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Complexes formed from [60]Fullerene and Calix[4]naphthalenes

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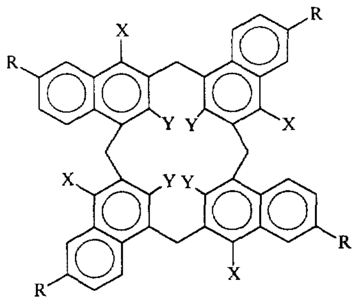
Abstract: The complexation of the *endo*-type calix[*4*]naphthalenes **2** and its tetra-*tert*-butylated derivative derivative, **3** with [60]fullerene and fullerite mixture has been studied in various organic solvents. Spectrophotometric methods show that in dilute solution 1:1 complexes are formed between **2** or **3** with [60]fullerene. Strong association constant values (K_{ass}) were observed for **2** and **3** with both [60]fullerene and fullerite mixture. © 1999 Elsevier Science Ltd. All rights reserved.

In 1994, Atwood *et al.* [1] and Shinkai *et al.* [2] reported that[60]fullerene is selectively sequestered from carbon soot using *p-tert*-butylcalix[*8*]arene. Since then, several studies have been published which have delineated parameters that are required for the optimal formation of [60]fullerene-calixarene inclusion complexes. In a recent study utilizing a number of different calix[*n*]arenes Shinkai *et al.* [3] concluded that an important requirement for effective inclusion of [60]fullerene in solution is that the calix[*n*]arenes have preorganized cone conformations and a proper inclination of the benzene rings. These authors also concluded that a deep inclusion of [60]fullerene into the calix[*n*]arene cavity as expected for calix[*8*]arenes, is not a necessary prerequisite for inclusion.

A class of calix[*4*]arene-related molecules which in principle possess deeper cavities, are the calix[*4*]naphthalenes. In 1993 [4] and 1995 [5] we reported the syntheses of all four isomers of the *exo*-calix[*4*]naphthalenes e.g. **1**. Andreetti *et al.* in 1993 [6] also reported an example of an *endo*-type calix[*4*]naphthalene, **2**. Our own work[7] with the variable-temperature ^{1}H- NMR of this molecule indicates that the molecule adopts a crown or cone conformation at low temperatures. We reasoned therefore that **2** and its 6-*tert*-butylated derivative,[8] **3** could serve as potentially effective hosts for inclusion of [60]fullerene and other guests. In the solid state **2** adopts a "pinched cone" conformation and its unit cell contains a pair of molecules in which a naphthalene unit of one molecule is situated within the hydrophobic cavity of the second molecule.[8] In principle, therefore, efficient inclusion could occur since multi π-π-interactions between [60]fullerene and the calix[*4*]naphthalenes are possible.



1: R = Y = H ;X = OH
2: R = X = H ;Y = OH
3: R = Bu^t ; X = H ;Y = OH

When solutions of **2** or **3** in toluene, benzene or carbon disulfide were added to solutions of [60]fullerene in the same respective solvents, the magenta coloured solutions of the [60]fullerene changed colour, and after standing for several days, dark red-brown precipitates were produced. In the

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case of **3**, ruby-red rod-like crystals were formed, but thus far single crystal X-ray diffraction analyses have eluded us since the crystals diffracted very weakly and only very low angle peaks could be observed.

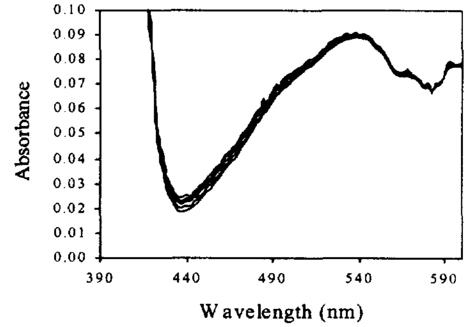

Figure 1. Absorbance spectra of mixtures of [60]fullerene (1.08×10^{-4} mol dm^{-3}) and **2** ($2.46 - 9.16 \times 10^{-4}$ mol dm^{-3}) in toluene at 25 °C.

The spectral change induced by the addition of [**2**], for example, to solutions of [60]fullerene can be seen in Figure 1. The most obvious changes are seen at λ= 430 nm. A continuous variation (Job's)[9] plot , an example of which is shown in Figure 2, of Δ A_{430} *vs.* [**2**]/[C_{60}]+ [**2**] (where [C_{60}] + [**2**] = 0.100 mmol dm^{-3}) in each of the three different solvents at 25 °C gave maxima at 0.5, indicating 1:1 complex formation at these low concentration levels. Analysis of the mole ratio data, an example of which is also shown in Figure 2, using the Benesi-Hildebrand equation[10] provided the association constants (K_{ass}) shown in Table 1 and also indicates 1:1 complex formation.

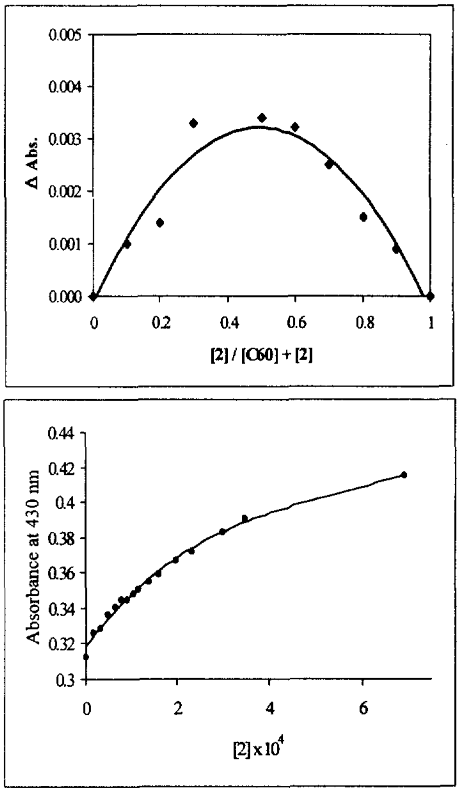

Figure 2. Continuous variation plot (top) and absorbance at 430 nm vs [**2**] plot (lower) in toluene at 25 °C.

As expected, the observed K_{ass} values are relatively higher than those observed with calix[*n*]arenes, but unexpectedly, the trend in the values obtained for [60]fullerene-**2** and [60]fullerene-**3** complexes in the different solvents were opposite to the trends reported by Haino *et al.* [11] In particular, the values obtained in carbon disulfide in our cases, namely $3.4 \pm 0.1 \times 10^3$ and $6.9 \pm 0.1 \times 10^3$ dm^3 mol^{-1} respectively, are higher than the highest value of $2.1 \pm 0.1 \times 10^3$ dm^3 mol^{-1} reported by Haino *et al.* for a calix[5]arene in toluene solution.[11] In both cases with pure [60]fullerene the K_{ass} values increase from benzene to toluene to carbon disulfide. In a more recent paper, Haino *et al* [12] report higher K_{ass} values, but the host molecules that they employed were all bridged calix[5]arenes.

Thus, it appears as though in addition to the enhanced π-π interactions that may be occurring due to the presence of the extra aromatic rings on the naphthalene units, that a solvophobic[13] effect may be occurring. Dormann *et al* [14] have shown by thermal gravimetry that carbon disulfide can form a 4:1 complexes with calix[*4*]- and calix[*6*]arenes, whereas toluene forms only 1:1 and 1.5:1 complexes respectively. It is possible that similar solvent-complexation could be occurring in our cases and that the displacement of solvent molecules to form [60]fullerene-**2** and [60]fullerene-**3** complexes could result in a favourable entropic effect which is typical in solvophobic processes. We are in the process of determining the thermodynamic parameters (ΔH and ΔS) for these compounds.[15] We are also presently determining these solvent-complexation properties of calix[4]naphthalenes using measurements of partial molal volume changes. Using such a methodology, Issac *et al.*[16] have shown that two toluene molecules are displaced upon complexation of [60]fullerene with *p*-benzylcalix[5]arene but they do not report any comparable data with any other solvents.

The trend in association constants for fullerite-**2** is opposite to that observed with pure [60]fullerene-**2**. This is in agreement with the trend reported by Haino *et al*[11] but with fullerite-**3** there is no apparent similar trend, although in both fullerite-**2** and fullerite-**3** the K_{ass} values in benzene solvent are an order of magnitude higher than those observed with [60]fullerene-**2** and [60]fullerene-**3** in the same solvent. In general, fullerite mixture shows higher K_{ass} values than pure [60]fullerene. At present we are unable to rationalize the data with fullerite although it is possible that there could be additional complexation of **2** and **3** with [70]fullerene that is present in the mixture. We are also presently investigating the complexation properties of **2** and **3** with pure [70]fullerene itself.

Table 1. K_{ass} of **2** and **3** with [60]fullerene and fullerite at 25 °C.

	(C_{60})(**2**)	(C_{60})(**3**)	(Fullerite)-(**2**)	(Fullerite)-(**3**)
Benzene	457 ± *40*	295 ± *13*	5,130 ± *300*	4,900 ± *570*
Toluene	631 ± *51*	676 ± *28*	4,170 ± *96*	1,050 ± *18*
Carbon disulfide	3,390 ± *180*	6,920 ± *330*	1,620 ± *120*	6,480 ± *610*

Further evidence for the inclusion of [60]fullerene in the cavity of **3** can be obtained from the down-field shifts observed in the ^{1}H NMR spectral data of [60]fullerene-**3** in toluene-d_8. A down-field shift of 0.093 ppm for the OH and 0.017 ppm for the *t*-Bu groups are found. Ikeda *et al.* observed similar, down-field shifts of 0.01 ppm for the OH and 0.02 ppm for the *t*-Bu groups in their C_{60}-hexahomooxocalix[3]arene complex.[17]

The +FAB-MS for the precipitate from the toluene solutions of [60]fullerene-**3** reveals a more complex pattern of peaks than what is observed for corresponding spectrum of crystals derived from toluene solutions of **3** alone. No M^+ peak for [60]fullerene-**3** is observed, but additional peaks are evident (among others) at 720 (C_{60}); 784(M^{2+}); 876 (M+ (toluene)$_2$)$^{2+}$; 968 (M+ (toluene)$_4$)$^{2+}$.

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