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Eric B. Brouwer[a b]; Gary D. Enright[b]; John A. Ripmeester[a b]
[a] Ottawa-Carleton Chemistry Institute, Department of Chemistry, Carleton University, Ottawa, Ontario, Canada [b] Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada

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COMMUNICATION

Guest-induced asymmetry in the structure of p-tert-butylcalix[4]arene-nitrobenzene[1]

ERIC B. BROUWER[a,b], GARY D. ENRIGHT[b] and JOHN A. RIPMEESTER*[a,b]

[a]Ottawa-Carleton Chemistry Institute, Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario K1S 5B6 Canada; [b]Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6 Canada.

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Nitrobenzene and p-tert-butylcalix[4]arene form a 1:1 inclusion compound in which the calixarene is significantly distorted from its usual 4-fold symmetry as evident from ^{13}C NMR spectroscopy and X-ray diffraction.

When considering the important factors which govern molecular recognition in p-**tert**-butylcalix[4]arene and related complexes it is of interest to note that so far all evidence suggests a rather weak influence of the guest on host geometry.[2] Structural[3] as well as modelling[4] studies suggest that the calix exists in the 4-fold symmetric cone conformation in the solid state as well as in solution. Observation of the chiral selectivity of *p*-sulfonatocalix[*n*]arenes towards chiral guests in solution does give a hint that distortion of the calixarene pocket is possible in order to incorporate specific guest shapes.[5] There is also an indication that the high symmetry observed for the p-**tert**-butylcalix[4]arene-toluene compound in the solid state may be a result of dynamic averaging rather than an intrinsic property of the calixarene.[6]

In order to further elucidate the importance of guest-host interactions, we examined over 20 new p-**tert**-butylcalix[4]arene-guest compounds by solid-state NMR;[7] most of these resulted in calixarene compounds with 4-fold symmetry of the host molecule. The only guests for which low-symmetry conformations were indicated were nitrobenzene and several methyl-substituted nitrobenzenes.

The p-**tert**-butylcalix[4]arene-nitrobenzene compound **1**[8] was chosen for more detailed study. The ^{13}C CP-MAS NMR spectrum of **1** (Fig. 1) indicates a significant lowering of symmetry from the 4-fold symmetric case[6] as some resonances split into as many as four components. This feature is most clearly illustrated by the central carbon of the **tert**-butyl group (C-7; δ 33.8–35.1 ppm). Therefore, each of the four p-**tert**-butylphenol monomer units of the host is expected to be unique and thus demonstrates clearly the guest-induced asymmetry.

The asymmetry of **1**, inferred from ^{13}C CP-MAS NMR spectroscopy, was confirmed by single-crystal X-ray diffraction.[9] Previous structural determinations of calixarene compounds have been hampered by symmetry-related disorder.[2–4] The asymmetry of **1** facilitates a much more reliable structure determination.

A representation of the asymmetric unit is shown in Fig. 2. Each p-**tert**-butylphenol monomer in the calixarene unit is unique and two of the subunits display a positional disorder of the **tert**-butyl groups with site occupancies of 0.57/0.43 and 0.79/0.21. The disordered **tert**-butyl groups are in close proximity to the aromatic ring of the included guest as well to that of a nitrobenzene in an adjacent host. The C_2 axis of the planar nitrobenzene is 67.9° off the z-axis. The nitro group is nestled between the two ordered p-**tert**-butylphenol units; the origin of the compound asymmetry arises from the steric requirements of the nitro group. The bond lengths and angles of the compound are as expected. Two guest-host contacts are significant. The nitrobenzene CN6 carbon is in van der Waals contact with carbons C42 (3.62 A) and C43 (3.52 A) of one p-**tert**-butylphenol unit to which the guest is nearly perpendicular (100.3°). Another close contact is between the nitrobenzene (CN2) and the methyls of an adjacent calixarene **tert**-butyl group (3.39 A; expected van der Waals contact *ca.* 4.0

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*Corresponding Author

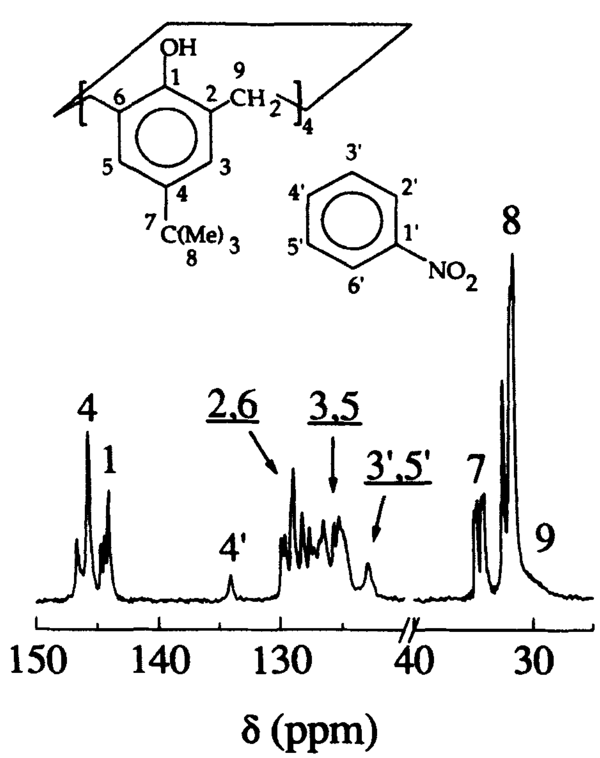

Figure 1 ^{13}C CP-MAS NMR spectrum of **1** at 293 K. The spectrum was collected on a Bruker CXP-180 spectrometer at 45.27 MHz utilizing a Bruker 7 mm double air bearing probe; spinning rate = 2.86 kHz; cross-polarization contact time = 3 ms; π/2 pulse = 5 ms; delay time = 3 s.

A). These contact points are probably the nestling points for the nitrobenzene guest.

Under dipolar dephasing conditions in the ^{13}C NMR experiment,[11] the nitrobenzene C-4' resonance disappears while C-3' and C-5' remain suggesting large amplitude of the guest molecule with the C-4'-H bond on the symmetry axis for the motion. This motion is also detected by ^{2}H NMR spectroscopy of p-**tert**-butylcalix[4]arene-nitrobenzene-d_5, **1'**. Fig. 3 shows the 290 K ^{2}H NMR spectrum of 1' which is typical of a 2-fold axial rotor at the fast motion limit.[12] Spectra taken at lower temperatures reflect the decrease in frequency of this motion until 200 K where the guest motion is frozen in. This motion was simulated[13] and the jump rates correlated to the temperature at which the spectra were collected. An Arrhenius plot of the inverse temperature vs the *ln* (jump rate) gives a barrier to 2-fold ring flips of 56.6 ± 1.3 kJ mol^{-1}. This barrier is significantly higher than observed for the guest in p-**tert**-butylcalix[4]arene-toluene (E_a = 34.0 ± 3.1 kJ mol^{-1}).[14]

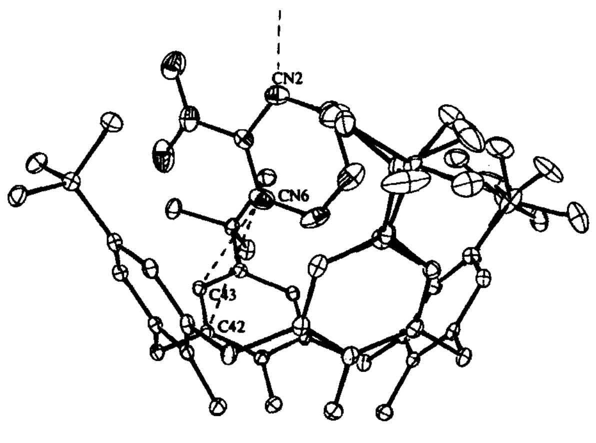

Figure 2 An ORTEP[15] plot of **1** with H atoms excluded for clarity. The thermal ellipsoids are drawn at the 30% probability level. The disorder observed in two of the four p-**tert**-butyl groups is apparent. The dashed lines correspond to the guest-host interactions indicated in the text.

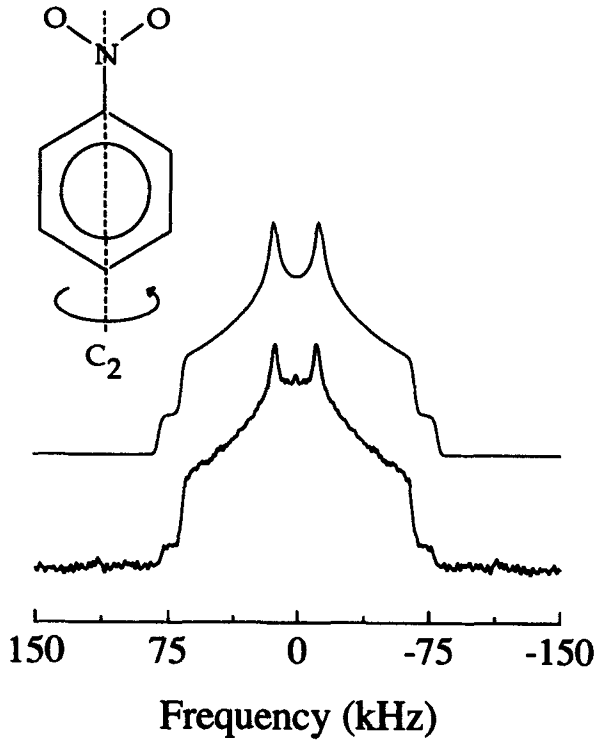

Figure 3 ^{2}H NMR spectrum of 1' at 290 K; *bottom*: observed, *top*: calculated. The spectrum was collected on a Bruker AMX-300 spectrometer at 46.05 MHz utilizing a Bruker 5 mm static probe and a quadrupolar echo sequence; echo spacings = 35 ms; delay time = 5 s; π/2 pulse = 2.5 ms.

The main feature of the guests responsible for inducing asymmetry seems to be the relatively large, asymmetric and inflexible part of the guest which protrudes from the calixarene cavity. In general, the results suggest that intermolecular contacts may well dominate any specific guest-host interactions in determining the structural details of these simple calixarene compounds.

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REFERENCES

1 Issued as NRCC No. 39074 (to be supplied in proof).

2 Gutsche, C. D. *Calixarenes*, RSC, Cambridge and London, 1989; *Calixarenes*, Vicens, J.; Bohmer, V. (Eds.), Kluwer, Dordrecht, 1990.

3 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; Komoto, T.; Ando, I.; Nakamoto, Y.; Ishida, S. *J. Chem. Soc., Chem. Commun.*, **1988**, 135; McKervey, M. A.; Seward, E. M.; Ferguson, G.; Ruhl, B. L. *J. Org. Chem.* **1986**, *81*, 3581; Bott, S. G.; Coleman, A. W.; Atwood, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 1709; Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.*, **1990**, 640; Atwood, J. L.; Orr, G. W.; Hamada, F.; Vincent, R. L.; Bott, S. G.; Robinson, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 2760.

4 Minn, H. H.; Chang, S.; No, K. T.; *Theor. Chim. Acta*, **1989**, *75*, 233; Grootenhuis, P. D. G.; Kollman, P. A.; Groenen, L. C.; Reinhoudt, D. N.; van Hummel, G. J.; Ugozzoli, F.; Andreetti, G. D. *J. Am. Chem. Soc.* **1990**, *112*, 4165; Drew, M. G. B.; in *Spectroscopic and Computational Studies of Supramolecular Systems*, Davies, J. E. D. (Ed.) Kluwer, Dordrecht, 1992; Guilbaud, P.; Varnek, A.; Wipff, G.; *J. Am. Chem. Soc.* **1993**, *115*, 8298.

5 Morozumi, T.; Shinkai, S. *J. Chem. Soc., Chem. Commun.*, **1994**, 1219.

6 Facey, G. A.; Dubois, R. H.; Zakrzewski, M.; Ratcliffe, C. I.; Atwood, J. L.; Ripmeester, J. A. *Supramol. Chem.*, **1993**, *1*, 199.

7 Acetone, acetylacetone, benzaldehyde, benzonitrile, benzylalcohol, benzylmercaptan, γ-caprolactone, chlorobenzene, dichloroethane, diethylether, ethylbenzene, 3-hydroxytetrahydrofuran, methylcyclohexane, α-methyl-γ-butyrolactone, 3-methyl-2-cyclopenten-1-one, 3-nitrotoluene, 4-nitrotoluene, nitrobenzene, propylene carbonate, pyridine, trimethylphosphate, tetrahydrofuran, and γ-valerolactone.

8 p-**tert**-Butylcalix[4]arene (265 mg, 0.408 mmol) was dissolved in nitrobenzene (4 mL), stirred, and heated at 100°C for 1 h. The clear yellow solution was cooled to room temperature which induced the formation of colourless crystals of **1** (189 mg, 0.245 mmol; 60% yield).

9 *Crystal data* for **1**: $C_{50}H_{61}NO_6$, $M_r = 772.04$. Orthorhombic, $Pc2_1n, a = 12.4355(4)$, $b = 12.9346(5)$, $c = 26.756(1)$ Å, $U = 4303.7(3)$ Å^3, $Z = 4$, $D_c = 1.191$ g cm^{-3}, $\mu = 0.59$ mm^{-1}. Of 5377 data collected on an Enraf-Nonius CAD-4 diffractometer, Cu-Kα, 2θ 2–140°, at 150 K, 5095 were observed [$I > 2.5\ \sigma(I)$]. The structure was solved by direct methods using the NRCVAX program.[10] $R = 0.041$, $R_w = 0.057$, GOF = 2.13.

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

11 Fyfe, C. A. *Solid-State NMR For Chemists*, CFC Press, Guelph, 1983.

12 Gall, C. M.; DiVerdi, J. A.; Opella, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 5039.

13 Greenfield, M. S.; Ronemus, A. D.; Vold, R. L.; Vold, R. R.; Ellis, P. D.; Raidy, T. E. *J. Mag. Res.* **1987**, *72*, 89.

14 Brouwer, E. B.; Ripmeester, J. A.; Enright, G. D. Submitted to *J. Incl. Phenom.*

15 Johnson, C. K. *ORTEP-A Fortran Thermal Ellipsoid Plot Program*, Technical Report ORNL-5138, Oak Ridge, 1976.