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Research Communication

Inclusion of Multi-ring Compounds by *p-tert*-Butylcalix[5]arene

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Abstract. The inclusion complex of *p-tert*-butylcalix[5]arene with tetralin has been characterized in the solid state by a single crystal X-ray diffraction study and by ^{13}C CP/MAS NMR experiments. A crystallographic mirror plane bisects the calix[5]arene and contains the tetralin molecule (which is dynamically disordered). The guest penetrates the upper rim of the calixarene and the experimental results indicate the saturated ring is imbedded most deeply. *p-tert*-Butylcalix[5]arene (tetralin) · 2 EtOH belongs to the monoclinic space group C2/m with $a = 22.187(6)$, $b = 15.823(6)$, $c = 18.168(5)$ Å, $\beta = 99.70(2)°$, and $D_c = 1.09$ g cm^{-3} for $Z = 4$. Refinement based on 1652 observed reflections led to a final R value of 0.081.

Key words. Calix[5]arene, multi-ring compound, tetralin, solid state NMR, X-ray diffraction.

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The inclusion of small molecules by calix[4]arenes is now well established as an important area of endeavor [1–4]. For the calix[6]- and calix[8]arenes, several structural studies [5, 6] have appeared, and for calix[6]arene important work on the complexation of metal-containing species [7] and of organics [8, 9] is available. Calix[5]arene is an excellent candidate for small molecule complexation, but difficulties with synthesis and purification [10] have limited the reports to one X-ray crystal structure (calix[5]arene · (acetone)$_2$, an exo-clathrate) [11] and two solution studies (both with water-soluble calix[5]arenes) [7a, 9]. We report herein the first solid state evidence for molecular inclusion by a calix[5]arene and the first structural evidence for the inclusion of a multi-ring compound by a calixarene.

In the only previous report of the complexation of multi-ring organic molecules by calix[5]arenes, Gutsche and Alam noted that "... calix[5]arene appears to be slightly too small to readily accept naphthalene ..." [9]. They further noted that the

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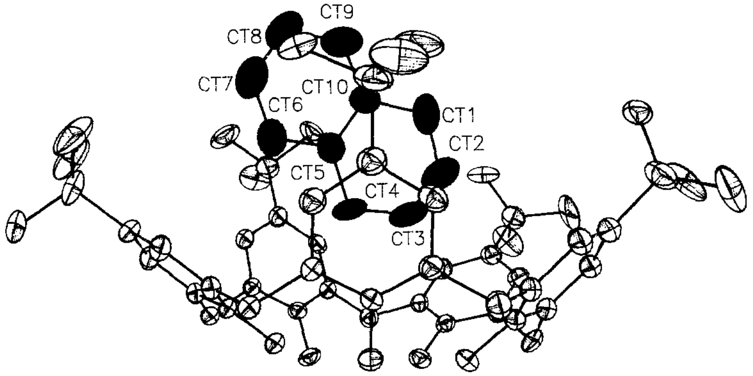

Fig. 1. Structure of the *p-tert*-butylcalix[5]arene inclusion complex with tetralin. The atoms of the tetralin rings have been darkened.

observation of solution complexation suggested that models had underestimated the size of the cavity. It was suggested that "complexation occurs by insertion of a portion of the aromatic hydrocarbon into the 'lower rim' of the calixarene." The X-ray structural study of the hydrocarbon soluble *p-tert*-butylcalix[5]arene with tetralin, Figure 1, shows that for this calixarene the cavity is large enough for insertion of a portion of the guest and that complexation occurs with insertion through the 'upper rim' [12].

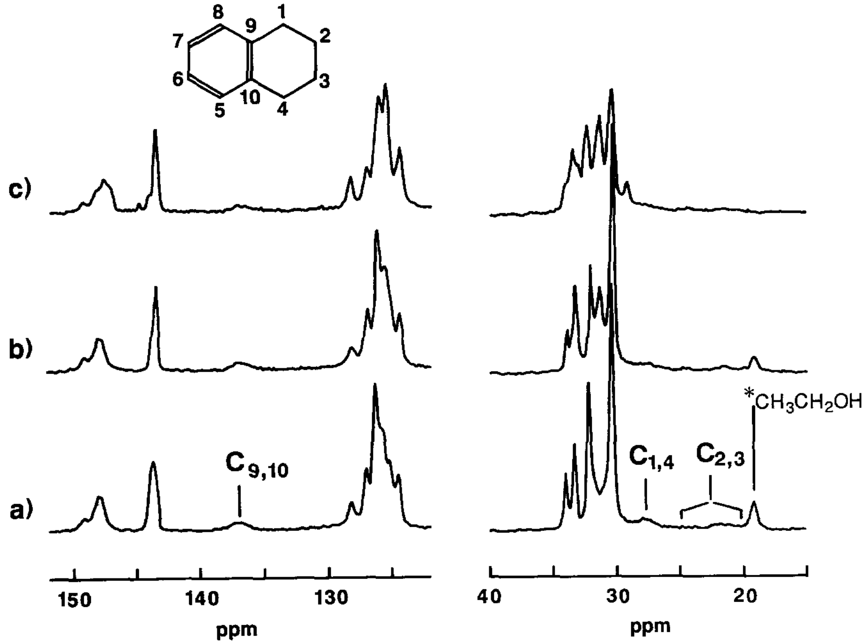

Fig. 2. ^{13}C CP/MAS NMR spectra of *p-tert*-butylcalix[5]arene with tetralin in the calix and incorporated ethanol: (a) initial sample; (b) sample after 8 h under vacuum at room temperature; (c) after removal of ethanol by heating under vacuum at 50° for 10 h. Inset shows carbon numbering scheme for tetralin.

A crystallographic mirror plane bisects the calix[5]arene and contains the multi-ring guest. The question of whether the aromatic or the aliphatic ring is most deeply imbedded cannot be answered with complete certainty. However, the tetralin molecule is not planar and the crystallographic restriction to planarity in this case implies disorder of the $—CH_2CH_2—$ unit. This should be reflected in higher thermal parameters which in turn implies that CT2 and CT3 belong to the saturated ring.

p-tert-Butylcalix[5]arene (tetralin) crystallizes from ethanol with inclusion of the solvent. As shown by CP MAS ^{13}C NMR spectra [13] (Figure 2), the ethanol can be completely removed by heating to 50° under a vacuum. However, the tetralin remains unchanged and the crystallinity is maintained, with only minor changes in the detailed host lattice structure. The best defined guest resonances are those of C1,4 at 27.8 ppm and C9,10 at 137.0 ppm, most of the others (solution values [14] 136.4 (C9,10), 128.8 (C5,8), 125.2 (C6,7), 29.3 (C1,4), 23.3 (C2,3)) being hidden by the dominant calix[5]arene lines. The line due to C2,3 appears complex and occurs between 21 and 25 ppm. This may be related to the disorder inferred from the crystallographic data. Dipolar dephasing experiments indicate that both the C2,3 methylenes of tetralin as well as the ethanol molecules have a dynamic component to their disorder.

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12. *p-tert*-Butylcalix[5]arene was prepared by the method of reference 10. This involved at one stage heating in tetralin at 155° for 6 h. After removal of the tetralin, the substance was recrystallized from ethanol. *p-tert*-Butylcalix[5]arene (tetralin) · 2 EtOH belongs to the monoclinic space group $C2/m$ with $a = 22.187(6)$, $b = 15.823(6)$, $c = 18.168(5)$ Å, $\beta = 99.70(2)°$, and $D_c = 1.09$ g cm^{-3} for $Z = 4$. Refinement based on 1652 observed reflections led to a final R value of 0.081.
13. Solid-state ^{13}C NMR spectra were obtained using cross-polarization (contact time 1 ms, delay 2 s, decoupling field amplitude 60 kHz) and magic angle spinning (3.25–3.55 kHz) on a Bruker CXP-180 spectrometer equipped with a Doty Scientific probe. Dipolar dephased spectra were obtained by leaving the decoupler off for 40 μs before initiating data acquisition.
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