ARTICLES

Study of Novel Interactions of Calixarene π-Systems with [60]- and [70]Fullerenes by the NMR Spectrometric Method

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Both [60]- and [70]fullerenes have been shown to form 1:1 supramolecular complexes with (i) 49,50,51,-52,53,54,55,56-octamethoxy-5,11,17,23,29,35,41,47-octa-(4-*tert*-butyl)calix[8]arene (**1**), (ii) 37,38,39,40,41,-42-hexamethoxy-5,11,17,23,29,35-hexa(4-*tert*-butyl)calix[6]arene (**2**), (iii) 37,39,41-trimethoxy-38,40,42-tri-hydroxy-5,11,17,23,29,35-hexa-(4-*tert*-butyl)calix[6]arene (**3**), and (4) 24,26-dimethoxy-25,27-dihydroxy-5,-11,17,23-tetra(4-*tert*-butyl)calix[4]arene (**4**) in carbon tetrachloride medium by NMR spectroscopy. Formation constants (K) of the above complexes have been determined from the systematic variation of NMR chemical shifts of specific protons of the calixarenes in the presence of [60]- and [70]fullerene. In one particular case it has been possible to show from the ^{13}C NMR signal that during inclusion the host (**3**) is preorganized in the conical conformation and the guest molecule approaches from the wider side containing the *tert*-butyl group.

1. Introduction

Calixarenes appeared as the third generation of supramolecular host compounds after crown ethers and cyclodextrins.[1−5] Calixarenes made up of phenol and methylene units have many conformational isomers because of two possible rotational modes of the phenol unit: the oxygen-through-the-annulas rotation and the para-substituent-through-the-annulas rotation. The conformational isomers thus yielded afford a great number of unique cavities with different size and shape. Fullerenes ([60]- and [70]-fullerene)[6,7] appeared as the third generation of carbon clusters after graphite and diamond. Following the initial discovery, fullerene research has continuously expanded due to both fundamental interest and wide ranging potential applications.[8] The interest in such novel materials has especially increased after the discovery of their superconductivity[9] in [60]fullerene−alkali metal salts, ferromagnetism,[10] and biological activity.[11,12] Theoretical calculation predicts that the LUMO of [60]- and [70]-fullerene can accept six electrons,[13−15] and electrochemical studies[16−18] reveal reduction potentials corresponding to ([60]fullerene)$^{n-}$ and ([70]fullerene])$^{n-}$, $n = 3−6$. Thus, the high electron affinity of [60]- and [70]fullerene makes them efficient electron acceptors,[10] and they form electron donor−acceptor (EDA) complexes with various electron donors like amines,[19−22] olefins,[23−25] etc. The study of formation of such complexes by [60]- and [70]fullerene in solution and in solid state is a field of current research.[26−34]

Since calixarenes have a cavity composed of benzene rings (which behave like π-donors) while fullerenes are π-systems with appreciable electron affinity, these two third-generation hosts and guests may have a chance to get involved in forming inclusion complexes, e.g., through $\pi-\pi$ interactions. This expectation has become actual by an accidental finding by Atwood et al.[35] and Shinkai et al.[36] that calix[8]arenes selectively include [60]fullerene in carbon soot and form precipitate with 1:1 stoichiometry. This is a very useful method of purification for obtaining [60]fullerene in large quantity and with high purity. More recently, it was shown that certain calixarenes and their analogues can interact with [60]- and [70]fullerenes even in solution.[37−40a] Since the formation constant (K) is an important parameter that shows whether inclusion has occurred or not, it is usually essential to determine K.

The method of determination of K of EDA complexes from NMR data was developed long ago by Mathur et al.[41] and by Hanna and Ashbaugh et al.[42] Recently from NMR study the formation of molecular complexes of [60]fullerene with various donors like aromatic hydrocarbons and methylpyridines have been reported.[43] Moreover, NMR data give important information about the possible conformations of calixarenes in solution.[44] Thus, NMR is a very useful tool by which host−guest complexation can be studied. The object of the present paper is an attempt along this line. Complexation of [60]- and [70]-fullerene with (i) 49,50,51,52,53,54,55,56-octamethoxy-5,11,-17,23,29,35,41,47-octa-(4-*tert*-butyl)calix[8]arene (**1**), (ii) 37,-38,39,40,41,42-hexamethoxy-5,11,17,23,29,35-hexa(4-*tert*-butyl)calix[6]arene (**2**), (iii) 37,39,41-trimethoxy-38,40,42-trihydroxy-5,11,17,23,29,35-hexa-(4-*tert*-butyl)calix[6]arene (**3**), and (4) 24,26-dimethoxy-25,27-dihydroxy-5,11,17,23-tetra(4-*tert*-butyl)calix[4]arene (**4**) has been studied in the present paper in carbon tetrachloride medium by the NMR method.

2. Materials and Methods

[60]Fullerene was obtained from Sigma. [70]Fullerene was obtained from SES Rsearch Corp., Houston, TX. The calixarenes

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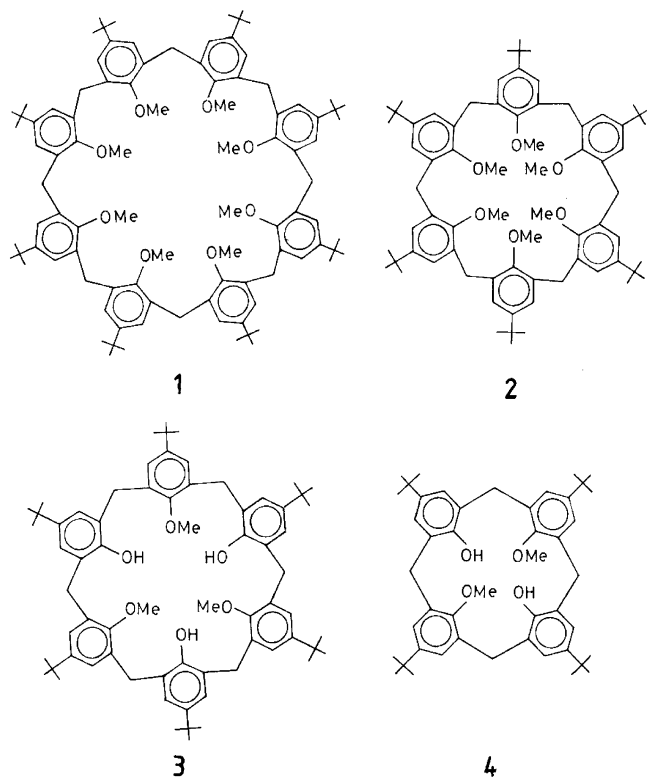* Corresponding author.

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Figure 1. Structures of the calixarenes studied.

TABLE 1: NMR Chemical Shifts of Methylene ($-CH_2$) Protons in [60]Fullerene−Calixarene Mixtures in CCl_4 Medium at Varying Concentrations of the Calixarenes ($T = 298$ K)

donor	$10^5[A]_0$, mol kg^{-1}	10^3[donor], mol kg^{-1}	Δ_{obs}, Hz
1	3.472	0.18	2.00
		0.29	1.77
		0.31	1.75
		0.37	1.66
2	3.472	0.58	2.00
		1.62	1.82
		2.13	1.74
		2.69	1.65
3	2.777	1.38	4.61
		1.61	4.16
		1.82	3.73
		2.92	3.52
		2.10	3.14
4	3.333	0.915	104.46
		1.67	72.05
		1.81	68.04
		1.85	66.05
		2.29	55.02
		2.44	54.94
		2.51	56.11

TABLE 2: NMR Chemical Shifts of Methylene Protons in Calixarenes−[70]Fullerene Mixtures in CCl_4 Medium at Varying Concentrations of the Calixarenes ($T = 298$ K)

donor	$10^5[A]_0$, mol kg^{-1}	10^3[donor], mol kg^{-1}	Δ_{obs}, Hz
1	2.052	1.71	18.41
		1.73	18.00
		1.81	17.80
		1.85	17.22
		1.94	16.51
2	1.488	1.32	18.21
		1.40	17.20
		1.42	18.20
		1.60	16.22
3	0.7068	0.86	1.20
		1.21	1.18
		1.77	0.98
		2.18	0.65
4	2.051	1.55	50.09
		1.80	45.45
		2.00	38.12
		2.25	38.51
		2.27	37.19
		2.31	36.11
		2.34	35.51
		3.54	25.01
		4.23	21.14

(Figure 1) were prepared as previously reported.[45−47] HPLC grade CCl_4 was used as solvent. ^{1}H NMR spectra of the calixarenes and calixarene−[60]fullerene and calixarene−[70]-fullerene mixtures in solution of CCl_4 were recorded on a Bruker AC-200 (200 MHz) NMR spectrometer with $CDCl_3$ as an internal lock.

3. Results and Discussion

To determine the formation constant (K) of a molecular complex C between the molecules of A and B

$$A + B \rightleftharpoons C, \quad K = [C]/([A][B]) \tag{1}$$
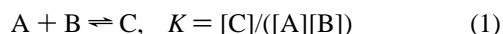
one requires knowledge of the equilibrium concentrations of the species A, B, and C.

Both [60]- and [70]fullerenes have no protons, and so the formation equilibria of [60]fullerene−calixarene and [70]-fullerene−calixarene complexes have been studied in the present report on the basis of changes in chemical shift of B protons on complexation; the derivation of the working formula was discussed in one of our previous publications.[43]

The working formula is

$$[B]_0 = \Delta_0[A]_0(1/\Delta_{obs}) - 1/K \tag{2}$$

where $\Delta_{obs} = \delta_{obs}^{(B)} - \delta_0^{(B)}$ = observed chemical shift of a B proton in the equilibrium mixture of A and B relative to that in free B and $\Delta_0 = \delta_c^{(B)} - \delta_0^{(B)}$ = chemical shift of the same B proton in the pure complex relative to that in the free B molecule. Thus, a linear plot of $[B]_0$ against $1/\Delta_{obs}$ is expected, from the intercept and slope of which K and Δ_0, respectively, can be evaluated. Experimental data for Δ_{obs} at a number of concentrations of B keeping that of A fixed are shown in Tables 1 and 2. In all cases, excellent linear plots in accordance with eq 2 were obtained, two such plots being shown in Figure 2.

Results of regression analysis and values of K and Δ_0 obtained therefrom are shown in Table 3.

Variation of the $-CH_2-$ and *tert*-butyl proton signals in the ^{1}H NMR spectra of one typical case, namely, [70]fullerene·**1** with change in concentration of **1**, is shown in Figure 3. With a fixed concentration of [70]fullerene, the observed Δ decreases as the donor concentration increases. Similar features were observed with all the donors studied (Tables 1 and 2). The values of maximum Δ_{obs} (for $-CH_2-$ proton) in all the cases range from 0.650 to 104.46 Hz. Such values are much greater than that expected from the solvation effect (ca. 0.5 Hz). Except for the calix[4]arene (**4**), the Δ_{obs} values are very much similar to those obtained by Hanna and Ashbaugh[42] for TCNQ complexes with a series of methylbenzenes and also for some complexes of [60]fullerene with a series of aromatic hydrocarbons and methylpyridines.[43] The formation constant values of the presently studied [60]- and [70]fullerene complexes are comparable in magnitude to those ($\sim10^3-10^4$ dm^3 mol^{-1}) of inclusion complexes of the same two fullerenes in bridged calix[5]arenes studied in CS_2 and *o*-dichlorobenzene medium by the absorption spectrophotometric method.[40b]
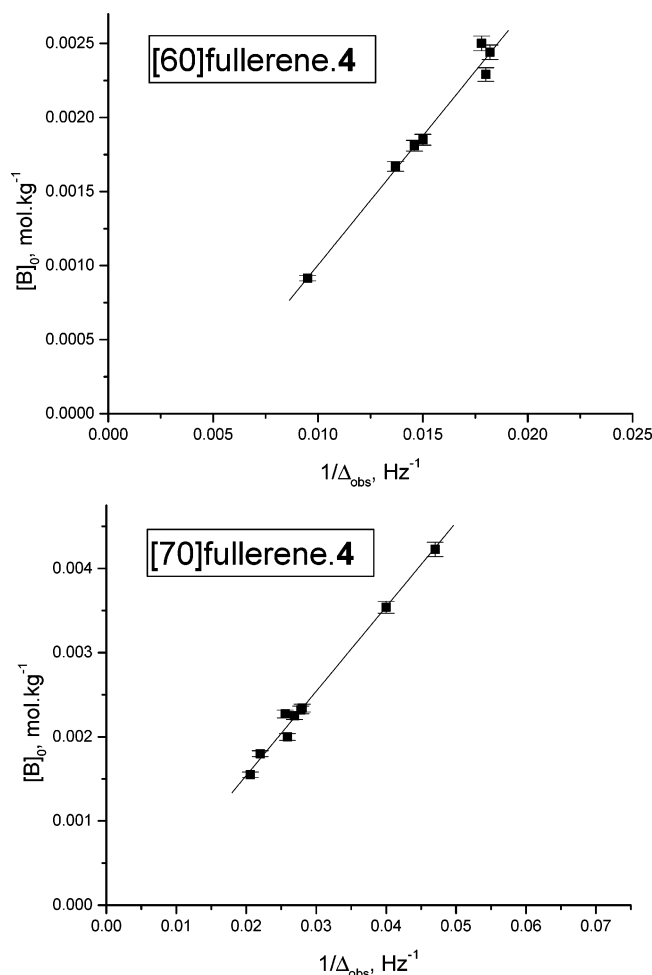
Figure 2. Plots of $[B]_0$ vs $1/\Delta_{obs}$ for [60]fullerene·**3** and [70]fullerene·**4** complexes.

The formation constants reported in Table 3 on the basis of the present experimental data obey the following trend: K of

TABLE 3: Formation Constants of the Complexes of [60]- and [70]Fullerene with Calixarenes and Chemical Shifts of the Pure Complexes Relative to the Respective Calixarenes ($T = 298$ K)

	formation constants, kg mol^{-1}		Δ_0, Hz	
calixarenes	[60]fullerene complex	[70]fullerene complex	[60]fullerene complex	[70]fullerene complex
1	2800 ± 50	4700 ± 200	35 ± 5	1700 ± 200
2	100 ± 10	2100 ± 230	570 ± 10	2200 ± 800
3	5700 ± 950	4500 ± 500	270 ± 50	200 ± 60
4	1350 ± 50	2150 ± 50	5240 ± 190	4800 ± 265

[60]fullerene·**3** > K of [60]fullerene·**1** > K of [60]fullerene·**4** > K of [60]fullerene·**2** and K of [70]fullerene·**1** $\cong$ K of [70]-fullerene·**3** > K of [70]fullerene·**4** > K of [70]fullerene·**2**.

Such trends can be rationalized as follows: The calixarenes **1** and **3** are capable of forming an inclusion complex with the fullerenes. The other calixarenes (**2** and **4**) do not. This is because **1** is a calix[8]arene with a suitable large cavity size and **3**, which is a calix 3-OH,3-OMe[6]arene, can preorganize itself into a conical configuration through intramolecular H-bonding at the lower rim and the fullerene ball approaches from the wider upper rim. This has been further substantiated by a ^{13}C NMR study discussed in the later part of this section. Both **3** and **4** have −OH groups and can preorganize into conical conformation. But the cavity of **4**, which is a calix 2-OH, 2-OMe[4]arene, does not become wide enough even after preorganization. This explains why K of the complex of **3** is higher than that of **4** with both [60]- and [70]fullerenes. The perimethylated calix[6]arene **2** does not form inclusion complexes with the fullerenes; they form EDA complexes (which is supported by the appearance of CT bands reported in one of our previous works[39]). Since [70]fullerene has a higher electron affinity[34] (by about 0.2 eV), the [70]fullerene complex of EDA type is expected to have a higher formation constant than the corresponding [60]fullerene complex. However, this cannot be the cause of about 20 times increase in K of the complexes of calixarene **2** in changing the acceptor from [60]- to [70]fullerene.
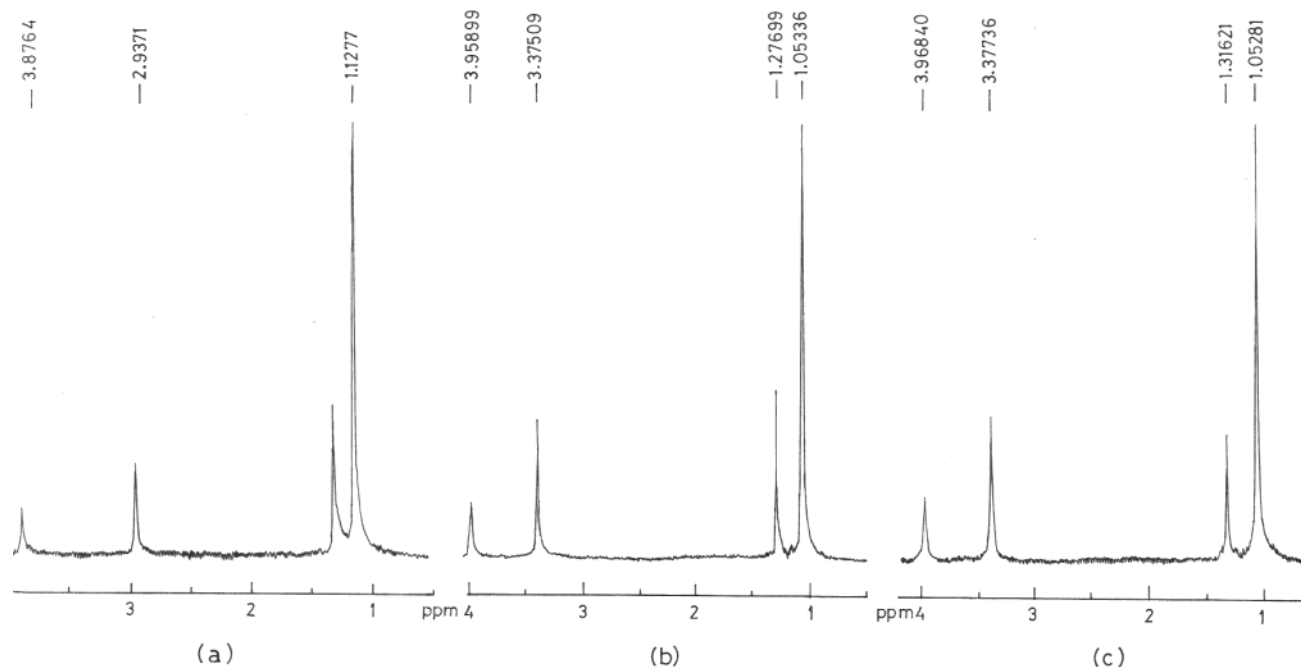

Figure 3. ^{1}H NMR spectrum of (a) **1** in CCl$_4$ in absence of [70]fullerene, (b) **1** (1.94×10^{-3} mol kg^{-1}) + [70]fullerene (2.052×10^{-5} mol kg^{-1}) in CCl$_4$, and (c) **1** (1.71×10^{-3} mol kg^{-1}) + [70]fullerene (2.052×10^{-5} mol kg^{-1}) in CCl$_4$ medium.

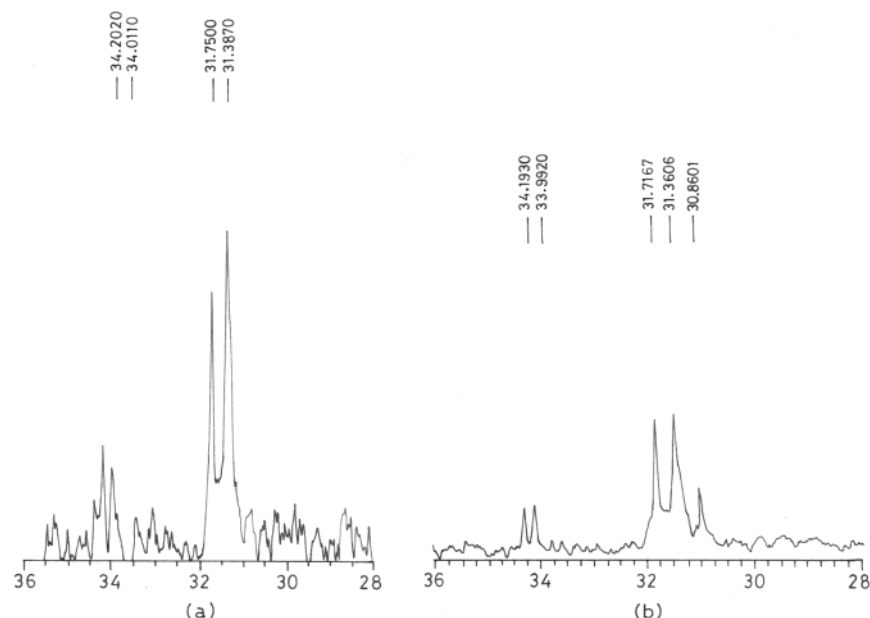**Figure 4.** ^{13}C NMR spectrum of (a) **3** (14.79 mol kg^{-1}) in CCl$_4$ in the absence of [60]fullerene and (b) **3** (14.79 mol kg^{-1}) + [60]fullerene (1.6835 × 10^{-5} mol kg^{-1}) in CCl$_4$ medium.

Formation constants of non-inclusion complexes involve many energy terms (in particular, solvation), and it is not always possible to explain their order only in terms of the electron-accepting power of the concerned acceptors.

^{13}C NMR spectra of compound **3** in the presence and absence of [60]fullerene in CCl$_4$ medium were also recorded in order to determine the direction of approach of the fullerene host toward the cavity of the guest. As expected, the *tert*-butyl group shows two signals (δ 31.7500 and 31.3870 ppm) in the absence of [60]fullerene, but in the presence of the latter these two signals are very slightly perturbed and a new signal appears at 30.8601 ppm (Figure 4). This indicates that the three methyl groups of *tert*-butyl do not remain equivalent after complexation. The guest molecule approaches the cavity from the *tert*-butyl side (wider rim), and despite rapid reversible exchange between the complexed and uncomplexed states, at least one $-CH_3$ of the *tert*-butyl group always remains within the ring current of the fullerene ball. Such $-CH_3$ exhibits a ^{13}C chemical shift different from that of the other $-CH_3$ members of the *tert*-butyl groups. The [60]fullerene carbon signal was obtained at 142.174 ppm in a mixture containing 14.79 mol kg^{-1} of compound **3** and 1.6835 × 10^{-5} mol kg^{-1} of [60]fullerene in CCl$_4$ medium. Compared to the chemical shift of pure [60]-fullerene (δ = 142.5 ppm) as measured in the present experiment and also reported in two earlier works,[48,49] this is an upfield displacement due to complexation. The chemical shift of the isolated pure complex was estimated as follows.

Derivation of Working Formula for Determination of K from ^{13}C NMR Data. Let us consider the formation equilibrium described in eq 1. If P_A and P_C are the probabilities of finding A molecules in the free and complexed forms, respectively, then the observed chemical shift of a particular carbon of A is given by

$$\delta_{obs}^{(A)} = P_A\delta^{(0)} + P_C\delta^{(C)} \qquad (3)$$

where $\delta^{(0)}$ and $\delta^{(C)}$ are the chemical shifts of the same carbon in pure A and in the complex C. We can write the above equation as

$$\delta_{obs}^{(A)} = P_A\delta^{(0)} + P_c\delta^{(c)}$$
$$= (1 - P_c)\delta^{(0)} + P_c\delta^{(c)}$$
$$= \delta^{(0)} + P_c(\delta^{(c)} - \delta^{(0)})$$

or

$$\delta_{obs}^{(A)} - \delta^{(0)} = P_c(\delta^{(c)} - \delta^{(0)}) \qquad (4)$$

Denoting $\delta_{obs}^{(A)} - \delta^{(0)}$ by Δ_{obs} and $\delta^{(c)} - \delta^{(0)}$ by $\Delta^{(0)}$, we have

$$\Delta_{obs} = P_c\Delta^{(0)} \qquad (5)$$

Now

$$P_c = [C]/([C] + [A]) = [C]/[A]_0 \qquad (6)$$

where [C] and [A] are respectively the equilibrium concentrations of the complex and free A and [A]$_0$ is the initial concentration of A in the mixture before complexation. Combination of eqs 5 and 6 gives

$$\Delta_{obs} = [C]\Delta^{(0)}/[A]_0 \qquad (7)$$

Now under the approximation [B]$_0$ ≫ [A]$_0$ the formation constant (K) can be written as

$$K = [C]/([B][A])$$
$$= [C]/\{([B]_0 - [C])([A]_0 - [C])\}$$
$$= [C]/\{[B]_0([A]_0 - [C])\}$$

since under the above approximation [B]$_0$ − [C] ≈ [B]$_0$. Hence, $1/K = \Delta^{(0)}[B]_0/\Delta_{obs} - [B]_0$ (utilizing eq 7) or

$$B_0 = (\Delta^{(0)}[B]_0/\Delta_{obs}) - 1/K \qquad (8)$$

This equation has been used for estimating the complexation-induced chemical shift of the ^{13}C atom of the [60]fullerene in

the pure complex. The derivation is analogous to that required for determination of K from the ^1H chemical shift.[43] The only difference is that the probability P_c of finding A, i.e., [60]-fullerene in the complexed state is given by $P_c = [AB]/[A]_0$. Using the value of K (=5700 mol kg^{-1}), $[B]_0$ (=14.79 mol kg^{-1}), and Δ_{obs} for the ^{13}C signal in eq 8, we evaluated Δ_0 and thence $\delta^{(c)}$ for the [60]fullerene·**3** complex. An upfield shift of 0.33 ppm of the [60]fullerene ^{13}C signal due to complexation was found. This estimated chemical shift value is well in agreement with the experimental value (0.35 ppm) obtained earlier by Haino et al.[40a]

4. Conclusions

Both [60]- and [70]fullerenes are shown to form 1:1 supramolecular complexes with the calixarenes under study. Of them, the calixarene **3** in particular forms a stronger inclusion complex with both [60]- and [70]fullerenes owing to preorganization, and the host fullerenes approach the cavity from the side of the wider rim containing *tert*-butyl groups. The peri-methylated calix[8]arene (**1**) forms a stronger inclusion complex with [70]fullerene than with [60]fullerene. This is possible if inclusion in (**1**) occurs mainly through $\pi-\pi$ interaction—[70]-fullerene with a higher electron affinity of 2.73 eV (compared to 2.65 eV of [60]fullerene) is a better electron acceptor.

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