

# Octaphenylcyclotetrasiloxane confinement of C<sub>60</sub> into double columnar arrays

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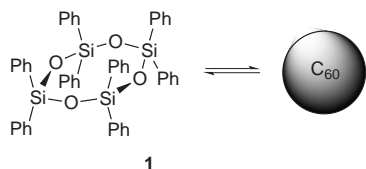
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**Excess octaphenylcyclotetrasiloxane [ $\{\text{SiPh}_2(\mu\text{-O})_4\}$ ] and C<sub>60</sub> in toluene affords the 1 : 1 supramolecular complex as a hemi-toluene solvate where the fullerenes are arranged in double columnar arrays shrouded by edge on, interlocking siloxanes.**

Host-guest and supramolecular chemistry of the electron-deficient fullerenes has focused mainly on the use of more traditional host or receptor molecules including cyclodextrins,<sup>1</sup> and container molecules with hydrophobic pockets lined with aromatic rings, notably calixarenes,<sup>2-6</sup> resorcinarenes,<sup>7</sup> and cyclotriveratrylene and related molecules.<sup>8,9</sup> A recent development is the confinement of C<sub>60</sub> and C<sub>70</sub> (and other globular molecules) in complementary cavities of rigid nickel( $\pi$ ) macrocycles.<sup>10</sup> Here the interaction may be synergic with the likelihood of fullerene to metal electron density flow as well as the reverse for the unsaturated rings of the host in contact with the fullerene. However, in general, encouraging inherently weak host-guest interactions involving a fullerene is facilitated by the complementarity of curvature of the host with that of the fullerene, as is having a host with a rigid structure such that there is no pre-organisation energy requirement prior to complexation with the fullerene.<sup>10</sup>

In further exploring the use of rigid receptor molecules to 'recognise' fullerenes we have investigated the interplay of octaphenylcyclotetrasiloxane [ $\{\text{SiPh}_2(\mu\text{-O})_4\}$ ] with C<sub>60</sub> and find it forms a 1 : 1 complex in the solid state. In principle, the siloxane can act as a multi-divergent receptor molecule with six concave surfaces surrounding the central core. Molecular mechanics suggests that these surfaces have complementarity of curvature with that of C<sub>60</sub> and that there is little pre-organisation for complexation which is associated with simple torsion along the Si-C bonds. Despite this, the isolated complex has the siloxane acting as a single receptor site with C<sub>60</sub>, in one of the four cavities which is edge-on relative to the tetrasiloxane plane (1). This is unexpected given that the two faces above and below

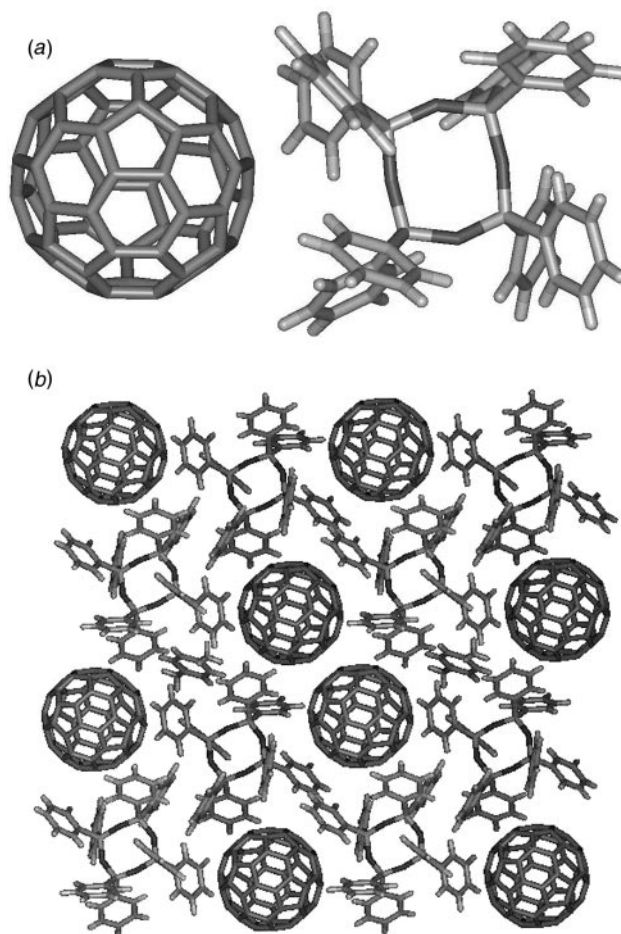


the siloxane plane have deeper cavities. Rather a phenyl ring of one siloxane molecule is directed into one of these cavities of another siloxane. This was also found in the structure of the siloxane itself but had been overlooked,<sup>11</sup> and surprisingly there is no inter-siloxane molecule  $\pi$ -stacking. The structure is also noteworthy in that the fullerenes are aligned in double columnar arrays; this structural motif is unusual, restricted to an organometallic inclusion complex<sup>12</sup> and a charge transfer complex with a thiafulvalene.<sup>13</sup> Moreover, this is the first report of a siloxane-C<sub>60</sub> host-guest complex, and C<sub>70</sub> fails to form a complex under similar conditions.

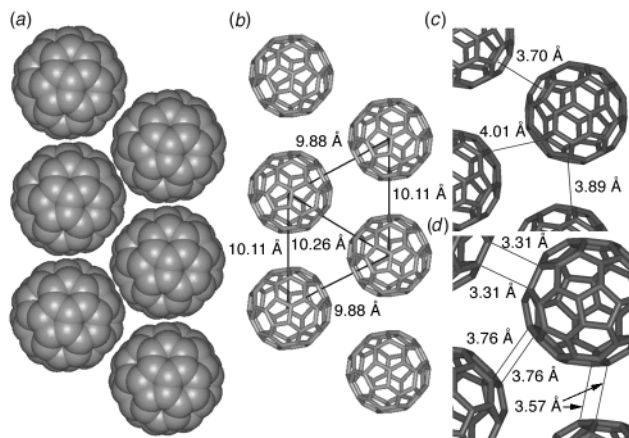
Dark red crystals of the 1 : 1 complex as a toluene hemi-solvate, [ $\{\text{SiPh}_2(\mu\text{-O})_4\}$ ]C<sub>60</sub>(toluene)<sub>0.5</sub>, were obtained by slow diffusion of Pr<sup>4</sup>OH vapour into a toluene solution of C<sub>60</sub> and

excess siloxane, ratio *ca.* 1 : 10.<sup>†</sup> Many other ratios and solvents, and solvent mixtures, were unsuccessful in forming the complex. The IR of the complex showed the superposition of peaks corresponding to the three components in the lattice, as expected for weakly associated species. In solution, UV-VIS studies show very little change in the range 400 to 800 nm, unlike in other systems,<sup>5,8,13</sup> and there was little change in the NMR spectroscopic data. Thus the interactions in solution are inherently weak.

In the structure derived from X-ray diffraction studies,<sup>‡</sup> a molecule of each of the supramolecular synthons and half a toluene molecule residing over a centre of inversion comprise the asymmetric unit; results are presented in Fig. 1 and 2. The side-on interaction of the fullerene with the siloxane is unsymmetrical; two of the four phenyl rings attached to the same silicon centre have the closest contacts to the fullerene at 3.70 Å. The two phenyl rings on the other silicon associated with the same edge of the siloxane are positioned such that there



**Fig. 1** The structure of [ $\{\text{SiPh}_2(\mu\text{-O})_4\}$ ]C<sub>60</sub>(toluene)<sub>0.5</sub> showing (a) the two interacting supramolecular synthons, and (b) the extended interplay projected down the axis, the direction of the double columnar arrays of fullerenes; the toluene molecules are disordered over centres of inversion.



**Fig. 2** The double columnar array of fullerenes in  $[\{\text{SiPh}_2(\mu\text{-O})_4\}\text{C}_{60}(\text{toluene})_{0.5}]$  showing (a) space filling packing, (b) fullerene centroid-centroid separations, (c) inter-fullerene ring centroid separations, and (d) closest fullerene contacts.

is no  $\pi$ -stacking between the two components, and indeed, the protons on the phenyl rings are the atoms in immediate contact with the fullerene [Fig. 1(a)]. This type of C–H $\cdots$ C<sub>60</sub> interaction has precedence in one other structure, notably that of  $[\text{C}_{60} \subset (\text{L})_2]$  (L = *p*-benzylhexahomooxalix[3]arene).<sup>3</sup>

In the upper and lower cavity of the siloxane, there are either one or two phenyl rings orientated with the C–H groups towards the centre of the siloxane ring. These orientations preclude any interaction of the fullerene in the clefts. One ‘upper’ phenyl ring of one siloxane molecule is pointing into the ‘lower cavity’ of the same siloxane one unit cell away in the direction of the *a* axis [Fig. 1(b)]. This interlocking stacking motif is similar to that found in the crystal structures of the pure siloxane.<sup>11</sup> The predilection towards this type of stacking for the siloxane may be one of the factors influencing its interplay with the fullerene.

Fig. 2 shows the pairs of C<sub>60</sub> columns. Analysis of the centroid-to-centroid distances of the C<sub>60</sub> molecules shows that the packing is not as regular as close packing, with the positions of the C<sub>60</sub> molecules in one column slightly offset, so they are closer to one of the nearest neighbours in the other column. The centroid-to-centroid distances are 10.11 Å within a column and either 9.88 or 10.26 Å between columns for the nearest neighbours. The shortest of these distances compare with the very short, dipole induced inter-fullerene distances in the single columnar arrays of C<sub>60</sub> found in a calix[4]arene–C<sub>60</sub> complex, viz. 9.8782(5) Å.<sup>6</sup> Within a single column of C<sub>60</sub> molecules, the closest centroid to centroid approach for two C<sub>60</sub> rings is 3.89 Å, with the rings offset, so that the centroids are not directly opposite each other. The closest approach between C<sub>60</sub> ring centroids occurs between the columns at 3.70 Å. The closest C $\cdots$ C contact is 3.31 Å. The siloxane molecules appear to interact between columns, and with other C<sub>60</sub> and toluene molecules [Fig. 1(b)]. With a few exceptions,<sup>3,4,8</sup> inter-fullerene interactions play a major role in the structures of supramolecular complexes of C<sub>60</sub>,<sup>2,5–8,10,12,13</sup> and this is further corroborated in the present structure. Establishing the ground rules for inter-fullerene interactions is important in understanding the competing interactions associated with the formation of discrete host–guest supermolecules.

This report clearly demonstrates the ability of a simple siloxane to self-assemble with C<sub>60</sub>. From here there is the exciting prospect of stronger binding by incorporating extended aryl arms on the siloxane, and to extend the work to the analogous octa-aryloctasiloxanes  $[\{\text{Si}(\text{aryl})(\mu\text{-O})\}_8]$ .

The support of this work by the Australian Research Council is gratefully appreciated.

## Notes and references

† *Synthesis of  $[\{\text{SiPh}_2(\mu\text{-O})_4\}\text{C}_{60}(\text{toluene})_{0.5}]$* : Slow diffusion of Pr<sup>3+</sup>OH into a toluene solution of C<sub>60</sub> (10 mg, 0.014 mmol) and the siloxane (100 mg, 0.130 mmol) in toluene (5 ml) over four weeks afforded colourless crystals (60 mg) of the siloxane which were separated manually from the deep red needles of the fullerene–siloxane complex, 4 mg, 19% yield. Found: C, 85.92; H, 2.60. C<sub>111.5</sub>H<sub>43.5</sub>O<sub>4</sub>Si<sub>4</sub> requires, C, 85.85; H, 2.84%.

‡ *Crystal data for  $[\{\text{SiPh}_2(\mu\text{-O})_4\}\text{C}_{60}(\text{toluene})_{0.5}]$* : Data were collected on an Enraf Nonius KappaCCD diffractometer with Mo–K $\alpha$  radiation ( $\lambda = 0.71073$  Å) and were corrected for Lorentzian and polarisation effects but not absorption. The structure was solved by direct methods (SHELXS-97) and refined anisotropically with full-matrix least-squares on  $F^2$  (SHELXL-97). Hydrogen atoms were located in the difference map and refined isotropically. C<sub>111.5</sub>H<sub>43.5</sub>O<sub>4</sub>Si<sub>4</sub>,  $M = 1559.3$ , triclinic, space group  $P\bar{1}$ ,  $a = 10.1145(4)$ ,  $b = 19.0653(8)$ ,  $c = 19.2258(7)$  Å,  $\alpha = 82.250(5)$ ,  $\beta = 75.960(5)$ ,  $\gamma = 78.414(5)^\circ$ ,  $U = 3509.0(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.476$  g cm<sup>–3</sup>,  $T = 123(1)$  K,  $\mu = 0.153$  mm<sup>–1</sup>, 22635 reflections collected, 12344 unique ( $R_{\text{int}} = 0.065$ ), 7715 reflections observed, 1241 parameters,  $R_1 = 0.0513$  (observed data),  $wR_2 = 0.1063$  (all data). CCDC 182/1250. See <http://www.rsc.org/suppdata/cc/1999/1139/> for crystallographic data in .cif format.

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