Solid-state NMR and diffraction studies of *p*-*tert*-butylcalix[4]arene·nitrobenzene·xenon†

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Xenon is enclathrated in the *p*-*tert*-butylcalix[4]arene cavity and behaves both as a guest and a cavity probe; ^{129}Xe NMR and X-ray diffraction data show Xe to occupy two cavity sites defined by static disordered host *tert*-butyl groups.

The *p*-*tert*-butylcalix[4]arene (*t*-BC) cavity (interatomic distance *d ca.* 10 Å at the upper rim, *d ca.* 3.8 Å at the lower rim: with a depth of *ca.* 4 Å) is a micropore‡ that to date, has not been examined by any of the common solid-state void space characterization techniques.[1] ^{129}Xe NMR spectroscopy is one such technique that is particularly sensitive to micropore geometry and size.[2]

We have previously reported *t*-BC compounds with aliphatic guests prepared by vapour diffusion of the guest into a saturated solution of *t*-BC in nitrobenzene.[3] In a similar fashion (in which Xe replaces the aliphatic guest), *t*-BC·$C_6H_5NO_2$·Xe **1**, is prepared.§ This first example of a *t*-BC·gas clathrate[4] is characterized by both single-crystal X-ray crystallography (XRD) as well as ^{129}Xe NMR spectroscopy using a complementary approach. Importantly, for the first time, ^{129}Xe NMR spectral features are related to specific single-crystal XRD structural aspects.

The XRD structure of **1** (Fig. 1)¶ confirms that the host geometry is identical to that of *t*-BC·$C_6H_5NO_2$ **2**.[5] In **1**, 17% of the cavities are occupied by Xe, with the remainder occupied by nitrobenzene. The off-axis orientation of the nitrobenzene guest is similar in the two structures. Whereas substitution of nitrobenzene by Xe does not influence the position of the disordered host *tert*-butylphenol groups (two of the four groups disordered), it does change the ratio of disordering in *tert*-butylphenol group *C* to 0.66 : 0.34 from 0.79 : 0.21 (Fig. 1). If the relationship between nitrobenzene content and the ratio of group *C tert*-butylphenol disorder present in **2** is constant, the change in disordering in **1** is consistent with Xe solely occupying a cavity defined by the majority disordered position in group *C*.

Xe sits at the centre of the cavity, 4.33 Å from the basal plane defined by the four phenolic oxygens. Xe shows no protrusion from the cavity and is in fact, located deep in the cavity relative to other *t*-BC·guest species. The closest Xe···host contacts are to the lower three carbons of each *p*-*tert*-butylphenol unit [C(1),C(2),C(6)], with an average distance of 4.13 Å from these carbons to Xe; these distances are slightly greater than the sum of the van der Waals radii (4.0 Å). The closest approach of a *t*-BC carbon to the Xe along the direction perpendicular to the capping *t*-BC bilayer is 5.4 Å.

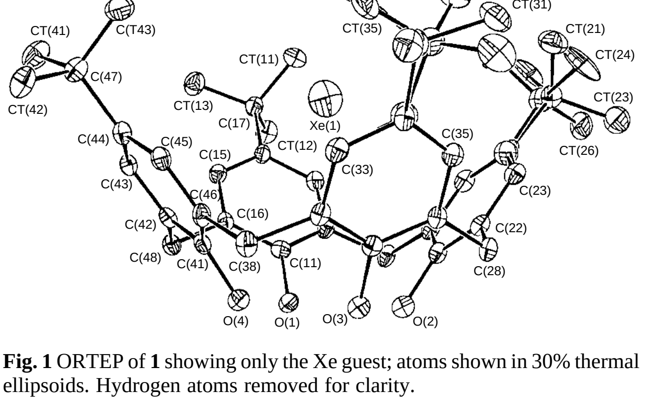

Fig. 1 ORTEP of **1** showing only the Xe guest; atoms shown in 30% thermal ellipsoids. Hydrogen atoms removed for clarity.

The two lines (δ_{iso} 59, I = 0.6, site I; δ_{iso} 64, I = 0.4, site II) in the ^{129}Xe CP MAS NMR spectrum [Fig. 2(*a*)] indicate that Xe samples two inequivalent sites which possess slightly different Xe occupancies and void space volumes, as indicated by the intensity and Δ_{iso} values respectively.

The components of the chemical shift anisotropy (CSA) tensors are obtained for the two sites from the static ^{129}Xe CP NMR spectrum [Fig. 2(*b*)], and reflect both the chemical environment and symmetry of the two cavity sites. The spectrum was fitted [Fig. 2(*c*)][6] using a two-site model employing the ^{129}Xe NMR δ_{iso} values from the MAS spectrum (site I: δ_{iso} 59; $\Delta\delta$ = 27 ppm; δ_{11} 49; δ_{22} 54; δ_{33} 76; site II: δ_{iso} 64, $\Delta\delta$ = 19 ppm, δ_{11} 56, δ_{22} 60, δ_{33} 75).‖

Both Xe powder patterns are characterized by somewhat asymmetric CSA tensors (η = 0.3), and accurately reflect the

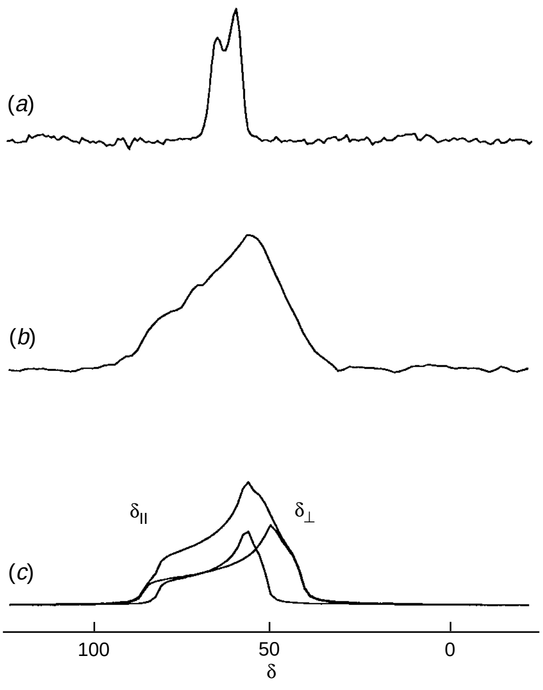

Fig. 2 49.8 MHz ^{129}Xe CP NMR spectra of **1**: (*a*) with MAS, 1219 transients; recycle time: 2 s; TD = 512; 20 Hz line broadening; ν = 2.65 kHz; (*b*) static 2080 transients; recycle time: 3 s; TD = 256; (*c*) fitted spectra. Both experimental spectra were collected on a Bruker CXP-180 NMR spectrometer with a Doty 7 mm spinning probe: π/2 pulse = 3.5 μs; contact time = 3.5 ms; 16 K points; SW = 20 kHz.

small departures from axial symmetry of both calix cavities. The least shielded component of both patterns ($\delta_{33} = \delta_{\parallel}$ is along the z axis, and since $\delta_{\parallel}{}^{\mathrm{I}} = \delta_{\parallel}{}^{\mathrm{II}}$, the two cavities share similar dimensions along this axis. Since $\delta_{\parallel}$ is the least shielded CSA component, the CSA tensor has positive anisotropy indicative of a prolate spheroidal cavity.[7,8] The difference in the δ_{11} and δ_{22} values for the two patterns indicates that Xe samples different dimensions in the xy plane for each cavity.

Because Xe sits in a cavity defined by the majority disordered position in *tert*-butylphenol group *C*, only the positional disordering in *tert*-butylphenol group *B* (0.57 : 0.43) influences cavity size. Disordering in *B* gives two cavities of dimensions of 10.15 × 10.52 Å (majority site) and 10.15 × 10.65 Å (minority site) defined by the central carbon of the *tert*-butyl groups (Fig. 3). Two cavities differing in one dimension in the xy plane by 0.17 Å result from the disordering in *B*. The differences along the z axis arising from the *tert*-butylphenol disordering are insignificant ($\Delta d < 0.03$ Å).

Specific features of each technique can now be correlated. On the basis of the position and intensities of the two ^{129}Xe NMR lines I and II are assigned to the majority of (10.15 × 10.52 Å) and minority (10.15 × 10.65 Å) cavities respectively. The intensities of the ^{129}Xe NMR lines agree with the ratio of *tert*-butylphenol disordering in *B* determined by XRD. The presence of two Xe sites indicates that, in contrast to the dynamic *tert*-butylphenol disordering observed in t-BC·C_6H_5Me,[9] *tert*-butylphenol *B* disordering in **1** is static. Finally, the degree of ^{129}Xe NMR δ shielding of the two sites is consistent with the cavity size/δ_{iso} relationship for void spaces,[7] and is to date the largest clathrate cavity defined by ^{129}Xe NMR in such a fashion (although ring-current effects[10] from the aromatic host walls likely interfere with any quantitative determinations of the cavity size). For comparison, Xe in zeolite A (one Xe per α cage, *d ca.* 9.8 Å), gives δ_{iso} 75.[11]

In summary, the t-BC·$C_6H_5NO_2$·Xe compound illustrates three key features: (*i*) it is the first example of gas inclusion in the t-BC cavity, (*ii*) since Xe behaves both as a guest and a probe, specific XRD and NMR data may (for the first time) be correlated, and (*iii*) NMR data establishes that the host *tert*-butylphenol disordering is static.

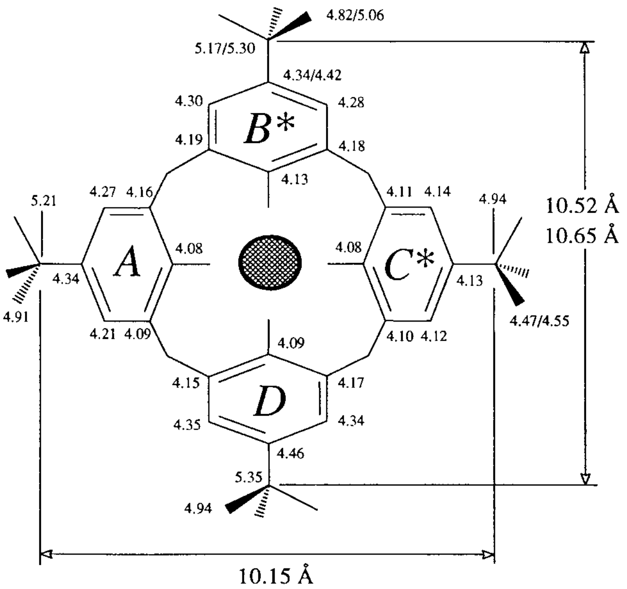

Fig. 3 The Xe position in the t-BC cavity in **1**. The smaller numbers indicate the distance (in Å) to Xe, and the larger numbers indicate the cavity dimensions in the Xe xy plane; two values reflect disordering in carbon atoms. The starred letters indicate disordered *p-tert*-butylphenol units: *B* 57 : 43; *C* 66 : 34.

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Footnotes

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‡ ^{13}C CP MAS NMR evidence shows that solid empty t-BC takes up small hydrocarbons on contact with the liquid.

§ *Synthesis*: A saturated nitrobenzene solution of *p-tert*-butylcalix[4]arene (T = 80 °C) is cooled to room temp. in a closed vessel pressurized with Xe (2 atm).

¶ *Crystal data* for **1**: $C_{48.98}H_{60.15}O_{5.66}N_{0.83}Xe_{0.17}$, $M_w = 773.43$, $T = 150$ K, orthorhombic, space group $Pc2_1n$, $a = 12.4872(7)$, $b = 12.8909(8)$, $c = 26.6893(17)$ Å, $U = 4296.2(5)$ Å^3, $Z = 4$, $F(000) = 1666.76$, $D_c = 1.199$ g cm^{-3}, μ(Cu-Kα) = 1.63 mm^{-1}. Intensities of 5416 reflections were measured on an Enraf-Nonius CAD-4 diffractometer using Cu-Kα radiation (graphite monochromator, θ–2θ scan mode). Three standard reflections were measured to monitor crystal stability. Absorption corrections were not applied. The structure was solved by using NRCVAX suite of programs.[12] Refinement converged at $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.048$, $R_w = [\Sigma w(|F_o| - |F_c)^2/\Sigma w|F_o|^2]^{1/2} = 0.062$ and GOF = $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2} = 1.92$ for 4258 reflections with $I \geqslant 2.50(I)$. Two of the four *tert*-butylphenol groups were disordered in 0.57 : 0.43 and 0.66 : 0.34 ratios. The final Fourier difference map showed no residual density outside of −0.290 and 0.210 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/426.

|| $|\delta_{33} - \delta_{\mathrm{iso}}| > |\delta_{22} - \delta_{\mathrm{iso}}|$, $|\delta_{11} - \delta_{\mathrm{iso}}|$; $\Delta\delta = \delta_{33} - \delta_{\mathrm{iso}}$; $\delta_{\mathrm{iso}} = (\delta_{11} + \delta_{22} + \delta_{33})/3$; $\eta = |\delta_{22} - \delta_{11}|/|\delta_{33} - \delta_{\mathrm{iso}}| = 0.3$; uncertainties: ±2 ppm.

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