Supplementary Material (ESI) for Chemical Communications

Supplementary Information

The structures of *p-tert*-butylcalix[4]arene and *p-tert*-pentylcalix[4]arene has been published before. The sublimed structure of *p-tert*-octylcalix[4]arene was determined by small-molecule X-ray diffraction method as described below.

Data collection, structure solution and refinement:
X-Ray intensity data were measured at 173 K on a Bruker SMART 1000 CCD diffractometer (MoKa, graphite monochromator). Empirical absorption corrections were applied (SADABS). The structures were solved by direct methods (SHELXS-97). In each case, the model was expanded by difference electron density synthesis and refined by full-matrix least-squares against F^2 using all data (SHELXL-97). Where possible, hydrogen atoms were included in calculated positions as riding atoms except where noted.

Crystal data for Octyl: $C_{60}H_{88}O_4$, M = 873.30, colorless prism, 0.25 × 0.25 × 0.20 mm^3, monoclinic, space group $P2_1/c$ (No. 14), a = 11.3633(17), b = 38.624(6), c = 12.6614(19) Å, β = 101.881(2)°, V = 5438.0(14) Å^3, Z = 4, D_c = 1.067 g/cm^3, F_{000} = 1920, MoKα radiation, λ = 0.71073 Å, T = 173(2)K, $2\theta_{max}$ = 54.3º, 47813 reflections collected, 12034 unique (R_{int} = 0.0919). The structure was solved and refined using the programs SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and to prepare the figures. Final *GooF* = 1.057, *R1* = 0.0786, *wR2* = 0.1791, *R* indices based on 6101 reflections with $I > 2\sigma(I)$ (refinement on F^2), 738 parameters, 30 restraints. *L*p and absorption corrections applied, μ = 0.064 mm^{-1}. Two octyl groups were disordered over two positions and modeled accordingly. All four hydroxyl hydrogen atoms were also modeled as disordered over two positions each.