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# Influence of *para*-Substituents and Solvents on Selective Precipitation of Fullerenes by Inclusion in Calix[8]arenes

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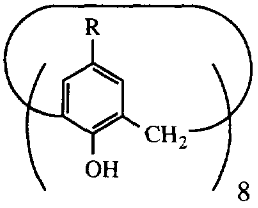
***Abstract:*** Twelve calix[8]arene derivatives ($1_8$R) with different *para*-substituents (R) were synthesized and applied to selective precipitation of $C_{60}$ and $C_{70}$ from benzene and toluene. $1_8$Pr$^i$ and $1_8$Bu$^t$ precipitates from benzene and toluene, forming a 1:1 complex with $C_{60}$ whereas only $1_8$Bu$^t$ precipitates from benzene, forming a 1:2 $1_8$Bu$^t$ / $C_{70}$ complex. The spectroscopic studies of the precipitate complexes are also reported.

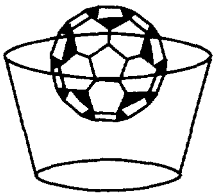
Fullerenes are a novel family of caged compounds which have a variety of scientific potentials as electron-carriers, π-basic donors and acceptors, host molecules, *etc.*[1] In spite of a broad demand for and a scientific interest in them the progress of this chemistry has been suppressed and hampered by their very extensive commercial price. This situation stimulated us to develop a practical purification method for their commercial use. Quite adventitiously, we came across "serendipity" that 5,11,17,23,29,35,41,47-octa-*tert*-butylcalix[8]arene-49,50,51,52,53,54,55,56-octol ($1_8$Bu$^t$) which has an inner cavity comparable with the size of $C_{60}$, selectively forms a 1:1 complex with $C_{60}$ and precipitates from a toluene solution.[2,3] This is a new purification method incomparably superior to a conventional column chromatography method.[4-6] At almost the same time, Atwood et al. have reported the same method and other results that calix[6]arene-37,38,39,40,41,42-hexol forms a 1:2 complex with $C_{60}$ and that 5,11,17,23,29,35-*tert*-butylcalix[6]arene-37,38,39,40,41,42-hexol forms a 1:2 complex with $C_{70}$.[3] The spectroscopic studies showed that in the $1_8$Bu$^t$·$C_{60}$ complex, (i) $C_{60}$ molecules are isolated discretely by $1_8$Bu$^t$,[2] (ii) the intramolecular hydrogen bonds among OH groups, characteristic of calix[n]arenes,[7] are partially cleaved,[2] (iii) the Bu$^t$ groups exist near the π-basic surface of $C_{60}$,[2] and (iv) $1_8$Bu$^t$ adopts a symmetrical conformation, either "cone" or "1,3,5,7-alternate".[8] In spite of our efforts the preparation of a single crystal for X-ray analysis has been unsuccessful so far, but one can explain the inclusion and selective precipitation mechanisms to some extent on the basis of several lines of spectroscopic information. Generally saying, "polyols" are soluble only in water or methanol but $1_8$Bu$^t$ with eight OH groups is soluble in toluene. The unusual solubility is ascribed to "sheltering" of the OH groups in the intramolecularly hydrogen-bonded ring. Upon inclusion of $C_{60}$ in $1_8$Bu$^t$, a conformational change is induced, the intramolecular hydrogen-bonding interaction is partially destroyed, and the complex precipitates because of the aggregation through the intermolecular hydrogen-bonding interaction. This is the most likely mechanism at present.

If the above hypothesis is correct, the OH groups are indispensable to selective inclusion of $C_{60}$. In contrast, it is not yet clear if the Bu$^t$ groups are indispensable or if calix[8]arenes can include other fullerene homologs (*e.g.*, $C_{70}$). Here, we synthesized 12 different calix[8]arenes and tested their inclusion ability for $C_{60}$ and $C_{70}$. Interestingly, we have found that they form not only a 1:1 complex but also a 1:2 calix[8]arene / fullerene complex. These complexes were carefully characterized by using solid-state $^{13}C$ NMR spectroscopy.

Compounds $\mathbf{1}_8$R (see Table 1) were synthesized according to the methods in the references.[9-11] The typical treatment method is as follows: a toluene (or benzene) solution (5 ml) of $C_{60}$ (or $C_{70}$) (0.005 mmol) and a same solution (5 ml) of calix[8]arene (0.01 mmol) were mixed. The combined solution was stirred at room temperature for 12 h. The results are summarized in Table 1.



$\mathbf{1}_8$R



$\mathbf{1}_8$Bu$^t$·$C_{60}$ complex

Table 1. Precipitation Tests with $\mathbf{1}_8$R in Toluene and Benzene[a)]

| Calix[8]arene | From toluene | | From benzene | |
|---|---|---|---|---|
| | $C_{60}$ | $C_{70}$ | $C_{60}$ | $C_{70}$ |
| $\mathbf{1}_8$H | N | N | N | N |
| $\mathbf{1}_8$Me | P' | N | P' | N |
| $\mathbf{1}_8$Et | N | N | P'(100) | P'(90) |
| $\mathbf{1}_8$Pr$^n$ | N | N | N | N |
| $\mathbf{1}_8$Pr$^i$ | P(50) | N | P(100) | N |
| $\mathbf{1}_8$Bu$^n$ | N | N | N | N |
| $\mathbf{1}_8$Bu$^s$ | N | N | N | N |
| $\mathbf{1}_8$Bu$^t$ | P(100) | N | P(100) | P(70) |
| $\mathbf{1}_8$Am$^n$[b)] | N | N | N | N |
| $\mathbf{1}_8$Am$^t$[b)] | N | N | N | N |
| $\mathbf{1}_8$Oct$^t$ | N | N | N | N |
| $\mathbf{1}_8$Ph | N | N | N | N |

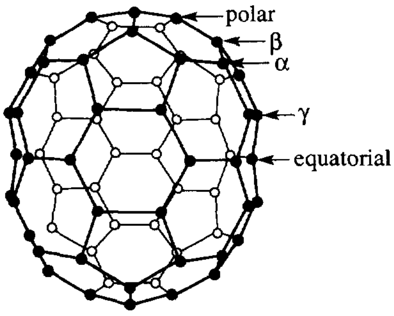
a) P: the precipitate was formed. N: the precipitate was not formed. P': the precipitate was formed but the stoichiometry was not reproducible. The value in the parenthesis indicates the recovery yield of $C_{60}$ or $C_{70}$ (%).
b) Am denotes the amyl group.

The precipitation including $C_{60}$ from toluene was observed for $\mathbf{1}_8$Me, $\mathbf{1}_8$Pr$^i$, and $\mathbf{1}_8$Bu$^t$ but none of calix[8]arenes could precipitate $C_{70}$. From benzene, on the other hand, $\mathbf{1}_8$Et in addition to the foregoing three calix[8]arenes precipitated $C_{60}$ and even $C_{70}$ was precipitated by $\mathbf{1}_8$Et and $\mathbf{1}_8$Bu$^t$. The results show that the

$C_{60}$ complexes are less soluble than the $C_{70}$ complexes and benzene is poorer solvent than toluene. Also, the $1Bu^t$ complexes were less soluble than other complexes: *e.g.*, the $1_8Bu^t \cdot C_{60}$ precipitate can stably exist in refluxing benzene whereas the $1_8Pr^i \cdot C_{60}$ precipitate is dissolved in it.

The stoichiometry was estimated by the elemental analysis. As in the $1_8Bu^t \cdot C_{60}$ precipitate from toluene,[2] $1_8Bu^t$ and $C_{60}$ always resulted in the 1:1 stoichiometry regardless of solvent. $1_8Pr^i$ also formed a 1:1 complex with $C_{60}$. Interestingly, the $1_8Bu^t \cdot C_{70}$ precipitate from benzene showed the 1:2 $1_8Bu^t$ / $C_{70}$ stoichiometry. In $1_8Me \cdot C_{60}$, $1_8Et \cdot C_{60}$, and $1_8Et \cdot C_{70}$ the precipitates were actually formed but the stoichiometry was not reproducible, ranging from 1:1 to 1:4 $1_8R$ / $C_{60}$ (or $C_{70}$). This is probably because $1_8Me$ and $1_8Et$ cannot form stable complexes with $C_{60}$ (or $C_{70}$) enough to afford the single complex species.

Previously, we had fully characterized the $1_8Bu^t \cdot C_{60}$ complex by spectroscopic methods.[2] We here characterized the $1_8Bu^t \cdot (C_{70})_2$ complex. To answer the question how calix[8]arenes include two $C_{70}$ fullerenes, solid-state $^{13}C$ NMR spectra of $1_8Bu^t \cdot (C_{70})_2$ and free $C_{70}$ were compared.[12] Interestingly, only one set of $C_{70}$ peaks (four separate peaks + one shoulder) was observed for the CP-MAS $^{13}C$ NMR spectrum of $1_8Bu^t \cdot (C_{70})_2$. The HD-MAS (MAS with $^1H$ high-power decoupling) $^{13}C$ NMR spectrum of $1_8Bu^t \cdot (C_{70})_2$ was also measured because the carbon without $^1H$-$^{13}C$ dipolar interaction may not appear in CP-MAS. The number and chemical shifts of $C_{70}$ resonances in the HD-MAS spectrum were similar to those in the CP-MAS spectrum. These results strongly support the view that two $C_{70}$ molecules in $1_8Bu^t \cdot (C_{70})_2$ are totally equivalent. Chemical shifts[13] of $C_{70}$ peaks in $1_8Bu^t \cdot (C_{70})_2$ (ppm) and in free $C_{70}$ (in parentheses) were 151.1 (polar, 151.1), 147.9 ($\alpha$, 148.2), 145.0 ($\gamma$, 145.6), and 130.3 (equatorial, 131.0), respectively.[14] Clearly, most $C_{70}$ peaks showed the small but significant up-field shift and the order of its magnitude was equatorial (-0.7) > $\gamma$ (-0.6) > $\alpha$ (-0.3) > polar (0.0). $T_1$ values[15] of $C_{70}$ peaks in $1_8Bu^t \cdot (C_{70})_2$ (sec) and in free $C_{70}$ (in parentheses) were 20.9 (polar, 3.17), 8.97 ($\alpha$, 3.42), 12.1 ($\gamma$, 3.30), and 11.7 (equatorial, 3.77), respectively . The finding that all $C_{70}$ peaks can be analyzed by using a single $T_1$ value indicates the equivalency of two $C_{70}$ molecules in $1_8Bu^t \cdot (C_{70})_2$. The very long $T_1$ observed for the polar carbon in $1_8Bu^t \cdot (C_{70})_2$ suggests that the rotational motion of $C_{70}$ around the minor axis is strongly suppressed by complexation. Thus, we consider that two $C_{70}$ molecules are incorporated into $1_8Bu^t$ from the major axis and rotate rapidly around the major axis.



Although it is not yet clear how $1_8Bu^t$ includes two $C_{70}$ molecules, it is clear that $1_8Bu^t$ shows a wide inclusion ability toward fullerene homologs and the selectivity is rather governed by the solubility of the complexes. Also, it has become clear that the $Bu^t$ group is most favorable among para-alkyl substituents but the complexation is not limited to the $Bu^t$ group. Further crystallographic and spectroscopic investigations are currently continued in this project.

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