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COMMUNICATION

Phase transition and dynamic structure in the toluene clathrate of t-butylcalix[4]arene

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Variable temperature solid-state ^{13}C NMR and differential scanning calorimetry were used to show that the toluene clathrate of t-butylcalix[4]arene undergoes a symmetry lowering phase transition at 248.0 K. ^{2}H NMR was used to show that the high symmetry of the complex at room temperature is due to dynamic disorder of the toluene guest, which is most easily described as an axial rotor.

In understanding the factors which govern molecular recognition in inclusion compounds often the presence of disorder and dynamic processes complicate matters considerably. For instance, t-butylcalix[4]arene, being a relatively flexible host molecule,[1] seems to display an unusually high degree of symmetry in complexing the toluene molecule. Both guest and host display four-fold symmetry,[2] with the high toluene symmetry achieved through a two-fold disorder about the long molecular axis. If the disorder is static, then the four-fold symmetry of each individual calixarene cavity does not match the two-fold toluene symmetry. On the other hand, toluene may achieve the higher apparent symmetry by the presence of dynamic disorder. In the latter case one may expect a symmetry lowering of the entire host-guest unit when the motion slows down to some critical rate. In this communication we report evidence for a dynamic room temperature structure and a symmetry lowering transition at low temperatures.

Figure 1a shows the ^{13}C CP/MAS NMR spectrum of the t-butylcalixarene-toluene complex.[3] This is in agreement with that reported by Komoto *et al.*[4], although the improved resolution allows a complete assignment of all guest and host lines. The multiplicity of the host lattice lines is consistent with the four-fold symmetry of the calixarene unit. On lowering the temperature, the spectrum does not change very much, until below 248 K a much more complicated pattern appears (Fig. 1b, c). Such a sudden change is often indicative of a phase transition, the presence of which was confirmed by differential scanning calorimetry (DSC), which showed a weak peak at 248.0 K. The heat of transition derived from the peak area was 0.398 J g^{-1}.

Perhaps the most significant change in the ^{13}C spectrum (Fig. 1c) is the doubling of the toluene C-1′ line. This suggests that the asymmetric unit in the low temperature phase contains two inequivalent calixarene-toluene guest-host units. Some of the host lattice lines also show increased splitting in the low temperature

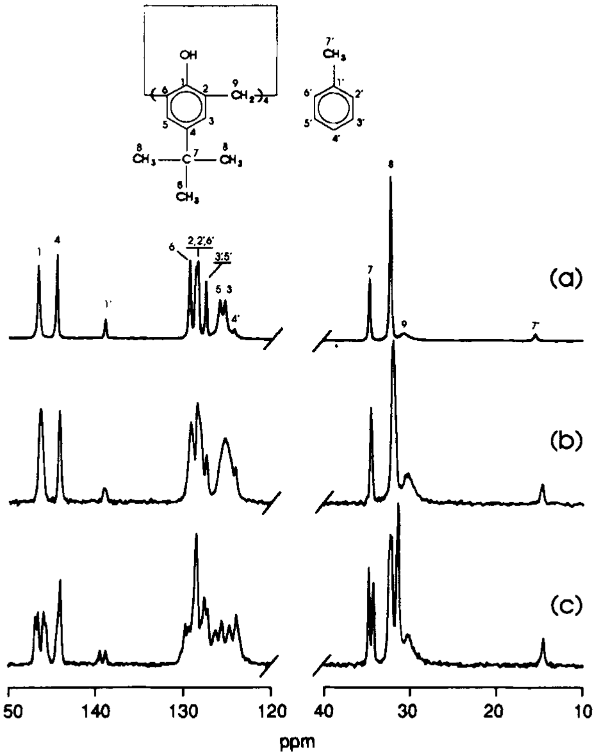

Figure 1 ^{13}C CP/MAS NMR spectra of the t-butyl calix(4)arene toluene clathrate obtained at 45.28 MHz; (a) 298 K; (b) 250 K; (c) 230 K.

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phase. The C-1 host lattice line shows quadrupling, as does the C-8 t-butyl line. This suggests that the two individual calixarene-toluene units also have reduced symmetry. The splitting pattern is consistent with the presence of either a two-fold axis or a mirror plane in each guest-host unit, so that each calix unit now has a symmetry that matches that of the guest. Of course, the correctness of this explanation will have to await the determination of the detailed crystal structure in the low temperature phase.

The ^{2}H NMR lineshape of the complex prepared with toluene-d_8 was recorded at room temperature[3] in order to check for dynamic effects. Figure 2 shows that there are three overlapping axially symmetric Pake doublets with relative intensities 1:3:4 which can be assigned to three distinct types of C-D bonds in the molecule. The four-fold disorder observed in the room temperature crystal structure suggests that the toluene may be regarded as an axial rotor. In this case the methyl group symmetry axis and the C4-D bond lie along the rotation axis, so that there should be no averaging of the methyl group quadrupole coupling constant (QCC) beyond that expected for methyl group rotation, and the C4-D QCC should have essentially its rigid lattice value. The remaining four C-D bonds have the bond axes oriented approximately at 60 degrees to the rotation axis, giving rise to considerable motional narrowing. The simulated lineshape (QCC's: C-4′ = 171 KHz, C-2′,3′,5′,6′ = 16.0 KHz, C-methyl = 47.2 KHz, all $\eta = 0$) shows that this model is largely correct, but that in addition to axial rotation there must be a small-angle libration of the rotation axis as well.

Clearly, in order to understand the four-fold symmetry of the complex at room temperature in terms of molecular recognition it is necessary to identify the toluene molecule as an axial rotor.

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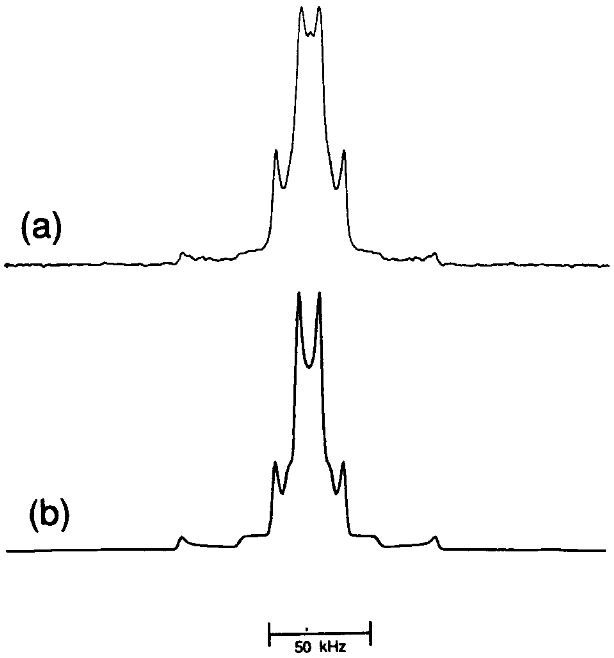

Figure 2 ^{2}H NMR lineshape of toluene-d_8 trapped in the t-butyl calix-(4)-arene clathrate at room temperature. (a) Experimental (b) simulated.

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3 Variable temperature CP/MAS ^{13}C NMR spectra were obtained on a Bruker CXP-180 NMR spectrometer at a frequency of 45.28 MHz utilizing a Doty 7 mm double air bearing probe. Matched rf field amplitudes were 60 KHz, with contact times of 3 msec and delay times of 2 sec. ^{2}H NMR spectra were obtained at a frequency of 27.6 MHz with a quadrupole echo sequence. Echo spacings were 35 usec, delay times 60 sec and the 90° pulse length was 1.7 usec.

4 Komoto, T.; Ando, I.; Nakamoto, Y.; Ishida, S.; *J.C.S. Chem. Comm.* **1988**, 135.