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Solid-state supramolecular array through cooperative π–π interactions of 1-(2-methoxyphenyl)-*o*-carborane

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Abstract—Dicarba-*closo*-dodecaborane (carborane) has received much attention as a building block for supramolecular assemblies and bioactive compounds. Among the carborane isomers, 1,2-dicarba-*closo*-dodecaborane (*o*-carborane) has unique chemical properties, including the ability of the *o*-carborane C–H hydrogens to form H-bonds. We have designed and synthesized 1-(2-methoxyphenyl)-*o*-carborane **1a** to study its ability to form an intramolecular H-bond between the *o*-carborane C–H hydrogen and various H-bond acceptors both in solution and in the solid state. Intramolecular H-bonding ability in solution was evaluated by means of ^{1}H NMR spectroscopic measurements of the C–H hydrogen signal. The signal of the C–H hydrogen of **1a** showed a remarkable downfield shift in $CDCl_3$ and various other solvents, i.e., the shift was almost solvent-independent. We suggest that **1a** forms an intramolecular H-bond in these solvents. Crystal structure analysis of **1a** showed a C–H···O distance of 2.05 Å and a nearly planar torsion angle C(2)–C(1)–C(7)–C(8) of 6.5°, indicating intramolecular C–H···O H-bond formation in the solid state. The crystal packing of **1a** indicates that a supramolecular array is stabilized by cooperative π–π stacking interactions among the methoxyphenyl groups and by hydrophobic interactions of the *o*-carborane cages. DFT calculations indicate that the strength of the intramolecular H-bond of **1a** is about 3.53 kcal/mol. These observations indicate the potential value of *o*-carborane in supramolecular chemistry and materials chemistry; it should be possible to design novel materials by utilizing both the H-bonding ability of the *o*-carborane C–H hydrogen and the high hydrophobicity of the *o*-carborane cage.

1. Introduction

The potential application of 1,2-dicarba-*closo*-dodecaborane, *o*-carborane, as a building block for bioactive compounds, supramolecular assemblies, and macrocyclic molecules containing carboranes (carboracycles) has been the subject of many reports.[1] *o*-Carborane is an icosahedral structure and each vertex bears a hydrogen atom. It has high hydrophobicity, which is similar to that of hydrocarbons and forms strong hydrophobic interactions with various molecules.[2] Furthermore, the C–H hydrogens of *o*-carborane are highly acidic (pK_a=22.0), owing to the electron deficiency of the carborane cage, and consequently have the potential for hydrogen-bond (H-bond) formation.[3] These contrasting features, i.e., high hydrophobicity and H-bonding ability, both favor strong intramolecular or intermolecular interactions. Thus, supramolecular assemblies utilizing *o*-carborane are expected to be mainly generated through hydrophobic interaction and H-bonding via the acidic *o*-carborane C–H vertices. *o*-Carborane C–H hydrogens interact with various substituents, such as halogens[4] and π-rich systems,[5] as well as H-bond acceptors.[6] It is especially interesting in relation to the potential of *o*-carborane C–H hydrogen for H-bond formation that 3-iodo-*o*-carborane forms a beautiful zigzag network structure through intermolecular C–H···I interactions as shown in the crystal structure.[4b] Interactions involving *o*-carborane C–H hydrogen in crystal structures have been studied in detail,[7] and also there are two reports concerning solution structures.[8]

We have reported that 1-(2-methoxyphenyl)-*o*-carborane (**1a**) exhibits an intramolecular C–H···O interaction between the C–H hydrogen and the oxygen atom of the methoxyl group in various solvents.[9] In this article, we confirm and extend our observations of an intramolecular C–H···O interaction both in solution and in the solid state by means of ^{1}H NMR spectroscopy and X-ray crystal structure analysis. We also present the results of density functional theory (DFT) calculations, which further support our findings.

Keywords: *o*-Carborane; C–H···O interaction; Hydrogen bond; Supramolecular array; ^{1}H NMR study; DFT calculations.
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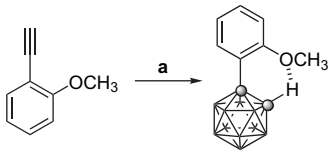
2. Results and discussion

2.1. The C–H···O interaction of 1-(2-methoxyphenyl)-*o*-carborane in solution

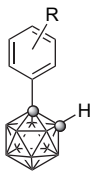
In contrast to *inter*molecular interactions, *intra*molecular interactions are largely immune to the molecular environment. As a result, they can be investigated at a high level of accuracy by employing a variety of methods. Bearing this in mind, we designed 1-(2-methoxyphenyl)-1,2-dicarba-*closo*-dodecaborane **1a** as a candidate for intramolecular H-bond formation between *o*-carborane C–H hydrogen and various substituents introduced at the *ortho* position of the benzene ring. Compound **1a** was readily synthesized by the cyclization of an acetylene derivative with decaborane(14) in the presence of acetonitrile as a Lewis base, as shown in Scheme 1.[10]



Scheme 1. Synthesis of 1-(2-methoxyphenyl-*o*-carborane) **1a**. Reagents: (a) decaborane(14), CH_3CN, benzene.

The ^1H NMR chemical shift values of C–H hydrogen of *o*-carborane in **1a** and its derivatives, measured at 25 °C in $CDCl_3$ with a 270 MHz NMR spectrometer, are summarized in Table 1. The chemical shift value of C–H hydrogen in phenyl-*o*-carborane **1b** was 3.97 ppm, which was taken as a reference value in this study. The introduction of a substituent into the benzene ring of **1b** shifts the C–H hydrogen signal owing to the anisotropic effect.[11] The chemical shift values of 3-nitrophenyl-*o*-carborane **1c** and 4-nitrophenyl-*o*-carborane **1d** were 4.03 and 4.02 ppm, respectively, reflecting the electron-withdrawing effect of the nitro group. An electron-donating group, such as the amino group, shifted the C–H hydrogen signal to upper field (Table 1; **1e** and **1f**). We have already reported that the remarkable downfield shift of the C–H hydrogen of **1a** was not due to anisotropic or steric effects of the methoxyl group, but rather due to the formation of an intramolecular H-bond.[12] Compounds **1g** and **1h**, which can be easily prepared by nitration of **1a** and subsequent reduction, exhibited interesting chemical shift changes. The introduction of a nitro group as an electron-withdrawing group at the *para* position to the methoxyl group in **1a** led to a remarkable upfield shift of the *o*-carborane C–H hydrogen ^1H NMR signal (Table 1; **1g**), in spite of the introduction of the electron-withdrawing group. In addition, the introduction of an amino group into **1a** induced a slight downfield shift of the C–H hydrogen signal (Table 1; **1h**) in opposition to the general electronic effect. These interesting results can be ascribed to the interplay between intramolecular C–H···O interaction and the electronic effects of the two oxygen atom lone-pairs.

Table 1. Effect of nitro or amino group on the ^1H NMR chemical shift values of *o*-carborane C–H hydrogen



Compound	Substituent (R)	Chemical shift $CDCl_3$ (ppm)
1a	OCH_3	5.36
1b	H	3.97
1c	3-NO_2	4.03
1d	4-NO_2	3.93
1e	3-NH_2	4.02
1f	4-NH_2	3.83
1g	2-OCH_3–5-NO_2	5.18
1h	2-OCH_3–5-NH_2	5.38

To seek further evidence of H-bond formation between the oxygen atom in the methoxyl group and *o*-carborane C–H hydrogen in solution, we evaluated solvent effects on the *o*-carborane C–H hydrogen signals of **1a** and **1b** by ^1H NMR study (Table 2). The chemical shift value of the C–H hydrogen in **1b** was the smallest in benzene-d_6, 2.92 ppm, and the largest in DMSO-d_6, 5.79 ppm. There was a remarkable solvent effect on the ^1H NMR spectrum of **1b**, and the difference (Δppm) was 2.87 ppm. The effects in the case of **1b** were caused by the shielding effect of the solvent benzene ring and by intermolecular H-bond formation with oxygen of DMSO.[11] The C–H hydrogen of **1b** may also form a H-bond in $CDCl_3$, CD_3CN or CD_3OD (3.97, 4.67, and 5.09 ppm, respectively). On the other hand, the C–H hydrogen of **1a** exhibited remarkable downfield shifts in all solvents (benzene-d_6, 5.22 ppm; $CDCl_3$, 5.36 ppm; CD_3CN, 5.71 ppm; CD_3OD, 5.67 ppm; DMSO-d_6, 5.98 ppm), and there was no solvent effect. The differences are very small (e.g., 0.76 ppm), although there should be a shielding effect of the aromatic ring in benzene-d_6. We conclude from the above results that the C–H hydrogen of **1a** forms a stable, intramolecular H-bond with the oxygen atom of the methoxyl group, while the C–H hydrogen of **1b** interacts with solvent molecules.

Table 2. Comparison of chemical shift values between **1a** and **1b** in various deuterated solvents

Solvent	Chemical shift (ppm) of **1b**	Chemical shift (ppm) of **1a**
Benzene-d_6	2.92	5.22
$CDCl_3$	3.97	5.36
CD_3CN	4.67	5.71
CD_3OD	5.09	5.67
DMSO-d_6	5.79	5.98
Δ ppm (max−min)	2.87	0.76

2.2. The C–H···O interaction of 1-(2-methoxyphenyl)-*o*-carborane in the solid state: X-ray diffraction study of 2-methoxyphenyl-*o*-carborane

Colorless crystals of **1a** were grown from a mixed solution of *n*-hexane and ethyl acetate by slow evaporation of the solvents. The structure of **1a** in the solid state was confirmed by single-crystal X-ray diffraction analysis (Fig. 1). Crystal data of **1a** are shown in Table 3. The aromatic rings of

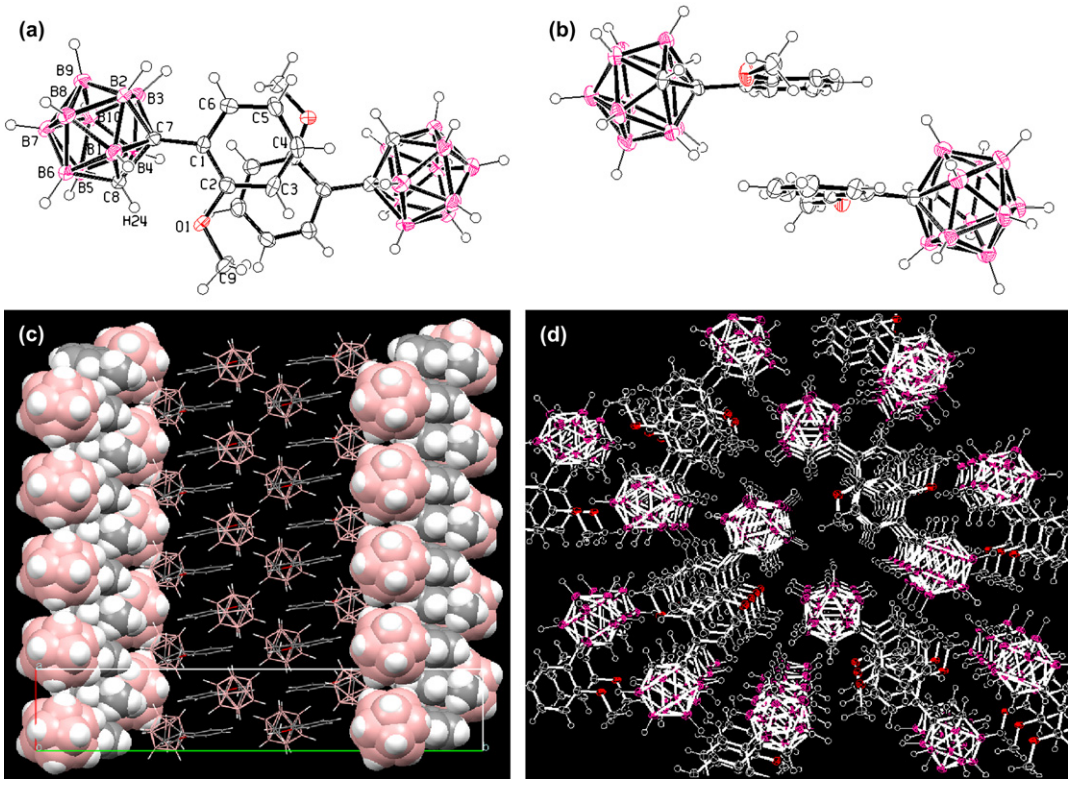


Figure 1. Various views of the X-ray structure of **1a**: (a) molecular structure with offset π–π stacking interactions (top view). (b) Molecular structure with offset π–π stacking interactions (side view). (c) Packing diagram of the supramolecular array (side view). (d) Packing diagram of the supramolecular array (top view).

Table 3. Crystal data of **1a**

Compound	**1a**
Formula	$C_9H_{18}B_{10}O$
M_r	250.33
Recryst. solvent	Ethyl acetate–*n*-hexane
Crystal system	Monoclinic
Lattice parameter	
a (Å)	7.120(12)
b (Å)	38.470(7)
c (Å)	10.351(18)
β (°)	95.625(3)
V (Å^3)	2821.8(8)
Space group	*P*2(1)/*n*
Z value	8
ρ_{calc} (Mg/m^3)	1.178
Absorption coefficient (mm^{-1})	0.06
Crystal size (mm^3)	0.45×0.30×0.20
Temperature (K)	150
2*θ* max (°)	55.0
Reflections collected	15,047
Independent reflections	5995 [*R*(int)=0.0973]
Data/restraints/parameters	5995/0/451
Goodness-of-fit on F^2	0.72
Residuals: *R*, R_w	0.0583, 0.117
Largest diff. peak and hole (e Å^{-3})	0.242 and −0.231

compound **1a** form a parallel-displaced stacked structure stabilized by intermolecular π–π interactions (Fig. 1(a) and (b)). In compound **1a**, the torsion angle of C(2)–C(1)–C(7)–C(8) is nearly planar, being 6.5(4)°. The bond distance between H(24) and O(1) in the crystal structure of **1a** is 2.05(3) Å [(H)C(8)···O(1) is 2.77(4) Å], which is considerably shorter than the sum (2.72 Å) of the van der Waals radii of hydrogen and oxygen.[13] The torsion angle formed by the intramolecular H-bond, C(8)–H(24)···O(1), was 133(2)°. Compound **1a** forms a pseudo-planar six-membered ring O(1)–C(2)–C(1)–C(7)–C(8)–H(24) connected through an intramolecular C–H···O bond. Thus, we have confirmed that **1a** forms an intramolecular C–H···O bond in the solid state, as it does in solution.[9] Geometrical parameters of **1a** in comparison with those reported for 1-phenyl-*o*-carborane are shown in Table 4.[14] The bond lengths of **1a** related to intramolecular C–H···O bond formation were C(8)–H(24) 0.92(3) Å, C(8)–C(7) 1.669(4) Å, C(7)–C(1) 1.509(4) Å, C(1)–C(2) 1.411(4) Å, C(2)–O(1) 1.385(3) Å, and O(1)–C(9) 1.438(3) Å. The bond lengths of C(8)–C(7) and C(1)–C(2) are extended in comparison with those of 1-phenyl-*o*-carborane. The bond length of C(2)–O(1) is shorter than the normal C–O bond (1.43 Å). In the stacked complex of **1a**, the distance and azimuthal angle between the centroids of two aromatic rings are 4.123 Å and 4.04°, respectively (Fig. 1(c) and (d)). This intermolecular π–π stacking interaction is of a parallel-displaced (PD) type. According to high-level gas-phase theoretical calculations on the benzene dimer, the interaction between parallel-displaced benzene molecules amounts to 2.8 kcal/mol whereas those between the T-shaped and parallel benzene molecules are slightly weaker being 2.7 and 1.8 kcal/mol, respectively.[15] Interestingly, **1a** forms a favorite supramolecular array through consecutive intermolecular π–π stacking between alternately oriented methoxyphenyl groups. This π–π interaction seems to be quite strong, because the center-to-center distance between the aromatic rings of **1a** is shorter than that of standard aromatic–aromatic π–π interaction distances observed in the solid state; the standard distance is about 5 Å.[16] Judging from the azimuthal angle, we suggested the possibility that

Table 4. Comparison of selected geometrical parameters of **1a** and 1-phenyl-*o*-carborane

Distance and angle	**1a**	1-Ph-*o*-carborane
C(1)–C(2)	1.411(4)	1.398(2)
C(2)–C(3)	1.373(4)	1.391(2)
C(1)–C(6)	1.397(4)	1.385(2)
C(1)–C(7)	1.509(4)	1.511(2)
C(7)–C(8)	1.669(4)	1.649(2)
C(7)–B(1)	1.735(5)	1.736(2)
C(7)–B(2)	1.715(5)	1.716(2)
C(7)–B(3)	1.720(4)	1.724(2)
C(7)–B(4)	1.742(5)	1.742(2)
C(8)–B(1)	1.711(5)	1.718(2)
C(8)–B(4)	1.714(5)	1.722(2)
C(8)–B(5)	1.685(5)	1.698(2)
C(8)–B(6)	1.678(5)	1.701(2)
B(1)–B(6)	1.777(5)	1.780(2)
B(5)–B(6)	1.775(5)	1.786(3)
B(4)–B(5)	1.777(5)	1.784(2)
C(2)–C(1)–C(7)	125.7(3)	121.26(14)
C(6)–C(1)–C(7)	117.5(3)	119.60(13)
C(1)–C(7)–C(8)	123.0(2)	118.76(12)

cooperative effects enhance the strength of the ensuing π–π stacking interactions. Moreover, besides these cooperative π–π interactions in the crystal, the supramolecular array is supported by hydrophobic interactions among the carborane cages of **1a**.

2.3. DFT calculation study of 2-methoxyphenyl-*o*-carborane

To investigate the effects of substituents on the intramolecular H-bond, C–H···O, we performed a series of DFT calculations on **1a**, **1g**, and **1h**. The geometries of the three molecules were optimized at the PBE1PBE/DGDZVP level of theory. Frequency calculations confirmed that the computated geometries represent real vibrational frequencies and, hence, they are all local minima on the corresponding potential energy surfaces. As shown in Figure 2, the H-bond distance computed for **1a** is 2.054 Å, which agrees well with the experimental value of 2.05(3) Å (see above). The introduction of a nitro group at C-5 in the substituted phenyl ring has the effect of lengthening the C–H···O bond by ~0.02 Å (2.076 Å) whereas the introduction of an amino group has the effect of shortening the C–H···O bond by 0.06 Å (2.049 Å). Clearly, these two groups exert opposing electronic effects on the intramolecular H-bond, thereby either weakening or strengthening it. This result is confirmed by the experimental values of the chemical shift of the *o*-carborane C–H hydrogen (Table 1) and by the magnitude of the natural charge born by the oxygen atom involved in the formation of the intramolecular H-bond being −0.58 au (**1a**), −0.57 au (**1g**), and −0.59 au (**1h**).

Next, we set out to estimate the strength of the intramolecular H-bonds of **1a**, **1g**, and **1h**. To begin with, we optimized the geometries of the corresponding rotamers having the torsion angle (H)C–C–C–C(OMe) set at 180°. Note that this approach can be employed only when the molecular skeleton that supports the intramolecular H-bond does not change significantly when the latter is disrupted, for example, upon rotation about a single bond. This, however, is not always the case.[17] The energy difference between the H-bonded and non-H-bonded forms of these three molecules provides the following estimate of the H-bond strength: 3.53 kcal/mol (**1a**), 2.39 kcal/mol (**1g**), and 4.09 kcal/mol (**1h**). If the simple rule of thumb that stronger interaction energies correspond to shorter H-bond distances is accepted, then the above energy values are fully consistent with the computed distances of the C–H···O bonds of **1a**, **1g**, and **1h** (Fig. 2).

3. Conclusions

We have designed and synthesized 1-(2-methoxyphenyl)-*o*-carborane **1a**, and evaluated its ability to form a H-bond both in solution and in the solid state. NMR spectroscopic measurements and X-ray diffraction analyses indicate that compound **1a** forms an intramolecular H-bond between the *o*-carborane C–H hydrogen and the oxygen atom of the methoxyl group in both states. DFT calculations indicate that the C–H···O interaction energy of **1a** is 3.53 kcal/mol. Finally, it is noteworthy that, in the crystal state, **1a** forms a supramolecular array, which is stabilized by cooperative π–π stacking interactions among the substituted phenyl rings and by hydrophobic interactions among the *o*-carborane cages. The present results demonstrate that *o*-carborane molecules would be useful building blocks in supramolecular and materials chemistry, owing to the combination of the H-bonding ability of the *o*-carborane C–H hydrogen and the high hydrophobicity of the *o*-carborane cage.

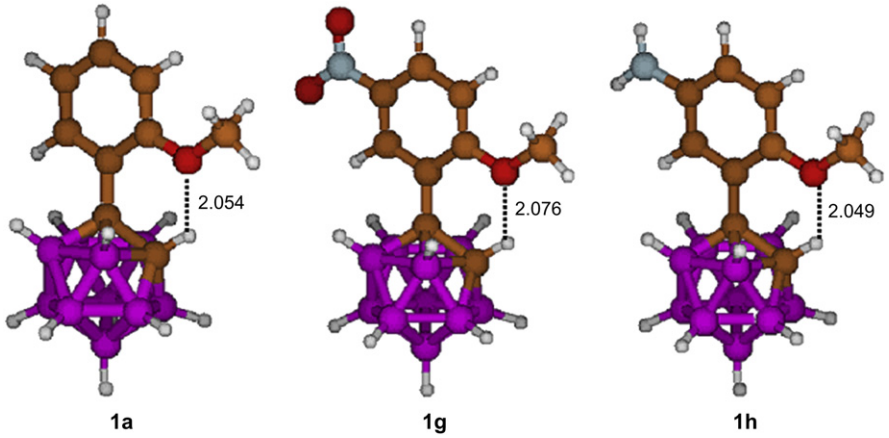


Figure 2. DFT-optimized structures of **1a**, **1g**, and **1h** (the H-bond distances are given in Å).

4. Experimental section

4.1. General considerations

Melting points were determined with a Yanaco micromelting point apparatus and were not corrected. ^{1}H NMR, ^{13}C NMR, and ^{10}B NMR spectra were recorded with JEOL JNM-EX-270, JNM-LA-400, and JNM-LA-600 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 splitting patterns are designated as follows: s (singlet), d (doublet), and m (multiplet). Mass spectra were recorded on a JEOL JMS-DX-303 spectrometer. Elemental analyses were performed with a Perkin–Elmer 2400 CHN spectrometer. Thin layer chromatography (TLC) was conducted on Merck DC-platten Kieselgel $60F_{254}$ with UV detection.

4.2. 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 s.r.o. (Prague, Czech Republic). Compounds **1b–1f**[18] were prepared according to the literature.

4.2.1. 1-(2-Methoxyphenyl)-1,2-dicarba-*closo*-dodecaborane (1a). A mixture of decaborane(14) (3.05 g, 25.0 mmol) and 2-methoxyethynylbenzene (3.0 g, 22.7 mmol) in 10 mL of dry CH_3CN and 40 mL of dry benzene was refluxed for 72 h under an Ar atmosphere. The solvent was removed under reduced pressure. The resulting residue was purified by silica gel column chromatography with *n*-hexane to give 2.72 g (48%) of the title compound as a colorless solid. Colorless needles (AcOEt–*n*-hexane); mp 132–133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.50–3.50 (br m, 10H), 3.85 (s, 3H), 5.36 (s, 1H), 6.89 (dd, J=1.1, 8.4 Hz, 1H), 6.96 (ddd, J=1.1, 7.3, 8.1 Hz, 1H), 7.32 (ddd, J=1.5, 7.3, 8.4 Hz, 1H), 7.61 (dd, J=1.5, 8.1 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ (ppm) 55.8, 59.9, 75.0, 112.2, 121.2, 121.3, 130.7, 132.4, 155.9; ^{11}B NMR (192 MHz, $CDCl_3$) δ (ppm) −13.6, −11.5, −9.3, −3.8; MS (EI) *m/z*: 250 (M^+, 100%). Anal. Calcd for $C_9H_{18}B_{10}O$: C, 43.18; H, 7.25. Found: C, 42.89; H, 7.30.

4.2.2. 1-(2-Methoxy-5-nitrophenyl)-1,2-dicarba-*closo*-dodecaborane (1g). A solution of **1a** (100 mg, 0.40 mmol) in 2 mL of CH_2Cl_2 was added dropwise to a solution of 2 mL of concentrated HNO_3 and concentrated H_2SO_4 (15:85 v/v) at 0 °C. The mixture was stirred at room temperature for 4 h, then poured onto ice, and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The resulting residue was purified by silica gel column chromatography with 1:3 AcOEt–*n*-hexane to give 83 mg (70%) of the title compound as a colorless solid. Colorless needles (AcOEt–*n*-hexane); mp 224–225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 1.50–3.50 (br m, 10H), 4.00 (s, 3H), 5.18 (s, 1H), 7.02 (d, J=9.2 Hz, 1H), 8.24 (dd, J=2.6, 9.2 Hz, 1H), 8.58 (d, J=2.6 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ (ppm) 56.9, 59.3, 73.0, 112.4, 122.3, 126.4, 128.5, 141.6, 160.4; ^{11}B NMR (192 MHz, $CDCl_3$) δ (ppm) −12.0, −10.3, −8.1, −7.5, −2.0; MS (EI) *m/z*: 295 (M^+, 100%). Anal. Calcd for $C_9H_{17}B_{10}NO_3$: C, 36.60; H, 5.80; N, 4.74. Found: C, 36.40; H, 6.05; N, 4.76.

4.2.3. 1-(2-Methoxy-5-aminophenyl)-1,2-dicarba-*closo*-dodecaborane (1h). A solution of **1g** (355 mg, 1.20 mmol) in 60 mL of EtOH was hydrogenated over 10% Pd–C (120 mg) at room temperature for 1 h under atmospheric pressure of hydrogen. After removal of the catalyst by filtration, the filtrate was concentrated to give 286 mg (90%) of the title compound as a brown solid. Brown prisms (AcOEt–*n*-hexane); mp 144–145 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ (ppm) 1.50–3.50 (br m, 10H), 3.51 (s, 2H), 3.76 (s, 3H), 5.38 (s, 1H), 6.64 (dd, J=2.6, 8.7 Hz, 1H), 6.71 (d, J=8.7 Hz, 1H), 6.94 (d, J=2.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ (ppm) 56.3, 59.8, 75.0, 113.9, 117.2, 118.9, 121.8, 140.2, 148.9; ^{11}B NMR (192 MHz, $CDCl_3$) δ (ppm) −12.3, −10.0, −8.1, −2.7; MS (EI) *m/z*: 265 (M^+, 100%); HRMS Calcd for $C_9H_{19}B_{10}NO$: 265.2470. Found: 265.2485.

4.3. X-ray crystallography

Details of data collection and structure refinement for **1a** are given in Table 1. Diffraction data were obtained with a Rigaku AFC7S four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ=0.71073 Å). Generally, indexing was performed from three oscillation images exposed for 4.0 min, and a total of 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[19] and refined by the full matrix least-squares technique on F2 using SHELXL-97.

4.4. Method of calculation

All the DFT calculations were performed with the parallel version of the Gaussian 03 (version C.02) software package.[20] The hybrid functional of Perdew, Burke, and Ernzerhof,[21] hereafter referred to as PBE1PBE, was employed in combination with the DGauss double-zeta valence polarization (DGDZVP) basis set.[22,23] Atomic charges were computed with the natural population analysis method of Weinhold and co-workers,[24] which is known to overcome some of the deficiencies of the canonical Mulliken-type population analysis. Pre- and post-processing were performed with the GaussView (version 3.0)[25] and Molden (version 4.4)[26] graphical user interfaces.

4.5. Supplementary data

Supplementary crystallographic data for this paper can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1223 336033; or deposit@ccdc.cam.ac.jk). CCDC: 655977 contain the supplementary crystallographic data for this paper.

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