Fullerenes Enclosed in Bridged Calix[5]arenes

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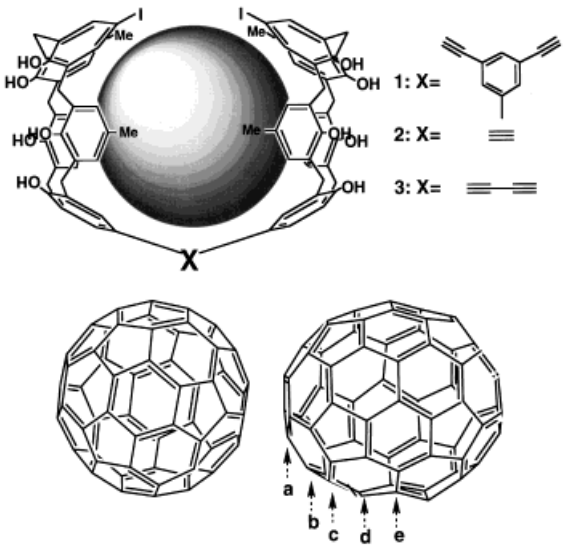
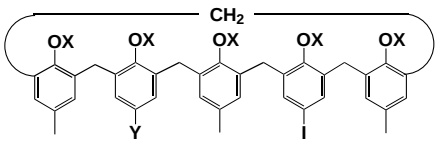
The development of host molecules for the inclusion of fullerenes is of interest in the direct purification of fullerenes,[1] although they can be separated and purified by chromatography.[2] The selective formation of a clathrate of *p-tert*-butylcalix[8]arene with C_{60} was used successfully to isolate C_{60}.[1a, 1b] The clathrate has a micellelike structure, and the host bound both C_{60} and C_{70} with a C_{60}/C_{70} selectivity of around 5/1.[1c] Thus, the design and synthesis of host molecules with reverse selectivity is of particular interest. We have reported that calix[5]arene receptors can strongly bind C_{60} in organic solvents[3] to give crystalline complexes with 1/1 and 2/1 host/guest ratios.[4] The structure of the crystalline 2/1 complex gave us a good suggestion of how two calix[5]arene units should be linked to give shape-selective receptors with well-defined cavity sizes. Thus, we synthesized host molecules for fullerenes that bind C_{70} preferentially to C_{60}. Here we report the synthesis of the host molecules **1**–**3** and their binding behavior towards C_{60} and C_{70} (Scheme 1).

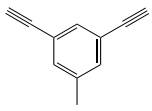


Scheme 1.

The starting material for the synthesis of the receptors was the readily available calix[5]arene derivative **4**,[3] which was converted into the pentaacetate **5**. A coupling reaction between **5** and **7** followed by removal of the acetyl groups furnished the desired receptor **1** in high yield. The palladium-catalyzed coupling of **5** with trimethylsilylacetylene followed by removal of the trimethylsilyl group afforded **6**.



4: X = H, Y = I
5: = Ac, = I
6: = Ac, = C≡CH



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The receptor **2** was prepared by the coupling of **5** and **6** with palladium(0) as catalyst followed by deprotection. Oxidative coupling of two molecules of **6** with cupric acetate and removal of the acetyl groups afforded the receptor **3**.

To the best of our knowledge, the association constant of the complex of C_{60} with the host **1** of $(76 \pm 5) \times 10^3$ dm^3 mol^{-1} in toluene is the largest yet reported in organic solvents (Table 1). It is more than 36 times larger than the corresponding value of C_{60} and **4** in the same solvent ($(2.1 \pm 0.1) \times 10^3$ dm^3 mol^{-1}),[3] and this clearly indicates an effective cooperation between the two calix[5]arene cavities. The association constants of the host/C_{60} complexes are solvent dependent and decrease in the order toluene $\geq$ benzene $>$ CS_2 $>$ 1,2-dichlorobenzene.

Table 1. Association constants [dm^3 mol^{-1}] of the complexes of **1**–**3** with fullerenes.

Solvent	Fullerene	**1**	**2**	**3**
toluene	C_{60}	$(76 \pm 5) \times 10^3$	$(83 \pm 2) \times 10^2$	$(27 \pm 1) \times 10^2$
	C_{70}	$(163 \pm 16) \times 10^3$	$(85 \pm 13) \times 10^3$	$(55 \pm 2) \times 10^2$
benzene	C_{60}	$(47 \pm 2) \times 10^3$	$(57 \pm 2) \times 10^2$	$(30 \pm 1) \times 10^2$
	C_{70}	$(72 \pm 7) \times 10^3$	$(49 \pm 1) \times 10^3$	$(41 \pm 5) \times 10^2$
CS_2	C_{60}	$(54 \pm 8) \times 10^2$	$(15 \pm 1) \times 10^2$	$(67 \pm 1) \times 10$
	C_{70}	$(96 \pm 3) \times 10^2$	$(66 \pm 2) \times 10^2$	$(103 \pm 4) \times 10$
o-dichloro-	C_{60}	$(30 \pm 2) \times 10^2$	$(12 \pm 1) \times 10^2$	$(44 \pm 5) \times 10$
benzene	C_{70}	$(41 \pm 1) \times 10^2$	$(190 \pm 2) \times 10$	$(49 \pm 2) \times 10$

All the bridged hosts bind C_{70} preferentially to C_{60}. The association constant of the complex of **1** with C_{70} has its largest value of $(163 \pm 16) \times 10^3$ dm^3 mol^{-1} in toluene. The binding selectivity of **2** for C_{70}/C_{60} is highest in toluene with a value of 10.2, but is lower in other solvents (benzene: 8.6, CS_2: 3.6, 1,2-dichlorobenzene: 1.6). The same trend was observed for the other hosts (**1** and **3**), although their selectivity ratios were smaller than those of **2**.

To obtain information on the orientation of the bound guests with respect to the host cavity, ^{13}C NMR spectra of C_{70} were measured in the presence and absence of **1**. Complexation induced shift (CIS) values of the five sets of nonequivalent carbons of the guest were obtained from the differences between these chemical shifts ($\Delta\delta$). The up-field shift is largest for the carbon atoms at the poles of C_{70} (Scheme 1, a, $\Delta\delta = 1.77$) and decreases towards the equator [$\Delta\delta = 1.55$ (b), 1.16 (c), 0.81 (d) 0.69 (e)]. This indicates that the carbon atoms at the poles reside the deepest within the cavity. The CIS of each set of nonequivalent carbons depends on the orientation of the guest within the host cavity. They were estimated by molecular-mechanical calculations with the Amber* force-field model,[5] with summation of the local anisotropic magnetic contribution of the 11 aromatic rings of

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the host, by using our ring-current program.[6] In the calculated structure of lowest energy (Figure 1A), the estimated induced shift of the equatorial carbons is the smallest.

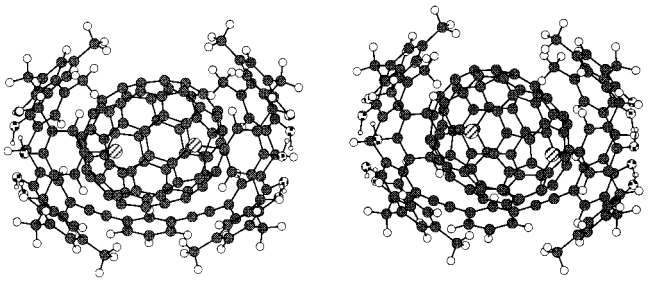

Figure 1. Assumed structures of supramolecular complex of **1** and C_{70} used in the calculation of chemical shifts.

However, in the structure with the second lowest energy (B), the corresponding value for the equatorial carbon atoms ($\Delta\delta = 1.202$) is larger than the induced shifts of the carbon atoms in positions d ($\Delta\delta = 1.119$) and c ($\Delta\delta = 1.185$). Apparently, structure B cannot reproduce the observed chemical-shift trend. Since molecular-mechanics calculations give "frozen" structures, the effect of thermal motion must be included. To take into account the dynamic movement of the host and guest molecules, a molecular dynamics simulation was carried out with a stochastic dynamic treatment at 300 K.[5] The calculation of a 2000 ps simulation revealed rapid movement of the guest within the host cavity. The average induced shifts of the guest carbon atoms were estimated from 500 structures monitored at 4 ps intervals during the simulation period. The calculated induced shifts[7] [$\Delta\delta = 1.651$ (a), 1.376 (b), 1.159 (c), 0.920 (d), 0.834(e)] showed good agreement with the experimental values (correlation coefficient $R^2 = 0.984$). Thus, molecular dynamics simulation analysis is efficient in reproducing the structure and the movement of the supramolecular complex with apolar guests such as fullerenes.

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[7] Our ring-current program was developed for calculating the induced shift of protons $\Delta\delta(^1H)$. We estimated the induced shift of all the carbon atoms of the guest by assuming that they are protons. By comparing the calculated and experimental values for benzene, we found that the induced shift for ^{13}C can be estimated by multiplying $\Delta\delta(^1H)$ by 0.6 [$\Delta\delta(^{13}C) = 0.6\,\Delta\delta(^1H)$]. The $\Delta\delta(^{13}C)$ values are lower because the paramagnetic term, which can be neglected for the chemical shift of ^1H, contributes significantly to the chemical shift of ^{13}C.[8] The uncorrected $\Delta\delta$ values of the five groups of equivalent carbon atoms in C_{70} (standard deviation) are 2.74(26) (a), 2.29(21) (b), 1.93(11) (c), 1.53(16) (d), 1.39 (26) (e).

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