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Synthesis of a New Cavitand. 2 C_{60} Complex

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A new cavitand 2 and its complexation with fullerene to afford complex 3 was prepared and characterized by spectroscopic methods. Macrocycle 2 was studied in solution by NMR, and in the solid state by ^{13}C CP-MAS, NMR and X-ray diffraction. The macrocycle 2 can host 2 fullerene C_{60} molecules in its structure. For the complex 3, $\pi-\pi$, CH$-\pi$ and $n-\pi$ interactions were observed by ^{13}C CP-MAS and FTIR spectroscopy. MM and MD calculations were carried out.

Keywords: Cavitands, fullerene, supra molecular complex crystal structure, MM and MD calculations

INTRODUCTION

Recently, the construction of supramolecular complexes with fullerene and calix[*n*]arenes ($n = 3-8$) has had a great development [1-13]. Because of their ability to form complexes, calixarenes have been employed for the separation of mixtures of C_{60} and C_{70}. This type of complexation has been extended to other macromolecules such as azacrown [14], cyclotriveratrylenes [15,16], porphyrazines [17] and resorcinarenes [18,19]. In our search for building blocks for the synthesis of cavitands, we become interested in macrocycles of structure I, which can be easily obtained in high yields by acid-catalized condensation of resorcinol with aldehydes [20]. The synthesis of cavitands from resorcinarenes provides organic compounds that contain an enforced concave cavity sufficiently large to accommodate other molecules or ions [21]. These cavitands are extremely rigid, and in general they adopt a crown-like conformation, with C_{4v} symmetry in solid state, and only a slight deviation from this structure in solution [22]. In the present work we report our findings on the interactions of fullerenes with cavitand **2**, forming a new solid-state complex. This corresponds to C_{60} and **2**, in a 1:2 (**3**) ratio.

RESULTS AND DISCUSSION

The starting material for the synthesis of the host **2** was the readily available resorcinarene **1** which was converted into cavitand **2** by treatment with $ClBrCH_2$.

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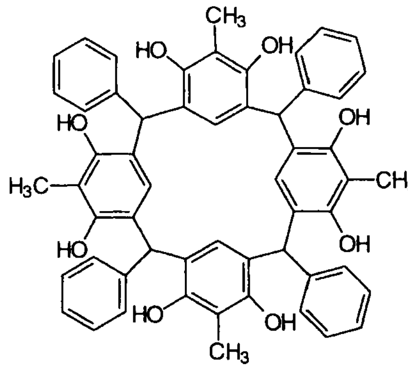
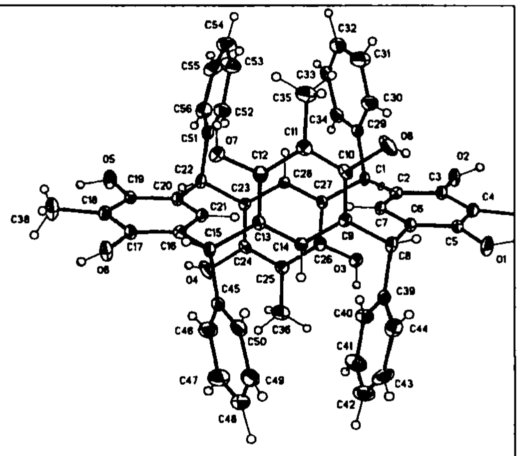
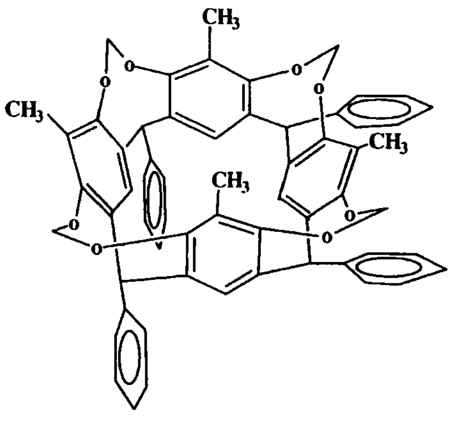


1



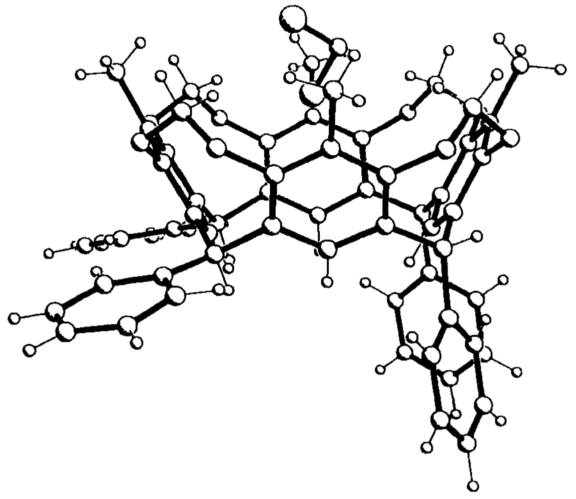
X-ray structure of 1

The ^1H NMR analysis of metacyclophane **2** in $CDCl_3$ at room temperature indicated the presence of conformer **2**. The signals from δ7.60 to δ7.16 (20H) which were attributed to the benzene protons oriented axially and equatorially. The aromatic hydrogens of the methyl resorcinol moiety resonates at δ7.02 and δ6.52 for the aromatic hydrogens axially and equatorially to the ansa cycle respectively. For O—CH_2—O were observed four doublets at δ: 6.01 (*d*, 2H outer of CH_2, $J = 6.80\,Hz$), 5.65 (*d*, 2H outer of CH_2, $J = 7\,Hz$), 4.47 (*d*, 2H inner of CH_2, $J = 7\,Hz$) and 4.37 (*d*, 2H inner of CH_2, $J = 7\,Hz$). A singlet at δ5.05 was assigned to the benzylic hydrogens.



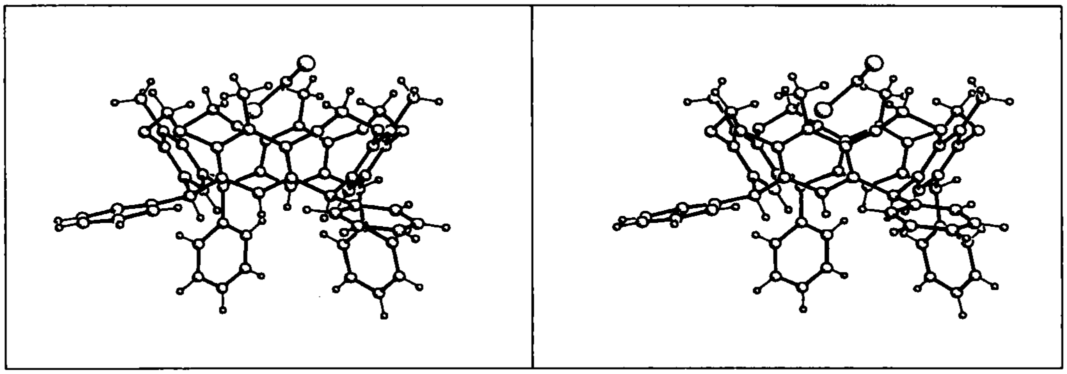
Cavitand 2

For the methyl groups three signals were observed at δ2.13, δ2.03 and δ1.93. The cavitand **2** was crystallized by slow evaporation of CH_2Cl_2, and the X-ray crystallographic determination was performed at room temperature. As a result we observe two phenyl substituents oriented axially, two equatorially, and with one guest molecule of dichloromethane in the bowl.



X-ray structure of cavitand 2

To prepare the supramolecular complex with fullerene, a CH_2Cl_2 solution of **2** (124 mg, 0.138 mmol) was added to a benzene solution



Side view of the cavitand **2**

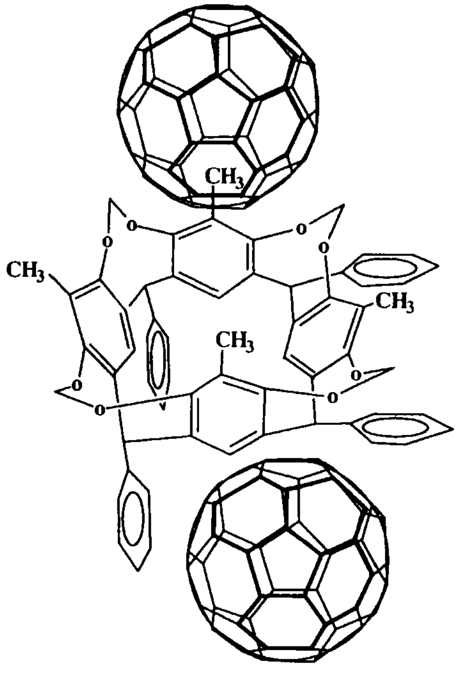
of C_{60} (100 mg, 0.138 mmol), and stirred vigorously at 80°C for 3.5 days. After this period, a brown precipitate was formed.

The solid was filtered and washed with benzene affording 120 mg (60 %) of compound **3**. Elemental analysis results were consistent with a 1 : 2 stoichiometry. Anal. Calcd. for $C_{60}H_{48}O_8 \cdot C_{60} \cdot 2CH_2Cl_2$: C, 87.15; H, 2.07. Found: C, 87.36; H, 1.54. Several attempts to obtain the 1 : 1 ratio complex between the macrocycle and the fullerene, under various conditions proved to be futile.

IR spectroscopy (KBr) of complex **3** indicates that the C—O—C bonding normally present at 1150 and 1243 cm^{-1} in the cavitand was partially disrupted and shifted to 1058 and 1181 cm^{-1}.

The UV-vis spectra in methanol show three signals at 208, 256 and 327 nm and the cavitand shows only one signal at 206 nm. The signal at 256 nm possibly arises from interactions between the π electron cloud of the fullerene and the π electron cloud of the macrocycle.

The ^{13}C CP-MAS NMR spectrum of **2** (Fig. 1A) shows a signal at δ_c10.48 ppm assigned to the methyl groups, two signals at δ_c40.00 and δ_c 42.51 are attributed to the methine carbons, the signal at 55.79 and 98.38 ppm were assigned to the O—CH_2—O moiety. For the aromatic carbons, oriented axially and equatorially, a broad strong signal at 128.169 ppm was observed: A signal at 136 ppm was assigned to the ipso C—CH_3 group, and two additional signals for the Ar—O at 140.20 and 153.89 ppm.



Complex **3**

Comparative analysis of the solid state ^{13}C CP-MAS NMR spectra of **2**, with that of the 2 : C_{60} complex **3** (Fig. 1B) implies a major conformational change for **2**. One signal is found at 10.07 ppm for the methyl groups, and that for the methyne carbons is diminished and shifted at 32.89 to 40.62 ppm. For the O—CH_2—O the only signal is also diminished and appears at

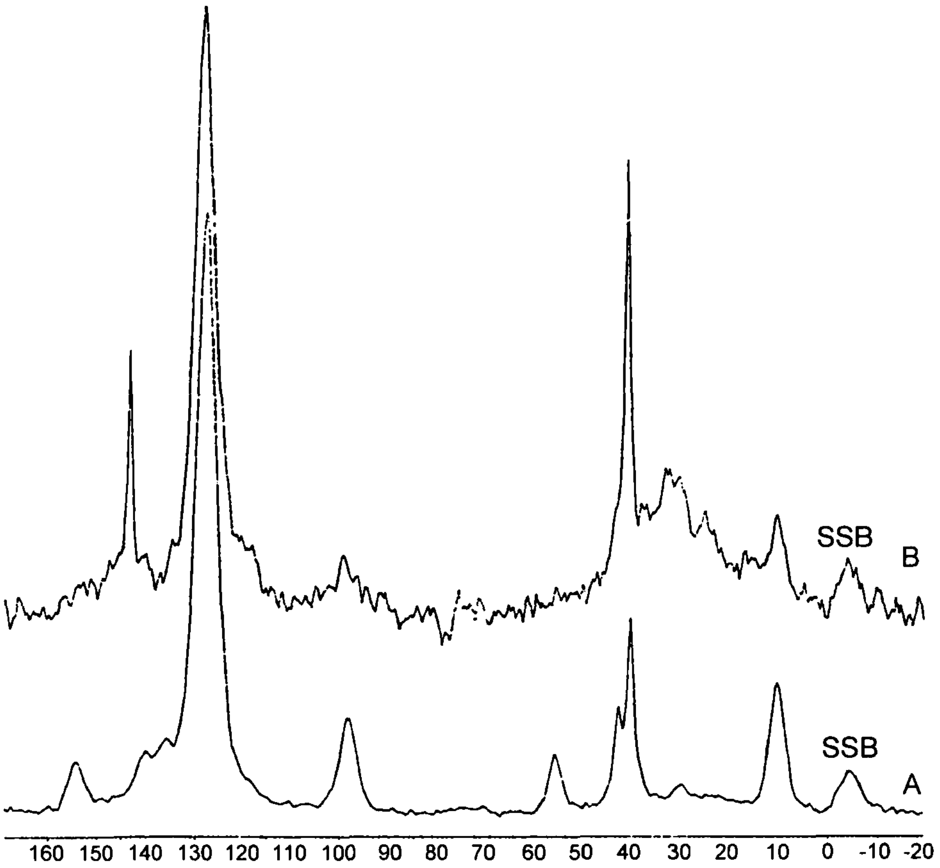


FIGURE 1 (A) ^{13}C CP-MAS NMR of 2. (B) ^{13}C CP-MAS NMR of 1 : 2C_{60}. All the spectra were taken at room temperature.

TABLE I Crystal data and structure refinement for cavitand

Identification code	nara
Empirical formula	$C_{61}H_{50}Cl_2O_8$
Formula weight	981.91
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 17.301(3)$ Å $\alpha = 90°$ $b = 15.072(3)$ Å $\beta = 107.18(1)°$ $c = 21.346(2)$ Å $\gamma = 90°$
Volume	5318(2) $Å^3$
Z	4
Density (calculated)	1.226 Mg/m^3
Absorption coefficient	1.537 mm^{-1}
F (000)	2056
Crystal size	0.48 × 0.28 × 0.28 mm orange-prism
θ range for data collection	2.90 to 56.75°
Index ranges	$0 \leq h \leq 18$, $0 \leq k \leq 16$, $-23 \leq \ell \leq 22$
Reflections collected	7378
Independent reflections	7101 ($R_{int} = 0.0795$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7101/0/670
Goodness-of-fit on F^2	1.022
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.11$, $wR2 = 0.29$
R indices (all data)	$R1 = 0.19$, $wR2 = 0.38$
Extinction coefficient	0.0014(3)
Largest diff. peak and hole	0.65 and -0.27 $eÅ^{-3}$

99.12 ppm. For the aromatic carbons, the signal appears at 128.35 ppm, and for the Ar—O signals and fullerene the signal appears at 143.52 ppm.

All the data of the spectroscopic analysis indicate a supramolecular complex, and all the assayed cases establish a stoichiometry of 1:2 between the macrocycle and the fullerene. In order to understand why this unique stoichiometry is favored, calculations were done by using the semi-empirical molecular orbital methods AM1 and HF/6-31. As a result it was found [23] that the fullerene might be bounded to the macro cycle either from above or from below, with similar interaction energies. Moreover, it was found that the macrocycle has high rigidity. This lack of deformation facilitates the bonding of a second fullerene without any interference of the first one. This is not the case for more flexible macro cycles [2], where the bonding of the first molecule from above or from below deforms others parts of the molecule, making difficult the bonding of a second molecule.

Conclusions

Rigid host **2** and somewhat flexible host **1** greatly resemble each other in their bowl structures, but host **2** is less symmetrical. The organization of the bowl in **2** appear to be associated with the hydrogen bonds between the oxygen atoms of the resorcinol and the dichloromethane. The new cavitand **2** can host two molecules of fullerene C_{60} **3**. We also observed from spectroscopic data interactions CH – π, π – π and n – π when the guest is C_{60}.

EXPERIMENTAL SECTION

General Remarks

Infrared (IR) spectra were recorded on a Nicolet FT-IR Magna 700 Spectrometer. ^{1}H- and ^{13}C-NMR spectra were collected on a Varian Unity 500 operating at 500 and 125 MHz, respectively. For both ^{1}H and ^{13}C, chemical shifts are expressed in ppm relative to tetramethylsilane (Me_4Si 0.00 ppm) used as an internal standard. The ^{13}C CP-MAS NMR spectra were collected on a Bruker spectrometer at 125 MHz for carbon-13. Elemental analyses were performed at Galbraith Laboratories, INC. Knoxville. FAB$^+$ mass spectra were taken with a JEOL JMS AX505 HA mass spectrometer. X-ray crystallographic data were collected at – 50°C on a Siemens P/4 diffractometer for **1** and room temperature for cavitand **2**.

Metacyclophane (1)

Metacyclophane **1** was synthesized according to a procedure previously reported [17].

It was obtained by treatment of 2.0 g (16.1 mmol) of 2-methylresorcinol and 1.8 ml (16.1 mmol) of benzaldehyde. A solid product 2.68 g (72%), was obtained. This solid was washed successively with methanol and dichloromethane. The residue, a white solid was crystallized from DMSO to afford 1.97 g (53%) of stereoisomer mp > 350°C. IR (KBr): 3532, 3027, 2923, 1607, 1476, 1449, 1320, 1237, 1192, 1093, 1028, 916, 754, 703, 575 cm^{-1} .^{1}H NMR (DMSO-*d*) δ6.86(*m*, 12H), 6.65(*m*, 8H), 6.19(*s*, 2H), 5.36(*s*, 2H), 5.62(*s*, 2H), 2.10(*s*, 6H), 1.92(*s*, 6H). ^{13}C NMR (DMSO-*d*) δ9.18($\underline{C}H_3$), 9.64($\underline{C}H_3$), 43.56 ($\underline{C}$H—Ph), 110.53($\underline{C}$—CH_3), 111.06($\underline{C}$—CH_3), 121.88($\underline{C}$—CH—Ph), 122.59($\underline{C}$—CH—Ph), 124.54(Ph), 125.78(Ar—H), 126.92(Ph—H), 129.02(Ph—H), 127.86(Ar—H), 143.08(PhC-ipso), 150.32(Ar—OH), 150.56(Ar—OH). Anal. Calcd for $C_{56}H_{51}O_8$: C, 79.15; H, 5.65; O, 15.07. found; C, 79.12; H, 5.62; O, 15.09.

Cavitand (2)

Cavitand **2** was synthesized according to a procedure previously reported [22].

It was obtained by treatment of 2 g (2.35 mmol) of **1** in DMSO (50 ml) and 0.61 ml (9.43 mmol) of $ClBrCH_2$ after 10 min was added

1.6 g of K_2CO_3 in 50 ml of DMSO. The reaction mixture was stirred for 40 h and then resulting suspension was vacuum filtered through filter paper. This solid was washed successively with a 1L of 1N aqueous NaCl solution, water and finally with methanol. The residue, a orange solid was crystallized from CH_2Cl_2 to afford 1.70 g (80%) of stereoisomer mp > 300°C, IR (KBr): 3548, 3399, 1600, 1407, 1427, 1243, 1150, 1098, 975, 731, 705 cm^{-1}. ^1H NMR ($CDCl_3$)δ7.60 – 7.16 (br, 20H), 7.02(*s*, 2H), 6.93(*s*, 2H), 6.52(*s*, 2H), 6.01(*d*, 2H, $J = 6.8$ Hz), 5.65(*d*, 2H, $J = 7.0$ Hz), 5.05(*s*, 2H), 4.47(*d*, 2H, $J = 7.0$ Hz), 4.37(*d*, 2H, $J = 7.0$ Hz), 2.13(*s*, 3H), 2.03(*s*, 6H), 1.93(*s*, 3H), ^{13}C NMR ($CDCl_3$) δ10.48 ($\underline{C}H_3$), 40.9($\underline{C}H$—Ar), 42.30($\underline{C}H$—Ar), 56.49(O—CH_2—O), 125.8 – 129.07 (Ar), 135.83(PhC-ipso), 140.33(Ar—O), 145.85(Ar—O). ^{13}C CP-MAS NMR Chemical shifts 10,48($\underline{C}H_3$), 40.00(CH—Ph), 42.51 (CH—Ph), 55.79(CH_2), 98.38(CH_2), 128.16(Ph), 136.71($\underline{C}$ ipso), 140.20(C—O), 153.89($\underline{C}$—OH). Anal. Calcd. for $C_{60}H_{48}O_8 \cdot CH_2Cl_2$ C, 74.69; H, 5.10. Found: C, 74.65; H, 5.00.

Complex: Cavitand 1: 2C60 (3)

A DMSO solution of **1** (117 mg, 0.138 mmol) was added to a benzene solution of C_{60} (100 mg, 0.138 mmol), and the mixture stirred vigorously at 80°C for 3.5 days. After this period, a brown precipitated was formed. The solid was filtered from the colorless solution and washed with benzene affording 153 mg of complex **3**. Elemental analysis results were consistent with a 1 : 2 stoichiometry. IR (KBr): 3415, 2911, 475, 1427, 1181, 1058, 1023, 953, 772, 576, 526 cm^{-1}. ^{13}C CP-MAS NMR Chemical shifts 10,07($\underline{C}H_3$), 32.89(CH—Ph), 40.62($\underline{C}H$—Ph), 99.12(CH_2), 128.35(Ph), 143.52. Anal. Calcd. for $C_{60}H_{48}O_8 \cdot 2C_{60} \cdot 2CH_2Cl_2$. C, 87.15; H, 2.07. Found: C, 87.61; H, 1.37.

Acknowledgements

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Notes

Crystal data for **1**: $C_{35.25}H_{45.75}S_{3.25}O_{7.50}$. $M = 693.66$ Monoclinic, space group C2/c. $a = 29.781(6)$, $b = 10.836(2)$, $c = 24.261(4)$ Å, $U = 7071(2)$ Å^3. Dc ($Z = 8$) = 1.303 mg cm^{-3}. F(000) = 2954, μ(Cu–Kα) = 1.537 mm^{-1}. 8287 reflections, 8133 (R_{int} = 5.3%) independent reflections ($2\theta_{\text{max}} = 113.5°$). $R = 0.080$ ($I > 2\sigma(I)$), $wR = 0.016$ (on F^2).

Crystal data for **2**: $C_{61}H_{50}Cl_2O_8$. $M = 981.91$. Monoclinic, space group $P2_1/n$. $a = 17.301(3)$, $b = 15.072(30)$, $c = 21.346(2)$ Å, $P = 107.18(1)°$, $U = 5318(2)$ Å^3. Dc ($Z = 4$) = 1.226 mg cm^{-3}. F(000) = 2056, μ(Cu – Kα) = 1.537 mm^{-1}. 7378 reflections, 7101 (R_{int} = 7.9%) independent reflections ($2\theta_{\text{max}} = 113.5°$). $R = 0.11$ ($I > 2\sigma(I)$), $wR = 0.029$ (on F^2).