Supramolecular complexation of [60]fullerene with hexahomotrioxacalix[3]naphthalenes: a new class of naphthalene-based calixarenes

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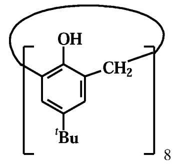
The hexahomotrioxacalix[3]naphthalenes **4** and **5** which are members of a new class of inherently chiral naphthalene-based calixarenes were evaluated for their supramolecular complexation properties with [60]fullerene ("C_{60}"). The X-ray structure of a $(\mathbf{5})_2\cdot C_{60}$ clathrate was obtained and compared with the supramolecular complexation data obtained by a ^1H NMR study of **4** and **5** with C_{60} in benzene-d_6 and toluene-d_8.

Introduction

The supramolecular (*i.e.* non-covalent or ionic) complexation of fullerenes with a variety of macromolecular hosts is a subject of extensive ongoing interest.[1] In particular, the independent discovery by Atwood[2] and Shinkai[3] and their co-workers that *p-tert*-butylcalix[8]arene **1** selectively sequestered [60]fullerene ("C_{60}") from a mixture of higher fullerenes and thus led to an efficient purification of C_{60}, has resulted in many studies involving C_{60} and other calixarenes. The calixarenes themselves are extensively studied due to their remarkable synthetic versatility as molecular building blocks for the design of novel and varied supramolecular hosts.[4] Recently, Shinkai and co-workers[5] showed that *p-tert*-butylhexahomotrioxacalix[3]arene **2** and its various derivatives[6] formed inclusion complexes with C_{60} in solution. In 1998 Fuji and co-workers[7] reported the first X-ray crystal structure of a $C_{60}\cdot\mathbf{2}$ complex and also of a C_{60} complex with *p*-bromohexahomotrioxacalix[3]arene **3**. Earlier this year the synthesis of a new class of supramolecular host molecules which are naphthalene-based analogues of **2** was reported.[8] Hexahomotrioxacalix[3]naphthalene **4** and its *tert*-butylated analogue **5** showed poor alkali-metal cation complexation properties, however they show much stronger complexing abilities with C_{60}. We herein describe the first X-ray structure of a supramolecular complex formed between C_{60} and a calixnaphthalene-type[9] molecule, and a solution complexation study using ^1H NMR spectrometry.[10]



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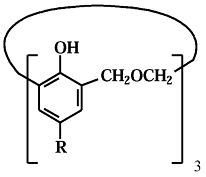
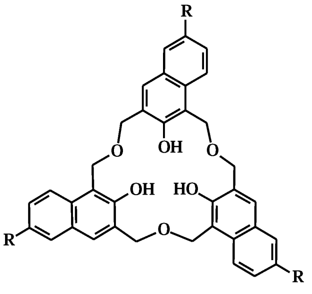


2: R = ^{t}Bu
3: R = Br
6: R = H



4: R = H
5: R = ^{t}Bu

Results and discussion

Supramolecular 1 : 1 complex formation between **4** (for example) and C_{60} in solution, can be represented by eqn. (1).

$$C_{60} + \mathbf{4} \rightleftharpoons C_{60}\cdot\mathbf{4} \tag{1}$$

The corresponding association constant K_{assoc} can be defined by eqn. (2),

$$K_{assoc} = [C_{60}\cdot\mathbf{4}]/([C_{60}][\mathbf{4}]) \tag{2}$$

and can be determined using the NMR version of the Benesi–Hildebrand equation[11] which is shown in eqn. (3),[10]

$$1/\Delta\delta = 1/(\Delta\delta_{max} \times K_{assoc}[C_{60}]_o) + 1/\Delta\delta_{max} \tag{3}$$

where $\Delta\delta$ is the change in chemical shift upon addition of C_{60}, referenced to uncomplexed **4**, and $\Delta\delta_{max}$ is the difference in chemical shifts between those observed in **4** and in the complex, while $[C_{60}]_o$ is the total concentration of C_{60}. The value of K_{assoc} is determined from the slope and intercept obtained from a linear regression analysis of the "double reciprocal linear plot" of $1/\Delta\delta$ *vs.* $1/[C_{60}]_o$. Table 1 lists the values of K_{assoc} at 298 K which were determined for C_{60} with each of **4** and **5** in toluene-d_8 or benzene-d_6. The calculations were based upon the chemical shift changes observed for "H_f". The K_{assoc} values listed here are higher than the values reported for the analogous calixarenes: Shinkai and co-workers[5] reported a value of 35 ± 5 $dm^3\ mol^{-1}$ for the complex of **2** with C_{60} in toluene using UV-VIS measurements, while Fuji and co-workers[7] reported values of 35.6 ± 0.3 $dm^3\ mol^{-1}$ for the same complex under the same conditions, and 9.1 ± 1.0 $dm^3\ mol^{-1}$ for the complex of **6** with C_{60} in toluene. Fuji and co-authors also reported a K_{assoc} value of 14.9 ± 2.0 $dm^3\ mol^{-1}$ for the complex of **3** with C_{60} in toluene. To our knowledge, there have been no reports on other solution studies on these systems.

The larger K_{assoc} values observed in the present study are consistent with our earlier findings[12] on the complexation of C_{60} with the closely-related calix[4]naphthalenes. In that study the major attractive interactions for the complex formation between C_{60} and the naphthalene ring-containing host molecules was postulated to be due to the π–π interactions between C_{60} and both of the fused aromatic rings in each naphthalene

Table 1 K_{assoc} values for C_{60} complexes with **4** and **5** in toluene-d_8 and benzene-d_6

	Toluene-d_8	Benzene-d_6
4 : Run 1	146 ± 7	119 ± 7
4 : Run 2	154 ± 2	112 ± 5
Mean values	150 ± 5	116 ± 6
5 : Run 1	300 ± 9	444 ± 14
5 : Run 2	292 ± 9	438 ± 30
Mean values	296 ± 9	441 ± 23

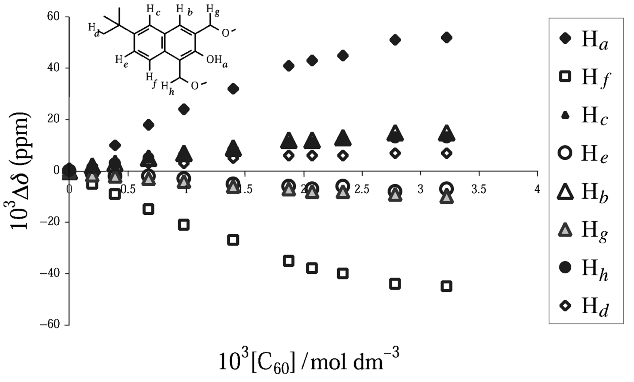


Fig. 1 Plot of chemical shift changes $\Delta\delta$ *vs.* $[C_{60}]$ for protons H_{a-h} of **5** in toluene-d_8.

unit, *via* a deep cavity inclusion. The values of K_{assoc} are affected by several factors, among which is the solvent. Haino *et al.*[13] showed that the stability of the complex increases as the solubility of C_{60} in the appropriate solvent decreases, since less energy is required for the desolvation of C_{60} which must necessarily precede its complexation with a host molecule. This would explain the higher K_{assoc} value found for the C_{60}·**5** complex in benzene-d_6 as compared to that in toluene-d_8, since the solubility of C_{60} is higher in toluene (2.1–3.2 mg cm^{-3}) than in benzene (1.4–1.9 mg cm^{-3}).[14]

We previously presented a discussion on the solvophobic effect on the values of K_{assoc} in which it was proposed[15] that the solvophobic effect, which is mainly entropic, also plays a role in our systems and in similar ones, even in non-aqueous solvents. Recently, we reported the partial molar volume study that showed that the change in molar volume upon complex formation between C_{60} and calix[4]naphthalenes was related to a solvophobic factor. From a similar partial molar volume study undertaken with these hexahomotrioxacalix[3]naphthalenes and C_{60},[16] it is concluded that the solvophobic effect is the larger one in the case of C_{60}·**4** complex formation in toluene. This explains the higher K_{assoc} value for C_{60}·**4** complex formation in toluene-d_8 compared to that in benzene-d_6.

The stoichiometry of the complex in each solution was determined to be 1 : 1 from both the Job Plot[17] and the mole ratio method. Fig. 1 shows the mole ratio plot for the chemical shifts of all eight of the protons in **5**. It is evident that the hydroxy proton "H_a" and the aromatic proton labelled "H_f" experience the largest changes in their chemical shifts. This implies that the C_{60} guest is included deep into the cavity of **5** (and **4**—*data not shown*), an interpretation which is also supported by the relatively much smaller changes in the chemical shift of the *tert*-butyl protons. The +mesomeric effect from the naphthol hydroxy group imparts greater electron density into the naphthalene rings, thereby enhancing the π–π interactions between the electron-rich naphthalene rings and the C_{60} guest. As a result, a significant shielding effect is experienced by aromatic proton H_f and a corresponding deshielding effect is experienced by the hydroxy proton. By contrast, Shinkai and co-workers[5] observed larger chemical shift changes for the *tert*-butyl protons than for the hydroxy and aromatic protons of the shallower cavity-bearing compound **2**.

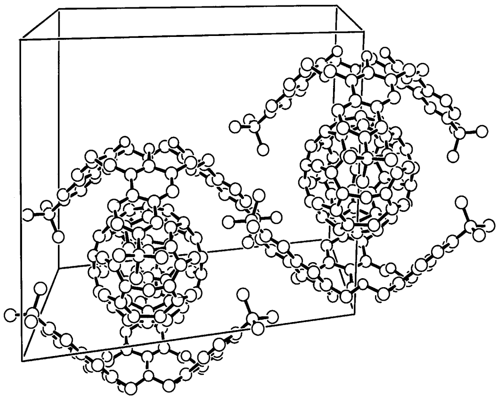


Fig. 2 X-Ray partial packing diagram for **5** in which the other molecules have been removed for clarity.

The spectral changes induced by the addition of **4** or **5** to solutions of C_{60} were seen at $\lambda = 430$ nm, a finding that is similar to that observed earlier with calix[4]naphthalenes.[18]

Deep red prism crystals having a $(\mathbf{5})_2$·C_{60} stoichiometry were obtained from the slow evaporation of a toluene-d_8 solution of C_{60} and **5**. The single-crystal X-ray structure shown in Fig. 2, reveals that the complex has C_{3i} symmetry and contains an encapsulated C_{60} molecule within the cavity defined by two molecules of **5**. The C_{60} molecule adopts a nesting position at the van der Waals contact distance between the two concave surfaces of the hexahomotrioxacalixnaphthalene. The 18-membered macrocycle of each of the two molecules of **5** line up with a six-membered ring in C_{60}, compelling the three adjacent, fused six-membered rings of the C_{60} to reside above the three electron rich naphthalene units of **5** to maximize the π–π interactions. Methyl–π interactions similar to those observed in many diverse clathrates of *tert*-butylcalixarenes,[19] are also evident here as revealed by the methyl groups of each of the *tert*-butyl groups which are directed toward the faces of the remaining six-membered rings in the "equatorial belt" of the C_{60}. Each of the two molecules of **5** which are in *cone* conformations are staggered with respect to each other, thereby minimizing any potential steric repulsion between them.

The C_{60} group in the complex is highly disordered or rotating and as a result the *R* values are high; however, this phenomenon with other C_{60} examples has been noted by others,[20,21] and attempts to refine the *R* factor by modelling this disorder would not be practical or meaningful.[22]

There are other instances that have been reported for C_{60}·calixarene complexes, whose solid state compositions have been revealed by their X-ray structures to be different from their solution compositions. For example, Haino *et al.*[13] and Yanase *et al.*[23] have reported different solution- and solid-state stoichiometries for C_{60}·calix[5]arene complexes. Atwood *et al.*[24] have reported 2 : 1 solid-state structures for the complexes between *p*-benzylhexahomotrioxacalix[3]arene and C_{60}, whereas in solution, it had 1 : 1 stoichiometry. On the other hand, Fuji *et al.*[7] reported the X-ray structures for the complexes of C_{60} with both **2** and **3**, and found them to exist as 1 : 1 complexes in both the solid- and solution-states.

All of the reported X-ray structures show back-to-back stacking of the respective calixarene·C_{60} complexes, in which intermolecular phenolic hydrogen-bonding is present. By comparison, our X-ray structure also shows similar back-to-back stacking of the **5**·C_{60} complexes, but with intermolecular methyl–π interactions being evident.

As noted by others[24,25] symmetry considerations play a significant role in complex formation. Thus, the presence of a common C_3 symmetry element in both **5** and C_{60} facilitates the alignment of both the host and the guest thereby maximizing the number of points of contact within the resulting complex.

In conclusion, it has been demonstrated that supramolecular complexation of C_{60} with the new class of naphthalene-based homooxacalixarenes represented by **4** and **5**, can exist in both the solid state and in solution. The X-ray structure of the C_{60} complex with **5** reveals it to have different stoichiometry from that observed in solution, as determined by ^{1}H NMR spectrometry.

Experimental

Compounds **4** and **5** were prepared according to the methods described previously.[8] All ^{1}H NMR spectra were recorded at 298 K on a BRUKER Avance Instrument at 500 MHz, using a 16 K data table for a 10.0 ppm sweep width having a digital resolution of 0.321 Hz. The solvents used were toluene-d_8 (99.6%) and benzene-d_6 (99.6%). Mass determinations were done on a CAHN-27 Electromicro-balance which is capable of mass determinations to 5×10^{-6} g. To obtain the association constants K_{assoc} corresponding to complex formation, changes in the chemical shifts ($\Delta\delta$) as a function of [C_{60}] were determined. Approximately 1.000 mg amounts of the host compound were dissolved in 1.00 ml of the desired solvent in an NMR tube, to which portions of C_{60} (approximately 0.100 mg amounts) were added. After sonication for 15 min to dissolve all of the C_{60} the NMR data was collected. At least 8–10 data points were collected for each run and a duplicate data set was obtained for each run. The changes in δ were plotted against [C_{60}] for each run, and the resulting plots (see Fig. 1) show plateaux at around a 1 : 1 ratio of C_{60} and **4** or **5**, indicating the formation of a 1 : 1 complex in each case. These molar ratios were confirmed from Job plots[17] in which the mole fraction of C_{60} was plotted against the mole fraction of **4** or **5** multiplied by $\Delta\delta$ for which the maxima are around 0.5. To calculate K_{assoc} values, the slopes and the intercepts obtained from linear regression analyses of Benesi–Hildebrand "linear double reciprocal" plots[11] were used.

X-Ray crystallographic data

The crystal used was a deep red crystal of $C_{108}H_{54}O_6$ having approximate dimensions of 0.64 × 0.11 × 0.11 mm which was mounted on a glass fibre. All data was collected on a Bruker P4/CCD system with graphite monochromated Mo-Kα radiation and a rotating anode generator. Cell constants and an orientation matrix for data collection corresponded to an R-centred trigonal cell (laue class: −3) with dimensions $a = 23.136(2)$ Å, $c = 17.217(2)$ Å and $V = 7981(1)$ Å^3. For $Z = 6$ and $M = 1447.61$, the calculated density is 1.81 g cm^{-3}. Based on the systematic absences of *hkil*, $-h + k + l \pm 3n$, packing considerations, a statistical analysis of intensity distribution and the successful solution and refinement of the structure, the space group was determined to be *R*-3 (#148). The data were collected at 193 ± 1 K on a Bruker P4/CCD diffractometer with graphite monochromated Mo-Kα radiation. The full hemisphere of data was collected with 30 s, 0.3 deg frames to a maximum 2θ value of 53.0°. A total of 14183 reflections were measured of which 3647 ($R_{\text{int}} = 0.096$) were unique. The linear absorption coefficient, μ, for Mo-Kα radiation is 1.1 cm^{-1}. The Siemens area detector absorption routine (SADABS) was used to correct the data with maximum and minimum effective transmissions of 0.9879 and 0.9326 respectively. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods[26] and expanded using Fourier techniques.[27] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement on F^2 was based on 1744 observed reflections and 247 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement *R* factors given by eqn. (4).

$$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.154 wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2} = 0.462 \quad (4)$$

The standard deviation of an observation of unit weight[28] (*i.e.* "Goodness of Fit Indicator") $[\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$, where N_o = number of observations, and N_v = number of variables, was 1.47. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.25 and −0.40 e$^-$ Å^{-3}, respectively. Neutral atom scattering factors were taken from Cromer and Waber.[29] Anomalous dispersion effects were included in F_{calc},[30] the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley.[31] The values for the mass attenuation coefficients are those of Creagh and Hubbell.[32] All calculations were performed using the teXsan[33] crystallographic software package of Molecular Structure Corporation except for refinement, which was performed using SHELXL-97.[28] CCDC 166077. See http://www.rsc.org/suppdata/p2/b1/b105019m/ for crystallographic files in .cif or other electronic format.

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