ARTICLE

OBC
www.rsc.org/obc

Preferential precipitation of C_{70} over C_{60} with *p*-halohomooxacalix[3]arenes

Naoki Komatsu *
Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto 606-8502, Japan

Received 19th August 2002, Accepted 21st October 2002
First published as an Advance Article on the web 27th November 2002

Preferential precipitation of C_{70} from a toluene solution of C_{60} and C_{70} was accomplished with *p*-trihalohomooxacalix[3]arenes ($\mathbf{1}_3$·X·X·X) prepared by the reductive coupling of diformylphenols. Heavy halogens, Br and/or I, are essential at the *para* position of $\mathbf{1}_3$·X·X·X for obtaining good yields and selectivities. C_{70} with up to 92% purity was obtained after the preferential precipitation.

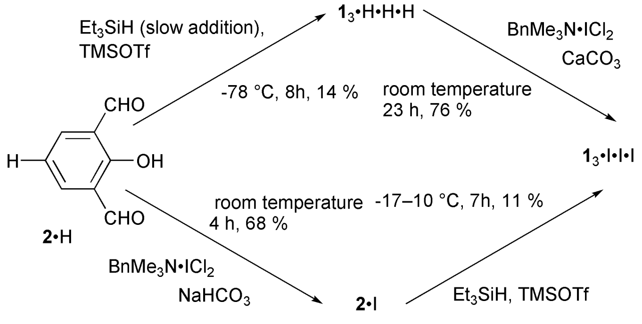
Introduction

Encapsulation of fullerenes is a subject of current interest in the fields of supramolecular and fullerene chemistry.[1–8] A practical goal in this area of chemistry is to develop an efficient method for the separation of specific size and/or isomers of fullerenes from mixtures.[9] Actually, selective complexation of fullerenes has so far been reported with calixarenes,[10–22] cyclodextrins,[15,23–25] cyclotriveratrylenes[26–28] and metalloporphyrins.[29] In 1992, selective extraction of C_{60} into a water layer was accomplished using γ-cyclodextrin[25] and water soluble calix[8]arene[22] by Wennerström and Verhoeven and their co-workers, respectively. Selective precipitation from an organic solution of a fullerene mixture, which is a more practical method by which to separate fullerenes, was reported in 1994 using *p-tert*-butylcalix[8]arene[19,20] and cyclotriveratrylene[28] by Shinkai and Atwood and their co-workers. More recently, a few bridged or cyclic dimers were found to encapsulate C_{70} preferentially to C_{60} in solution.[14,17,26,29] However, no host molecules preferentially precipitating C_{70} have been reported except for one example using *p-tert*-butylcalix[6]arene.[16,20] Herein is described a selective precipitation of C_{70} over C_{60} with *p*-halohomooxacalix[3]arenes.

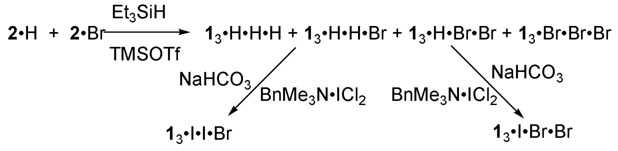
Results

Synthesis of homooxacalix[*n*]arenes ($\mathbf{1}_n$·R)

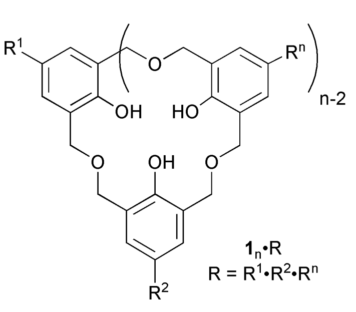
The homooxacalix[*n*]arenes ($\mathbf{1}_n$·R) were prepared according to the recent report based on the reductive coupling of 4-substituted-2,6-diformylphenols (**2**·R).[30] *p*-Triiodohomooxacalix[3]arene ($\mathbf{1}_3$·I·I·I) was prepared stepwise from 2,6-diformylphenol (**2**·H)[31] through a combination of iodination[32,33] and reductive coupling[30] (Scheme 1) because diformylation of *p*-iodophenol[34] gave **2**·I in very low yield. *p*-Trihalohomooxacalix[3]arenes with different halogens, $\mathbf{1}_3$·I·I·Br and $\mathbf{1}_3$·I·Br·Br, were prepared through the iodination[33] of the corresponding $\mathbf{1}_3$·H·H·Br and $\mathbf{1}_3$·H·Br·Br as shown in Scheme 2. Other *p*-halohomooxacalix[3]arenes with different substituents, $\mathbf{1}_3$·I·I·Bz (Bz = CH_2Ph), $\mathbf{1}_3$·I·Bz·Bz, $\mathbf{1}_3$·I·I·Oct′ (Oct′ = 1,1,3,3-tetramethylbutyl) and $\mathbf{1}_4$·I·I·I·Oct′, were prepared by reductive heterocoupling between 4-substituted-2,6-diformylphenol (**2**·R) and the tris(trimethylsilyl) ether of 4-substituted-2,6-bis(hydroxymethyl)-;phenol (**4**·R)[30] which was prepared *via* **3**·R as shown in Scheme 3. The 2,6-bis(hydroxymethyl)phenols with benzyl and *tert*-octyl substituents (**3**·Bz and **3**·Oct′) were prepared according to the reported method.[35] Since the direct hydroxymethylation of *p*-iodophenol was reported to fail, **3**·I was prepared in a similar indirect route starting from the commercial compound to that described in ref. 36. The trimethylsilylation of **3** was carried out with *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BTSTA) in acetonitrile to give **4** in high yields after rapid column chromatography with hexane and careful evaporation of the solvents.[37,38]



Scheme 1



Scheme 2



Precipitation of C_{70} with homooxacalix[*n*]arenes

Thus prepared homooxacalix[*n*]arenes with a variety of *para*-substituents were first examined for precipitation of C_{70} (Table 1). About 70% of C_{70} was precipitated by $\mathbf{1}_3$·I·I·I from a toluene solution of C_{70} (*ca.* 1 mg cm^{-3}) as a complex (runs 1 and 2). Under similar conditions, however, no precipitate was observed for C_{60} with $\mathbf{1}_3$·I·I·I (run 3). These contrasting results clearly show a potential of $\mathbf{1}_3$·I·I·I for separation of C_{70} from a mixture of C_{60} and C_{70}.

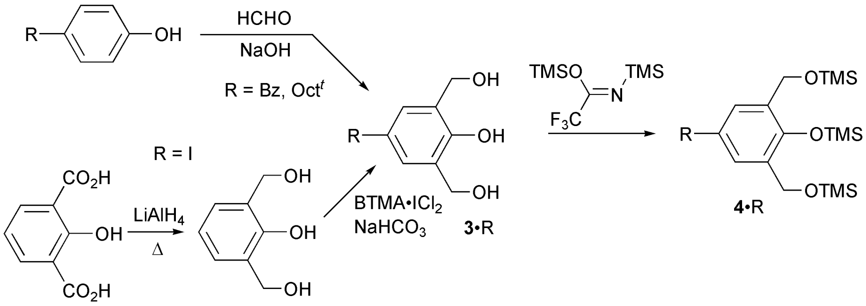
The number of alkyl groups and the nature of the halogens at the *para* position of *p*-halohomooxacalix[*n*]arenes (*n* = 3 or 4) remarkably affected the yield of C_{70} (runs 4–9). *p*-Iodohomooxacalix[*n*]arenes (*n* = 3 or 4) with one alkyl group afforded

DOI: 10.1039/b208107e

Table 1 Precipitation of C_{70} with *p*-halohomooxacalix[*n*]arenes with various substituents[a]

	Host (**1**$_n$·R)					Precipitate	
Run	*n*	R	Weight/mg (μmol)	C_{70}/mg (μmol)	Toluene/cm^3	Weight/mg	Yield (%) of C_{70}[b]
1	3	I·I·I	24.1 (31)	51.3 (61)	48	52.5	71
2	3	I·I·I	52.8 (67)	111.6 (130)	96	109.2	67
3	3	I·I·I	4.3 (5.5)	3.8 (5.3)[c]	4.5	0	0[c]
4	3	I·I·Bz[d]	12.7 (17)	30.2 (36)	21.5	9.6	22
5	3	I·I·Oct^t[e]	24.0 (31)	54.8 (65)	43	16.1	20
6	4	I·I·I·Oct^t[e]	15.8 (15)	31.5 (37)	21.5	9.2	20
7	3	I·Bz·Bz	5.1 (7.1)	4.7 (5.6)	3.5	trace	~0
8[f]	3	I·Bz·Bz[d]	5.6 (7.8)	4.7 (5.6)	5.5	trace	~0
9	3	Br·Br·Br	45.9 (71)	111.1 (130)	96	52.5	33

[a] Mixtures were stirred at room temperature overnight unless otherwise noted. [b] Calculated from recovery (%) of C_{70} from the filtrate. [c] C_{60}. [d] Bz = CH_2Ph. [e] Oct^t = 1,1,3,3-tetramethylbutyl. [f] At −30 °C.



Scheme 3

C_{70} precipitates in low yields (runs 4–6), while only a trace amount of precipitate was obtained using *p*-iodohomooxacalix[3]arene with two alkyl groups (runs 7–8). *p*-Tribromohomooxacalix[3]arene gave C_{70} complex in 33% yield (run 9), which is less than half of the yield with *p*-triiodohomooxacalix[3]arene (runs 1 and 2). A similar precipitation experiment with a more concentrated toluene solution of C_{70} (2.5 mg cm^{-3}) has been carried out with *p-tert*-butylcalix[6]arene which gives C_{70} complex in 31% yield.[20]

Preferential precipitation of C_{70} over C_{60} with homooxacalix[3]arenes

Selective precipitation of C_{70} from fullerene mixtures was carried out under more concentrated conditions than those in Table 1.[39] The results are summarized in Table 2. The selectivity and the yield of C_{70} strongly depend on the nature of the halogens at the *para* position of the host molecules. The order of efficiency in the purification of C_{70} followed the size of the halogens, I > Br > Cl > F (runs 2, 7, 13 and 14). As compared to **1**$_3$·I·I·I and **1**$_3$·Br·Br·Br, **1**$_3$·Cl·Cl·Cl gave low selectivity (run 12) or low yield of C_{70} (run 13), and **1**$_3$·F·F·F afforded low yield of C_{70} with the highest purity (run 14). When **1**$_3$·I·I·I or **1**$_3$·Br·Br·Br was added to the toluene solution of a fullerene mixture (C_{60} : C_{70} = 1 : 1, w/w), the ratios of C_{60} : C_{70} and the yields of C_{70} of the precipitates were 21 : 79–38 : 62 and 75–91%, respectively (runs 2, 7 and 9–11). The purity of C_{70} in the precipitates increased to 92% and 88% from 83% and 80%, respectively, after the selective precipitation (runs 1 and 8). The attempt to obtain pure C_{70} by this method was not successful; 92% purity is the upper limit of this purification. *p*-Iodohomooxacalix[3]arenes with one or two Br groups, **1**$_3$·I·I·Br and **1**$_3$·I·Br·Br (runs 3 and 6), afforded almost the same results as that of **1**$_3$·I·I·I (run 2), while the ones with one alkyl group, **1**$_3$·I·I·Bz and **1**$_3$·I·I·Oct^t (Oct^t = 1,1,3,3-tetramethylbutyl), gave much lower yields of C_{70} (runs 4 and 5). These results show that three heavy halogens are essential for obtaining both good yield and selectivity. The selectivity seems to be similar to the reported ones with *tert*-butylcalix[6]arene.[16,20] When other solvent systems were used instead of toluene, similar results were obtained (runs 10 and 11). The precipitate from a toluene solution of the fullerene mixture (C_{60} : C_{70} : $C_{>70}$ = 2 : 6 : 2) with **1**$_3$·I·I·I included a considerable amount of higher fullerenes ($C_{>70}$) along with C_{70}; that is, **1**$_3$·I·I·I cannot discriminate C_{70} and $C_{>70}$, which is another limitation of this method for the purification of fullerenes. When a toluene solution of **1**$_3$·I·I·I was added to a toluene solution of raw fullerene mixture (fullerene extract, C_{60} : C_{70} = 8 : 2), precipitation was not observed to give a dark brown homogeneous solution.

In order to recover the fullerene and reuse the host molecules, liberation of the complexes was carried out. Since the binding of the C_{70} complexes with **1**$_3$·I·I·I, **1**$_3$·I·I·Br and **1**$_3$·I·Br·Br was very tight, it was very difficult to liberate the fullerene by a simple way like that used for the *tert*-butylcalix[8]arene-C_{60} complex.[19,20] Eventually, C_{70}-**1**$_3$·I·I·I was dissolved in *o*-dichlorobenzene (ODCB), and the host molecules were extracted with basic aqueous solution.

Discussion

The host : guest ratio of the **1**$_3$·I·I·I–C_{70} and **1**$_3$·Br·Br·Br–C_{70} complexes is calculated to be about 2 : 5 and 1 : 3 from the results of the elemental analyses.† The ratio was reported to be 1 : 2 in *p-tert*-butylcalix[6]arene–C_{70},[20] *p-tert*-butylcalix[6]arene–C_{60} and calix[6]arene–C_{70} complexes,[16] 1 : 1 in **1**$_3$·Br·Br·Br–C_{60},[40] **1**$_3$·Bu^t·Bu^t·Bu^t–C_{60},[41] *p-tert*-butylcalix[5]arene–C_{60}[41] and *p*-methylcalix[5]arene–C_{60} complexes,[42] and 2 : 1 in **1**$_3$·Bz·Bz·Bz–C_{60} (Bz = CH_2Ph),[43] *p*-phenylcalix[5]arene–C_{60},[11] hexahomotrioxacalix[3]naphthalene–C_{60},[13] and *p*-diiodotrimethylcalix[5]arene–C_{60} complexes.[42,44] Such an unprecedented large capacity of *p*-trihalohomooxacalix[3]arenes for C_{70} may be attributed to its shallow cavity, intermolecular π–π interactions among the guest molecules,[45] the large van der Waals radii of the heavy halogens, and strong van der Waals interactions between the heavy halogens and the guests.[44,46] Unfortunately, a crystal structure of the complexes has not been determined yet.

---

† Anal. Calcd for $C_{398}H_{42}I_6O_{12}$ (2 : 5 complex): C 82.76, H 0.73, I 13.18; found: C 83.14, H 0.84, I 12.61%. Anal. Calcd for $C_{234}H_{21}Br_3O_6$ (3 : 1 complex): C 88.71, H 0.67, Br 7.57; found: C 88.66, H 0.65, Br 7.67%.

Table 2 Selective precipitation of C_{70} with *p*-halohomooxacalix[3]arenes with various substituents[a]

	Host ($\mathbf{1}_3$·R)		Fullerene mixture		Precipitate		
Run	R	Weight/mg (μmol)	C_{60}(mg)/C_{70}(mg) (ratio)	Toluene/cm^3	C_{60} : C_{70}[b]	Yield (%)[c]	Filtrate C_{60} : C_{70}[b]
1	I·I·I	6.9 (8.8)	2.6/13.0 (17 : 83)	7	8 : 92	93	63 : 37
2	I·I·I	12.8 (16)	20.3/20.4 (50 : 50)	11	24 : 76	88	86 : 14
3	I·I·Br	17.0 (23)	20.2/20.2 (50 : 50)	11	24 : 76	93	91 : 9
4[d]	I·I·Bz[e]	11.6 (15)	10.2/9.9 (51 : 49)	11	14 : 86	18	55 : 45
5[d]	I·I·Oct′[f]	41.3 (53)	20.9/21.7 (49 : 51)	17	11 : 89	20	55 : 45
6	I·Br·Br	15.3 (22)	19.6/20.1 (49 : 51)	11	24 : 76	90	87 : 13
7	Br·Br·Br	15.3 (24)	20.1/19.8 (50 : 50)	11	38 : 62	91	84 : 16
8	Br·Br·Br	11.5 (18)	4.0/16.2 (20 : 80)	7	12 : 88	84	45 : 55
9	Br·Br·Br	8.0 (12)	10.0/9.8 (50 : 50)	6	23 : 77	75	76 : 24
10	Br·Br·Br	7.4 (11)	9.8/10.0 (50 : 50)	10 + 5[g]	22 : 78	79	78 : 22
11	Br·Br·Br	7.3 (11)	10.2/9.8 (51 : 49)	5 + 5[h]	21 : 79	76	78 : 22
12	Cl·Cl·Cl	11.6 (23)	9.7/9.7 (50 : 50)	5	48 : 52	93	67 : 33
13	Cl·Cl·Cl	12.1 (24)	20.2/20.1 (50 : 50)	11	37 : 63	63	63 : 37
14	F·F·F	10.9 (24)	9.8/9.8 (50 : 50)	5	6 : 94	19	55 : 45

[a] Mixtures were stirred at room temperature overnight unless otherwise noted. [b] Weight ratio based on area ratio in HPLC. [c] Yield of C_{70} in the precipitates was calculated from the weights of C_{60} and C_{70}, and the C_{60} : C_{70} ratios of the precipitates and filtrates. [d] At −30 °C for 2 days. [e] Bz = CH_2Ph. [f] Oct′ = 1,1,3,3-tetramethylbutyl. [g] Toluene (10 cm^3) + hexane (5 cm^3). [h] 1,1,2,2-Tetrachloroethane (5 cm^3) + hexane (5 cm^3).

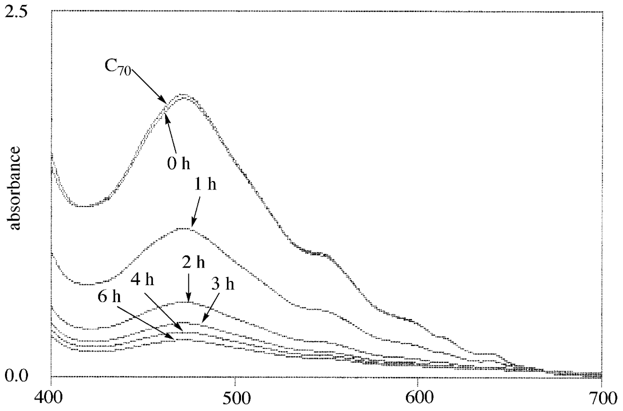
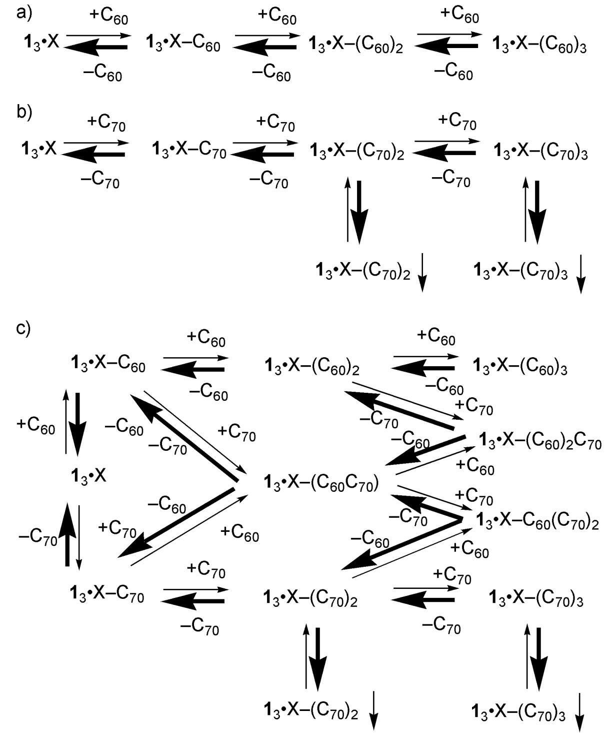


Fig. 1 Time-course of the absorption spectra of C_{70} (2.0×10^{-4} M)–*p*-triiodohomooxacalix[3]arene ($\mathbf{1}_3$·I·I·I, 8.4×10^{-3}M) in toluene at 20 °C.

The time-course of the change in absorption spectra of C_{70} was measured in the presence of $\mathbf{1}_3$·I·I·I in toluene at 20 °C as shown in Fig. 1. The brown color of C_{70} discharged gradually as the precipitation of C_{70}-$\mathbf{1}_3$·I·I·I proceeded with time. Although a monotonous decrease in the absorption spectra was observed, there was no significant change in the shape of the spectra, indicating that no stable complex existed in solution. On the other hand, no spectroscopic change occurred in the solution of C_{60} and $\mathbf{1}_3$·I·I·I, indicating that no complex or precipitate formed under the conditions.

The results mentioned above imply that most of the starting compounds, $\mathbf{1}_3$·I·I·I and the fullerenes, exist separately in solution, and that the complexes with two or three C_{70}, which should exist in a small amount in solution, form precipitates (Scheme 4b), while the C_{60} complexes do not precipitate at all (Scheme 4a). On the preferential precipitation of the fullerene mixture, at least one of the complexes, $\mathbf{1}_3$·I·I·I–$C_{60}C_{70}$, $\mathbf{1}_3$·I·I·I–$(C_{70})_2C_{60}$, and $\mathbf{1}_3$·I·I·I–$(C_{60})_2C_{70}$, is considered to precipitate along with the C_{70} complexes, because there is always some C_{60} in the precipitate (Scheme 4c).



Scheme 4

Experimental

^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were obtained on a JEOL JNM-FX400 in $CDCl_3$ with Me_4Si as internal standard. Chemical shifts are reported in *δ* and the coupling constants (*J*) are in Hz. MALDI-TOF-MS analyses were performed by a Shimadzu/Kratos KOMPACT MALDI II using an ethanol–water solution of 2,5-dihydroxybenzoic acid or α-cyano-4-hydroxycinnamic acid as a matrix. High resolution mass spectra were recorded on an Applied Biosystems, Marier (ESI-MS). Absorption spectra were measured in toluene on a Hitachi UV2001. HPLC analyses were performed at 35 °C on a Shimadzu LC-10 equipped with an Imtakt Cadenza CD-C18 column (100 × 4.6 mm) with hexane–propan-2-ol = 4 : 6 (v/v) as an eluent at 0.8 cm^3 min^{-1} using UV detection at 285 nm. Melting points were determined with a Yanaco MP-J3 apparatus and are uncorrected. Flash chromatography was performed with a Wakogel C-300. CH_2Cl_2 was freshly distilled from CaH_2 under argon.

Synthesis of 4-substituted-2,6-diformylphenols (2·R)

Compounds **2**·R were prepared according to the literature method[34] except for 4-iodo-2,6-diformylphenol.

2,6-Diformyl-4-fluorophenol (2·F). Yield 20 %; mp 108–109 °C (Found: C, 57.05; H, 2.97. Calc. for $C_8H_5FO_3$: C, 57.15; H, 3.00%); δ_H 7.69 (2H, d, *J* 7.2, Ar–H), 10.22 (2H, s, CHO), 11.39 (1H, s, OH); δ_C 123.3, 123.8, 153.1, 157.9, 159.8, 191.0.

4-Benzyl-2,6-diformylphenol (2·Bz). Yield 47%; mp 105–107 °C (Found: C, 75.04; H, 4.94. Calc. for $C_{15}H_{12}O_3$: C, 74.99; H, 5.03%); δ_H 4.00 (2H, s, CH_2), 7.16–7.34 (5H, m, Ph–H), 7.78 (2H, s, Ar–H), 10.19 (2H, s, CHO), 11.50 (1H, s, OH); δ_C 40.4, 123.0, 126.7, 128.7, 128.8, 133.1, 137.7, 139.5, 162.1, 192.1.

2,6-Diformyl-4-iodophenol (2·I). Since the diformylation of 4-iodophenol gave the desired product only in 3% yield, 2,6-diformylphenol (**2**·H)[31] was iodinated with benzyltrimethylammonium dichloroiodate (BTMA·ICl_2) in the presence of $NaHCO_3$.[33]

To a CH_2Cl_2–methanol (40 cm^3 : 16 cm^3) solution of **2**·H (0.60 g, 4.0 mmol) was added BTMA·ICl_2 (1.6 g, 4.6 mmol) and $NaHCO_3$ (2.3 g, 27 mmol), and the resulting yellow suspension was stirred at room temperature for 9 hours. After filtration through a Celite-SiO_2 bed, the filtrate was concentrated and submitted to flash column chromatography on silica gel to give **2**·I (0.77 g, 68%). Mp 145–148 °C (Found: C, 35.09; H, 1.73. Calc. for $C_8H_5IO_3$: C, 34.81; H, 1.83%); δ_H 8.22 (2H, s, Ar–H), 10.16 (2H, s, CHO), 11.55 (1H, s, OH); δ_C 80.8, 125.0, 154.6, 162.9, 190.8.

Synthesis of 4-substituted-2,6-bis(hydroxymethyl)phenols (3·R)

Compounds **3**·R were prepared according to the literature method[35] except for 4-iodo-2,6-bis(hydroxymethyl)phenol.

4-Benzyl-2,6-bis(hydroxymethyl)phenol (3·Bz). Mp 92–93 °C (ethyl acetate) (Found: C, 73.76; H, 6.57. Calc. for $C_{15}H_{16}O_3$: C, 73.74; H, 6.61%); δ_H 2.47 (2H, s, OH), 3.87 (2H, s, CH_2Ph), 4.75 (4H, d, *J* 2.4, CH_2O), 6.89 (2H, s, Ar–H), 7.14–7.29 (5H, m, CH_2Ph), 7.92 (1H, s, ArOH).

4-*tert*-Octyl-2,6-bis(hydroxymethyl)phenol (3·Oct^t). Mp 63–66 °C (ethyl acetate) (Found: C, 69.76; H, 9.74. Calc. for $C_{16}H_{30}O_4$($C_{16}H_{26}O_3$ + ½ethyl acetate): C, 69.64; H, 9.74%); δ_H 0.72 (9H, s, $C(CH_3)_3$), 1.32 (6H, s, $C(CH_3)_2$), 1.68 (2H, s, CH_2), 4.81 (4H, s, CH_2O), 7.05 (2H, s, Ar–H).

4-Iodo-2,6-bis(hydroxymethyl)phenol (3·I)[36]**.** A commercial 2-methoxyisophthalic acid was demethylated in aqueous HI solution at reflux temperature,[47] reduced to dimethanol with lithium aluminum hydride,[48] and iodinated with BTMA·ICl_2 in the presence of $NaHCO_3$.[36]

Typical procedure for the synthesis of 4-substituted-2,6-bis(trimethylsilyloxymethyl)phenol trimethylsilyl ethers (4·R)

To an acetonitrile solution (30 cm^3) of **3**·Oct^t was added BTSTA (4.5 cm^3, 17 mmol) dropwise over 5 minutes at room temperature under Ar. The resulting pale yellow solution was stirred for 22 hours, the mixture was concentrated on a rotary evaporator and rapidly passed through a short column using hexane as eluent. After careful concentration on a rotary evaporator, the desired compound, **4**·Oct^t, was obtained as a colourless oil containing a small amount of hexane in almost quantitative yield, and used immediately in the next coupling reaction.

4-*tert*-Octyl-2,6-bis(trimethylsilyloxymethyl)phenol trimethylsilyl ether (4·Oct^t). δ_H 0.14 (18H, s, TMS), 0.23 (9H, s, TMS), 0.69 (9H, s, $C(CH_3)_3$), 1.36 (6H, s, $C(CH_3)_2$), 1.71 (2H, s, CH_2), 4.65 (4H, s, CH_2O), 7.27 (2H, s, Ar–H).

4-Benzyl-2,6-bis(trimethylsilyloxymethyl)phenol trimethylsilyl ether (4·Bz). δ_H 0.11 (18H, s, TMS), 0.22 (9H, s, TMS), 3.94 (2H, s, CH_2Ph), 4.61 (4H, s, CH_2O), 7.09 (2H, s, Ar–H), 7.17–7.29 (5H, m, Ph).

4-Iodo-2,6-bis(trimethylsilyloxymethyl)phenol trimethylsilyl ether (4·I). δ_H 0.16 (18H, s, TMS), 0.24 (9H, s, TMS), 4.57 (4H, s, CH_2O), 7.60 (2H, s, Ar–H).

Synthesis of homooxacalix[*n*]arenes *via* reductive coupling

7,15,23-Triiodo-2,3,10,11,18,19-hexahomo-3,11,19-trioxacalix[3]arene-25,26,27-triol (*p*-triiodohomooxacalix[3]arene, 1$_3$·I·I·I). As shown in Scheme 1, two synthetic routes were followed from **2**·H. The reductive homocoupling of **2**·H and **2**·I afforded **1$_3$**·H·H·H and **1$_3$**·I·I·I in 14% and 11% yields, respectively, following the reported procedure.[30] The **1$_3$**·H·H·H obtained was iodinated according to the following procedure: a yellow solution of **1$_3$**·H·H·H (0.13 g, 0.32 mmol) and BTMA·ICl_2 in dichloromethane (30 cm^3)–methanol (12 cm^3) was stirred at room temperature for 0.5 hour. Then, $CaCO_3$ (0.20 g, 2.0 mmol) was added to the mixture. After being stirred for 19 hours, the suspension was filtered through Celite, and the filtrate was concentrated to about a half in volume and washed with 5% $NaHSO_3$ (30 cm^3) twice. The combined water layer was extracted with dichloromethane (30 cm^3) once, and the dichloromethane layers were combined, concentrated and chromatographed on silica gel to give **1$_3$**·I·I·I (0.19 g, 76%) as a white solid. Mp >300 °C (Found: C, 36.72; H, 2.64. Calc. for $C_{24}H_{21}I_3O_6$: C, 36.67; H 2.69%); δ_H 4.62 (12H, s, CH_2), 7.42 (6H, s, Ar–H), 8.67 (3H, s, OH); δ_C 70.3, 81.1, 126.4, 138.3, 155.6; MALDI-TOF-MS (pos): calcd. for $C_{24}H_{21}I_3NaO_6$ 809.12, found 809.06 (M + Na$^+$).

7,15,23-Trifluoro-2,3,10,11,18,19-hexahomo-3,11,19-trioxacalix[3]arene-25,26,27-triol (*p*-trifluorohomooxacalix[3]arene, 1$_3$·F·F·F). **1$_3$**·F·F·F was prepared according to the reported procedure.[30] Yield 29%; mp 218–220 °C (Found: C, 62.06; H, 4.63. Calc. for $C_{24}H_{21}F_3O_6$: C, 62.34; H, 4.58%); δ_H 4.66 (12H, s, CH_2), 6.86 (6H, d, Ar–H), 8.55 (3H, s, OH); δ_C 70.8, 115.9, 116.2 (d, *J* 23), 125.1 (d, *J* 7.1), 151.7 (d, *J* 2.3), 155.6 (d, *J* 240); MALDI-TOF-MS (pos): calcd. for $C_{24}H_{21}F_3NaO_6$ 485.41, found 485.40 (M + Na$^+$).

7,15-Diiodo-23-benzyl-2,3,10,11,18,19-hexahomo-3,11,19-trioxacalix[3]arene-25,26,27-triol (1$_3$·I·I·Bz). **1$_3$**·I·I·Bz was prepared according to the reported procedure[30] using 2,6-diformyl-4-iodophenol (0.19 g, 0.72 mmol), 2,6-bis(trimethylsilyloxymethyl)-4-benzylphenol trimethylsilyl ether (0.17 g, 0.31 mmol), trimethylsilyl trifluoromethanesulfonate (0.26 cm^3, 1.4 mmol), triethylsilane (0.24 cm^3, 1.5 mmol) and dichloromethane (20 cm^3). Yield 6%; δ_H 3.86 (2H, s, CH_2Ph), 4.61 (4H, s, CH_2), 4.62 (4H, s, CH_2), 4.65 (4H, s, CH_2), 6.94 (2H, s, Bz–Ar–H), 7.11–7.26 (5H, m, Bz), 7.41 (2H, s, I–Ar–H), 8.45 (1H, s, Bz–Ar–OH), 8.76 (2H, s, I–Ar–OH); δ_C 40.82, 70.23, 70.30, 71.27, 80.97, 123.84, 126.04, 126.42, 126.65, 128.41, 128.77, 130.40, 132.39, 138.18, 138.26, 141.09, 153.85, 155.69; MALDI-TOF-MS (pos): calcd. for $C_{31}H_{28}I_2NaO_6$ 772.81, found 773.14 (M + Na$^+$).

15,23-Dibenzyl-7-iodo-2,3,10,11,18,19-hexahomo-3,11,19-trioxacalix[3]arene-25,26,27-triol (1$_3$·I·Bz·Bz). **1$_3$**·I·Bz·Bz was prepared according to the reported procedure[30] using 4-benzyl-2,6-diformylphenol (0.10 g, 0.42 mmol), 2,6-bis(trimethylsilyloxymethyl)-4-iodophenol trimethylsilyl ether (0.11 g, 0.22 mmol), trimethylsilyl trifluoromethanesulfonate (0.14 cm^3, 0.80 mmol), triethylsilane (0.14 cm^3, 0.88 mmol) and dichloromethane (12 cm^3). Yield 26%; δ_H 3.84 (4H, s, CH_2Ph), 4.59 (2H, s, CH_2), 4.63 (2H, s, CH_2), 4.63 (2H, s, CH_2), 6.92 (4H, s, Bn–Ar–H), 7.07–7.26 (10H, m, Ph), 7.38 (2H, s, I–Ar–H), 8.54 (2H, s, Bn–Ar–OH), 8.85 (1H, s, I–Ar–OH); δ_C 40.82, 70.24, 71.23, 80.86, 123.90, 124.13, 126.01, 126.72, 128.39, 128.77, 130.30, 130.37, 132.26, 138.14, 141.16, 153.95, 155.80.

7,15-Diiodo-23-*tert*-octyl-2,3,10,11,18,19-hexahomo-3,11,19-trioxacalix[3]arene-25,26,27-triol (1$_3$·I·I·Oct^t). **1$_3$**·I·I·Oct^t was prepared according to the reported procedure[30] using 2,6-diformyl-4-iodophenol (0.20 g, 0.73 mmol), 2,6-bis(trimethylsilyloxymethyl)-4-*tert*-octylphenol trimethylsilyl ether (0.15 g, 0.31 mmol), trimethylsilyl trifluoromethanesulfonate (0.26 cm^3, 1.4 mmol), triethylsilane (0.24 cm^3, 1.5 mmol) and dichloromethane (20 cm^3). Yield 17%; δ_H 0.71 (9H, s, $\mathrm{C(CH_3)_3}$), 1.30 (6H, s, $\mathrm{C(CH_3)_2}$), 1.67 (2H, s, $\mathrm{–CH_2–Bu}^t$), 4.62 (4H, s, $\mathrm{CH_2}$), 4.63 (4H, s, $\mathrm{CH_2}$), 4.70 (4H, s, $\mathrm{CH_2}$), 7.09 (2H, s, Oct^t–Ar–H), 7.43 (4H, s, I–Ar–H), 8.40 (1H, s, Oct^t–Ar–OH), 8.79 (2H, s, I–Ar–OH); δ_C 31.54, 31.84, 32.32, 37.83, 56.80, 70.16, 70.31, 71.77, 80.95, 122.99, 126.44, 126.75, 127.56, 138.12, 138.26, 141.67, 152.99, 155.70; MALDI-TOF-MS (pos): calcd. for $\mathrm{C_{32}H_{38}I_2NaO_6}$ 795.49, found 795.48 (M + Na$^+$).

31-*tert*-Octyl-7,15,23-triiodo-2,3,10,11,18,19,26,27-octahomo-3,11,19,27-tetraoxacalix[4]arene-33,34,35,36-tetraol ($\mathbf{1_4}$·I·I·I·Oct^t). This compound was obtained in a small amount (3.8 mg) as a byproduct in the preparation of **1**$_3$·I·I·Oct^t; δ_H 0.71 (9H, s, $\mathrm{C(CH_3)_3}$), 1.29 (6H, s, $\mathrm{C(CH_3)_2}$), 1.67 (2H, s, $\mathrm{–CH_2–Bu}^t$), 4.63 (8H, s, $\mathrm{CH_2}$), 4.64 (4H, s, $\mathrm{CH_2}$), 4.69 (4H, s, $\mathrm{CH_2}$), 7.09 (2H, s, Oct^t–Ar–H), 7.41–7.44 (6H, m, I–Ar–H), 8.01 (1H, s, Oct^t–Ar–OH), 8.30 (1H, s, I–Ar–OH), 8.37 (2H, s, I–Ar–OH); δ_C 31.56, 31.85, 32.33, 37.80, 56.73, 70.27, 70.38, 70.38, 71.87, 80.90, 80.90, 123.02, 126.41, 126.46, 126.82, 127.72, 138.33, 138.43, 138.54, 141.60, 153.17, 155.76, 155.88; MALDI-TOF-MS (pos): calcd. for $\mathrm{C_{40}H_{45}I_3NaO_8}$ 1057.55, found 1057.79 (M + Na$^+$).

Synthesis of *p*-trihalohomooxacalix[3]arenes (1$_3$·I·I·Br and 1$_3$·I·Br·Br, Scheme 2)

p-Bromohomooxacalix[3]arenes (**1**$_3$·H·H·Br and **1**$_3$·H·Br·Br) were obtained in 3% yield after the purification of the mixture from the reductive coupling of 2,6-diformylphenol (**2**·H) and 4-bromo-2,6-diformylphenol (**2**·Br).[30] The **1**$_3$·I·I·Br and **1**$_3$·I·Br·Br were obtained by iodination of **1**$_3$·H·H·Br and **1**$_3$·H·Br·Br with BTMA·$\mathrm{ICl_2}$ (2.2 and 1.1 equiv.) in the presence of $\mathrm{NaHCO_3}$ (4.6 and 2.3 equiv.), respectively, in dichloromethane–methanol (5 : 2 v/v) followed by a similar work-up to that in the synthesis of **1**$_3$·I·I·I.

23-Bromo-7,15-diiodo-2,3,10,11,18,19-hexahomo-3,11,19-trioxacalix[3]arene-25,26,27-triol ($\mathbf{1_3}$·I·I·Br). δ_H 4.62 (2H, s, $\mathrm{CH_2}$), 4.63 (2H, s, $\mathrm{CH_2}$), 4.64 (2H, s, $\mathrm{CH_2}$), 7.25 (2H, s, Ar–H), 7.42 (4H, s, Ar–H), 8.65 (1H, s, OH), 8.67 (2H, s, OH); δ_C 70.33, 70.34, 70.51, 81.07, 111.26, 125.77, 126.27, 132.27, 138.18, 154.62, 155.45; HRMS (EI): calcd. for $\mathrm{C_{24}H_{20}BrI_2O_6}$ 736.8527, found 736.8541.

15,23-Dibromo-7-iodo-2,3,10,11,18,19-hexahomo-3,11,19-trioxacalix[3]arene-25,26,27-triol ($\mathbf{1_3}$·I·Br·Br). δ_H 4.63 (2H, s, $\mathrm{CH_2}$), 4.64 (2H, s, $\mathrm{CH_2}$), 4.64 (2H, s, $\mathrm{CH_2}$), 7.25 (4H, s, Ar–H), 7.43 (2H, s, Ar–H), 8.66 (2H, s, OH), 8.68 (1H, s, OH); δ_C 70.34, 70.53, 81.06, 111.27, 125.79, 126.29, 132.22, 132.28, 132.33, 138.14, 138.19, 138.25, 154.64, 155.46; HRMS (EI): calcd. for $\mathrm{C_{24}H_{20}Br_2IO_6}$ 688.8677, found 688.8683.

General procedure for the precipitation of the complex of fullerene with homooxacalix[*n*]arene (Tables 1 and 2)

To a toluene solution of fullerene was added a toluene solution of homooxacalix[*n*]arene, and the mixture was stirred at room temperature. After filtration of the formed precipitate, the filtrate was concentrated and washed with acetone thoroughly to give the recovered fullerene. The ratios of $\mathrm{C_{60}}$: $\mathrm{C_{70}}$ in both precipitate and filtrate were determined by HPLC.

Recovery of fullerene from the C$_{60}$/C$_{70}$–1$_3$·I·I·I complex

To an *o*-dichlorobenzene solution (12 cm^3) of the complex (12.4 mg) was added 1 M NaOH (10 cm^3), and the resulting heterogeneous solution was vigorously stirred at room temperature for an hour. After separation of the two layers, the organic layer was washed with 1 M NaOH (15 cm^3) twice. The combined water extracts were made acidic with conc. HCl and extracted with dichloromethane (20 cm^3) three times and toluene (30 cm^3) once. Concentration of the combined dichloromethane extracts gave pure **1**$_3$·I·I·I (3.7 mg). On the other hand, the *o*-dichlorobenzene layer was combined with toluene extract, dried over $\mathrm{MgSO_4}$ and concentrated *in vacuo* to give liberated fullerenes (9.0 mg).

Acknowledgements

The author is grateful to Professors Keiji Maruoka, Atsuhiro Osuka and Kazumi Matsushige (Kyoto University) for their encouragement, Dr Tomonari Wakabayashi (Kyoto University) for his helpful suggestions, Mr Itaru Yazawa (Imtakt Co.) for his kind offering of a HPLC column (Cadenza CD-C18), Mr Koji Sasaki for his assistance of measuring HRMS, and Messrs Takashi Onozawa and Susumu Kosugiyama (Tokyo Chemical Industry Co., Ltd.) for their assistance with experiments and their kind donation of some reagents. A part of this work was supported by a Grant-in-Aid for Research for Young Researchers from Kyoto University-Venture Business Laboratory (KU-VBL).

References

1 S. Shinkai and A. Ikeda, *Pure Appl. Chem.*, 1999, **71**, 275.
2 A. L. Balch and M. M. Olmstead, *Coord. Chem. Rev.*, 1999, **185–186**, 601.
3 S. Shinkai and A. Ikeda, *Gazz. Chim. Ital.*, 1997, **127**, 657.
4 T. Braun, *Fullerene Sci. Technol.*, 1997, **5**, 615.
5 A. Ikeda and S. Shinkai, *Chem. Rev.*, 1997, **97**, 1713.
6 C. L. Raston, in *Comprehensive Supramolecular Chemistry*, ed. G. W. Gokel, Pergamon, Oxford, 1996, vol. 1, pp. 777–787.
7 P. Lhotak and S. Shinkai, *J. Synth. Org. Chem., Jpn.*, 1995, **53**, 963.
8 E. C. Constable, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 2269.
9 J. Theobald, *Sep. Sci. Technol.*, 1995, **30**, 2783.
10 T. Haino, Y. Yamanaka, H. Araki and Y. Fukazawa, *Chem. Commun.*, 2002, 402.
11 M. Makha, M. J. Hardie and C. L. Raston, *Chem. Commun.*, 2002, 1446.
12 T. Haino, H. Araki, Y. Yamanaka and Y. Fukazawa, *Tetrahedron Lett.*, 2001, **42**, 3203.
13 S. Mizyed, M. Ashram, D. O. Miller and P. E. Georghiou, *J. Chem. Soc., Perkin Trans. 2*, 2001, 1916.
14 J. Wang, S. G. Bodige, W. H. Watson and C. D. Gutsche, *J. Org. Chem.*, 2000, **65**, 8260.
15 K. Komatsu, K. Fujiwara, Y. Murata and T. Braun, *J. Chem. Soc., Perkin Trans. 1*, 1999, 2963.
16 J. L. Atwood, L. J. Barbour, C. L. Raston and I. B. N. Sudria, *Angew. Chem., Int. Ed.*, 1998, **37**, 981.
17 T. Haino, M. Yanase and Y. Fukazawa, *Angew. Chem., Int. Ed.*, 1998, **37**, 997.
18 T. Suzuki, K. Nakashima and S. Shinkai, *Tetrahedron Lett.*, 1995, **36**, 249.
19 T. Suzuki, K. Nakashima and S. Shinkai, *Chem. Lett.*, 1994, 699.
20 J. L. Atwood, G. A. Koutsantonis and C. L. Raston, *Nature*, 1994, **368**, 229.
21 R. M. Williams, J. M. Zwier and J. W. Verhoeven, *J. Am. Chem. Soc.*, 1994, **116**, 6965.
22 R. M. Williams and J. W. Verhoeven, *Recl. Trav. Chim. Pays-Bas*, 1992, **111**, 531.
23 T. Andersson, M. Sundahl, G. Westman and O. Wennerström, *Tetrahedron Lett.*, 1994, **35**, 7103.
24 T. Andersson, G. Westman, O. Wennerström and M. Sundahl, *J. Chem. Soc., Perkin Trans. 2*, 1994, 1097.
25 T. Andersson, K. Nilsson, M. Sundahl, G. Westman and O. Wennerström, *J. Chem. Soc., Chem. Commun.*, 1992, 604.
26 H. Matsubara, S. Oguri, K. Asano and K. Yamamoto, *Chem. Lett.*, 1999, 431.
27 H. Matsubara, A. Hasegawa, K. Shiwaku, K. Asano, M. Uno, S. Takahashi and K. Yamamoto, *Chem. Lett.*, 1998, 923.
28 J. W. Steed, P. C. Junk, J. L. Atwood, M. J. Barnes, C. L. Raston and R. S. Burkhalter, *J. Am. Chem. Soc.*, 1994, **116**, 10346.

29 J.-Y. Zheng, K. Tashiro, Y. Hirabayashi, K. Kinbara, K. Saigo, T. Aida, S. Sakamoto and K. Yamaguchi, *Angew. Chem., Int. Ed.*, 2001, **40**, 1858.

30 N. Komatsu, *Tetrahedron Lett.*, 2001, **42**, 1733.

31 C. Zondervan, E. K. van den Beuken, H. Kooijman, A. L. Spek and B. L. Feringa, *Tetrahedron Lett.*, 1997, **38**, 3111.

32 B. Krenke and W. Friedrichsen, *J. Chem. Soc., Perkin Trans. 1*, 1998, 3377.

33 S. Kajigaeshi, T. Kakinami, H. Yamasaki, S. Fujisaki, M. Kondo and T. Okamoto, *Chem. Lett.*, 1987, 2109.

34 L. F. Lindoy, G. V. Meehan and N. Svenstrup, *Synthesis*, 1998, 1029.

35 P. D. Hampton, Z. Bencze, W. Tong and C. E. Daitch, *J. Org. Chem.*, 1994, **59**, 4838.

36 G. T. Crisp and P. D. Turner, *Tetrahedron*, 2000, **56**, 407.

37 P. Chirakul, P. D. Hampton and E. N. Duesler, *Tetrahedron Lett.*, 1998, **39**, 5473.

38 P. D. Hampton, C. E. Daitch and E. N. Duesler, *New. J. Chem.*, 1996, **20**, 427.

39 A. N. Ponomarev, B. M. Aksel'rod, V. T. Barchenko, V. P. Belousov, Z. S. Egorova, I. V. Igonchenkov, A. Y. Isakov, O. Y. Kut'eva, V. A. Nikitin, D. V. Nikitin, S. V. Ruzaev, A. V. Rumyantsev, O. S. Tulyakov, N. A. Charykov, M. E. Yudovich and A. L. Yurin, *Russ. J. Phys. Chem.*, 2000, **74**, 1942.

40 K. Tsubaki, K. Tanaka, T. Kinoshita and K. Fuji, *Chem. Commun.*, 1998, 895.

41 A. Ikeda, Y. Suzuki, M. Yoshimura and S. Shinkai, *Tetrahedron*, 1998, **54**, 2497.

42 T. Haino, M. Yanase and Y. Fukazawa, *Tetrahedron Lett.*, 1997, **38**, 3739.

43 J. L. Atwood, L. J. Barbour, P. J. Nichols, C. L. Raston and C. A. Sandoval, *Chem. Eur. J.*, 1999, **5**, 990.

44 T. Haino, M. Yanase and Y. Fukazawa, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 259.

45 L. A. Bulavin, I. I. Adamenko, V. M. Yashchuk, T. Y. Ogul'chansky, Y. I. Prylutskyy, S. S. Durov and P. Scharff, *J. Mol. Liq.*, 2001, **93**, 187.

46 S. Talukdar, P. Pradhan and A. Banerji, *Fullerene Sci. Technol.*, 1997, **5**, 547.

47 G. R. Sprengling and J. H. Freeman, *J. Am. Chem. Soc.*, 1950, **72**, 1982.

48 J. H. Freeman, *J. Am. Chem. Soc.*, 1952, **74**, 6257.