2.58. Both structures were solved by direct methods using the NRCVAX program.[14]

12 Schneider, H.-J.; Guttes, D.; Schneider, U. *J. Am. Chem. Soc.* **1988**, *110*, 6449.

13 Nishikiori, S.; Ratcliffe, C. I.; Ripmeester, J. A. *J. Phys. Chem.* **1990**, *94*, 8098.

14 Gabe, E. J.; Le Page, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Cryst.*, **1989**, *22*, 384.