Pergamon

Tetrahedron Letters, Vol. 38, No. 12, pp. 2107-2110, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)00318-3

Solution Complexes Formed from C_{60} and Calixarenes. On the Importance of the Preorganized Structure for Cooperative Interactions

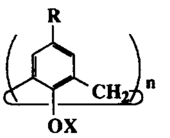
Atsushi Ikeda, Makoto Yoshimura, and Seiji Shinkai*

Department of Chemical Science & Technology, Faculty of Engineering,
Kyushu University, Fukuoka 812, Japan

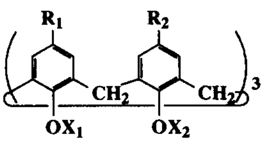
Abstract: In order to find calix[n]arenes which can interact with C_{60} in solution we have screened 28 different calix[n]arenes by spectroscopic methods. We eventually discovered such three calix[n]arenes (**1**$_5$·Bu^t·H, **2**$_6$·Bu^t·Bu^t·H·H, and **3**$_3$·Bu^t·H). They commonly possess a cone conformation and a benzene ring inclination suitable to C_{60} inclusion. We believe that this finding will open a door to new fullerene-calix[n]arene inclusion chemistry. © 1997 Elsevier Science Ltd.

In 1994, we[1] and Atwood *et al.*[2] discovered that *p-tert*-butylcalix[8]arene selectively includes C_{60} in carbon soot and forms the precipitate with 1 : 1 stoichiometry. This is a very novel and very useful purification method to obtain C_{60} in the large quantity and with high purity.[3] It has been believed that the origin of selective inclusion stems from the conformity of the C_{60} size with the calix[8]arene cavity. However, when this complex was solubilized in solution (*e.g.*, by heating or using good solvents), it dissociated into each component, and any spectroscopic indication for the complex formation could not be found.[4] This means that this complex can stably exist only in the solid state. So far, inclusion complexes of C_{60} are obtained in an aqueous system with cyclodextrins and water-soluble calixarenes.[5] However, C_{60} has a practical solubility only in certain organic solvents: therefore, it seems more useful for C_{60} to be treated in organic solvents, for example, for further derivatization and functionalization.

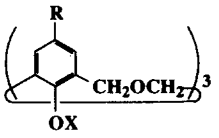
To find a breakthrough for this problem we previously introduced electron-rich aniline or 1,3-diaminobenzene derivatives into calix[6]arene, expecting that the charge-transfer interaction acts as a driving-force for C_{60} inclusion: the association constants (K) were 7.9-110 dm^3 mol^{-1} in toluene.[6] On the other hand, Atwood *et al.*[7] found that excess cyclotriveratrylene (CTV) and C_{60} in toluene results in micelle-like aggregation of the fullerenes which is spectrophotometrically detectable. This implies that the CTV-C_{60} interaction is not so strong as to disperse C_{60} particles discretely but does exist even in toluene solution. This finding has stimulated us to screen the potential inclusion ability of many calixarene derivatives we have synthesized so far. After examination of 28 calixarene



1$_n$·R·X
(n = 4, 6, 8)



2$_6$·R$_1$·R$_2$·X$_1$·X$_2$



3$_3$·R·X

derivatives[8] we have eventually discovered that calix[5]arenes and homooxacalix[3]arenes (and calix[6]arene more weakly than the former two) do interact with C_{60} in toluene.

Compounds tested for a calix[4]arene series are 1_4·Bu^t·H, 1_4·H·H, and 1_4·H·Me, but in toluene at 25 °C none of them showed any significant change in their absorption spectroscopy ([C_{60}] = 1.00×10^{-4} mol dm^{-3}, [1_4·R·X] = (1 ~ 50) × 10^{-4} mol dm^{-3}). Compounds tested for a calix[8]arene series are 1_8·H·H, 1_8·Me·H, 1_8·OMe·H, 1_8·OMe·Me, 1_8·OCH$_2$Ph·H, 1_8·Et·H, 1_8·Pr^i·H, 1_8·Ph·H, 1_8·*n*-Amyl·H, and 1_8·*t*-Amyl·H. Again, none of them showed any significant spectroscopic change.

For a calix[6]arene series we tested 13 compounds: 2_6·Bu^t·Bu^t·H·H, 2_6·Bu^t·Bu^t·Me·Me, 2_6·H·H·H·H, 2_6·H·H·Me·Me, 2_6·Bu^t·H·Me·Me, 2_6·Bu^t·Br·Me·H, 2_6·Bu^t·H·Me·H, 2_6·Bu^t·Bu^t·H·Me, 2_6·OMe·OMe·Me·Me, 2_6·Ph·Ph·H·H, 2_6·Bu^t·Bu^t·Bu^n·Bu^n, 2_6·H·H·Bu^n·Bu^n, and 2_6·H·H·CH$_2$COOEt·CH$_2$COOEt. Among them only 2_6·Bu^t·Bu^t·H·H induced a slight spectroscopic change in the C_{60} band (Fig. 1). 1_5·Bu^t·H induced a greater spectroscopic change than 2_6·Bu^t·Bu^t·H·H (Fig. 1), but its *O*-methyl derivative, 1_5·Bu^t·Me was totally ineffective. Interestingly, 3_3·Bu^t·H induced a large spectroscopic change at 420-480 nm region (Fig. 1), indicating that a significant interaction does exist between C_{60} and homooxacalix[3]arene even in toluene. Again, its *O*-methyl derivative, 3_3·Bu^t·Me was ineffective.

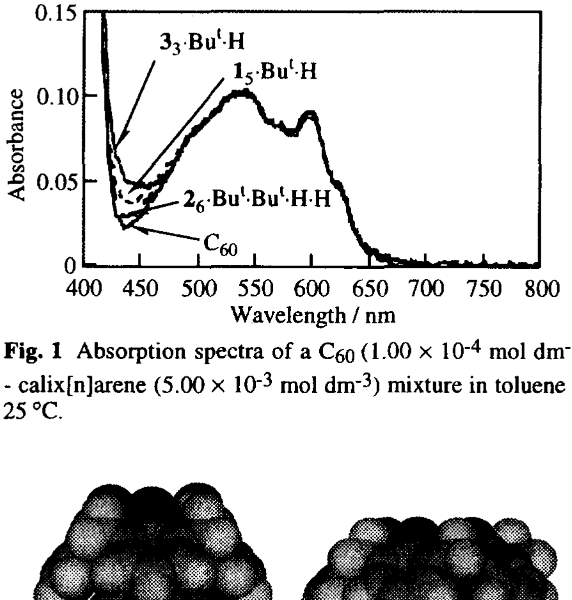


Fig. 1 Absorption spectra of a C_{60} (1.00×10^{-4} mol dm^{-3}) - calix[n]arene (5.00×10^{-3} mol dm^{-3}) mixture in toluene at 25 °C.

The foregoing findings support the view that C_{60} is included by a few selected calixarenes. From the extensive screening we can now conclude that the primary prerequisite for C_{60} inclusion is that the OH groups on the lower rim are not substituted. The secondary prerequisite is the ring size that the interaction is observed only for unmodified calix[5]arene, calix[6]arene, and homooxacalix[3]arene. Previously, we theoretically estimated the most stable conformations of unmodified calix[n]arenes, which showed good agreements with those determined by X-ray crystallographic analyses.[9] From comparison of the structure of the stablest conformers with the C_{60} globular structure we noticed that the cavities of these calixarenes are too small to deeply "include" C_{60} but have an inclination of the benzene rings to enjoy a multi-point contact with the C_{60} surface: that is, they can interact as a local "cap" for C_{60} (Fig. 2). This

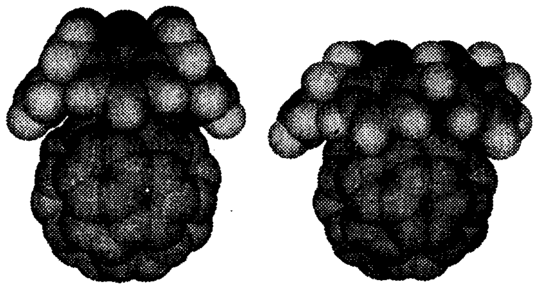

1_4·H·H 1_5·H·H

Fig. 2 Possible interactions of 1_4·H·H and 1_5·H·H with C_{60}. 1_4·H·H and 1_5·H·H are energy-minimized with MM3(92). 1_5·H·H can provide a benzene ring inclination suitable to C_{60}-binding whereas 1_4·H·H cannot.

requirement is also satisfied by 3_3·Bu^t·H. This second prerequisite allows us to consider that the major driving-force for C_{60} inclusion is a π–π interaction (including the charge-transfer-type interaction) and/or a solvophobic effect. To fully enjoy this effect the calix[n]arenes are required to be preorganized in a cone conformation through intramolecular hydrogen-bonds among OH groups.

To obtain further insights into C_{60} inclusion we chose 3_3·Bu^t·H which showed the largest spectral change. A continuous variation plot of A_{437} *vs.* [C_{60}] / ([C_{60}] + [3_3·Bu^t·H]) (where [C_{60}] + [3_3·Bu^t·H]) = 3.00 mmol dm^{-3}) in toluene at 25 °C gave a maximum value at 0.5, indicating the formation of a 1 : 1 complex. The analysis of a plot of A_{460} *vs.* [3_3·Bu^t·H] (Fig. 3 : where [C_{60}] = 0.5 mmol dm^{-3}) according to the Benesi-Hildebrand equation provided the association constant $K = 64 \pm 5$ dm^3 mol^{-1}. This value is nearly half of the K for a calix[6]arene bearing three 1,3-diaminobenzene units (110 dm^3 mol^{-1}).[6]

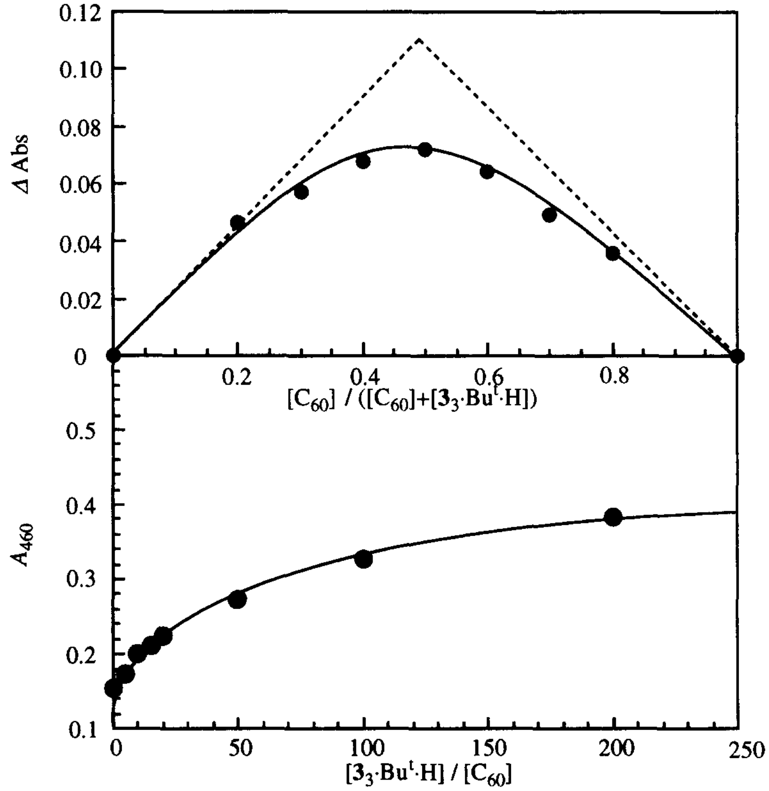


Fig. 3 A continuous variation plot (upper) and an A_{460} *vs.* [3_3·Bu^t·H] plot (lower) in toluene at 25 °C.

^{1}H and ^{13}C NMR spectra were measured in toluene-d_8 at 25 °C ([C_{60}] = 5.6 mmol dm^{-3}, [3_3·Bu^t·H] = 20 mmol dm^{-3}: judging from K = 64 dm^3 mol^{-1}, 52% of C_{60} are included in the 3_3·Bu^t·H cavity). In the ^{1}H NMR spectrum the slight down-field shift was observed for *t*-Bu (+0.02 ppm), ArH (+0.01 ppm), and OH (+0.01 ppm) protons. In the ^{13}C NMR spectrum the significant down-field shift was observed for CH_3 (+0.06

ppm), CH_2 (+0.17 ppm), and Ar (+0.04 ~ 0.08 ppm) carbons whereas C_{60} carbons move to higher magnetic field (143.23 → 143.21 ppm). These NMR data are commensurate with the proposal that C_{60} is included in the calix[3]arene cavity.

C_{60} (5.0 mg; 6.9×10^{-6} mol) and **3**$_3$·Bu^t·H (40 mg; 6.9×10^{-5} mol) were solubilized into toluene (4.0 ml) by sonication and the resultant solution was left at room temperature for one week. The dark brown precipitate was formed from this solution. The elemental analysis data supported the 1 : 1 stoichiometry of this complex (Found: C, 88.89; H, 3.88 %. Calcd for the 1 : 1 complex: C, 88.87; H, 3.73%). In the IR spectrum (KBr disk) the characteristic bands for **3**$_3$·Bu^t·H were scarcely affected by C_{60} inclusion: *e.g.*, 3369 → 3368 cm^{-1}, 2957 → 2960 cm^{-1}, 1486 → 1487 cm^{-1}, 1080 → 1080 cm^{-1}, and 879 → 877 cm^{-1}. This supports the view that **3**$_3$·Bu^t·H is well preorganized for C_{60} inclusion.

In conclusion, the present study demonstrated that such calix[n]arenes that have a preorganized cone conformation and a proper inclination of the benzene rings can interact with C_{60} even in solution. This means that deep inclusion of C_{60} into the calix[n]arene cavity, as expected for calix[8]arenes, is not a prerequisite for C_{60} inclusion. We believe that the present results will open a door to new inclusion chemistry between fullerenes and calix[n]arenes.

REFERENCES AND NOTES

1. Suzuki, T.; Nakashima, K.; Shinkai, S. *Chem. Lett.*, **1994**, 699-702.
2. Atwood, J. L.; Koutsantonis, G. A.; Raston, C. L. *Nature*, **1994**, *368*, 229-231.
3. Constable, E. C. *Angew. Chem. Int. Ed. Engl.*, **1994**, *33*, 2269-2271.
4. Suzuki, T.; Shinkai, S.; unpublished results: also see Suzuki, T.; Nakashima, K.; Shinkai, S. *Tetrahedron Lett.*, **1995**, *36*, 249-252.
5. Anderson, T.; Nilsson, K.; Sundahl, M.; Westman, G.; Wennerström, O. *J. Chem. Soc., Chem. Commun.*, **1992**, 604-606; Yoshida, Z.; Takekuma, H.; Matsubara, Y. *Angew. Chem. Int. Ed. Engl.*, **1994**, 33, 1597-1599; R. M. Williams and J. W. Verhoeven, *Recl. Trav. Chim. Pays-Bas*, **1992**, *111*, 531-532.
6. Araki, K.; Akao, K.; Ikeda, A.; Suzuki, T.; Shinkai, S. *Tetrahedron Lett.*, **1996**, *37*, 73-76.
7. Atwood, J. L.; Barnes, M. J.; Gardiner, M. G.; Raston, C. L. *J. Chem. Soc., Chem. Commun.*, **1996**, 1449-1450.
8. For the source of the calix[n]arenes used herein refer to my review article and references cited therein: Shinkai, S. *Tetrahedron*, **1993**, *49*, 8933-8968.
9. Harada, H.; Shinkai, S. *J. Chem. Soc., Perkin Trans. 2*, **1995**, 2231-2242.

(*Received in Japan* 6 *January* 1997; *revised* 12 *February* 1997; *accepted* 14 *February* 1997)