

Solution volume studies of a deep cavity inclusion complex of C₆₀: [*p*-benzylcalix[5]arene ⊂ C₆₀]

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Molecular complexation of C₆₀ with *p*-benzylcalix[5]arene in toluene is associated with a partial molar volume change of +195 cm³ mol⁻¹ which is consistent with the displacement of two toluene molecules from the cavity of the calixarene.

Inclusion of fullerenes in container molecules is of interest in the direct purifying of fullerenes from fullerite, and the opportunities that such host-guest complexes have as nanometer size components in building up novel supramolecular arrays.¹⁻¹⁷ Further developments require gaining control over inherently weak host-guest interactions which are in competition with fullerene-fullerene, solvent-host and guest-solvent interactions, and is compounded by the essentially spherical, non-polarised nature of C₆₀.^{10,15} Container molecules which form discrete complexes with C₆₀ and/or C₇₀ include calix[6,8]arenes,⁵⁻¹³ cyclotrimeratrylene (CTV),^{14,15} γ -cyclodextrin,¹⁶ and azacrown ethers.¹⁷ Only three of these complexes have been structurally authenticated, a bis-mixed *p*-methyl/iodo-substituted calix[5]arene complex with C₆₀,¹³ and two

complexes of CTV with C₆₀ of composition (C₆₀)_{*n*}(CTV), (*n* = 1, 1.5). The latter structures are based on 'ball-and-socket' local host-guest supermolecules with the gross structures dominated by fullerene-fullerene interactions. The solid-state structure of another complex, the 1:1 complex of *p*-Bu^t-calix[8]arene with C₆₀ has been predicted as containing a micelle-like triangular aggregate of three fullerenes shrouded by three host molecules, each in a double cone conformation.¹⁰ Similar micelle-like species are formed in the confines of a mesoporous silica with mean pores size diameter of 5.4 nm.¹²

In solution there is some evidence for the formation of solvated host-guest supermolecules^{13,15} which can lead to micelle-like species.¹⁵ We now further explore host-guest chemistry in solution for C₆₀ in the presence of *p*-benzylcalix[5]arene **1** using high-precision densitometry to measure the change in partial molar volume ($\Delta\bar{V}$) on complexation. This technique has been recently employed to measure the partial molar volume of C₆₀ in different organic solvents¹⁸ but has not been used previously for studying supramolecular assemblies in

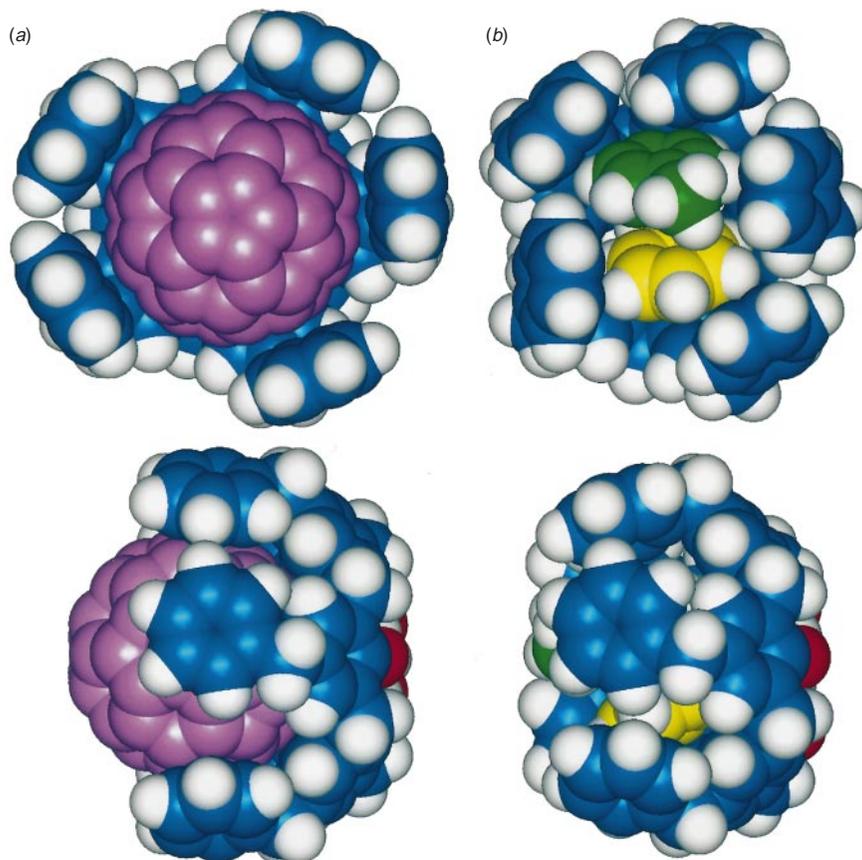
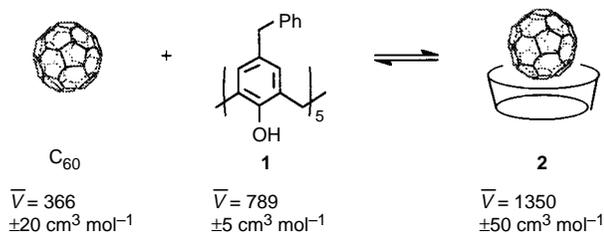


Fig. 1 Space filling molecular mechanics structures of (a) [*p*-benzylcalix[5]arene ⊂ C₆₀] and (b) [*p*-benzylcalix[5]arene ⊂ (toluene)₂] [Insight II/Discover with standard CVFF forcefields; structure minimised using the conjugate gradients algorithm with a convergence criterion of the average derivative being <0.001 kcal mol⁻¹ (1 cal = 4.184 J)]



Scheme 1

solution. Choice of calixarene **1** was based on the availability of a deep cavity with a large internal surface area offering π -cloud overlap with the electron deficient fullerene. Furthermore, this overlap is optimised by the matching of the C_5 symmetry of the calixarene cavity with a C_5 symmetry axis of the fullerene.

p-Benzylcalix[5]arene, **1**, was prepared by a variation of a published procedure.¹⁹ On heating a toluene solution of **1** with C_{60} (1 : 1) the characteristic magenta colour of C_{60} in solution changed to red and crystals slowly precipitated on cooling, albeit as the 2 : 1 calixarene to C_{60} complex.[†] However, titration of C_{60} with **1** in toluene revealed the appearance of a shoulder in the visible spectrum around 450 nm which was unchanged for concentrations of **1** in excess of 1.0 equiv., indicating 1 : 1 stoichiometry of the complex in solution. This is consistent with a recent finding that a *p*-methyl/iodo-substituted calixarene forms a 1 : 1 complex in solution,¹³ while a 2 : 1 complex precipitates from solution. ¹H and ¹³C NMR analysis of solutions of **1** and C_{60} (1 : 1) revealed little change on complexation other than a small downfield shift (0.2 ppm) in the ¹H resonance for the phenolic protons which is consistent with proximity of the O centres to the electron deficient C_{60} and a commensurate upfield shift (0.3 ppm) in the ¹³C resonance for C_{60} .¹³

Molecular modelling of the 1 : 1 complex (Fig. 1) shows that while much of the fullerene is in the cavity of the calixarene an area is exposed for intimate contact with a fullerene of another supermolecule. In solution, the absence of an interfullerene resonant band at 460 nm¹⁵ rules this out and the spectrum is similar to that obtained on mixing C_{60} in toluene with a toluene solution of an allyl substituted CTV where there is formation of solvated host-guest species.¹⁵ Interestingly, this CTV is like *p*-benzylcalix[5]arene in having extended arms. When a toluene solution of **1** is added to a mesoporous silica containing pre-mobilised C_{60} , a broad band at 460 nm appears which is assigned as an interfullerene resonant transition.¹² Thus in the confines of the mesopores there is some association of the supermolecules *via* fullerene-fullerene interactions, but not so in solution, and also in the solid state where the fullerene is most likely completely shrouded by two calixarenes.

The partial molar volumes of C_{60} , calixarene **1** and the 1 : 1 complex **2** in toluene at infinite dilution (Scheme 1) were determined using a Parr high-precision, vibrating-tube density meter at 25.35 ± 0.05 °C. At least three density measurements were made at three–six concentrations over the range 6.5×10^{-4} – 2.0×10^{-3} M and extrapolated to $c = 0$. The partial molar volume measured for C_{60} in toluene was in good agreement with the range given by Ruelle *et al.* (358.3–364.4 cm³ mol⁻¹).¹⁸ The partial molar volume of **2** was calculated assuming a negligible dissociation to C_{60} and calixarene as indicated by the UV spectrum. The uncertainties in the volume measurements for C_{60} and **2** are perhaps somewhat larger than usual (5% for C_{60} , 4% for **2**) owing to the sparing solubility of these compounds in toluene which precludes density measurements over a wider concentration range.

The reaction volume ($\Delta\bar{V}_{c \rightarrow 0}$) on complex formation is, therefore, +195 cm³ mol⁻¹ which is equivalent to the partial

molar volume of *ca.* 1.8 toluene molecules.¹⁸ This value can be interpreted in terms of the displacement of two toluene molecules from the cavity of the calixarene by C_{60} . This interpretation is supported by molecular mechanics using BIOSYM software.²⁰ Several minimised conformations for toluene molecules within the *p*-benzylcalix[5]arene cone were found. In particular, the toluene molecules with the same orientation (either both methyl groups orientated towards or away from the O rim) or reverse orientations (as shown in Fig. 1) gave rise to similar system energies. The minimised complex [*p*-benzylcalix[5]arene $\subset C_{60}$] and two free toluene molecules is favoured energetically by approximately 28 kcal mol⁻¹ over the minimised complex comprising [*p*-benzylcalix[5]arene] \subset (toluene)₂ and free C_{60} .

One practical implication of this positive reaction volume is that elevated pressures would, perhaps unexpectedly, disfavour complex formation.

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Footnotes and References

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† *p*-Benzylcalix[5]arene (7.5 mg, 7.6 μ mol) in toluene (1 ml) and C_{60} (5.5 mg, 7.6 μ mol) in toluene (1 ml) were filtered into a common vessel and heated to 80 °C for 30 min. On cooling dark red crystals were obtained which were washed with hexane, yield 80–90%, and analysed as (**1**)₂ C_{60} ·8C₆H₅Me.

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