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Synthesis of distorted molecules based on spatial control with icosahedral carboranes

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Abstract

In the crystal structure of 1,2-bis(*o*-carboranyl)benzene (**2**), the benzene ring is remarkably twisted out of planarity, owing to the steric bulkiness of two adjacent carboranyl groups. In the carboracycle (**3**), the two benzene rings are slantingly stacked owing to spatial control by the carborane cages.

Keywords: Carboranes; Conformation; Molecular design

1. Introduction

On account of their high boron contents, chemical and thermal stabilities, rigid near-spherical geometry and hydrophobic character, the icosahedral carboranes (dicarba-*closo*-dodecaboranes) can serve as chemical building blocks for various applications in the materials sciences and biomedical sciences. The high boron contents and chemical and thermal stability of the carboranes have been utilized in the preparation of thermostable polymers [1] and carrier molecules for boron neutron capture therapy [2]. The spherical geometry and hydrophobic character have been utilized in the preparation of materials for liquid crystals [3]. Recently, we have examined their electronic properties in the field of physical organic chemistry [4] and attempted to apply their spherical geometry and hydrophobic character to the development of novel biologically active molecules, which interact hydrophobically with receptors [5].

On the other hand, carboranes have attracted increasing attention as building blocks for the design and synthesis of molecules with defined shapes, such as rings and rigid rods, because of their potential applications to nanoarchitecture and functionalized molecules. The 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 *o*-, *m*-, and *p*-carboranes bear relatively acidic protons that can be replaced with metal and organic groups. Substituents can also be introduced at certain boron vertices. The construction of linear [6] and macrocyclic [7] molecules, in which carboranes are linked through organic groups or mercury atoms [8], has also progressed. We have reported the construction of aromatic multilayered molecules [9] by utilizing the *cis*-preference of *N*-methyl aromatic ureas [10] in combination with regulation of the *C*-substituent on the 1,2-dicarba-*closo*-dodecaborane (*o*-carborane) cage, and the construction of macrocyclic compounds composed of 1,7-dicarba-*closo*-dodecaborane (*m*-carborane) moieties linked *via* their carbon vertices through

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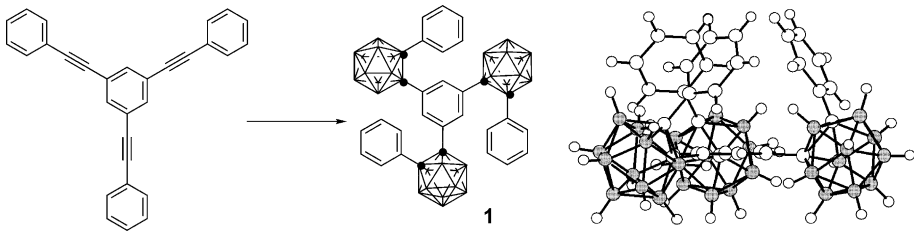


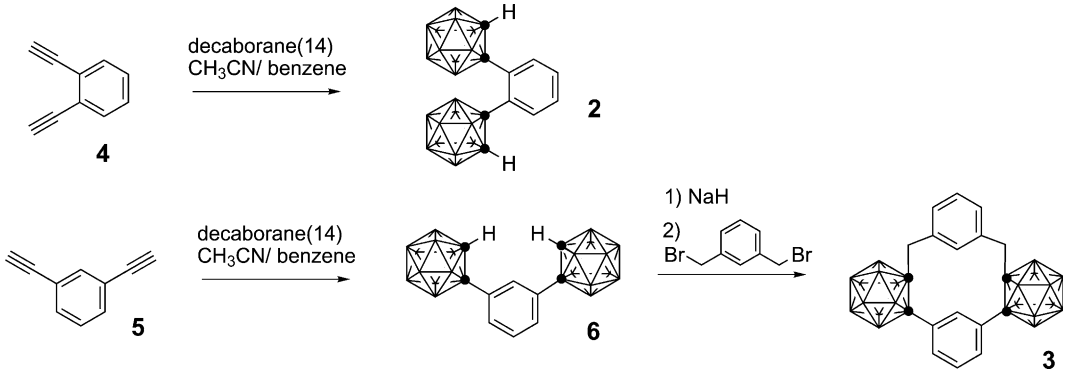
Fig. 1. Construction of 3D structure (**1**) from an arylacetylenic array.

N,*N*′-dimethyldiphenylurea groups as a new type of carboracycle [11]. We have also presented the synthesis and structural analysis of bis- and tris(2-phenyl-*o*-carboran-1-yl)benzenes (**1**) [12]. The last examples indicate the usefulness of the carborane cage in constructing three-dimensional structures from planar arylacetylenic arrays. In addition to these features of carboranes, it should be possible to utilize the bulkiness of the carborane cage to synthesize new kinds of strained molecules. We here describe the synthesis and structural analysis of two unusual strained aromatic compounds composed of benzene nuclei linked with *o*-carborane (**2** and **3**) (see Fig. 1).

2. Results and discussion

The syntheses of the designed molecules, 1,2-bis(*o*-carboran-1-yl)benzene (**2**) and the carboracycle **3**, are outlined in Scheme 1. The precursors, 1,2- and 1,3-diethynylbenzenes (**4** and **5**) were prepared by palladium-catalyzed coupling of ethynyltrimethylsilane with iodobenzene, followed by desilylation [13]. The reaction of decaborane(14) with acetylenic compounds in the presence of a Lewis base is general for the preparation of C-substituted *o*-carborane derivatives. Reaction of **4** with decaborane(14) in acetonitrile-benzene under reflux for 3 days afforded 1,2-bis(*o*-carboran-1-yl)benzene (**2**) in 10% yield. The procedure using Et_2S as a Lewis base instead of acetonitrile has been applied to the synthesis of bis-aryl-substituted *o*-carboranes [14], aryl derivatives containing more than one carborane substituent [15]. However, this procedure was not effective for the preparation of **2**. On the other hand, reaction of the **5** with decaborane(14) in acetonitrile-benzene under reflux for 2 days afforded 1,3-bis(*o*-carboran-1-yl)benzene (**6**) in 44% yield. Treatment of **6** with α,α′-dibromo-*m*-xylene in the presence of sodium hydride afforded the carboracyle **3** in 77% yield.

Observation of the ^{1}H NMR spectrum of **2** did not reveal any noteworthy feature, except for a low-field shift of protons neighboring the electron-withdrawing carboranyl groups. However, X-ray crystallographic analysis revealed the characteristic structure of **2**, which is shown in Fig. 2. The benzene ring of **2** is twisted unsymmetrically owing to the bulkiness of the *o*-carboranyl groups on adjacent positions. Interatomic distances, bond angles and deviations from the optimum plane of the benzene ring of **2** are given in Fig. 3 and Table 1. The C(1)–C(2) bond length (1.435(3) Å) of the benzene ring is elongated, as are the C(1)–C(6) and C(2)–C(3) bond lengths. The angles C(1 cage A)–C(1)–C(2) and C(1)–C(2)–C(1 cage B) are expanded to 130.8(2)° and 132.8(2)°, and the angles of C(1 cage A)–C(1)–C(6), C(6)–C(1)–C(2), C(1)–C(2)–C(3), and C(1 cage B)–C(2)–C(3) are contracted. The angles at C(1) and C(2) in **2** imply a considerable amount of angular strain for sp^2-hybridised carbon atoms. The dihedral angle between C(1A)–(cage A)–C(1) and C(2)–C(1B) (cage B) is 26.7° and the C(3)–C(2)–C(1)–C(6) torsional angle is 12.6°. Other aromatic compounds with two bulky substituents on adjacent positions include 1,2-di(1-



Scheme 1. Preparation of strained molecules (**2** and **3**).

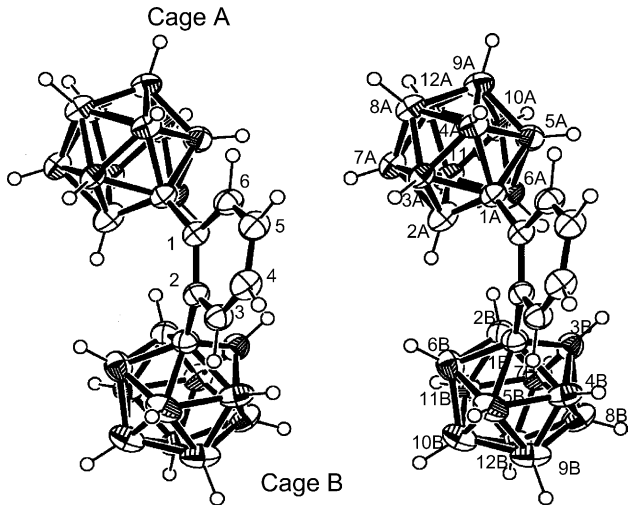


Fig. 2. Stereoview (parallel eyed) of **2** from the X-ray data.

adamantyl)benzene (**7**), which has been prepared by oxidation of 3,4-di(1-ada- mantyl)thiophene followed by Diels–Alder reaction with phenyl vinylsulfone [16]. Some geometrical parameters for **7** have been described in the literature [16] as preliminary results. The corresponding values reported for **7** are 16.6° for C(1(Ad))–C(1) and C(2)–C(1(Ad)), and 7.1° for the C(3)–C(2)–C(1)–C(6) torsional angle. Therefore, compound **2** should be useful for evaluating the effects of extremely bulky substituents on the 1,2-positions of benzene. Geometrical parameters for the two carborane cages of **2** in comparison to those reported for 1-phenyl-*o*-carborane [17] are shown in Table 1. The bond lengths of C(1)–C(2) (1.700(3) Å), C(1)–B(4) (1.774(3) Å), C(2)–B(6) (1.768(4) Å), C(2)–B(7) (1.751(3) Å), C(2)–B(11) (1.753(3) Å) in cages A are expanded in comparison with those of 1-phenyl-*o*-carborane. On the other hand, the bond lengths of B(3)–B(4) (1.713(3) Å) and B(3)–B(7) (1.738(3) Å) in cage A is shortened. The structure of the carborane cage A is distorted by compar- ison with that of cage B, while the bond lengths and bond angles around C(1) of the benzene ring are less distorted than those of C(2). On the other hand, five angles around C(1) of the both carborane cages (C(1A) and C(1B)) are distorted owing to the steric contact of the two carboranes. The bond angles of C(2)–C(1)–C(benzene) and B(6)–C(1)–C(benzene) in both carborane cages A, B are expanded, and the angles of B(4)–C(1)–C(benzene) in both carborane cages A, B are contracted (Table 1). Although a tentative structure of 1,2,4-tris(*o*-carborane)benzene was assigned to a product of trimerization of 1-ethynyl-*o*-carborane based on NMR, IR, MS and combustion data [18], structural analysis of the compound was not reported. Therefore, 1,2-bis(*o*-carboran-1-yl)benzene (**2**) has the most distorted benzene ring analyzed experimentally to date (see Table 2).

Another characteristic structure based on spatial control by carborane cages is seen in compound **3**. The crystal structure of **3** is shown in Fig. 5, and interatomic distances and bond angles of the carbon skeleton are shown in Fig. 6(a) and (b). The bond lengths of both benzene rings are 1.384(3)–1.394(3) Å, and the bond angles are 118.6(2)–121.9(2)°, which do not deviate from

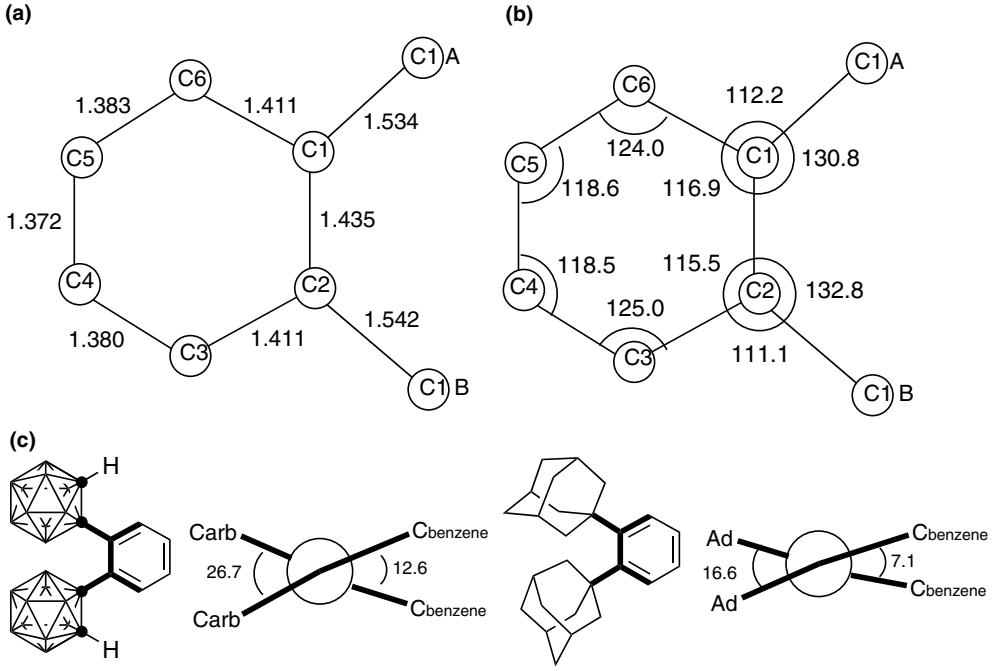


Fig. 3. Geometrical Parameters for benzene ring of **2** from the X-ray data. (a) Interatomic distances (Å). (b) Bond angles (°). (c) Comparison of key dihedral angles of **2** with 1,2-di(1-adamantyl)benzene (**7**).

Table 1
Comparison of geometrical parameters for the two carborane cages of **2**[a] and that of 1-phenyl-*o*-carborane[b]

Distance or angle	**2** cage A	**2** cage B	1-Ph-*o*-$C_2B_{10}H_{11}$[b]
C(1)–C(2)	1.700(3)	1.657(3)	1.649(2)
C(1)–B(3)	1.725(3)	1.754(3)	1.742(2)
C(1)–B(4)	1.774(3)	1.735(3)	1.724(2)
C(1)–B(5)	1.728(3)	1.750(3)	1.716(2)
C(1)–B(6)	1.717(3)	1.739(3)	1.736(2)
C(2)–B(3)	1.701(3)	1.717(3)	1.718(2)
C(2)–B(6)	1.768(4)	1.730(4)	1.722(2)
C(2)–B(7)	1.751(3)	1.714(3)	1.701(2)
C(2)–B(11)	1.753(3)	1.725(3)	1.698(2)
B(3)–B(4)	1.713(3)	1.748(3)	1.779(2)
B(3)–B(7)	1.738(3)	1.791(3)	1.780(2)
B(3)–B(8)	1.734(3)	1.778(4)	1.766(3)
B(4)–B(5)	1.766(4)	1.765(4)	1.783(3)
B(4)–B(8)	1.764(3)	1.751(4)	1.785(2)
B(4)–B(9)	1.748(3)	1.747(4)	1.780(2)
B(5)–B(6)	1.797(4)	1.776(4)	1.777(2)
B(5)–B(9)	1.777(3)	1.769(4)	1.784(2)
B(5)–B(10)	1.779(3)	1.783(4)	1.785(2)
B(6)–B(10)	1.780(3)	1.790(4)	1.764(2)
B(6)–B(11)	1.778(3)	1.793(4)	1.784(2)
B(7)–B(8)	1.764(3)	1.781(3)	1.772(3)
B(7)–B(11)	1.794(3)	1.776(4)	1.786(3)
B(7)–B(12)	1.776(4)	1.773(4)	1.773(3)
B(8)–B(9)	1.778(4)	1.768(4)	1.789(3)
B(8)–B(12)	1.782(3)	1.790(4)	1.789(2)
B(9)–B(10)	1.781(3)	1.778(4)	1.788(3)
B(9)–B(12)	1.788(4)	1.777(4)	1.782(3)
B(10)–B(11)	1.790(4)	1.785(4)	1.780(3)
B(10)–B(12)	1.786(3)	1.772(4)	1.794(3)
B(11)–B(12)	1.792(3)	1.766(3)	1.776(2)
C(1)–C(benzene)	1.534(2)	1.542(3)	1.511(2)
C(2)–C(1)–C(benzene)	123.9(2)	128.3(2)	118.76(12)
B(3)–C(1)–C(benzene)	117.8(2)	116.9(2)	116.70(11)
B(4)–C(1)–C(benzene)	115.1(2)	114.6(2)	121.82(12)
B(5)–C(1)–C(benzene)	120.0(2)	118.1(2)	122.26(12)
B(6)–C(1)–C(benzene)	125.4(2)	124.9(2)	117.52(11)

[a] For the atom numbering scheme, see Fig. 2.
[b] Data from Ref. [17b].

Table 2
Crystal data of carborane-containing compounds **2** and **3**

Compound	**2**	**3**
Formula	$C_{10}B_{20}H_{26}$	$C_{18}B_{20}H_{32}$
M_r	362.52	464.65
Recryst. solvent	*n*-hexane	Diethyl ether/*n*-hexane
Crystal system	Monoclinic	Monoclinic
Lattice parameter		
a (Å)	10.347 (4)	13.348 (2)
b (Å)	15.76 (1)	14.123 (2)
c (Å)	12.911 (9)	14.049 (2)
β (°)	98.17 (2)	97.814 (3)
V (Å^3)	2084.1499	2623.8 (7)
Space group	$P2_1/n$ (# 14)	$P2_1/n$ (# 14)
Z value	4	4
ρ_{calc} (g/cm^3)	1.155	1.176
μ (Mo Kα) (cm^{-1})	0.5	0.55
Temperature (°C)	15 ± 1	−170 ± 1
$2\theta_{max}$(°)	50.1	57.1
Number of observations	3317 ($I > 1.50s$ (I))	3077 ($I > 2.00s$ (I))
Number of variables	272	440
Goodness-of-fit (GoF)	3.26	0.95
Maximum shift/error in final cycle	0.02	0.26
Residuals: R, R_w	0.069, 0.092	0.047, 0.042
Maximum peak in final difference map (e Å^{-3})	0.31	0.28

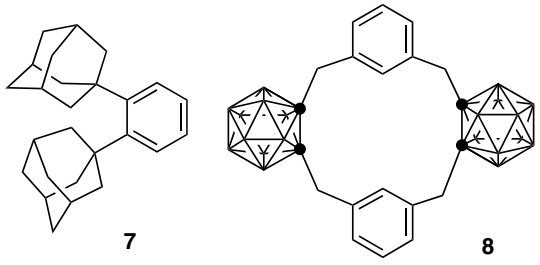


Fig. 4. Structures of related compounds.

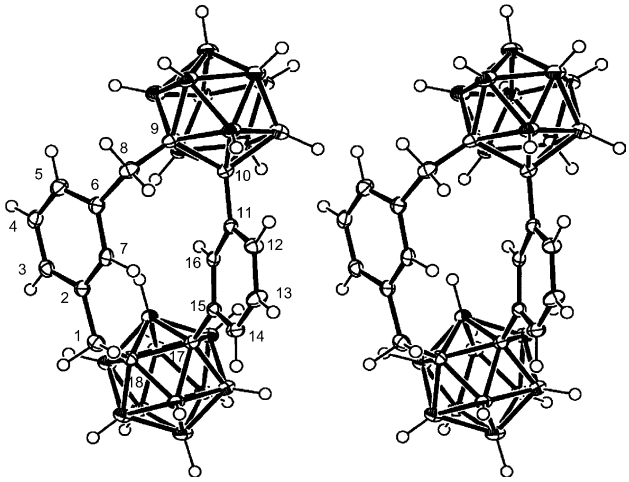


Fig. 5. Stereoview (parallel eyed) of **3** from the X-ray data.

standard values. However, the most characteristic feature of the structure appears to be the geometry of the two benzene rings, which is regulated by the 12-membered cyclic structure with the two metacyclophanes and the two carborane cages. The two benzene rings are stacked with the planes defined by the benzene rings meeting at an angle of 22.40°. This rigid conformation is retained in solution. The signal of the proton attached to the 2-position of the 1,3-xylylene group (C(7)) in the ^{1}H NMR spectrum appears at 4.09 ppm in $CDCl_3$, being significantly shifted to high-field from that of ordinary protons on a benzene ring. This is because the proton is located close to the other benzene ring. The distance between the proton and the ring-center of the other benzene ring is approximately 2.7 Å. The proton on the 2-position of the other benzene ring (C(16)) showed a more moderate high-field shift at 7.38 ppm, while the chemical shift was 7.66 ppm in the case of 1,3-bis(*o*-carboranyl)benzene (**6**). The chemical shifts of compound **3** are shown in Fig. 6(c). Macrocyclic compounds composed of carboranes linked by alkyl groups (carboracycles) have been reported [7]. Hawthorne et al. have

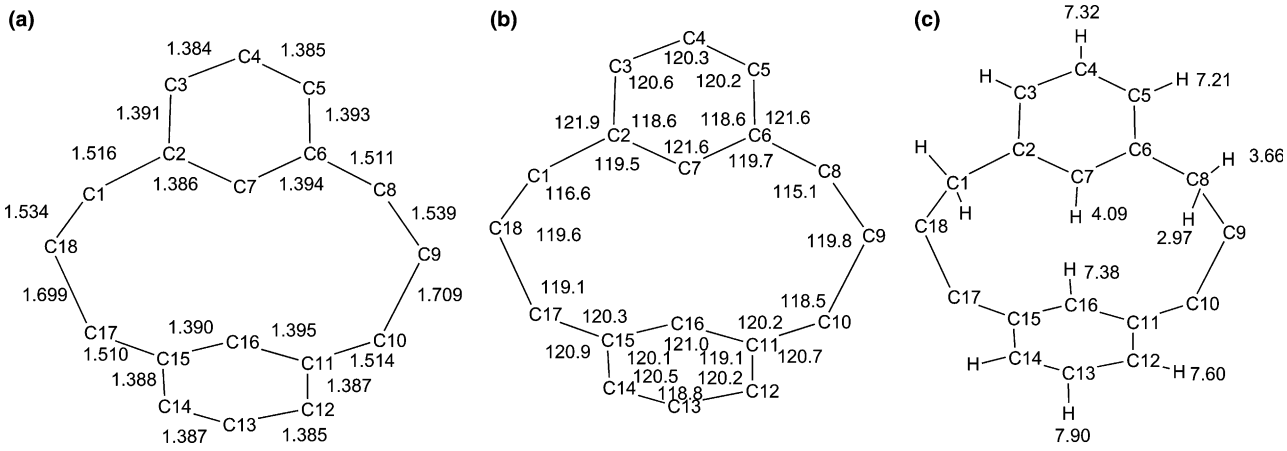


Fig. 6. Geometrical parameters for the carbon skeleton of **3** from X-ray analysis and ^{1}H NMR spectral data. (a) Interatomic distances (Å). (b) Bond angles (°). (c) Proton chemical shifts (ppm) in $CDCl_3$.

synthesized the 14-membered compound (**8**) with a combination of *o*-carborane and *m*-xylene units [7c]. In the case of **8**, the crystal structure revealed a bowl shape, in which the two benzene rings are situated at an angle of 80°. The protons at the 2-position of the 1,3-xylylene group are shifted to lower field, 7.84 ppm, in the ^{1}H NMR spectrum (in deuteroacetone), because the proton is situated near the plane of the other benzene ring (see Fig. 4).

3. Conclusion

We synthesized a molecule containing a distorted benzene ring (**2**) and an aromatic layered molecule (**3**), in which the structure features are regulated by the presence of bulky *o*-carborane cages. The results described here throw light on the steric effect of carboranes and should be helpful to develop a range of carborane-containing functionalized molecules that might find application in the field of supramolecular chemistry.

4. Experimental

4.1. General remarks

Melting points were obtained on a Yanagimoto micro hot stage without correction. Elemental analyses were carried out in the Microanalytical Laboratory, Faculty of Pharmaceutical Sciences, University of Tokyo, and were within ±0.3% of the theoretical values. Thin layer chromatography (TLC) was conducted on Merck DC-platten Kieselgel $60F_{254}$ (1.05715) with UV detection. ^{1}H NMR spectra were recorded with a JEOL JNM-A600 spectrometer (600 MHz) or JEOL JNM-FX-400 spectrometer (400 MHz), with tetramethylsilane (TMS) as an internal standard and chemical shifts are given in ppm as δ values from TMS. THF was distilled over sodium benzophenone ketyl. Benzene was distilled over calcium hydride and stored over sodium wire.

4.2. X-ray crystallography

X-Ray crystal structure analyses were performed on crystals of selected compounds [18]. Diffraction data were obtained with a Rigaku AFC7S four-circle diffractometer and a Rigaku RAXISIIC imaging plate diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71070 Å). Generally, indexing was performed from 3 oscillation images which were exposed for 4.0 min, and a total of 15 oscillation images within the 2θ value of 50.0° was collected in the case of using the imaging plate area detector.

4.3. Synthesis of 1,2-bis(o-carboran-1-yl)benzene 2

A solution of decaborane(14) (2.0 g, 16.4 mmol), 1,2-diethynylbenzene (**4**, 1.0 g, 7.9 mmol) and acetonitrile (4 ml) in dry benzene (40 ml) was refluxed under an Ar atmosphere for 72 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: *n*-hexane/dichloromethane 4:1) to afford **2** as a pale yellow solid (260 mg, 10%). The crude product was recrystallized from *n*-hexane. mp 198 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.5–3.3 (br, m, 20 H), 4.95 (br s, *2*H), 7.34 (*AA′BB′*, 2H), 7.75 (*AA′BB′*, *2*H); ^{13}C NMR (150.8 MHz, $CDCl_3$) δ 63.89 (cage C_2), 78.37 (cage C_1), 129.13 (Ar C_3, C_4), 132.70 (Ar C_1, C_6), 136.03 (Ar C_2, C_5); ^{11}B NMR (192.5 MHz, $CDCl_3$) δ −1.78 (2B), −3.26 (2B), −8.53 (8B), −10.24 (4B), −13.19 (4B); Anal. Calc. for $C_{10}H_{24}B_{20}$: C, 33.13; H, 7.23. Found: C, 33.37; H, 6.93%.

4.4. Synthesis of carboracycle 3

A solution of decaborane(14) (2.3 g, 19.0 mmol), 1,3-diethynylbenzene (**5**) (1.19 g, 9.4 mmol) and acetonitrile (5 ml) in dry benzene (50 ml) was refluxed under an Ar atmosphere for 48 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel (eluent: *n*-hexane/dichloromethane 4:1) to afford **6** as a colorless solid (1.48 g, 44%). The crude product was recrystallized from *n*-hexane to give colorless needles. M.p. 260–261 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 1.5–3.3 (br, m, 20H), 3.92 (br s, *2*H), 7.33 (t, $J = 8.1$ Hz, 1H), 7.51 (dd, $J = 2.0$ and 8.1 Hz, 2H), 7.66 (t, $J = 2.0$ Hz, 1H). Sodium hydride (60% in oil; 90 mg, 2.25 mmol) was washed with *n*-hexane, dried under reduced pressure and suspended in 5 ml of DME under an Ar atmosphere. A solution of 363 mg (1.0 mmol) of **6** in 5 ml of DME was added to it. This solution was stirred for 1 h, then 264 mg (1.0 mmol) of α,α′-dibromo-*o*-xylene was added and stirring was continued for 12 h at room temperature. The mixture was poured into 2 N HCl and the whole was extracted with ethyl acetate. The organic phase was washed with water and brine, dried over $MgSO_4$ and concentrated. Purification by column chromatography on silica gel (eluent: *n*-hexane/ethyl acetate 7:1) afforded 360 mg (77%) of **3** as a colorless solid. The crude product was recrystallized from diethyl ether/*n*-hexane to give colorless needles. M.p. >300 °C; ^{1}H NMR ($CDCl_3$) δ 1.5–3.3 (br, m, 20H), 2.97 (d, $J = 15.6$ Hz, 2H), 3.66 (d, $J = 15.6$ Hz, 2H), 4.09 (s, 1H), 7.21 (dd, $J = 1.8$ and 7.6 Hz, 2H), 7.32 (dd, $J = 7.1$ and 8.1 Hz, 1H), 7.38 (m, 1H), 7.60 (t, $J = 8.1$ Hz, 2H), 7.90 (dd, $J = 2.0$ and 8.1 Hz, 2H); ^{13}C NMR (150.8 MHz, $CDCl_3$) δ 40.28 (CH_2), 80.19 (cage C), 80.77 (cage C), 129.14 (Ar C_3, C_5), 129.28 (Ar C_4), 130.00 (Ar C_{12}, C_{14}), 130.74 (Ar C_{11}, C_{15}), 132.64 (Ar C_{13}), 132.76 (Ar C_7), 134.49 (Ar C_2, C_6), 137.95 (Ar C_{16}); ^{11}B NMR (192.5 MHz, $CDCl_3$) δ −1.54 (2B), −2.89 (2B), −8.07 (8B), −10.08 (6B), −10.86 (2B); Anal. Calc. for $C_{18}H_{32}B_{20}$: C, 46.53; H, 6.94. Found: C, 46.48; H, 6.85%.

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References

[1] R.E. Williams, Pure Appl. Chem. 29 (1972) 569–583.
[2] (a) M.F. Hawthorne, Angew. Chem., Int. Ed. Engl. 32 (1993) 950–984;
(b) A.H. Soloway, W. Tjarks, B.A. Barnum, F.G. Rong, R.F. Barth, I.M. Codogni, J.G. Wilson, Chem. Rev. 98 (1998) 1515–1562;
(c) Z.J. Lesnikowski, J. Shi, R.F. Schinazi, J. Organomet. Chem. 581 (1999) 156–169;
(d) W. Tjarks, J. Organomet. Chem. 614–615 (2000) 37–47.
[3] (a) A.G. Douglass, K. Czuprynski, W. Mierzwa, P. Kaszynski, Chem. Mater. 10 (1998) 2399–2402;
(b) A.G. Douglass, K. Czuprynski, W. Mierzwa, P. Kaszynski, J. Mater. Chem. 8 (1998) 2391–2398;
(c) P. Kaszynski, A.G. Douglass, J. Organomet. Chem. 581 (1999) 28–38;
(d) P. Kaszynski, Collect. Czech. Chem. Commun. 64 (1999) 895–956;
(e) K. Ohta, A. Januszko, P. Kaszynski, T. Nagamine, G. Sasnouski, Y. Endo, Liq. Cryst. 31 (2004) 1–12.
[4] (a) Y. Endo, Y. Taoda, Tetrahedron Lett. 40 (1999) 9073–9076;
(b) Y. Endo, T. Sawabe, Y. Taoda, J. Am. Chem. Soc. 122 (2000) 180–181;
(c) Y. Endo, Y. Taoda, Tetrahedron Lett. 42 (2001) 6327–6331;
(d) Y. Taoda, Y. Endo, Tetrahedron Lett. 44 (2003) 8177–8181.
[5] (a) Y. Endo, T. Iijima, K. Ohta, H. Kagechika, E. Kawachi, K. Shudo, Chem. Pharm. Bull. 47 (1999) 585–587;
(b) Y. Endo, T. Iijima, Y. Yamakoshi, M. Yamaguchi, H. Fukasawa, K. Shudo, J. Med. Chem. 42 (1999) 1501–1504;
(c) Y. Endo, T. Iijima, Y. Yamakoshi, A. Kubo, A. Itai, BioMed. Chem. Lett. 9 (1999) 3313–3318;
(d) Y. Endo, T. Yoshimi, T. Iijima, Y. Yamakoshi, BioMed. Chem. Lett. 9 (1999) 3387–3392;
(e) Y. Endo, K. Yaguchi, E. Kawachi, H. Kagechika, BioMed. Chem. Lett. 10 (2000) 1733–1736;
(f) Y. Endo, T. Iijima, Y. Yamakoshi, H. Fukasawa, C. Miyaura, M. Inada, A. Kubo, A. Itai, Chem. Biol. 8 (2001) 331–345;
(g) Y. Endo, T. Yoshimi, C. Miyaura, Pure Appl. 75 (2003) 1197–1205.
[6] (a) X. Yang, W. Jiang, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc 114 (1992) 9719–9721;
(b) J. Muller, K. Base, T.F. Magnera, J. Michl, J. Am. Chem. Soc. 114 (1992) 9721–9722;
(c) N.M. Colquhoun, P.L. Herbertson, K. Wade, I. Baxter, D.J. Williams, Macromolecules. 31 (1998) 1694–1696;
(d) W. Jiang, D.E. Harwell, M.D. Mortimer, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 35 (1996) 4355–4359.
[7] (a) R. Coult, M.A. Fox, W.R. Gill, P.L. Herbertson, J.A.H. MacBride, K. Wade, J. Organomet. Chem. 462 (1993) 19–29;
(b) E. Clegg, W.R. Gill, J.A.H. MacBride, K. Wade, Angew. Chem., Int. Ed. Engl. 32 (1993) 1328;
(c) W. Jiang, T. Chizhevsky, M.D. Mortimer, W. Chen, C.B. Knobler, S.E. Johnson, F.A. Gomez, M.F. Hawthorne, Inorg. Chem. 35 (1996) 5417–5426;
(d) W.R. Gill, P.L. Herbertson, J.A.H. MacBride, K. Wade, J. Organomet. Chem 507 (1996) 249–255.
[8] (a) X. Yang, C.B. Knobler, Z. Zheng, M.F. Hawthorne, J. Am. Chem. Soc. 116 (1994) 7142–7159;
(b) Z. Zheng, M. Diaz, C.B. Knobler, M.F. Hawthorne, J. Am. Chem. Soc. 117 (1995) 12338–12339;
(c) Z. Zheng, C.B. Knobler, M.D. Mortimer, G. Kong, M.F. Hawthorne, Inorg. Chem. 35 (1996) 1235–1243.
[9] (a) C. Songkram, A. Tanatani, R. Yamasaki, K. Yamaguchi, H. Kagechika, Y. Endo, Tetrahedron Lett. 41 (2000) 7065–7070;
(b) Y. Endo, C. Songkram, R. Yamasaki, A. Tanatani, H. Kagechika, K. Takaishi, K. Yamaguchi, J. Organomet. Chem. 657 (2002) 48–58.
[10] (a) A. Tanatani, H. Kagechika, I. Azumaya, R. Fukutomi, Y. Ito, K. Yamaguchi, K. Shudo, Tetrahedron Lett. 38 (1997) 4425–4428;
(b) K. Yamaguchi, G. Matsumura, H. Kagechika, I. Azumaya, Y. Ito, A. Itai, K. Shudo, J. Am. Chem. Soc. 113 (1991) 5474–5475.

[11] C. Songkram, R. Yamasaki, A. Tanatani, K. Takaishi, K. Yamaguchi, H. Kagechika, Y. Endo, Tetrahedron Lett. 42 (2001) 5913–5916.
[12] C. Songkram, R. Takaishi, K. Yamaguchi, H. Kagechika, Y. Endo, Tetrahedron Lett. 42 (2001) 6365–6368.
[13] S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, Synthesis (1980) 627–629.
[14] (a) M.M. Teplyakov, I.A. Khotina, Ts.L. Gelashvili, V.V. Kovshak, Dokl. Akad. Nauk. SSSR 271 (1980) 874–877;
(b) N.D. Tinker, K. Wade, T.G. Hibbert, PCT Int. Appl. WO 98/21216.
[15] W. Jiang, C.B. Knobler, M.F. Hawthorne, Inorg. Chem. 35 (1996) 3056–3058.
[16] (a) J. Nakayama, R. Hasemi, J. Am. Chem. Soc. 112 (1990) 5654–5655;
(b) J. Nakayama, R. Hasemi, K. Yoshimura, Y. Sugihara, S. Yamaoka, J. Org. Chem. 63 (1998) 4912–4924;
(c) J. Nakayama, personal communication. Part of the geometrical parameters for **7** have been described in the literature [16a] as preliminary results. Final results have not yet been published.
[17] (a) P.T. Brain, J. Cowie, D.J. Donohoe, D. Hnyk, D.W.H. Rankin, D. Reed, B.D. Reid, H.E. Robertson, A.J. Welch, M. Hofmann, P.v.R. Schleyer, Inorg. Chem. 35 (1996) 1701–1708;
(b) R.L. Thomas, G.M. Rosair, A.J. Welch, Acta Cryst. C 52 (1996) 1024–1026.
[18] K.P. Callahan, M.F. Hawthorne, J. Am. Chem. Soc. 85 (1973) 4574–4580.