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Conformational Control of Benzyl-*o*-carboranylbenzene Derivatives and Molecular Encapsulation of Acetone in the Dynamically Formed Space of 1,3,5-Tris(2-benzyl-*o*-carboran-1-yl)benzene

Chalermkiat Songkram,[†] Kiminori Ohta,[‡] Kentaro Yamaguchi,[§] Fabio Pichierri,[¶] and Yasuyuki Endo*[,‡]

[†]*Faculty of Pharmaceutical Sciences, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand,* [‡]*Faculty of Pharmaceutical Sciences, Tohoku Pharmaceutical University, 4-4-1 Komatsushima, Aoba-ku, Sendai 981-8558, Japan,* [§]*Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, 1314-1 Shido, Sanuki, Kagawa 769-2193, Japan, and* [¶]*G-COE Laboratory, Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aoba-yama 6-6-07, Sendai 980-8579, Japan*

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A 1,3,5-substituted benzene platform has been widely used in the fields of supramolecular chemistry and molecular recognition. Here, we show that 1,3,5-tris(2-benzyl-*o*-carboran-1-yl)benzene **6** exhibits solvent-dependent conformation in the crystalline state. Recrystallization from dichloromethane-*n*-pentane gave the anti conformation **6-*anti***, while recrystallization from methanol-acetone gave the syn conformation **6-*syn***, in which the three benzyl-*o*-carboranyl moieties are located to one side of the central benzene ring. Interestingly, one acetone molecule is captured in the π-rich space of **6-*syn*** and two complexes facing each other encapsulate two acetone molecules in a π-rich container formed by the eight benzene rings. The inclusion involves several weak interactions, that is, T-shaped C−H···π interactions, and C−H···O and C−H···π interactions. Two C−H···O interactions involving benzylic C−H hydrogens activated by the electron-withdrawing character of the *o*-carborane cage and the oxygen atom of the acetone seem to be the most important. DFT calculations indicate that the binding energy for entrapment of acetone is 6.6 kcal/mol. Inclusion of acetone is achieved through not only multiple C−H···O interactions but also a number of C−H···π interactions. The third benzyl-*o*-carborane moiety is fixed in the syn conformation by intramolecular and intermolecular C−H···π interactions.

Introduction

Supramolecular chemistry utilizing noncovalent interactions, such as ionic bonds, hydrogen bonds, van der Waals interactions, and $\pi-\pi$ stacking interactions, is becoming increasingly important in many research areas, particularly those involving molecular recognition.[1] Among noncovalent bonds, hydrogen bonds can be classified into four major groups, that is, very strong, strong, weak, and very weak hydrogen bonds, according to the bond energy and the kind of hydrogen bond acceptor and donor.[2] Molecular recognition and conformational control of small molecules with weak hydrogen bonds, such as OH···π, NH···π, CH···n (lone pair), and CH···π, are interesting and challenging topics. For example, entropically favored macrocyclic compounds such as cyclodextrins[3] and calix[*n*]arenes[4] can easily capture small molecules, because of the low flexibility of their pockets. In most cases, electrostatic interactions such as classical hydrogen bonds and ionic interactions trigger the molecular recognition and the complexations are enthalpy-dominated. Although one strong interaction is generally important for molecular recognition, the synergistic action of several weak interactions can also effectively stabilize complexes, owing to enthalpy factors.

1,3,5-Trisubstituted benzene has some molecular flexibility and is often utilized in the development of artificial receptors for small molecules, including peptides,[5] sugars,[6] cations,[7]

*To whom correspondence should be addressed: E-mail: yendo@tohoku-pharm.ac.jp Phone: +81-22-727-0142. Fax: +81-22-275-2013.

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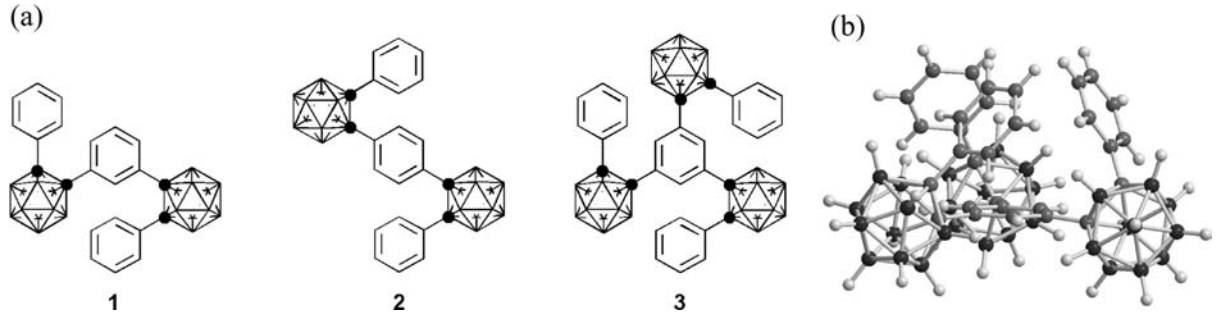

Figure 1. (a) Structures of phenyl-*o*-carboranylbenzene derivatives **1**, **2**, and **3**. (b) X-ray crystal structure of compound **3**, which adopts a syn conformation.

and anions.[8] In many cases, when three identical substituents are introduced onto the 1,3,5-benzene scaffold, there are only two conformational isomers, anti and syn.[9] The anti conformation is thermodynamically stable, but the syn conformation is often stabilized by the existence of intramolecular interactions among the arms of the 1,3,5-substituents and by intermolecular interactions between molecular recognition sites and small guests.[10] The 1,2-, 1,3-, and 1,4-substituted benzene structures also possess both anti and syn conformational isomers.[11] Although the conformations of 1,3- and 1,4-substituted benzene derivatives are controlled by various intramolecular and intermolecular interactions, the conformation of 1,2-substituted benzene compounds is highly dependent on straightforward steric repulsion, rather than weak interactions.[12] We are interested in the conformational control of 1,3-, 1,4-, and 1,3,5-substituted benzene scaffolds and molecular recognition based on weak interactions.

We have previously investigated molecular constructions with carborane cages.[13] Carborane, a boron cluster with an icosahedral structure and very high hydrophobicity similar to that of hydrocarbons, has been applied in boron neutron capture therapy (BNCT) for the treatment of cancer.[14] Carborane cages are also used as hydrophobic core structures of bioactive molecules[15] and are expected to be useful as components or building blocks in supramolecular architectures.[16] Carboranes have several desirable features in this regard. Their rigid three-dimensional structures hold substituents in well-defined spatial relationships. The two carbon vertices of carboranes bear relatively acidic protons and readily allow substitution with metal and organic groups, while the boron vertices can also support various substituents.[17] We have reported the syntheses and X-ray crystal structures of (2-phenyl-*o*-carboran-1-yl)benzene derivatives, 1,3-bis(2-phenyl-*o*-carboran-1-yl)benzene (**1**), 1,4-bis(2-phenyl-*o*-carboran-1-yl)benzene (**2**), and 1,3,5-tris (2-phenyl-*o*-carboran-1-yl)benzene (**3**) (Figure 1).[18] Compound **1**, with a *m*-substituted benzene platform, adopts a *syn* conformation through intramolecular C−H···π interaction, although there is a sterical disadvantage because of steric repulsion. In contrast, compound **2** has an anti conformation because of the absence of intermolecular C−H···π interactions. In the structure of **3**, the three terminal benzene rings point in the same direction (syn conformation) and the four benzene rings, including the benzene platform, form a pyramidal π-rich space via mutual C−H···π interactions, but the resulting space is too small even for the inclusion of small molecules (Figure 1).

Thus, we were interested in searching for compounds with more flexible structures consisting of π faces and highly

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hydrophobic parts, based on combinations of one or more benzyl-*o*-carborane moieties with a benzene platform, and along this line, we designed compounds **4**, **5**, and **6** with larger π-spaces. Here, we describe the synthesis and structural analysis of bis- and tris(2-benzyl-*o*-carboran-1-yl)benzene derivatives **4**−**6**.

Experimental Section

General Considerations. Melting points were determined with a Yanagimoto micro-melting point apparatus without correction. ^{1}H NMR, ^{13}C NMR, and ^{10}B NMR spectra were recorded with JEOL JNM-LA-400 and JNM-FX-400 spectrometers. Chemical shifts for ^{1}H NMR spectra were referenced to tetramethylsilane (0.0 ppm) as an internal standard. Chemical shifts for ^{13}C NMR spectra were referenced to residual ^{13}C present in deuterated solvents. Chemical shift values for ^{11}B spectra were referenced relative to external $BF_3 \cdot OEt$ (0.0 ppm, with negative values upfield). The chemical shifts are reported in ppm (δ scale) and all coupling constants (J) values are given in hertz (Hz). The splitting patterns are designed as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Mass spectra were recorded on a JEOL JMS-DX-303 spectrometer. Elemental analyses were performed by a Perkin-Elmer 2400 CHN spectrometer.

Materials. Unless otherwise noted, the reagents and solvents were purchased from Aldrich Chemical Co., Kanto Chemicals, Tokyo Kasei, or Wako Chemicals, Inc., and were used as received. Decaborane(14) was purchased from Katchem sro (Prague, Czech Republic). Compound **12** was prepared according to the literature.[19]

1,3-Bis(1,2-dicarba-*closo*-dodecaboran-1-yl)benzene (9). A solution of decaborane (**14**) (460 mg, 3.8 mmol), 1,3-diethynylbenzene **7** (237 mg, 1.9 mmol) and 1 mL of acetonitrile in 10 mL of dry benzene was refluxed for 48 h under an argon (Ar) atmosphere. After removal of the solvent, the residue was purified by column chromatography on silica gel with *n*-hexane/CH_2Cl_2 4:1 to afford 295 mg (43%) of the title compound as a colorless solid; colorless needles (CH_2Cl_2-*n*-hexane); mp 260−261 °C; ^{1}H NMR (396 MHz, $CDCl_3$) δ (ppm) 1.5−3.5 (brm, 20H), 3.92 (s, 2H), 7.33 (t, J = 8.2 Hz, 1H), 7.51 (dd, J = 2.0 Hz, 8.2 Hz, 2H), 7.66 (t, J = 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 60.1, 75.1, 127.6, 128.9, 129.4, 134.4; ^{11}B NMR (127 MHz, $CDCl_3$) δ (ppm) −12.7 (4B), −11.6 (4B), −10.9 (4B), −8.8 (4B), −3.9 (2B), −1.9 (2B); MS (EI) m/z 362 (M^+, 100%); HRMS calcd for $C_{10}H_{26}B_{20}$ 362.4041; found 362.4035; Anal. Calcd for $C_{10}H_{26}B_{20}$ C 33.13, H 7.23; found C 33.25, H 7.36.

1,4-Bis(1,2-dicarba-*closo*-dodecaboran-1-yl)benzene (10). A solution of decaborane (**14**) (4.0 g, 33 mmol), 1,4-diethynylbenzene **8** (2.0 g, 16 mmol), and 5 mL of acetonitrile in 50 mL of dry benzene was refluxed for 72 h under an Ar atmosphere. After removal of the solvent, the residue was purified by column chromatography on silica gel with *n*-hexane:AcOEt 10:1 to afford 3.4 g (59%) of the title compound as a colorless solid; colorless needles (CH_2Cl_2-*n*-hexane); mp >300 °C; ^{1}H NMR (396 MHz, $CDCl_3$) δ (ppm) 1.5−3.5 (brm, 20H), 3.92 (s, 2H), 7.45 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 59.9, 74.8, 128.0, 135.2; ^{11}B NMR (127 MHz, $CDCl_3$) δ (ppm) −12.7 (4B), −11.0 (8B), −8.8 (4B), −3.8 (2B), −1.9 (2B); MS (EI) m/z 362 (M^+, 100%); HRMS calcd for $C_{10}H_{26}B_{20}$ 362.4041; found 362.4039; Anal. Calcd for $C_{10}H_{26}B_{20}$: C 33.13, H 7.23; found C 33.25, H 6.98.

1,3-Bis(2-benzyl-1,2-dicarba-*closo*-dodecaboran-1-yl)benzene (4). To a suspension of NaH (60%, 88 mg, 2.2 mmol) in 4 mL of dry DME was added **9** (363 mg, 1.0 mmol) in one portion. After 15 min, benzyl bromide (0.3 mL, 25.2 mmol) was added, and the mixture was stirred for 24 h at room temperature. The reaction was quenched with 3 N HCl aqueous solution, and the whole was extracted with AcOEt. The organic phase was washed with water and brine, dried over Na_2SO_4, and then evaporated. The residue was purified by column chromatography on silica gel with *n*-hexane/AcOEt 10:1 to afford 234 mg (44%) of the title compound as a colorless solid; colorless needles (CH_2Cl_2-*n*-hexane); mp 201.0−202.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.4−3.4 (brm, 20H), 3.11 (s, 4H), 6.79 (dd, J = 2.0 Hz, 7.7 Hz, 4H), 7.20−7.28 (m, 6H), 7.58 (t, J = 7.7 Hz, 1H), 7.88 (dd, J = 1.9 Hz, 7.7 Hz, 2H), 8.06 (t, J = 1.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 41.2, 82.0, 82.2, 128.1, 128.5, 129.8, 129.9, 132.1, 133.4, 134.6, 134.9; ^{11}B NMR (126.9 MHz, $CDCl_3$) δ (ppm) −3.3 (4B), −9.8 (16B); MS (EI) m/z 542 (M^+, 100%); HRMS calcd for $C_{24}H_{38}B_{20}$ 542.4980; found 542.4980; Anal. Calcd for $C_{24}H_{38}B_{20}$ C 53.11, H 7.06; found C 53.08, H 7.08.

1,4-Bis(2-benzyl-1,2-dicarba-*closo*-dodecaboran-1-yl)benzene (5). To a suspension of NaH (60%, 88 mg, 2.2 mmol) in 4 mL of dry DME was added **10** (363 mg, 1.0 mmol) in one portion. After 15 min, benzyl bromide (0.3 mL, 25.2 mmol) was added, and the mixture was stirred for 24 h at room temperature. The reaction was quenched with 3 N HCl aqueous solution, and the whole was extracted with AcOEt. The organic phase was washed with water and brine, dried over Na_2SO_4, and then evaporated. The residue was purified by column chromatography on silica gel with *n*-hexane/AcOEt 7:1 to afford 182 mg (34%) of the title compound as a colorless solid; colorless needles (CH_2Cl_2-*n*-hexane); mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.4−3.4 (brm, 20H), 3.13 (s, 4H), 6.81 (dd, J = 1.5 Hz, 7.8 Hz, 4H), 7.19−7.27 (m, 6H), 7.77 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 41.3, 81.4, 82.0, 128.1, 128.5, 129.9, 131.9, 133.6, 134.6; ^{11}B NMR (126.9 MHz, $CDCl_3$) δ (ppm) −3.3 (4B), −9.8 (16B); MS (EI) m/z 542 (M^+, 100%); HRMS calcd for $C_{10}H_{26}B_{20}$ 542.4980; Found 542.4973; Anal. calcd for $C_{24}H_{38}B_{20}$ C 53.11, H 7.06; found C 53.18, H 7.09.

1,3,5-Tris(1,2-dicarba-*closo*-dodecaboran-1-yl)benzene (13). A solution of decaborane (**14**) (7.4 g, 61 mmol), 1,3,5-triethynylbenzene **12**[18] (3.0 g, 20 mmol, and 8 mL of acetonitrile in 80 mL of dry benzene was refluxed for 72 h under an Ar atmosphere. After removal of the solvent, the residue was purified by column chromatography on silica gel with *n*-hexane/AcOEt 4:1 to afford 4.5 g (45%) of the title compound as a colorless solid; colorless needles (CH_2Cl_2-*n*-hexane); mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.5−3.5 (brm, 30H), 3.88 (s, 4H), 7.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 60.2, 74.0, 128.8, 135.3; ^{11}B NMR (127 MHz, $CDCl_3$) δ (ppm) −12.1 (12B), −10.9 (6B), −8.7 (9B), −1.4 (3B); MS (EI) m/z 504 (M^+, 100%); HRMS calcd for $C_{12}H_{36}B_{30}$ 504.5827; found 504.5818; Anal. calcd for $C_{24}H_{38}B_{20} \cdot 0.1n$-hexane C 29.48, H 7.34; found C 29.44, H 7.31.

1,3,5-Tris(2-benzyl-1,2-dicarba-*closo*-dodecaboran-1-yl)benzene (6). To a suspension of 60% NaH (240 mg, 6 mmol) in 20 mL of dimethoxyethane (DME) was added **13** (500 mg, 1 mmol), in one portion. After 15 min, benzyl bromide (1.5 mL, 12.6 mol) was added. The reaction mixture was stirred for 24 h at room temperature, quenched with 3 N aqueous HCl solution, and extracted with AcOEt. The organic phase was washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel with *n*-hexane/AcOEt 8:1 to afford 340 mg (44%) of the title compound as a white solid; Colorless needles (CH_2Cl_2-*n*-hexane); mp 257−258 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.5−3.3 (brm, 30H), 3.12 (s, 6H), 6.77−6.79 (m,6H), 7.20−7.29 (m, 9H), 8.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 41.5, 80.5, 82.3, 128.4, 128.8, 129.7, 133.3, 134.1, 136.1; ^{11}B NMR (126.9 MHz, $CDCl_3$) δ (ppm) −9.54 (8B), −2.85 (2B); MS (EI) m/z 775 (M^+, 100%); HRMS calcd for $C_{12}H_{36}B_{30}$ 774.7235; found 774.7219; Anal. calcd for $C_{33}H_{54}B_{30}$ C 51.14, H 7.02; found C 51.25, H 7.03.

X-ray Crystallography. Details of data collection and structure refinement are given in Table 1. Diffraction data were

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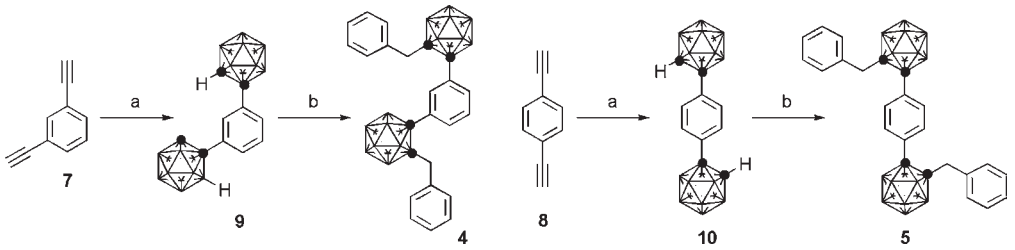
Table 1. Crystal Structure Data and Details of Structure Refinement for Compounds **4**, **5**, **6-*anti***, and **6-*syn*·acetone**

	4	**5**	**6-*anti***	**6-*syn*·acetone**
formula	$C_{24}B_{20}H_{38}$	$C_{24}B_{20}H_{38}$	$C_{33}B_{30}H_{54}$	$C_{33}B_{30}H_{54}(C_3H_6O)$
M_r	542.77	542.77	775.10	833.17
recyst. solvent	CH_2Cl_2-*n*-hexane	CH_2Cl_2-*n*-hexane	CH_2Cl_2-*n*-pentane	acetone-methanol
crystal system	monoclinic	monoclinic	triclinic	monoclinic
lacttice parameter				
a (Å)	10.9967(11)	12.68(2)	12.179(2)	12.051(2)
b (Å)	12.2368(12)	7.66(1)	20.038(3)	20.659(4)
c (Å)	12.0677(12)	33.06(3)	20.340(3)	19.909(4)
α (deg)			93.997(3)	
β (deg)	98.201(2)	90.62(3)	92.730(2)	90.598(3)
γ (°)			98.728(3)	
V (Å^3)	1607.3(2)	3208(7)	4885.6(1)	4956(1)
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/n$
D_{calcd} (g/cm^3)	1.121	1.124	1.013	1.116
Z value	2	4	4	4
R	0.043	0.069	0.099	0.058

Scheme 1. Synthesis of Bis(benzyl-*o*-carboranyl)benzene Derivatives **4** and **5**[a]



[a] Reagents: (a) decaborane (**14**), acetonitrile, benzene; (b) NaH, benzyl bromide, dimethoxyethane.

obtained with a Rigaku AFC7S four-circle diffractometer with graphite-monochromated Mo Ka radiation (λ = 0.71073 Å). Generally, indexing was performed from three oscillation images exposed for 4.0 min, and in total, 15 oscillation images within the 2θ value of 50.0° were collected with the imaging plate area detector. The structure was solved by direct methods using SHELXS-97[20] and refined by the full matrix least-squares technique on F^2 using SHELXL-97.

Method of Calculation. All the quantum mechanical calculations were performed with the parallel version of the Gaussian 03 software package running on a Linux PC cluster.[21] The PBE1PBE hybrid density functional was employed in combination with the 6-31G(d,p) basis set.[22,23] The computed binding energy ($-\Delta E$) was corrected for the basis-set superposition error (BSSE) using the counterpoise-correction method of Boys and Bernardi.[24] Pre- and postprocessing operations were carried out with the Molden (version 4.7) graphic software.[25]

Results and Discussion

Synthesis. Bis(2-benzyl-*o*-carboran-1-yl)benzene structures on a 1,3- or 1,4-substituted benzene platform, **4** and **5**, were synthesized from commercially available diethynylbenzenes, **7** and **8** (Scheme 1). The reaction of **7** or **8** with decaborane(14) in the presence of acetonitrile as a Lewis base afforded the corresponding bis(1-*o*-carboranyl)-benzenes **9** and **10** in 59% and 43% yields, respectively.[26] Compounds **9** and **10** were reacted with benzyl bromide in the presence of NaH as a base to afford *C*-benzylated compounds **4** and **5** in 34% and 44% yields, respectively.[27] 1,3,5-Tris(2-benzyl-*o*-carboran-1-yl)benzene **6** was synthesized as summarized in Scheme 2. Commercially available 1,3,5-tribromobenzene **11** was reacted with trimethylsilylacetylene under Sonogashira coupling conditions, followed by deprotection with K_2CO_3 in methanol to afford 1,3,5-triethynylbenzene **12** in 87% yield.[18] The ethynyl groups were converted to *o*-carborane cages by means of cyclization reaction with decaborane (**14**) to afford compound **13** in 47% yield.[26] Three *o*-carborane C−Hs of compound **13** were transformed into benzyl groups with benzyl bromide in the presence of NaH to afford the desired compound **6** in 44% yield.[27] The structures of the compounds were established by analytical data, including melting point, NMR spectrum (^{1}H, ^{11}B, and ^{13}C),

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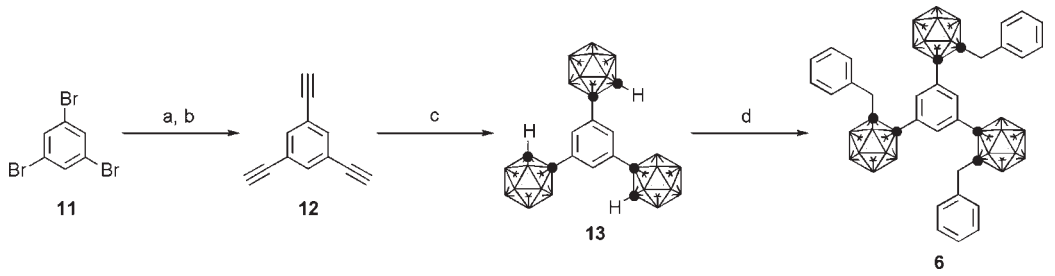
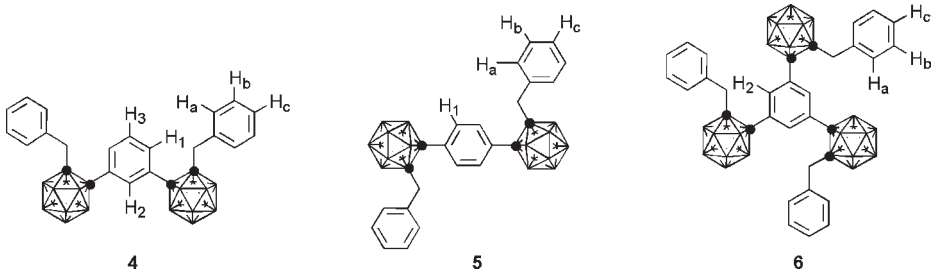
Scheme 2. Synthesis of 1,3,5-Tris(benzyl-*o*-carboranyl)benzene **6**[a]



[a] Reagents: (a) $Pd(PPh_3)_2Cl_2$, CuI, Et_3N, trimethylsilylacetylene, THF; (b) K_2CO_3, MeOH; (c) decaborane (**14**), acetonitrile, benzene; (d) NaH, benzyl bromide, dimethoxyethane.

Table 2. ^{1}H NMR Chemical Shift Values of Compounds **4**−**6** in $CDCl_3$ at Room Temperature



positions of protons		chemical shift values (ppm) of protons		
		4	**5**	**6**
central benzene ring	H_1	7.88	7.77	
	H_2	8.06		8.22
	H_3	7.58		
terminal benzene ring	H_a	6.78	6.81	6.78
	H_b	7.24	7.23	7.33
	H_c	7.22	7.23	7.33
benzylic methylene protons	CH_2	3.10	3.13	3.12

MS spectrum, IR spectrum, elemental analysis, and X-ray diffraction study (see Experimental Section).

^{1}H NMR Studies. Conformational behaviors of **4**, **5**, and **6** in solution were examined by means of ^{1}H NMR studies in $CDCl_3$ as a solvent. Table 2 summarizes the ^{1}H NMR chemical shift data of compounds **4**−**6**. All protons were assigned based on chemical shifts and coupling patterns and constants. There are three types of protons in the central benzene rings of **4**−**6**: those located between *o*-carborane and another proton, H_1, located between two *o*-carborane rings, H_2, and located between two protons, H_3. The terminal benzene ring also has three types of protons; *ortho*-position to the methylene part, H_a, *meta*-position, H_b, and *para*-position, H_c. On the central benzene ring, the *o*-carborane cage shifts the ^{1}H NMR signals of neighboring protons downfield because of both steric hindrance and the electron-withdrawing character of *C*-substituted *o*-carborane. Thus, the order of chemical shift values is as follows: $H_2 > H_1 > H_3$. Additionally, as the number of *o*-carborane moieties on the central benzene ring is increased, the proton signals are shifted downfield because of the electron-withdrawing character of *o*-carborane. The terminal benzene ring and methylene protons do not show any significant difference in chemical shift values among these compounds. They also did not show any chemical shift change at low temperature (233 K). All compounds are in rapid equilibrium between *syn* and *anti* conformations in solution.

X-ray Diffraction Analyses. Colorless crystals of **4** and **5** were grown from a mixed solution of CH_2Cl_2 and *n*-hexane by slow evaporation of the solvents. The structures of **4** and **5** in the solid state were confirmed by single-crystal X-ray diffraction analyses (Table 1). Both compounds crystallize in the monoclinic space group $P2_1/c$. Compound **4** has a *syn* conformation with two benzyl groups located on the same side of the central benzene ring (Figure 2). One benzylic C−H hydrogen of each benzyl group is located near the platform benzene ring with separations of 2.548 Å and 2.628 Å, respectively. One terminal benzene ring is perpendicular to the face of the other benzene ring and the associated hydrogen atom is aligned almost to the middle of the benzene ring with a centroid distance of 3.038 Å, which is consistent with a C−H$\cdots\pi$ interaction (T-shaped interaction). The C−H$\cdots\pi$ interactions are important for geometry generation, but not for the construction of the syn conformation, because the anti form can also exhibit this kind of C−H$\cdots\pi$ interaction. The latter C−H$\cdots\pi$ interaction enhances mutual attraction between the benzyl arms and acts as a major driving force for the formation of the syn conformation. The crystal structure of **5** showed anti conformation with two benzyl groups located on opposite

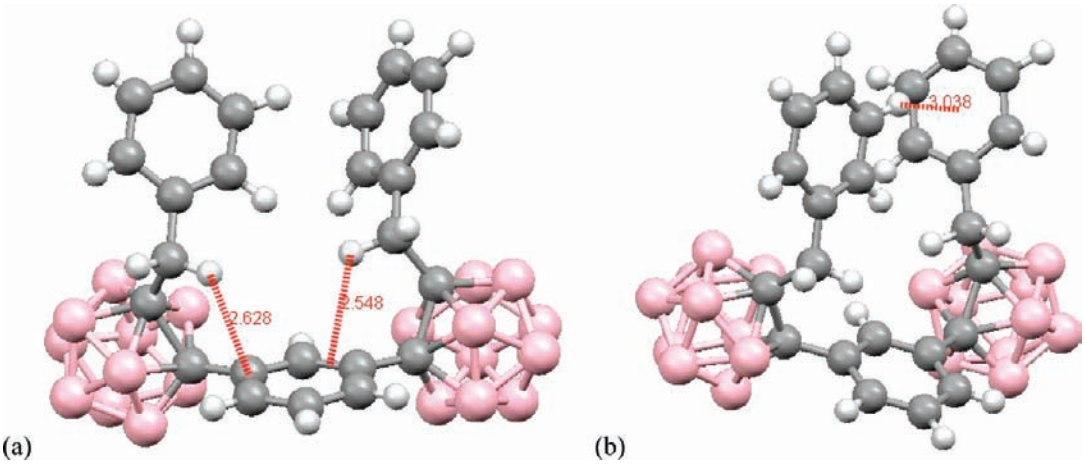


Figure 2. X-ray crystal structure of compound **4**. Hydrogen atoms of B−H bonds are omitted. (a) Benzylic C−H hydrogens form C−H···π interactions with the central benzene ring. (b) A T-shaped stacking is formed between the terminal benzene rings. The C−H···π interactions and distances are shown in red.

faces of the central benzene ring. Along with the intramolecular C−H···π interactions (2.657 Å) between benzylic C−H and the platform benzene ring, two kinds of intermolecular C−H···π interactions were apparent in the crystal structure (Figure 3a). The other benzylic C−H hydrogen interacts with a terminal benzene ring of another molecule with a distance of 3.141 Å. The C−H hydrogen of the terminal benzene ring is located obliquely on the platform benzene ring with the distance of 3.104 Å. That is, there is a distorted T-shaped interaction between the two benzene rings. Additionally, the terminal benzene rings exhibit intermolecular parallel stacking, and the distance between carbon atoms of the benzene rings is 3.594 Å, which is consistent with displaced $\pi-\pi$ stacking. In the packing structure of compound **5**, the *o*-carborane cage assembles through hydrophobic interaction, and *o*-carborane cages and benzene rings formed alternating hydrophobic and π layers (Figure 3b).

The structure of compound **6** was confirmed by X-ray diffraction studies of a single crystal grown in a mixed solvent of CH_2Cl_2 and *n*-pentane by slow evaporation (Table 2: **6-*anti***). Compound **6** crystallizes in the triclinic space group *P-1* in this solvent system. Crystalline **6-*anti*** showed anti conformation, with one benzyl group located on the opposite side of the platform benzene π-face (Figure 4). Two types of anti conformations are observed in the crystal structure and interact with each other through an intermolecular T-shaped C−H···π interaction with the distance of 2.843 Å. Six benzylic C−H hydrogens in the two anti conformers are in close contact with the carbon atoms of the central benzene rings, with distances in the range of 2.562−2.859 Å. One anti conformer forms an intramolecular T-shaped C−H···π interaction between two terminal benzene rings at the distance of 3.372 Å; this interaction motif is very similar to that observed in compound **4**. The crystal structure of **6-*anti*** is composed of just C−H···π interactions, as in the case of compound **4**.

On the other hand, crystals of compound **6-*syn*** obtained from acetone-methanol mixed solvent belonged to the monoclinic space group $P2_1/n$ (Table 2: **6-*syn*·acetone**). In contrast to the structure of **6-*anti***, the three benzyl arms are oriented in the same direction (*syn* conformation) and form a π-cavity which resembles the shape of a three-petaled flower. There is a T-shaped C−H···π interaction between terminal benzene rings with a distance of 3.589 Å. Interestingly, one acetone molecule was accommodated in the cavity formed by three benzyl groups of **6-*syn*** (**6-*syn*·acetone**). The oxygen of acetone was located in the interior of the cavity with the distance of 3.831 Å from the center of the platform benzene, but there is no interaction. Because of the electron-withdrawing ability of the *o*-carborane cage, the two benzylic C−H hydrogens are more acidic than the alkyl-substituted benzylic C−H hydrogens and approach the oxygen atom of the acetone with distances of 2.552 and 2.658 Å. The shortest distance from the oxygen atom to benzylic carbon is 3.272 Å, which is shorter than the sum of the van der Waals radii (C−H; 2.0, O; 1.4) and within the range of C−H···O interaction. The paired benzylic C−H hydrogens are directed outside the cavity. The C−H hydrogens of the third benzyl group are away from the oxygen with distances of 2.947 and 2.964 Å, which is beyond the range of C−H···O interaction. Since two hydrogen bonds, C−H···O, interact with the oxygen lone-pairs, the C−H hydrogens of the third benzyl group do not have the opportunity to form an additional hydrogen bond. The directions of the C−H hydrogens of the third benzyl group are fixed to a certain extent owing to the intramolecular T-shaped C−H···π interactions between the terminal benzene rings. Besides, both methyl groups of the acetone molecule form intermolecular C−H···π interactions with the three terminal benzene rings with the distances of 3.054, 3.346, and 3.516 Å. The inclusion of acetone is supported by C−H···O and C−H···π interactions, and the intermolecular C−H···O interaction might be the main driving force. The syn or anti form of the third benzyl-*o*-carborane moiety is controlled by intramolecular C−H···π interaction and intermolecular hydrogen bonding with acetone, by the C−H···π interaction, not the C−H···O interaction.

In the crystal structure of **6-*syn***, we found that two host molecules are symmetrically associated with each other and two acetone molecules are encapsulated into a π space formed by the six terminal benzene rings and two platform benzene rings. Complementary intermolecular T-shaped C−H···π interactions between the benzyl arms of the opposed host molecules are formed with the

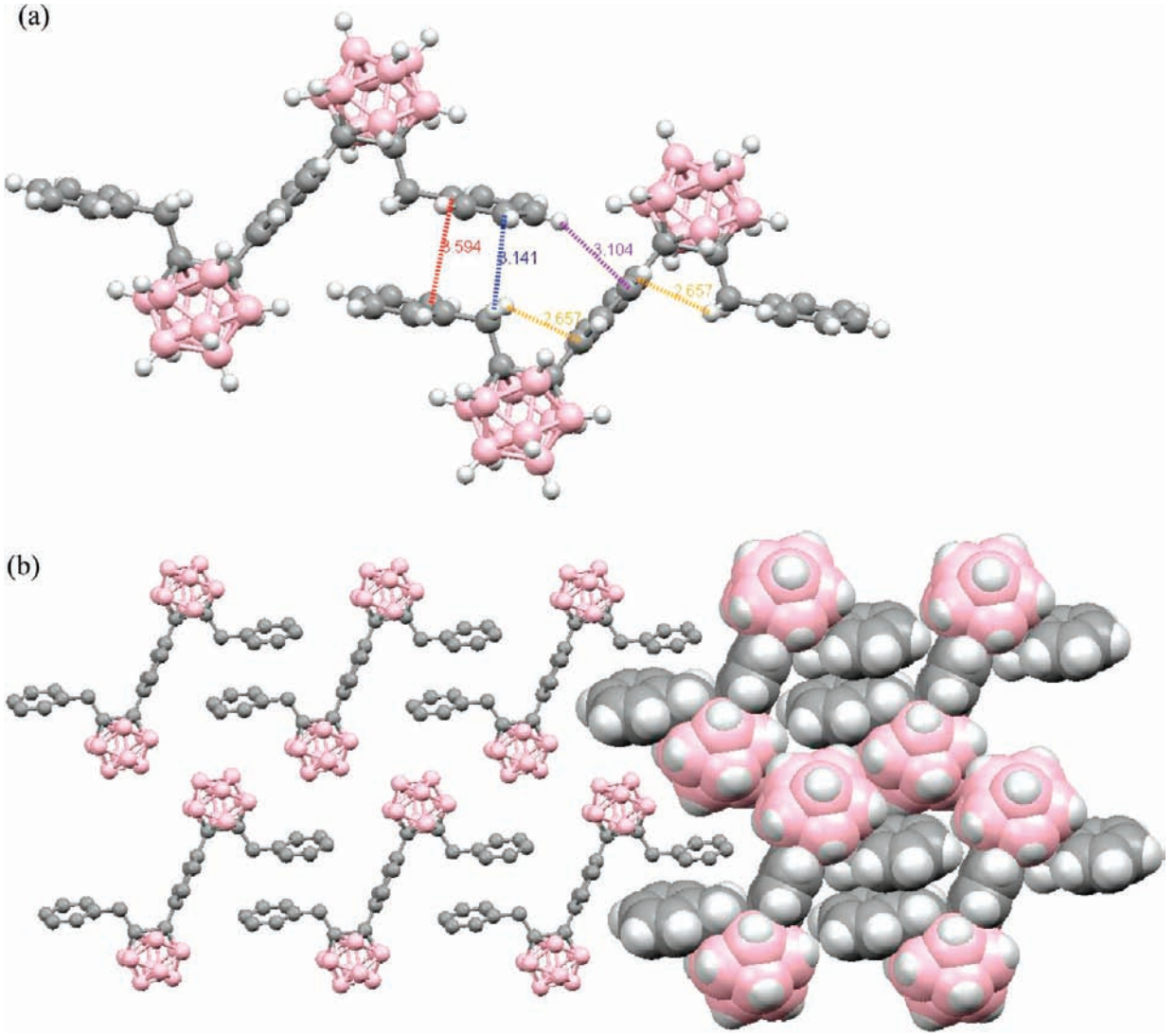


Figure 3. Crystal structures of compound **5**. (a) Compound **5** is arranged with an offset $\pi-\pi$ stacking (3.594 Å, red) and three different C−H$\cdots\pi$ interactions: an intramolecular C−H(benzylic)$\cdots\pi$(platform) interaction (2.657 Å, orange), an intermolecular C−H(benzylic)$\cdots\pi$(terminal) interaction (3.141 Å, blue), and a distorted T-shaped interaction (3.104 Å, purple). (b) Array structure showing crystal packing of compound **5** with a partial space filling model. Hydrogen atoms are omitted.

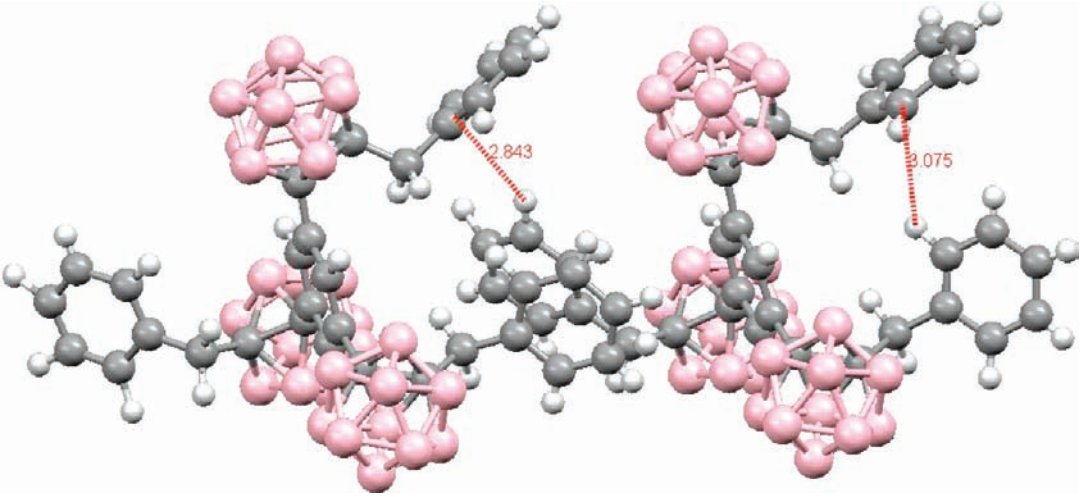


Figure 4. Crystal structure of **6-*anti*** crystallized from CH_2Cl_2-*n*-pentane. B−H bonds are omitted.

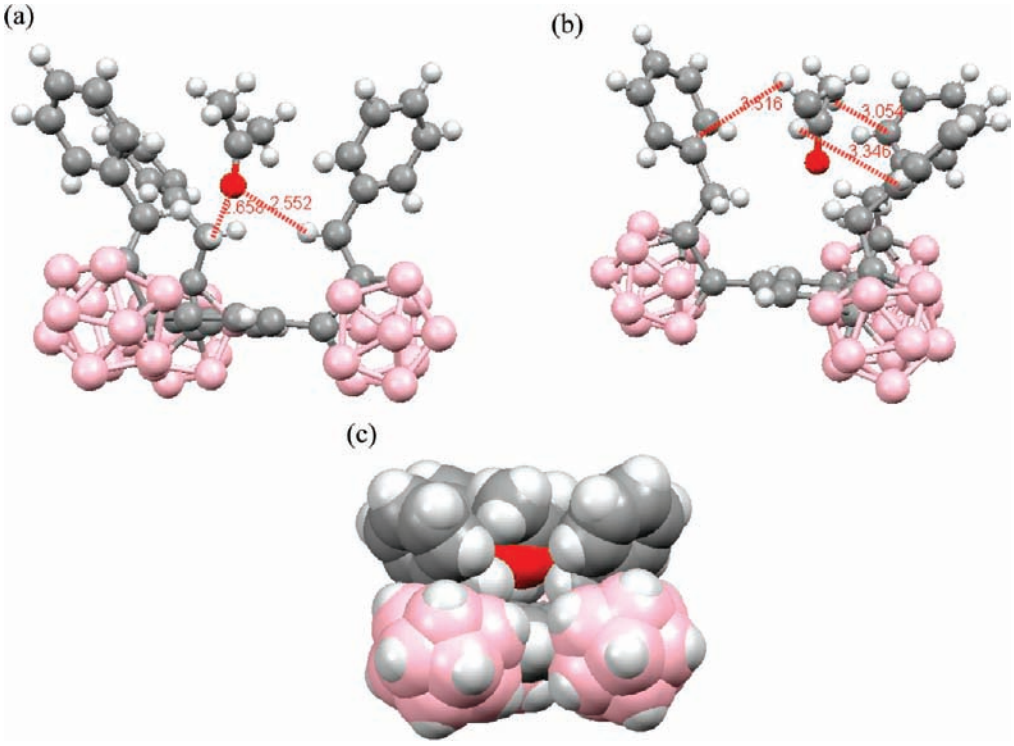


Figure 5. Crystal structure of **6-*syn*·acetone**. (a) Intramolecular C−H (benzylic)···O interaction is the main driving force of the host−guest complexation. The distances are 2.552 and 2.658 Å. B−H bonds are omitted. (b) C−H···π interactions between the terminal benzene rings and CH_3 groups of acetone. The closest distances between the C−H hydrogen and the benzene rings are 3.054, 3.346, and 3.516 Å. B−H bonds are omitted. (c) A space-filling model of the complex **6-*syn*·acetone**.

distance of 3.113 Å. Around the π-space formed by the two host molecules, two facing benzene rings are arranged parallel to each other; the dihedral angle between the planes of the benzene rings is 0°, and the distances are 7.161 Å, 11.641 Å, and 13.969 Å in the benzyl moieties, and 13.886 Å in the platform (Figure 6). There is a symmetric intermolecular interaction between the host−guest complexes, with a complementary C−H···π interaction between the methyl group of acetone and the benzyl group of the opposite host molecule, with the distance of 2.926 Å.

In the crystal packing structure of **6-*syn***, the capsule including two acetone molecules showed a supramolecular array structure like a π layer sandwich on hydrophobic *o*-carborane layers (Figure 7). The extended array of (**6-*syn*·acetone**)$_2$ showed an architecture with an acetone-encapsulating π-container placed between serpentine-like structures of *o*-carborane rings, which assemble owing to the high hydrophobicity of *o*-carborane to form a continuous structure.

There are two main types of interactions that are responsible for this encapsulation phenomenon. One is the driving force for the construction of the π-space, which is the intramolecular T-shaped C−H···π interactions between terminal benzene rings of the host molecule and the intermolecular T-shaped C−H···π interaction between the complementary host molecules. The other is the intermolecular interactions between the acetone and the host molecule, such as the C−H···O and the C−H···π interactions. These interactions play crucial roles in the stability of the *syn* conformation and the encapsulation of the acetone molecule in the π-container. In addition, the high hydrophobicity of the *o*-carborane cage determines the supramolecular array structure in the packing of (**6-*syn*·acetone**)$_2$.

DFT Calculation Study of the Complex 6-*syn*·acetone. We performed a series of density functional theory (DFT) calculations to shed light on the formation of complex **6-*syn*·acetone**. Our crystal structure analyses indicate that in the free (i.e., uncomplexed) form of **6-*anti***, one of the three phenyl-carborane units is oriented in the opposite direction to the other two phenyl-carborane units. Upon complexation with acetone, **6-*syn*·acetone**, however, all three phenyl substituents are located on the same side with respect to the plane containing the central arene ring. In this manner, the methylene units can form multiple hydrogen bonds with the carbonyl oxygen of acetone, thereby locking the guest inside the chalice-like cavity of the complex. Our DFT calculations indicate that the energy difference between the optimized geometries of the chalice-like conformer (Figure 8b) and the open conformer (Figure 8a) is only 0.7 kcal/mol, with the latter conformer being only slightly more stable than the former. The DFT-optimized structure of **6-*syn*·acetone**, shown in Figure 8c, is consistent with the crystal structure, although one should consider that the latter is subjected to crystal packing effects that are absent in the former. Each methylene moiety employs only one of its hydrogen atoms to form a C−H···O interaction with the carbonyl oxygen of acetone at distances of 2.446, 2.507, and 2.453 Å. The BSSE-corrected binding energy of the complex corresponds to 6.6 kcal/mol. Interestingly, the chalice-like conformer (Figure 8b) possesses a large dipole moment of 9.4 D, which is likely to stabilize the complex, as well as favoring the approach of small, polar molecules bearing electronegative atoms.

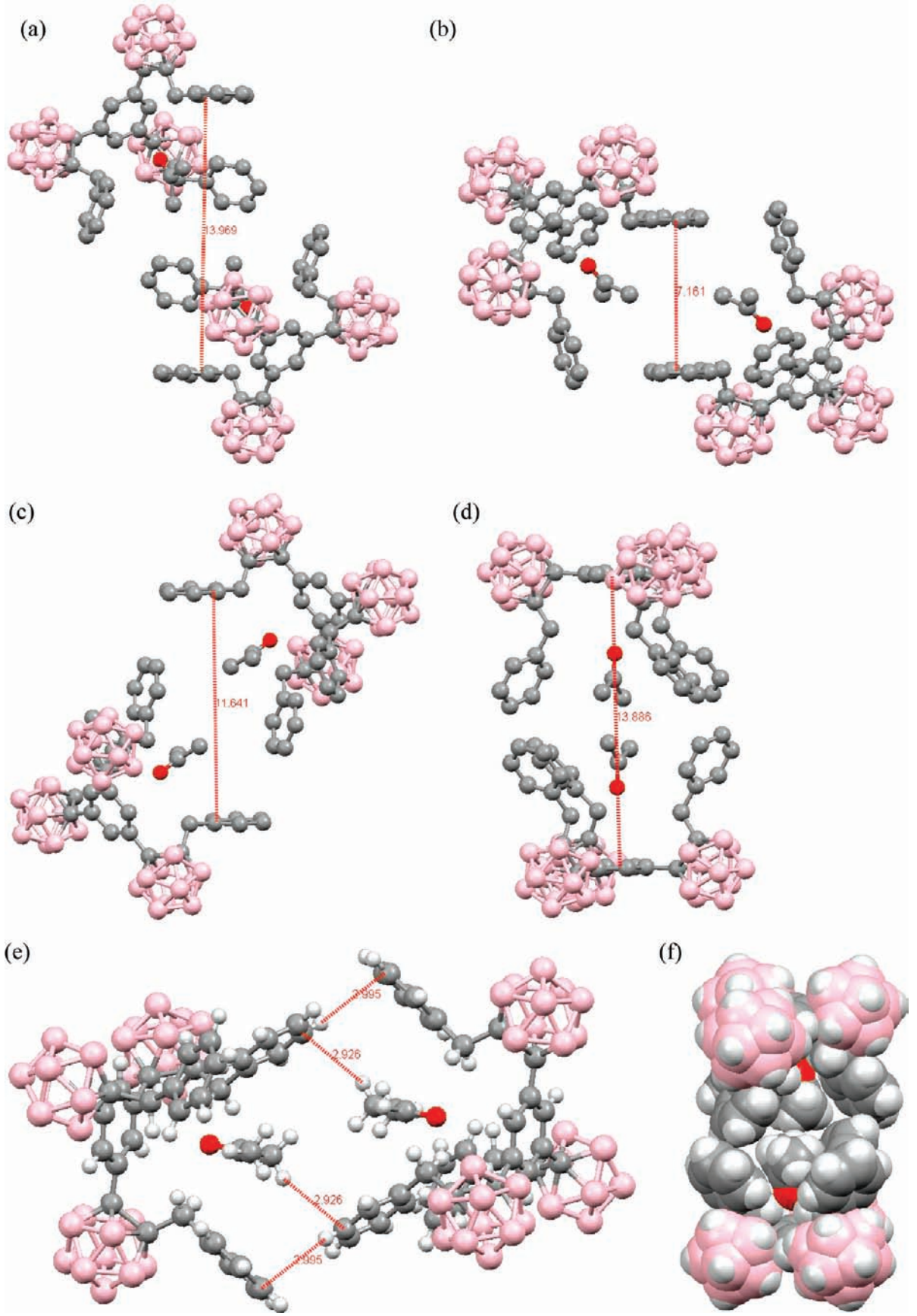


Figure 6. Encapsulation of two molecules of acetone in the octahedral π space formed from eight benzene rings of two molecules of **6-*syn***. (a)-(c) The distances of three complementary benzylic π faces in the π-container (7.161−13.169 Å). Hydrogen atoms are omitted. (d) The distance of a complementary π-face between the 1,3,5-benzene scaffolds of (**6-*syn*·acetone**)$_2$ (13.886 Å). Hydrogen atoms are omitted. (e) Complemetary bilateral C−H$\cdots\pi$ interactions of the π-container. B−H bonds are omitted. (f) A space-filling model of the capsule structure (**6-*syn*·acetone**)$_2$.

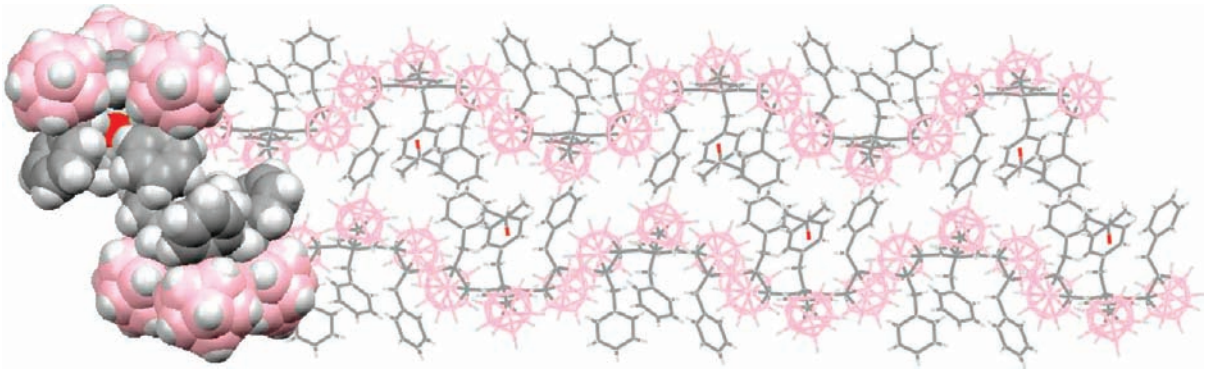


Figure 7. Packing structures of the capsule (**6-*syn*·acetone**)$_2$ with a partial space-filling model. The extended structure shows the up-and-down type arrangement of the supramolecular arrays.

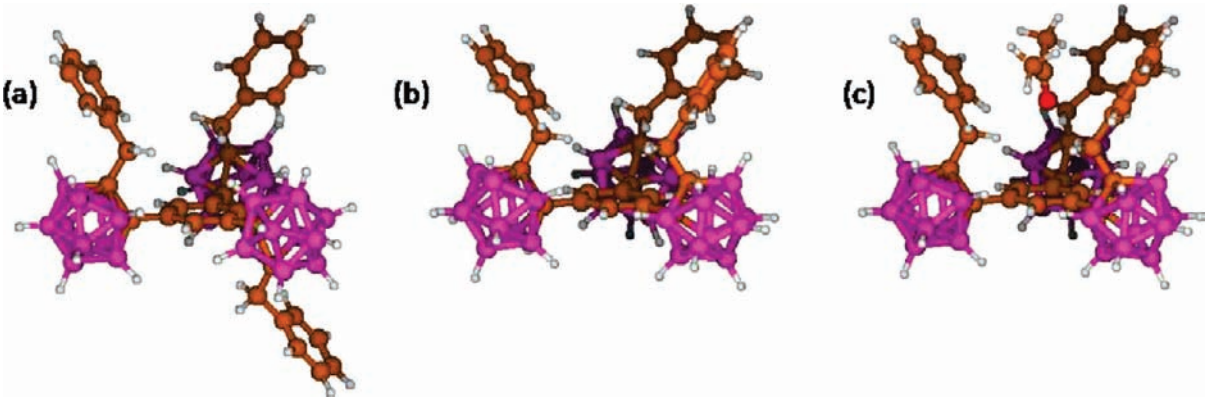


Figure 8. DFT-optimized structures of two conformers of **6** and complex **6-*syn*·acetone**. (a) The *anti* conformation of **6** (**6-*anti***). (b) The *syn* conformation of **6** (**6-*syn***). (c) The complex **6-*syn*·acetone**.

Conclusions

Focusing on the combination of high hydrophobicity, the orientation of substituents and the rigidity of the *o*-carborane cage, we designed and synthesized three compounds **4**−**6** with a benzene ring as a central core structure and benzyl-*o*-carborane moieties. We then examined and compared their X-ray crystal structures. Compounds **4** and **5** showed syn and anti conformations, respectively, thus reflecting differences in their weak intramolecular and intermolecular interactions. Compound **6**, on the other hand, showed solvent-dependent conformations: the *syn* conformation obtained from a mixed solvent of MeOH-acetone includes one acetone molecule in the space formed by the three benzyl groups and one platform benzene. The inclusion of the acetone molecule involves weak interactions, including T-shaped C−H···π, C−H···O, and C−H···π interactions. The C−H···O interactions between benzylic C−H hydrogens activated by the electron-withdrawing character of the *o*-carborane cage and the oxygen atom of the acetone seem to be the most important among them. DFT calculations indicated that the binding energy of the acetone complex is 6.6 kcal/mol. Furthermore, the complex is stabilized by the large dipole moment associated with the chalice-like conformation of the carborane receptor. The artificial capsule constructed from two molecules of **6-*syn*** via complementary intermolecular C−H···π interactions accommodates two acetone molecules in the π-space, and supramolecular architecture was generated as a result of the high hydrophobicity of the *o*-carborane cage.

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Supporting Information Available: Details of X-ray crystallographic data (CIF) and the results of DFT calculations. These materials are available free of charge via the Internet at http://pubs.acs.org.