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Complexation of Fullerenes with 5,5′-Biscalix[5]arene[1]

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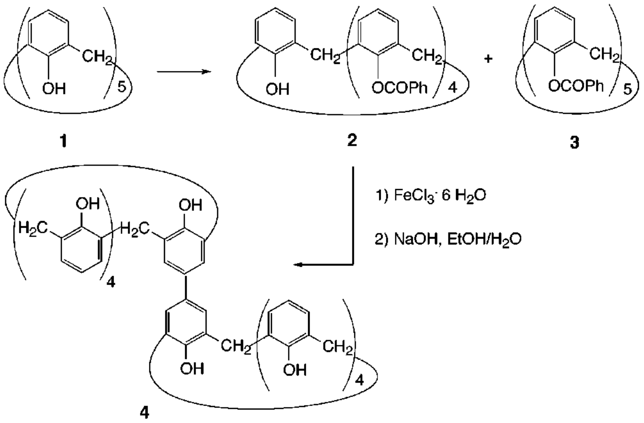
5,5′-Biscalix[5]arene, prepared by oxidative coupling of the tetrabenzoyl ester of calix[5]arene (shown by X-ray crystallographic analysis to have a **o**,u,u,d,u conformation), forms complexes with C_{60} ($K_{assoc} = 43\ M^{-1}$) and C_{70} ($K_{assoc} = 233\ M^{-1}$). The X-ray crystallographic structure of the C_{60} complex reveals its clamshell-shaped architecture, presumably the result of a change in the conformation of biscalix[5]arene from anti (uncomplexed) to syn (complexed).

Introduction

The complexation of fullerenes has been extensively studied in recent years.[2] Included among the macromolecular hosts that have been employed are the cyclodextrins,[3] azacrowns,[4] cyclotriveratrylenes,[5] dendrimers,[6] porphyrins,[7] calixarenes,[8−13] and other aromatic molecules.[14] Part of an ongoing investigation in our laboratory that is focused on the chemistry of the calixarenes[15] involves their use for fullerene complexation and has assumed considerable interest. In this connection the present article deals with the synthesis of a biscalix[5]arene and its complexation behavior toward C_{60} and C_{70}.

Synthesis of the Host Molecule. Neri and coworkers have described an oxidative coupling reaction that effects the direct upper rim to upper rim attachment of a pair of calix[4]arenes, calix[6]arenes, or calix[8]arenes, respectively, to yield 5,5′-biscalix[4, 6, or 8]arenes.[16] We have now extended this procedure to include calix[5]arene. The requisite starting material, the partially benzoylated calix[5]arene, was prepared by treating calix[5]arene (**1**) with benzoyl chloride in pyridine at 0 °C using the procedure of Gutsche and Lin.[17] The tetrabenzoyl ester **2** was isolated in 63% yield, accompanied by 10% of the pentabenzoyl ester **3**. The tetrabenzoyl ester, isolated by chromatographic separation, shows a fairly complicated pattern of resonances in the ArH and CH_2 region of the ^1H NMR spectrum,



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indicating it to be a mixture of conformers; only one of these crystallizes from solution. An X-ray crystallographic structure of the crystalline material (see Supporting Information) shows it to have a **o**,u,u,d,u conformation[18] (ArOH moiety the reference), while the X-ray crystallographic structure of the pentabenzoyl ester shows it to have a u,o,u,d,d conformation. That the tetrabenzoyl compound is a mixture of conformers is not detrimental to the formation of the target molecule, however, because the benzoyl groups are ultimately removed to yield a completely hydroxylated product in which the calix[5]arene rings assume the cone conformation. The coupling of **2** was effected with $FeCl_3 \cdot 6H_2O$ in refluxing MeCN, and the resulting product was saponified to provide a 42% yield of 5,5′-biscalix[5]arene (**4**). Unfortunately, it has not been possible to obtain crystals of **4** for X-ray analysis, so the representation of the orientation of its two rings as anti is only conjectural. However, this conjecture rests on good analogy, because the X-ray crystallographic structure of the closely related 5,5′-biscalix[4]arene, obtained by Neri and co-workers,[16] shows it to have the anti conformation.

Complexation Studies. The preferred solvent for studying the complexation of fullerenes is toluene. However, the biscalix[5]arene **4** is not sufficiently soluble in this solvent to provide effective complexation constants, so CS_2 was used as an alternative. By means of well-established procedures employing UV/vis spectral measurements,[9a,10d] association constants of 43 ± 5 M^{-1} with C_{60} and 233 ± 30 M^{-1} for C_{70} were measured, as shown in Table 1. Also shown in the Table are the corresponding association constants for the parent calix[5]arene **1**, which are 119 times lower for C_{60} and 4 times lower for C_{70}, leading to an unusually large K_{C70}/K_{C60} ratio for **1**. This is the consequence of the very low association constant for **1** in CS_2, much lower than in toluene. Presumably this is the result of competition between C_{60} and the solvent for complexation with the host molecule, the smaller SC_2 being more effective than the larger toluene in this regard. The largest K_{C70}/K_{C60} ratio previously observed in this laboratory was 3.8 for **1** in toluene solution; the smallest value was 0.48 for a biscalix[5]arene spanned between the upper rims by a CH_2-$CH{=}CHCH_2$ moiety[9a,b] (association constants for this compound with C_{60} and C_{70} are 1300 and 625 M^{-1}, respectively). Fukazawa and co-workers have reported association constants as high as 76000 M^{-1} for C_{60} and 163000 M^{-1} for C_{70} for a calix[5]arene bridged with a *m*-diethynylphenyl moety.[9j] To study the stoichiometry of the complexes in solution Job plots were constructed for $\mathbf{1 \cdot C_{60}}$ and $\mathbf{4 \cdot C_{60}}$ at three different wavelengths (420, 430, and 440 nm). In all cases the maximum ratio for $[C_{60}]/[C_{60} + \text{host}]$ occurred at 0.5, indicating a 1:1 ratio of host to guest as illustrated in Figure 1.

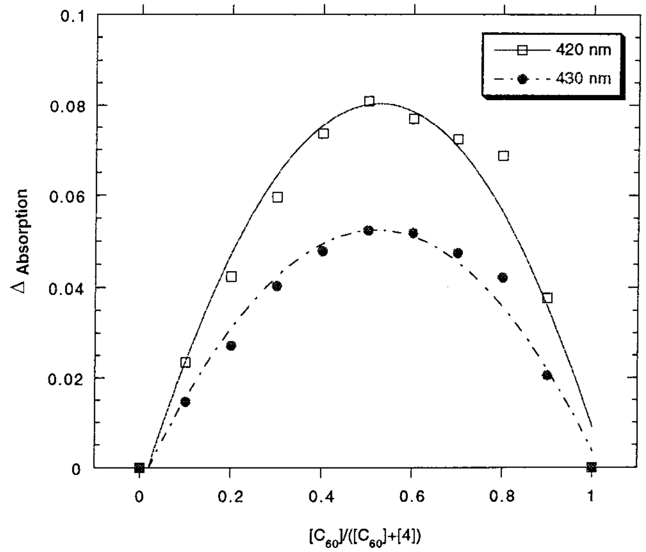

Figure 1. Job plot for 5,5′-biscalix[5]arene·C_{60} complex in CS_2 solution.

Table 1. Complexation Constants for Calixarenes 1 and 4 with C_{60} and C_{70} in CS_2 Solution

host molecule	K_{C60}, M^{-1}	$K_{C70,}$, M^{-1}	K_{C70}/K_{C60}
1	0.36 ± 0.05	58 ± 10	161
4	43 ± 5	233 ± 30	5.4

The complex of **4** with C_{60} was crystallized from toluene−CS_2, and an X-ray structure was obtained which shows the two rings of **4** to be syn to one another in a clamshell-like orientation with a pair of toluene molecules providing a cap, as illustrated in Figure 2. Thus, assuming that **4** exists in the anti conformation in the absence of a guest, it undergoes an anti to syn conversion upon complexation to maximize the interaction between host and guest, as illustrated in Figure 3. It is interesting to note that the biphenyl portion of the biscalix[5]arene is slightly bent, reflecting the attempt of the host to accommodate to the structure of its guest. Although an X-ray crystallographic structure of the complex of **4** with

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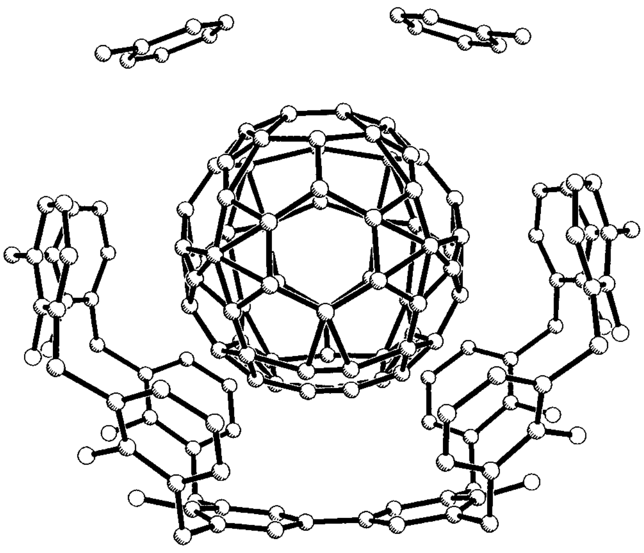

Figure 2. X-ray crystallographic structure of 5,5′-biscalix[5]-arene•C_{60} complex

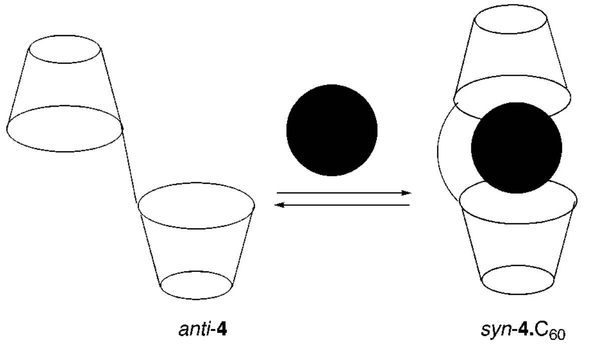

Figure 3. Conformational conversion of *anti*-**4** to *syn*-**4**•C_{60}.

C_{70} could not be obtained, the structure of the **4**•C_{60} complex suggests that the more elipsoidally shaped C_{70} might be better accommodated by *syn*-**4**, as suggested by the K_{C70}/K_{C60} complexation constant ratio of 5.4. Although X-ray crystallographic structures for simple calixarene•fullerene complexes such as calix[5]arene•C_{60} have been reported,[9h,i] the one for **4**•C_{60} represents the first for a biscalixarene•fullerene complex.

Experimental Section[19]

Tetrabenzoylcalix[5]arene (2). A 0.53 g (1 mmol) sample of calix[5]arene was dissolved in 10 mL of anhydrous pyridine, and 0.81 mL (7 mmol) of benzoyl chloride was added at ice-bath temperature. The mixture was stirred at 0 °C for 2.5 h. The reaction was then quenched by pouring the mixture into 100 mL of 2 N HCl, and the precipitate was collected by filtration and washed sequentially with 2 N NaOH, H_2O, and MeOH to give 0.82 g crude product. Purification by flash chromatography (eluent: hexane−$CHCl_3$−EtOAc, 5:1:1) and recrystallization from $CHCl_3$−CH_3OH gave 0.59 g. (63%) of **2** as a mixture of conformers: mp > 196 °C (dec); ^1H NMR ($CDCl_3$) δ 8.21−6.42 (m, 36H, ArH, OH), 3.84−3.26 (m, 10H, $ArCH_2Ar$); ^{13}C NMR ($CDCl_3$) δ 166.3, 165.1, 165.0, 164.9, 164.8, 164.7, 164.6, 164.4, 164.3, 163.6, 163.5,163.4, 153.8, 148.9, 148.6, 148.3, 148.0, 147.8, 147.4, 146.0, 135.3, 134.3, 134.1, 134.0, 133.7, 133.5, 133.3, 133.1, 132.9, 132.8, 132.6, 132.4, 132.3, 132.2, 131.9, 131.6, 131.2, 131.1, 130.9, 130.7, 130.6, 130.5, 130.3, 129.9, 129.8, 129.6, 129.5, 129.3, 129.1, 129.0, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.4, 127.2, 127.1, 126.7, 126.4, 126.3, 125.9, 125.7, 125.5, 125.4, 125.3, 125.1, 125.0, 124.8, 124.6, 118.5, 38.2, 35.8, 35.0, 31.4, 31.0, 30.8, 30.6, 29.7, 29.5; IR (KBr) 3427, 1732, 1450, 1265, 1170, 707 cm^{-1}. Anal. Calcd for $C_{63}H_{46}O_9$•0.25 CH_2Cl_2 (CH_2Cl_2 present in X-ray crystal structure): C 78.46; H 4.84. Found: C 78.85; H 4.87.

Pentabenzoylcalix[5]arene (3). From the flash chromatographic separation described above 10% of a mixture of the conformers of the pentabenzoyl ester **3** was isolated as a colorless solid: mp >260 °C (dec); ^1H NMR ($CDCl_3$) δ 8.28−5.67 (m, 40H, ArH), 3.94−3.11 (m, 10H, $ArCH_2Ar$); ^{13}C NMR ($CDCl_3$): δ 166.0, 165.3, 165.1, 165.0, 164.9, 148.9, 148.8, 148.3, 148.2, 147.8, 147.7, 147.6, 147.0, 146.9, 146.8, 134.8, 133.9, 133.8, 133.6, 133.4, 133.1, 132.8, 132.7, 132.5, 132.4, 132.3, 132.1, 131.9, 131.8, 131.7, 131.5, 131.4, 131.1, 131.0, 130.9, 130.8, 130.7, 130.5, 130.3, 130.1, 130.0, 129.8, 129.6, 129.4, 129.3, 129.0, 128.6, 128.4, 128.2, 128.1, 128.0, 126.1, 125.6, 125.2, 125.0, 124.7, 38.2, 37.2, 37.0, 36.2, 29.8, 29.3, 29.2, 29.0, 28.96, 28.92, 28.5, 28.4.; IR (KBr) 1730, 1450, 1267, 1167, 709 cm^{-1}. Anal. Calcd for $C_{70}H_{50}O_{10}$: C 79.98; H 4.79. Found: C 80.13; H 4.74. (See Supporting Information for X-ray crystal structure.)

5,5′-Bicalix[5]arene (4). A suspension of 0.51 g (0.54 mmol) of **2** and 1.16 g (4.32 mmol) of $FeCl_3$•$6H_2O$ in 50 mL of CH_3CN was refluxed with stirring. Additional aliquots of $FeCl_3$•$6H_2O$ (8 equiv) were added at 1 h intervals, until the starting material was no longer detected by TLC. The solvent was then removed by evaporation in vacuo, 2 N HCl was added to the residue, and the solid material was collected by filtration. The crude product was suspended in 85 mL of EtOH, and after addition of 13 mL of 15% aqueous NaOH, the mixture was refluxed with stirring for 7 h. Most of the EtOH was removed by evapration in vacuo, the resulting suspension was neutralized with 1 N HCl, and the solid material was collected by filtration. Flash chromatography with CH_2Cl_2−hexane (1:1) on silica gel gave 0.12 g (42%) of **4** as a colorless solid: mp > 252 °C (dec); ^1H NMR ($CDCl_3/CS_2$, 5:1); δ 8.94 (s, 2H, OH), 8.92 and 8.91(s, 4H each, OH), 7.26 (s, 4H, ArH), 7.21 (d, 16H, J = 7.6 Hz, ArH), 6.84 (t, 8H, J = 7.6 Hz, ArH), 3.87 (bs, 20H, $ArCH_2Ar$); ^{13}C NMR ($CDCl_3/CS_2$, 5:1): δ 150.0, 149.3, 134.6, 129.3, 129.2, 126.8, 126.7, 126.5, 121.7, 121.6, 31.5, 31.4. Anal. Calcd for $C_{70}H_{58}O_{10}$: C 79.38, H 5.52. Found: C 79.52, H 5.79. FAB-MASS in 3-NBA/GLY/TFA: m/z 1059 (M + 1).

Measurement of Complexation Constants. Complexation constants (K_{assoc}) were determined in CS_2 solution with a Cary 3 UV−vis spectrometer at 25 ± 5 °C. A 2.5 mL volume of fullerene stock solution (1×10^{-4} M) was placed in the sample cell and a 2.5 mL volume of CS_2 in the reference cell. A calculated amount of the host compound was added, with stirring, to the sample cell and the reference cell, and the absorption spectrum was recorded. Additional amounts of the host compound were then added to the two cells, and a spectrum was recorded after each addition. For example, the absorption in the range 425−450 nm for a C_{60} solution increased upon the addition of the host molecule, and the color of the solution changed from magenta to red, indicating the formation of a complex. Similarly, the absorption in the range 400−450 nm for a C_{70} solution increased upon the addition of the host molecule, and the color changed from red to colorless, again indicating the formation of a complex. The wavelengths for the maximum intensity changes were selected as 430 nm for C_{60} and 420 nm for C_{70}. From the absorption intensities at these wavelengths along with the concentrations of the host, the complexation constants of Table 1 were calculated using the Benesi−Hildebrand equation[20]

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[19] The melting points were measured in sealed and evacuated capillary tubes on a Mel-Temp apparatus (Laboratory Devices, Cambridge, MA) using a 500 °C calibrated against a thermocouple. ^1H and ^{13}C NMR spectra were recorded on a Varian XL-300 instrument at 300 and 75 MHz, respectively. Analytical samples were dried for at least 36 h at 100−140 °C and 1−2 mm of pressure and analyzed by Desert Analytics, Tucson, AZ.

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Job Plot Determinations. Nine solutions (solutions A) were prepared containing C_{60} in CS_2 in concentrations increasing in integral values from 1×10^{-4} to 9×10^{-4} M. Another nine solutions (solutions B) were prepared containing C_{60} and 5,5′-biscalix[5]arene (**4**) in integral concentration values such that the total concentration $[C_{60}] + [\mathbf{4}]$ remains constant at 10^{-3} M. The absorption intensities of all eighteen solutions were measured at several different wavelengths, and the absorption intensity of solution A was subtracted from that of the corresponding solution B. These values ($A - A_o$) were plotted against the value of $[C_{60}]/([C_{60} + [\mathbf{4}])$ as shown in Figure 1 for determinations at 420 and 430 nm. A maximum at 0.5 indicates the presence of a 1:1 complex.

X-ray Crystallography. Single crystals of **2** and **3** suitable for X-ray diffraction analysis were grown by slow evaporation (2−4 weeks) at room temperature in CH_2Cl_2 for **2** and acetone for **3**. To obtain a crystal of **4**·C_{60} for X-ray analysis a 2 mg sample of C_{60} was dissolved in 1 mL of toluene, mixed with 3 mg of **4** dissolved in 1 mL of CS_2, and slowly evaporated over a 2−4 week period.The single crystals of **2**, **3**, and **4·C_{60}** were glued to a glass fiber and mounted on a Bruker SMART CCD-based diffractometer. The frames were integrated with the SAINT software package[21] using a narrow-frame algorithm, and the structures were solved and refined using the SHELX-ZL software package.[22] An empirical absorption correction was applied. The C_{60} group in compound **4** is highly disordered even at 148 K. Attempts to fit the C_{60} structure were unsuccessful due to the multiple orientations. The *R* factor could be reduced by fitting large numbers of peaks with partial occupancy, but the results were meaningless. The largest peaks corresponding to the correct number of atoms were arbitrarily assigned as carbon and were refined anisotropically. Table 2 gives the crystal and refinement data for compounds **2**, **3**, and **4**·C_{60}.

Table 2. X-ray Data for Compounds 2, 3, and 4·C_{60}

	2	**3**	**4·C_{60}**
formula	$C_{64}H_{48}O_9CL_2$	$C_{73}H_{56}O_{11}$	$C_{144}H_{74}O_{10}$
FW	1031.9	1109.2	1964.0
T (K)	298	298	148
crystal structure	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/n$	$Pnma$
a (Å)	21/114(8)	14.023(2)	23.701(3)
b (Å)	12,295(5)	18.318(3)	30.019(4)
c (Å)	21.316(8)	23.293(4)	12.846(2)
α (deg)	90.00	90.00	90.00
β (deg)	102.781(3)	102.858(3)	90.00
γ (Å)	90.,00	90.00	90.00
Z	4	4	4
μ (mm^{-1})	0.180	0.085	0.089
reflections	7769	8372	6711
parameters	648	760	710
R_1; wR_2	0.138; 0.193	0.077; 0.221	0.098; 0.258

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Supporting Information Available: X-ray crystallographic structures for **2** and **3** and crystal data for **2**, **3**, and **4·C_{60}**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) SAINT Version 6.02, Bruker Analytical X-ray Systems, Inc; 1997−1999.

(22) SHELXTL Version 5.1, Bruker Analytical X-ray Systems, Inc; 1998.