Complexation of Fullerenes with Bis-calix[*n*]arenes Synthesized by Tandem Claisen Rearrangement[1]

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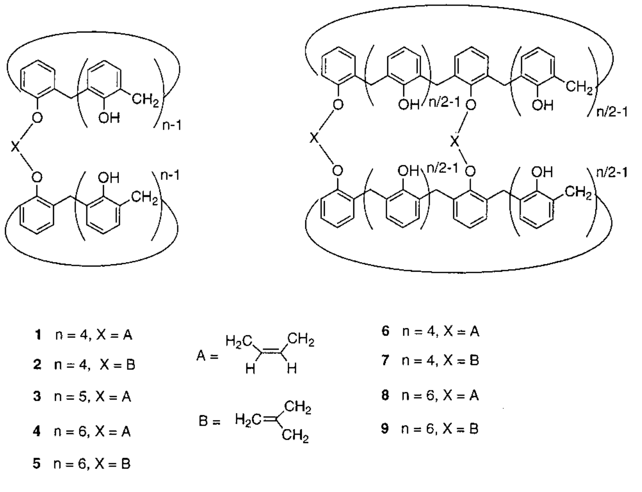
Abstract: Bis-calix[*n*]arenes that are singly and doubly bridged at the upper rims with 2-butenyl or 2-methylenepropyl moieties have been prepared by tandem Claisen rearrangement of bis-calix[*n*]arenes that are singly and doubly bridged via ether linkages at the lower rims with these same spanners. The complexation behavior of these bis-calixarenes toward C_{60} and C_{70} has been measured, and a calix[5]arene singly bridged at the upper rims with a 2-butenyl spanner and carrying allyl groups at all of the other available *p*-positions has been found to be particularly effective.

The remarkable versatility of the Claisen rearrangement[2] was further extended some years ago by the observation that double (tandem) sequences can be effected without the isolation of intermediates[3]. A more recent application of the tandem Claisen rearrangement was reported by Hiratani and co-workers[4] and provided the impetus for the present work. After its initiation two more reports from the Hiratani group describe the application of the procedure to the synthesis of calixarene-like compounds[5] and novel crownophanes.[6] We now demonstrate that the tandem Claisen rearrangement is also applicable to a variety of calixarenes[7] themselves, both singly and doubly bridged on the lower rims, providing compounds for complexation studies involving the fullerenes C_{60} and C_{70} as the guest molecules.

Synthesis of Bis-calixarenes. For the preparation of lower rim-bridged calixarenes the spanners derived from 1,4-dichloro-2-butene (DCB) and 3-chloro-2-chloromethyl-1-propene (CCMP) were used, following well-established calixarene etherification procedures[8] with some modification. When calix[4]arenes were mixed with DCB or CCMP in THF−DMF solution and treated with Me_3SiOK or NaH as the base, only the starting materials were recovered. However, when a stoichiometric amount of tetrabutylammonium iodide (TBAI) was added to the reaction mixtures containing 1 equiv of calixarene and 0.5 equiv of the alkylating agent in CH_2Cl_2 solution with NaH as the base, the bis-ethers **1** and **2** were obtained in yields of 84% and 51%, respectively. It is postulated that TBAI acts not only as a I^-/Cl^- exchange reagent to create a more reactive alkylating agent but also as a phase transfer agent. In similar fashion calix[5]arene was converted to **3** in 40% yield, and calix[6]arene to **4** and **5** in 59% and 51% yields, respectively.

Using procedures similar to those employed for converting calix[4]arenes to A,C-diethers,[9] 1 equiv each of calix[4]arene, DCB, and TBAI along with 0.5 equiv of K_2CO_3 in MeCN afforded a 41% yield of the doubly bridged **6**. When using CCMP instead of DCB, however, no pure products could be isolated, and the doubly bridged **7** was instead produced in 35% yield by the method described above for **2** (using equivalent amounts of calix[4]arene and CCMP). The products of etherification using equimolar amounts of calix[6]arene and the alkylating agents were obtained only as mixtures of the singly and doubly bridged bis-calixarenes, requiring flash chromatographic separation to afford 16% of **8** (along with 59% of **4**) and 23% of **9** (along with 51% of **5**). In none of the cases were products of intramolecular alkylation observed even though the reactions were carried out under high dilution conditions. The structures of all of the products of alkylation **1**−**9** are compatible



1 n = 4, X = A
2 n = 4, X = B
3 n = 5, X = A
4 n = 6, X = A
5 n = 6, X = B
6 n = 4, X = A
7 n = 4, X = B
8 n = 6, X = A
9 n = 6, X = B

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[1] Calixarenes. 48 in the series entitled "Calixarenes". For paper 47 cf. Sharma, S. K.; Kanamathareddy. S.; Gutsche, C. D. *Synthesis* **1997**, 1268.

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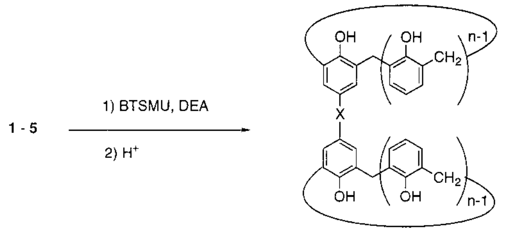
with the elemental analyses, the ^1H and ^{13}C NMR spectra and the mass spectral determinations of molecular weight.

Tandem Claisen Rearrangement of Bis-calixarenes. The simple Claisen rearrangement of the allyl ethers of calixarenes, effected by refluxing in *N,N*-diethylaniline, provided one of the earliest methods for introducing functionality into the para positions.[10] While the yields are ca. 74% for the tetraallyl ether of calix[4]arene, they fall to ca. 21% for the hexaallyl ether of calix[6]arene and dwindle to zero for the octaallyl ether of calix[8]arene. At the outset of the present work this was the method used in attempts to effect the tandem Claisen rearrangements of the bis-calixarenes, but only trace amounts of rearranged products could be isolated and identified. Providentially, at about the same time that these experiments were in progress an improved procedure was being devised in our laboratory[11] which showed that the yields of the simple Claisen rearrangements of the calixarene allyl ethers can be dramatically improved by carrying out the reaction in the presence of bis-(trimethylsilyl)-urea (2 equiv per phenolic unit).This reagent silylates the phenolic groups as they are generated during the rearrangement, thereby protecting them from further reaction (e.g., oxidation). Hydrolysis of the reaction mixture without isolation of the silyl ethers that are formed in the rearrangement then leads to the *p*-allylphenols in good to excellent yields. Using this procedure, the lower rim singly bridged bis-calixarene ethers **1**−**5** produced the upper rim-bridged calixarenes **10** (68%), **11** (61%), **12** (65%), **13** (76%), and **14** (93%). Even the lower rim doubly bridged bis-calixarene ethers **6**−**9** undergo tandem Claisen rearrangements in comparable fashion to give the upper rim doubly bridged bis-calixarenes **15** (15%), **16** (22%), **17** (33%), and **18** (70%). The structures of the rearrangement product **15**−**18** and **20** were all commensurate with the elemental analyses, the ^1H and ^{13}C NMR spectra, and the mass spectral molecular weight determinations. Considering the conformational contortions that must be involved in the transformations involving the doubly bridged calixarenes, it is surprising that yields of any magnitude are realized and provides further testament to the impressive versatility of the Claisen rearrangement.



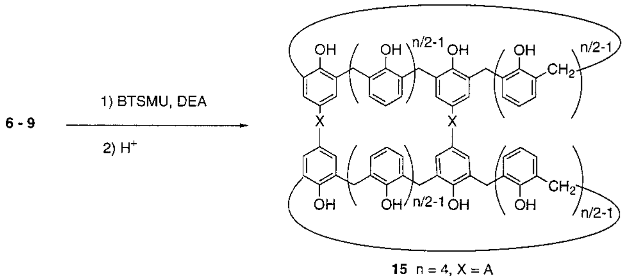
10 n = 4, X = A

11 n = 4, X = B

12 n = 5, X = A

13 n = 6, X = A

14 n = 6, X = B



15 n = 4, X = A

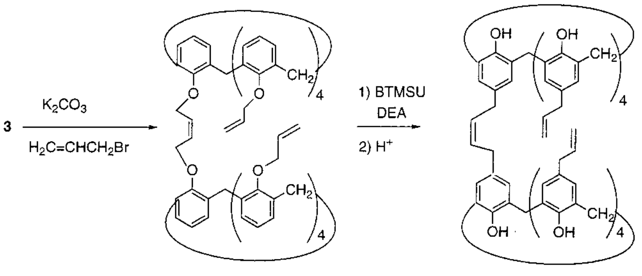
16 n = 4, X = B

17 n = 6, X = A

18 n = 6, X = B

It is interesting to note that the upper rim doubly bridged compound **15** has also been synthesized by McKervey and coworkers[12] by the action of $RuCl_2(CHPh)(PCy_3)_2$ on A,C-*p*-diallylcalix[4]arene. Obtained in 5% yield as a mixture of *E*- and *Z*-isomers, its elemental analysis and mass spectral parent peak are commensurate with the assigned structure. Its ^1H NMR spectrum shows more resonances than **15** and contains 76 instead of the required 56 hydrogens, but presumably this simply reflects the fact that it is a mixture.

As a further test of the improved method for effecting the Claisen rearrangement, the lower rim-bridged calix[5]arene **19** was converted to the upper rim-bridged calix[5]arene **20**, a compound also of interest for the complexation experiments described below. The mass spectrum of **20** shows a signal for the parent ion even though its precursor compound **19** fails to do so.



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Complexation of Fullerenes with Bis-calixarenes. The complexation of fullerenes with macromolecular hosts of various types has been extensively investigated in recent years, including inter alia the cyclodextrins,[13−16] azacrowns,[17] cyclotriveratrylenes,[18] and calixarenes.[19−35] A number of these compounds have been shown to form strong complexes; therefore, it was

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Table 1. Complexation Constants (K dm^{-3} mol^{-1}) of Calixarenes and Fullerenes at 25 °C in Toluene

calixarenes	K_{C60}	K_{C70}	K_{C70}/K_{C60}
calix[5]arene	30 ± 2	51 ± 3	1.7
p-tert-butylcalix[5]arene	9 ± 1	*a*	
bis-calix[5]arene **12**	93 ± 5	119 ± 6	1.3
bis-calix[6]arene **13**	32 ± 2	55 ± 3	1.7
bis-calix[6]arene **14**	27 ± 3	21 ± 2	0.8
p-allyl-bis-calix[5]arene **20**	1300 ± 65	625 ± 32	0.5
p-allylcalix[5]arene	292 ± 15	141 ± 8	0.5
p-allylcalix[6]arene	*a*	*a*	

[a] Binding too small for accurate measurement.

of interest to test the complexation behavior of the bis-calixarenes described above.

The complexation evaluations were carried out in toluene at 25 °C by measuring the intensity of absorption at 430 nm for C_{60} and 420 nm for C_{70}. As has been noted in other studies with the fullerenes, complexation with C_{60} results in a color change from magenta to red and from red to colorless with C_{70}. Application of the Benesi−Hildebrand treatment of the spectrophotometric measurements produced the complexation constants shown in Table 1. On the basis of these data it is concluded that (a) none of the doubly bridged bis-calixarenes (**15**−**18**) form measurable complexes with the fullerenes, presumably because of the difficulty of entry of the fullerene into the cavity of the bis-calixarene; (b) none of the singly bridged bis-calix[4]arenes form measurable complexes with fullerenes, presumably because of the small cavity size; (c) bis-calix[5]arenes **12** and **20** bind the fullerenes 2−5 times more tightly than the corresponding monocalix[5]arenes; (d) calix-[6]arene shows no measurable binding, whereas the bis-calix-[6]arenes **13** and **14** show modest binding with K_{assoc} values of 21−55 M^{-1}; (e) presumably because of their deeper cavities, *p*-allylcalix[5]arene and the *p*-allyl-bis-calix[5]arene **20** show the largest complexation constants, the 1300 value for the latter being about half that of the 2100 M^{-1} value reported by Fukazawa and co-workers[27a] for an A,C-*p*-iodocalix[5]arene although falling considerably short of the 76−163 × 10^3 M^{-1} values reported by this same group for some bis-calix[5]-arenes;[27b] (f) *p*-allylcalix[5]arene **20** shows selectivities with respect to C_{70}/C_{60} opposite to those of calix[5]arene and the bis-calix[5]arene **12**; (g) a Job's plot reveals that the stoichiometry of the complexation with the bis-calixarenes **12**−**14**, and *p*-allylcalix[5]arene with fullerene is 1:1.

Inspection of Table 1 shows that with calix[5]arene and bis-calix[6]arene the C_{70}/C_{60} complexation ratio is 1.7. Even though the complexation constants in these cases are rather small, the possibility of using such systems to enrich a fullerene mixture in C_{70} was explored. A 1-mL amount of a 2 × 10^{-4}M solution of a violet-colored 1:1 mixture of C_{60} and C_{70} was treated with 15 mg of calix[5]arene. The solution was allowed to stand at room temperature overnight, by which time it had become almost colorless and had deposited a black precipitate. After the precipitate was separated and purified it by washing with toluene, hexane, and $CHCl_3$, an HPLC analysis showed it to have an 83:17 ratio of C_{70}/C_{60} and to account for 91% of the C_{70} in the original sample.

Experimental Section[36]

1,4-Bis-(calix[4]arene-25,26,27-triol-28-oxy)-2-butene (1). To a solution of 0.42 g (1 mmol) of calix[4]arene in 40 mL of CH_2Cl_2 was added 0.08 g (2 mmol) of NaH (60% oil dispersion).The mixture was stirred for 30 min in an inert atmosphere, treated with 0.065 mL (0.5 mmol) of 1,4-dichloro-2-butene and 0.37 g (1 mmol) of tetrabutylammonium iodide, and stirred at room temperature for 24 h. The reaction mixture was washed with 1 N HCl, H_2O, and brine and then dried over anhydrous Na_2SO_4 to yield a yellow solid after evaporation of the solvent. Flash chromatography on silica gel (1:1 CH_2Cl_2−hexane eluent) followed by crystallization from $CHCl_3$−MeOH gave 0.38 g (84%) of **1** as colorless crystals: mp 172−174 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.67 (s, 2H, OH), 9.26 (s, 4H, OH), 7.09−6.63 (m, 26H, ArH and OCH_2CH), 4.92 (d, J = 5.4 Hz, 4H, OCH_2C), 4.40 (d, J = 13.1 Hz, 4H, $ArCH_2Ar$), 4.18 (d, J = 13.7 Hz, 4H, $ArCH_2Ar$), 3.47 (d, J = 13.1 Hz, 4H, $ArCH_2Ar$), 3.40 (d, J = 13.7 Hz, 4H, $ArCH_2Ar$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 151.1, 150.7, 149.2, 129.5, 129.2, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 126.5, 121.9, 121.0, 71.5, 31.8, 31.7. Anal. Calcd for $C_{60}H_{52}O_8$: C, 79.98; H, 5.82. Found: C, 79.79; H 5.72. FAB-MS [M + H] (m/z) = 901.

1,1-Bis-(calix[4]arene-25,26,27-triol-28-oxymethyl)-ethene (2). 2 was prepared in 51% yield by the procedure described above for **1** using 3-chloro-2-chloromethyl-1-propene. It was purified by flash chromatography on silica gel (1:1 CH_2Cl_2−hexane eluent) followed by recrystallization from $CHCl_3$−MeOH to give a colorless solid: mp 214−216 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 9.57 (s, 2H, OH), 9.25 (s, 4H, OH), 7.12−6.97 (m, 16H, ArH), 6.90 (t, J = 7.7 Hz, 2H, ArH), 6.68 (t, J = 7.5 Hz, 6H, ArH), 6.06 (s, 2H, $C{=}CH_2$), 5.07 (s, 4H, $ArOCH_2$), 4.47 (d, J = 13.2 Hz, 4H, $ArCH_2Ar$), 4.20 (d, J = 13.9 Hz, 4H, $ArCH_2Ar$), 3.55 (d, J = 13.2 Hz, 4H, $ArCH_2Ar$), 3.44 (d, J = 13.9 Hz, 4H, $ArCH_2Ar$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 151.0, 148.9, 139.7, 134.1, 129.6, 128.9, 128.8, 128.7, 128.5, 128.2, 128.1, 126.5, 122.1, 120.8, 120.6, 77.6, 31.9, 31.5. Anal. Calcd for $C_{60}H_{52}O_8 \cdot {}^1/_2CHCl_3$: C, 75.63; H, 5.55. Found: C, 75.34; H, 5.54. FAB-MS [M + H] (m/z) = 901.

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(36) Unless otherwise noted, starting materials were obtained from commercial suppliers and used without further purification. THF was freshly distilled from Na benzophenone. The melting points of all compounds melting above 250 °C were taken in sealed and evacuated capillary tubes on a Mel-Temp apparatus (Laboratory Devices, Cambridge, MA) using a 500 °C thermometer calibrated against a thermocouple. The melting points are uncorrected. A melting temperature preceded by a ">" sign indicates that the compound starts to decompose at that temperature but appears to actually melt at some higher temperature. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian XL-300 spectrometer at 300 and 75 MHz, respectively. Analytical samples were dried in a drying pistol under vauum for at least 36 h. Microanalyses were performed by Desert laboratories, Tucson, AZ. Thin-layer chromatography (TLC) was carried out on Analtech silica gel plates (absorbant thickness 250 mm) containing a fluorescent indicator. Column chromatography was carried out with J. T. Baker silica gel no. JT7042-2 (40−64 mm particles) on columns filled to a height of ca. 6 in. Elution rates were 2 in. min. Mass spectral determinations were carried out by the Mass Spectrometry Resource Center of Washington University, St. Louis, MO, partially supported by NIH Grant RR00954.

1,4-Bis-(calix[5]arene-31,32,33,34-tetrol-35-oxy)-2-butene (3). 3 was prepared by the procedure described above for **1** using calix[5]-arene. It was purified by flash chromatography on silica gel (2:1 CH_2Cl_2−hexane eluent) followed by recrystallization from $CHCl_3$−MeOH to give 40% yield of a colorless solid: mp >184 °C dec; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.03$ (s, 4H, OH), 7.92 (s, 4H, OH), 7.17 (d, $J = 7.5$ Hz, 4H, ArH), 7.12 (d, $J = 7.6$ Hz, 8H, ArH), 7.09 (d, $J = 7.6$ Hz, 4H, ArH), 7.03 (d, $J = 7.5$ Hz, 4H, ArH), 6.88 (t, $J = 7.6$ Hz, 2H, ArH), 6.79 (t, $J = 7.5$ Hz, 4H, ArH), 6.78 (t, $J = 7.5$ Hz, 4H, ArH), 5.90 (t, $J = 3.8$ Hz, 2H, $OCH_2CH{=}$), 4.53 (d, $J = 3.8$ Hz, 4H, OCH_2-$CH{=}$), 4.21 (d, $J = 14.2$ Hz, 4H, $ArCH_2Ar$), 3.97 (d, $J = 14.3$ Hz, 4H, $ArCH_2Ar$), 3.92 (d, $J = 13.3$ Hz, 2H, $ArCH_2Ar$), 3.63 (d, $J = 13.3$ Hz, 2H, $ArCH_2Ar$), 3.53 (d, $J = 14.2$ Hz, 4H, $ArCH_2Ar$), 3.51 (d, $J = 14.3$ Hz, 4H, $ArCH_2Ar$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 151.8, 150.1, 133.0, 129.5, 129.3, 129.1, 128.2, 127.3, 127.0, 126.8, 125.6, 121.5, 120.3, 71.5, 31.8, 31.1. Anal. Calcd for $C_{74}H_{64}O_{10}\cdot 3H_2O$: C, 76.14; H, 6.04. Found: C, 76.29; H, 5.95. FAB-MS [M] (*m/z*) = 1112.

1,4-Bis-(calix[6]arene-37,38,39,40,41-pentol-42-oxy)-2-butene (4). A solution containing 0.64 g (1 mmol) of calix[6]arene in 110 mL of THF−DMF (10:1) was cooled to 0 °C, treated with 0.77 g (6 mmol) of $KOSi(CH_3)_3$, and stirred 15 min. A solution of 0.15 g (1.2 mmol) of 1,4-dichlorobutene in 10 mL of THF was added, and the reaction mixture was stirred at room temperature for 20 h. The solvent was removed under vacuum, the residue was treated with 150 mL of cold 0.1 N HCl, the precipitate was separated by filtration, and the crude product was purified by flash chromatography on silica gel (1:1 CH_2Cl_2−hexane eluent) and recrystallized from $CHCl_3$−MeOH to afford 0.39 g (59%) of **4** as a colorless solid: mp >205 °C dec; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 9.45$ (brs, 6H, OH), 8.4 (brs 4H, OH), 7.12−6.71 (m, 36H, ArH), 6.52 (t, $J = 3.7$ Hz, 2H, $OCH_2CH{=}$), 4.89 (d, $J = 3.9$ Hz, 4H, $OCH_2CH{=}$), 3.72 (brs, 24H, $ArCH_2Ar$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.2, 151.2, 150.4, 149.3, 133.0, 129.5, 129.4, 129.1, 129.0, 128.7, 127.6, 127.5, 127.4, 127.3, 127.2, 125.9, 121.9, 121.2, 120.8, 70.9, 32.1, 31.9, 31.8. Anal. Calcd for $C_{88}H_{76}O_{12}$: C, 79.74; H, 5.78. Found: C, 79.18; H, 6.03. FAB-MS [M] (*m/z*) = 1324.

1,1-Bis-(calix[6]arene-37,38,39,40,41-pentol-42-oxymethyl)-ethene (5). 5 was prepared as described above for **4** using 3-chloro-2-chloromethyl-1-propene. It was purified by flash chromatography on silica gel (1:1 CH_2Cl_2−hexane eluent) followed by recrystallization from $CHCl_3$−MeOH and obtained in 51% yield as a colorless solid: mp >205.2−207.6 °C dec; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 9.76$ (s, 6H, OH), 8.71 (s, 4H, OH), 7.20−6.56 (m, 36H, ArH), 6.03 (s, 2H, $C{=}CH_2$), 5.17 (s, 4H, OCH_2), 4.40−3.40 (m, 24H, $ArCH_2Ar$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.8, 151.2, 150.4, 148.9, 140.6, 133.2, 129.7, 129.3, 129.0, 128.9, 127.7, 127.6, 127.5, 127.4, 127.0, 126.0, 122.2, 121.3, 120.9, 120.7, 76.2, 32.1, 31.9, 31.8. Anal. Calcd for $C_{88}H_{76}O_{12}\cdot {}^1/_2CHCl_3$: C, 76.73; H, 5.57. Found: C, 76.64; H, 5.76. FAB-MS [M] (*m/z*) = 1324.

25,25′,27,27′-Bis-(1,2-dioxymethylethene)-bis-(calix[4]arene-26,28-diol) (6). A suspension of 0.84 g (2 mmol) of calix[4]arene, 0.3 g (2 mmol) of K_2CO_3, 0.32 g (1 mmol) of tetrabutylammonium iodide, and 0.26 mL (2 mmol) of 1,4-dichloro-2-butene in 50 mL of CH_3CN was refluxed under N_2 for 36 h. The solvent was removed under vacuum, and the residue was distributed between 20 mL of CH_2Cl_2 and 10 mL of 0.1 N HCl. The organic layer was separated, washed with H_2O and brine, dried over Na_2SO_4, and the solvent removed by evaporation. The residue remaining was triturated with MeOH and purified by flash chromatography (2:1 CH_2Cl_2−hexane eluent) to give 0.30 g (41%) of **6** as a colorless solid: mp >312 °C dec; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 8.52$ (s, 4H, OH), 6.99 (d, $J = 7.5$ Hz, 8H, ArH), 6.90 (d, $J = 7.5$ Hz, 8H, ArH), 6.80 (t, $J = 7.5$ Hz, 4H, ArH), 6.68 (t, $J = 4.4$ Hz, 4H, $O{-}CH_2{-}CH{=}$), 6.52 (d, $J = 7.5$ Hz, 4H, ArH), 4.85 (d, $J = 4.9$ Hz, 8H, $OCH_2CH{=}$), 4.41 (d, $J = 12.7$ Hz, 8H, $ArCH_2Ar$), 3.32 (d, $J = 12.7$ Hz, 8H, $ArCH_2Ar$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9, 151.5, 134.2, 129.1, 128.9, 128.5, 128.4, 128.2, 128.1, 125.7, 119.1, 71.0, 31.7. Anal. Calcd for $C_{64}H_{56}O_8\cdot {}^1/_4\ CHCl_3$: C, 78.51; H, 5.77. Found: C, 78.30; H, 5.62. FAB-MS [M + H] (*m/z*) = 953.

25,25′,27,27′-Bis-(1,1-dioxymethylethene)-bis-(calix[4]arene-26,28-diol) (7). 7 was prepared following the procedure described above for **2** but using 1 mmol of 3-chloro-2-chloromethyl-1-propene. It was purified by flash chromatography on silica gel (2:1 CH_2Cl_2−hexane eluent) and was obtained in 35% yield as a colorless solid: mp >234 °C dec; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 8.77$ (s, 4H, OH), 7.04 (d, $J = 7.5$ Hz, 8H, ArH), 7.03 (d, $J = 7.4$ Hz, 8H, ArH), 6.83 (t, $J = 7.5$ Hz, 4H, ArH), 6.62 (t, $J = 7.4$ Hz, 4H, ArH), 5.95 (s, 4H, $CH_2C{=}CH_2$), 5.12 (s, 8H, OCH_2), 4.42 (d, $J = 12.9$ Hz, 8H, $ArCH_2Ar$), 3.42 (d, $J = 12.9$ Hz, 8H, $ArCH_2Ar$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 152.2, 139.9, 134.1, 129.3, 128.4, 125.7, 120.3, 119.4, 77.1, 32.3. Anal. Calcd for $C_{64}H_{56}O_8\cdot {}^1/_6CHCl_3$: C, 79.21; H, 5.52. Found: C, 79.57; H, 5.84. FAB-MS [M + H] (*m/z*) = 953.

37,37′,40,40′-Bis-(1,2-dioxymethylethene)-bis-(calix[6]arene-38,39,41,42-tetrol) (8). From the flash chromatography (2:1 CH_2Cl_2−hexane eluent) of crude product from **4** as described above 0.11 g (16%) of the doubly bridged compound **8** was isolated as a colorless solid: mp >260 °C dec; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.79$ (s, 8H, OH), 7.09 (d, $J = 6.0$ Hz, 4H, ArH), 7.08 (d, $J = 7.4$ Hz, 4H, ArH), 6.90−6.86 (m, 12H, ArH), 6.73 (d, $J = 6.0$ Hz, 8H, ArH), 6.66 (t, $J = 7.4$ Hz, 8H, ArH), 6.48 (t, $J = 4.2$ Hz, 4H, $OCH_2CH{=}$), 4.92 (d, $J = 4.7$ Hz, 8H, $OCH_2CH{=}$), 4.38 (d, $J = 13.8$ Hz, 8H, $ArCH_2Ar$), 3.93 (d, $J = 14.0$ Hz, 4H, $ArCH_2Ar$), 3.30 (d, $J = 13.8$ Hz, 8H, $ArCH_2Ar$), 3.28 (d, $J = 14.0$ Hz, 4H, $ArCH_2Ar$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1, 151.5, 133.2, 130.6, 129.1, 128.9, 128.6, 128.5, 128.0, 125.5, 120.5, 72.2, 31.9, 31.6. Anal. Calcd for $C_{92}H_{80}O_{12}$: C, 80.21; H, 5.85. Found: C, 79.97; H, 6.23. FAB-MS [M + H] (*m/z*) = 1377.

37,37′,40,40′-Bis-(1,1-dioxymethylethene)-bis-(calix[6]arene-38,39,41,42-tetrol) (9). 9 was prepared as described above for **5** and obtained in 23% yield as a colorless solid: mp >415 °C dec; ^1H NMR (300 MHz, $CDCl_3$) $\delta = 7.79$ (s, 8H, OH), 7.08 (d, $J = 7.2$ Hz, 8H, ArH), 6.85−6.82 (m, 20H, ArH), 6.69 (t, $J = 7.2$ Hz, 8H, ArH), 5.94 (s, 4H, $C{=}CH_2$), 4.86 (s, 8H, OCH_2), 4.31 (d, $J = 14.1$ Hz, 8H, $Ar{-}CH_2{-}Ar$), 3.82 (brs, 4H, $ArCH_2Ar$), 3.38 (d, $J = 13.7$ Hz, 12H, $ArCH_2$-Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 151.6, 140.8, 133.2, 129.2, 129.0, 128.7, 128.6, 128.0, 127.8, 125.5, 120.5, 75.7, 31.6, 31.4. Anal. Calcd for $C_{92}H_{80}O_{12}$: C, 80.21; H, 5.85. Found: C, 80.33; H, 6.00. FAB-MS [M + H] (*m/z*) = 1377.

Claisen Rearrangement (General Procedure). A suspension of calixarene (1 mmol), 1,3-bis(trimethylsilyl)urea (2 equiv per OH group) and diethylaniline (10 mL) was refluxed in inert atmosphere for 3−6 h. The reaction mixture was cooled to room temperature, 10 mL of $CHCl_3$ was added, and then the reaction mixture was washed three times with 6 mL of 1 N HCl. The organic layer was separated and concentrated under reduced pressure, and the residue was suspended in a mixture of CH_2Cl_2−CH_3OH (6−10 mL) and HCl (2N, 2 mL) and stirred for 10 h. The precipitate was removed by filtration, the filtrate was concentrated, and the residue was treated with 5 mL of MeOH to give a solid product which usually purified by flash chromatography followed by recrystallization.

1,4-Bis-(5-calix[4]arene-25,26,27,28-tetrol)-2-butene (10). 10 was prepared by Claisen rearrangement of **1** using the procedure described above and was purified by flash chromatography on silica gel (2:1 CH_2Cl_2−hexane eluent) to give a 68% yield of a colorless solid: mp 286−288 °C dec; ^1H NMR (300 MHz, $CDCl_3$) δ 10.19 (s, 8H, OH), 7.04 (d, $J = 7.5$ Hz, 8H, ArH), 7.01(d, $J = 7.7$ Hz, 4H, ArH), 6.84 (s, 4H, ArH), 6.71 (t, $J = 7.6$ Hz, 6H, ArH), 5.51 (t, $J = 3.7$ Hz, 2H, $ArCH_2CH{=}$), 4.23 (brs, 8H, $ArCH_2Ar$), 3.51 (brs, 8H, $ArCH_2Ar$), 3.12 (d, $J = 4.8$ Hz, 4H, $ArCH_2CH{=}$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.8, 148.7, 146.9, 134.3, 130.3, 129.0, 128.8, 128.3, 128.1, 122.3, 122.2, 38.0, 31.8, 31.7. Anal. Calcd for $C_{60}H_{52}O_8$: C, 79.98; H, 5.82. Found: C, 79.39; H, 5.67. FAB-MS [M] (*m/z*) = 900.

3,3′-Bis-(5-calix[4]arene-25,26,27,28-tetrol)-2-methyl-1-propene (11). 11 was prepared by Claisen rearrangement of **2** using the procedure described above and was purified by flash chromatography on silica gel (1:1 CH_2Cl_2−hexane eluent) to give a 61% yield of a colorless solid: mp 185−188 °C dec; ^1H NMR (300 MHz, $CDCl_3$) δ 10.21 (s, 8H, OH), 7.07−7.01 (m, 12H, ArH), 6.79 (s, 4H, ArH), 6.72 (t, $J = 7.5$ Hz, 6H, ArH), 4.78 (s, 2H, $(ArCH_2)_2C{=}CH_2$), 4.24 (brs, 8H, $ArCH_2$-Ar), 3.52 (brs, 8H, $ArCH_2Ar$), 3.00 (s, 4H, $(ArCH_2)_2C{=}CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.9, 148.8, 148.3, 147.1, 133.1, 129.5, 129.0, 128.9, 128.8, 128.3, 128.2, 128.0, 122.2, 113.3, 41.3, 31.8, 31.7. Anal.

Calcd for $C_{60}H_{52}O_8\cdot{}^1/_4$ $CHCl_3$: C, 77.74; H, 5.66. Found: C, 77.96; H, 5.84. FAB-MS [M + H] (*m*/*z*) = 901.

1,4-Bis-(5-calix[5]arene-31,32,33,34,35-pentol)-2-butene (12). 12 was prepared by Claisen rearrangement of **3** using the procedure described above and was purified by flash chromatography on silica gel (1:1 CH_2Cl_2−hexane eluent) followed by recrystallization from $CHCl_3$−MeOH to give a 65% yield of a colorless solid: mp 191−193 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.88 (s, 10H, OH), 7.17 (d, J = 7.4 Hz, 4H, ArH), 7.13 (d, J = 7.5 Hz, 4H, ArH), 7.05(d, J = 7.9 Hz, 4H, ArH), 7.02 (d, J = 9.2 Hz, 4H, ArH), 6.93 (s, 4H, ArH), 6.82 (t, J = 7.5 Hz, 4H, ArH), 6.69 (t, J = 7.5 Hz, 4H, ArH), 5.48 (s, 2H, ArCH$_2$*CH*═), 3.74 (brs, 20H, ArCH$_2$Ar), 3.17 (d, J = 2.3 Hz, 4H, Ar*CH$_2$*CH═); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 149.9, 148.1, 133.6, 130.3, 129.2, 129.1, 128.9, 126.7, 126.6, 126.5, 121.5, 121.4, 37.8, 31.3. Anal. Calcd for $C_{74}H_{64}O_{10}\cdot1.5\ H_2O$: C, 77.94; H, 5.92. Found: C, 77.75; H 6.14. FAB-MS [M] (*m*/*z*) = 1112.

1,4-Bis-(5-calix[6]arene-37,38,39,40,41,42-hexol)-2-butene (13). 13 was prepared by Claisen rearrangement of **4** using the procedure described above and was purified by flash chromatography on silica gel (2:1 CH_2Cl_2−hexane eluent) followed by recrystallization from $CHCl_3$−MeOH to give a 76% yield of a colorless solid: mp >271 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.4 (s, 12H, OH), 7.16−7.07 (m, 20H, ArH), 6.93 (s, 4H, ArH), 6.85−6.75 (m, 10H, ArH), 5.55 (brs, 2H, ArCH$_2$*CH*═), 3.81 (brs, 24H, ArCH$_2$Ar), 3.20 (d, J = 3.8 Hz, 4H, Ar*CH$_2$*CH═); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.7, 147.8, 134.0, 130.5, 129.5, 129.2, 127.4, 127.3, 121.9, 38.2, 32.2. Anal. Calcd for $C_{88}H_{76}O_{12}$: C, 79.74; H, 5.78. Found: C, 79.41; H, 5.81. FAB-MS [M] (*m*/*z*) = 1324.

3,3′-Bis-(5-calix[6]arene-37,38,39,40,41,42-hexol)-2-methyl-1-propene (14). 14, prepared by Claisen rearrangement of **5** using the procedure described above, was purified by flash chromatography on silica gel (2:1 CH_2Cl_2−hexane eluent) followed by recrystallization from $CHCl_3$−MeOH to give a 93% yield of a colorless solid: mp >275 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.37 (s, 12H, OH) 7.13−6.77 (m, 34H, ArH), 4.83 (s, 2H, (ArCH$_2$)$_2$C═*CH$_2$*), 3.86 (brs, 24H, ArCH$_2$Ar), 3.10 (s, 4H, (Ar*CH$_2$*)$_2$C═CH$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.6, 148.5, 147.9, 132.6, 130.0, 129.5, 127.4, 127.3, 127.1, 121.8, 113.2, 41.3, 32.2. Anal. Calcd for $C_{88}H_{76}O_{12}$: C, 79.74; H, 5.78. Found: C, 79.68; H, 6.01. FAB-MS [M + H] (*m*/*z*) = 1325.

5,5′,17,17′-Bis-(1,4-buten-2-yl)-bis-(calix[4]arene-25,26,27,28-tetrol) (15). 15, prepared by Claisen rearrangement of **6** using the procedure described above, was purified by flash chromatography on silica gel (2:1 CH_2Cl_2−hexane eluent) followed by recrystallization from $CHCl_3$−MeOH to give a 15% yield of a colorless solid: mp >325 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.93 (s, 8H, OH), 6.90 (d, J = 7.5 Hz, 8H, ArH), 6.80 (s, 8H, ArH), 6.63 (t, J = 7.5 Hz, 4H, ArH), 5.49 (brs, 4H, ArCH$_2$*CH*═), 4.17 (d, J = 14.0 Hz, 8H, ArCH$_2$Ar), 3.41 (d, J = 14.0 Hz, 8H, ArCH$_2$Ar), 3.24 (brs, 8H, Ar*CH2*CH═); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.5, 147.0, 133.2, 130.0, 128.8, 128.7, 128.2, 127.6, 121.9, 121.8, 37.1, 31.7. Anal. Calcd for $C_{64}H_{56}O_8\cdot{}^1/_4\ CHCl_3$: C, 78.51; H, 5.77. Found: C, 78.51; H, 5.71. FAB-MS [M] (*m*/*z*) = 952.

5,5′,17,17′-Bis-[3,3′-(2-methylpropen-1-yl)]-bis(calix[4]arene-25,26,27,28-tetrol) (16). 16, prepared by Claisen rearrangement of **7** using the procedure described above, was purified by flash chromatography on silica gel (1:1 CH_2Cl_2−hexane eluent) followed by recrystallization from $CHCl_3$−MeOH to give a 22% yield of a colorless solid: mp >310 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.93 s, 8H, OH), 6.98 (d, J = 7.5 Hz, 8H, ArH), 6.69 (s, 8H, ArH), 6.68 (t, J = 7.4 Hz, 4H, ArH), 4.73 (s, 4H, (ArCH$_2$)$_2$C═*CH$_2$*), 4.17 (d, J = 13.9 Hz, 8H, ArCH$_2$Ar), 3.43 (d, J = 13.9 Hz, 8H, ArCH$_2$Ar), 2.84 (s, 8H, (Ar*CH$_2$*)$_2$C═CH$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.1, 147.8, 146.5, 132.3, 129.9, 128.7, 128.2, 127.9, 121.4, 110.7, 42.4, 31.6. Anal. Calcd. for $C_{64}H_{56}O_8\cdot2CHCl_3$: C, 66.51; H, 4.90. Found: C, 66.70; H, 4.91. FAB-MS [M] (*m*/*z*) = 952.

5,5′,23,23′-Bis-(1,4-buten-2-yl)-bis-(calix[6]arene-37,38,39,40,41,42-hexol) (17). 17, prepared by Claisen rearrangement of **8** using the procedure described above, was purified by flash chromatography on silica gel (1:1 CH_2Cl_2−hexane eluent) followed by recrystallization from $CHCl_3$−MeOH to a 33% yield of a colorless solid: mp >290 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.43−10.24 (m, 12H, OH), 7.19 (d, J = 7.5 Hz, 4H, ArH), 7.09 (d, J = 7.5 Hz, 4H, ArH), 6.97 (s, 8H, ArH), 7.04−6.82 (m, 12H, ArH), 6.61 (t, J = 7.3 Hz, 4H, ArH), 5.45 (brs, 4H, ArCH$_2$*CH*═), 4.39 (d, J = 14.4 Hz, 4H, ArCH$_2$Ar), 4.26 (d, J = 13.8 Hz, 4H, ArCH$_2$Ar), 3.78 (d, J = 14.4 Hz, 4H, ArCH$_2$Ar), 3.56 (d, J = 14.1 Hz, 4H, ArCH$_2$Ar), 3.53 (d, J = 13.4 Hz, 8H, ArCH$_2$Ar), 3.24 (d, J = 14.5 Hz, 4H, ArCH$_2$Ar), 3.13 (bs, 8H, Ar*CH$_2$*CH═); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.8, 148.5, 148.3, 133.6, 130.7, 130.2, 129.7, 129.6, 129.4, 129.2, 129.0, 128.6, 128.4, 128.1, 127.3, 126.9, 126.8, 126.5, 122.4, 121.4, 38.7, 32.2, 32.0, 31.9. Anal. Calcd for $C_{92}H_{80}O_{12}$: C, 80.21; H, 5.85. Found: C, 79.81; H, 5.91. FAB-MS [M + H] (*m*/*z*) = 1377.

5,5′,23,23′-Bis-[3,3′-(2-methylpropen-1-yl)]-bis-(calix[6]arene-37,38,39,40,41,42-hexol) (18). 18, prepared by Claisen rearrangement of **9** using the procedure described above, was purified by recrystallization from $CHCl_3$−MeOH to give a 70% yield of a colorless solid: mp >430 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$−pyridine-d_5): δ = 7.32 (s, 4H, ArH), 7.30 (d, J = 7.5 Hz, 4H, ArH), 7.26 (d, J = 7.1 Hz, 4H, ArH), 7.09 (t, J = 7.5 Hz, 4H, ArH), 6.88 (d, J = 1.5 Hz, 4H, ArH), 6.82 (d, J = 7.5 Hz, 4H, ArH), 6.10 (t, J = 7.5 Hz, 4H, ArH), 5.32 (d, J = 7.4 Hz, 4H, ArH), 5.15 (s, 4H, (ArCH$_2$)$_2$C═*CH$_2$*), 4.27 (d, J = 14.0 Hz, 4H, ArCH$_2$Ar), 4.20 (d, J = 14.4 Hz, 4H, ArCH$_2$Ar), 3.52 (d, J = 14.0 Hz, 4H, ArCH$_2$Ar), 3.49 (d, J = 16.7 Hz, 4H, ArCH$_2$Ar), 3.47 (d, J = 13.8 Hz, 4H, ArCH$_2$Ar), 3.32 (d, J = 13.8 Hz, 4H, (Ar*CH$_2$*)$_2$C═CH$_2$), 3.17 (d, J = 16.7 Hz, 4H, ArCH$_2$Ar), 1.70 (d, J = 13.6 Hz, 4H, (Ar*CH$_2$*)$_2$C═CH$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.9, 148.7, 147.6, 147.3, 131.1, 129.5, 129.4, 129.1, 128.8, 128.7, 128.5, 128.3, 126.8, 125.9, 125.7, 125.6, 122.3, 121.0, 113.6, 40.6, 32.1, 30.5, 29.7. Anal. Calcd for $C_{92}H_{80}O_{12}$: C, 80.21; H, 5.85. Found: C, 80.13; H 5.84. FAB-MS [M + H] (*m*/*z*) = 1377.

1,4-Bis-(calix[5]arene-31,32,33,34-tetraallyloxy-35-oxy)-2-butene (19). A suspension 0.40 g (0.36 mmol) of **3** (vide supra), 0.70 g (5.76 mmol) of allyl bromide, and 0.8 g (5.76 mmol) of K_2CO_3 in 30 mL of acetone was refluxed 48 h in an inert atmosphere. The solvent was removed by evaporation and the residue was suspended in 15 mL of H_2O and sonicated for 2 min. The precipitate was removed by filtration, dried, and flash chromatographed on silica gel (1:1 $CHCl_3$−hexane eluent) to afford 0.42 g (81%) of **19** as a colorless solid: mp >102 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.11−7.01 (m, 20H, ArH), 6.86−6.75 (m, 10H, ArH), 5.59 (brs, 4H, OCH$_2$*CH*═CH$_2$ and ArCH$_2$*CH*═), 5.43 (brs, 6H, OCH$_2$*CH*═CH$_2$), 5.10−4.79 (m, 16H, OCH$_2$CH═*CH$_2$*), 4.11−3.27 (m, 40H, ArCH$_2$Ar and OCH$_2$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.2, 155.1, 155.0, 134.4, 134.3, 134.2, 134.1, 129.7, 129.5, 129.4, 128.1, 123.4, 123.2, 123.1, 116.2, 116.1, 73.2, 73.1, 68.9, 31.9, 31.8. Anal. Calcd for $C_{98}H_{96}O_{10}\cdot2H_2O$: C, 80.08; H, 6.86. Found: C, 80.31; H, 6.87.

1,4-Bis-(5,11,17,23-tetraallyl-29-calix[5]arene-31,32,33,34,35-pentol)-2-butene (20). 20, prepared by Claisen rearrangement of **19** using the procedure described above, was purified by flash chromatography on silica gel (3:2 CH_2Cl_2−hexane eluent) followed by recrystallization from hexane to give a 61% yield of a colorless solid: mp >102 °C dec; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.83 (s, 10H, OH), 6.99−6.96 (m, 20H, ArH), 5.91−5.87 (m, 8H, ArCH$_2$*CH*═CH$_2$), 5.59 (m, 2H, Ar−CH2−*CH*═), 5.07−4.96 (m, 16H, ArCH$_2$CH═*CH$_2$*), 3.80 (brs, 20H, ArCH$_2$Ar), 3.27 (d, J = 6.4 Hz, 16H, Ar*CH$_2$*CH═CH$_2$), 3.24 (d, J = 5.9 Hz, 4H, Ar*CH$_2$*CH═); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.4, 148.3, 137.8, 137.7, 133.8, 132.9, 130.4, 129.3, 126.6, 115.5, 39.2, 39.1, 38.0, 31.4, 29.7. Anal. Calcd for $C_{98}H_{96}O_{10}\cdot H_2O$: C, 81.07; H, 6.80. Found: C, 80.82; H, 6.85. FAB-MS [M] (*m*/*z*) = 1432.

Measurement of Complexation Constants. Complexation constants (K_{assoc}) were determined in toluene solution with a Cary 3 UV−vis spectrometer at 25 ± 0.5 °C. A 2.5-mL quantity of toluene was placed in the sample cell and the reference cell, and 25 μL of a 1×10^{-2} M fullerene stock solution in toluene was added to the sample cell to give a fullerene concentration of 1×10^{-4} M. 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, as shown in Figures 1 and 2 for C_{60} and C_{70}, respectively.

For example, the absorption in the range 425−450 nm for a C_{60} solution increased upon the addition of compound **20**, and the color of

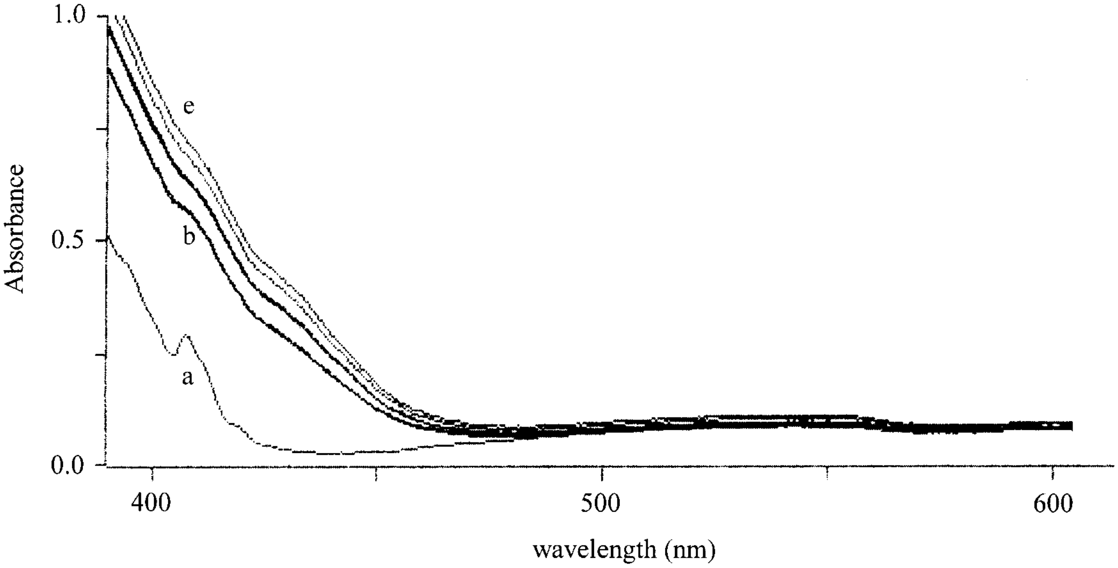

Figure 1. Absorption spectra of C_{60} (1.0×10^{-4} mol dm^{-3}) in the presence of **20** in toluene at 25 °C. The concentrations of **20** for curves a−e are 0.0, 1.0, 2.0, 3.0, 4.0 ($\times 10^{-3}$ mol dm^{-3}) respectively.

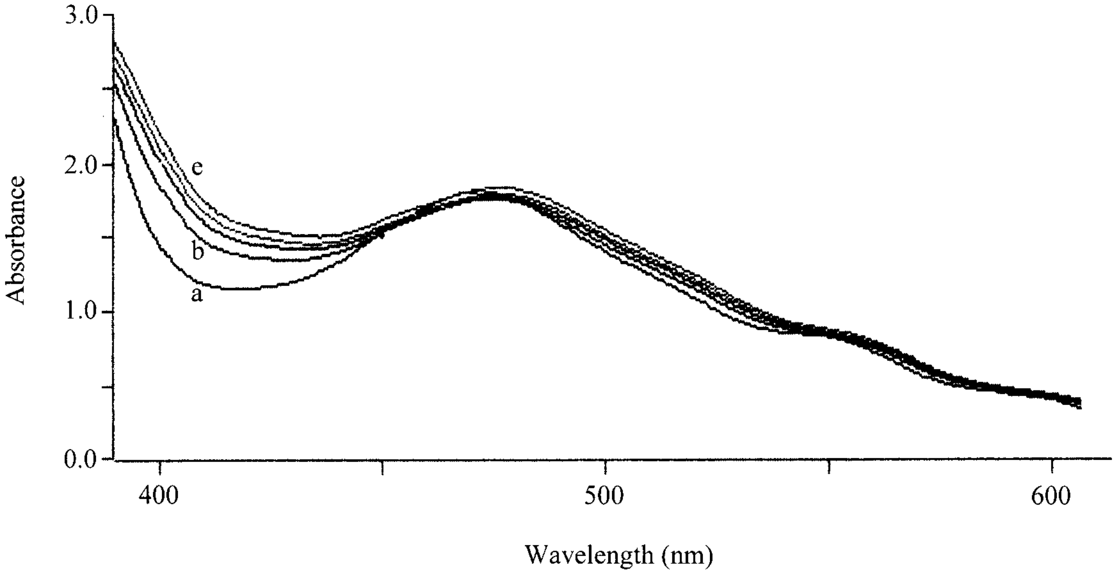

Figure 2. Absorption spectra of C_{70} (1.0×10^{-4} mol dm^{-3}) in the presence of **20** in toluene at 25 °C. The concentrations of **20** for curves a−e are 0.0, 1.0, 2.0, 3.0, 4.0 ($\times 10^{-3}$ mol dm^{-3}) respectively.

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 compound **20**, 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.

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