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Most Stable Conformation of the Cyclopropane Ring Attached at a Carbon Atom in a 1,2-Dicarba-*closo*-dodecaborane(12) System

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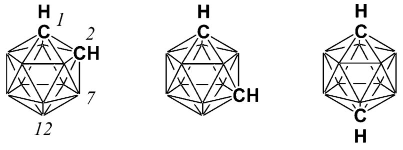
We obtained two crystal structures of electronically interesting dicarba-*closo*-dodecaborane(12)s (hereafter, "carboranes") substituted with a cyclopropyl group at a caged carbon atom, i.e., *C*-cyclopropyl-*o*-carborane (**4**) and *C*-cyclopropyl-*o*-carboranylphenylmethanol (**9**), at 123 K. In these *C*-cyclopropyl-*o*-carboranes, the cyclopropyl group adopted a slightly twisted perpendicular conformation with respect to the electron-deficient carbon−carbon (C−C) bond axis in the *o*-carborane cage. In contrast, it has previously been shown that a phenyl group substituted at the caged carbon atom, i.e., *C*-phenyl-*o*-carborane (**3**), is almost parallel to this axis at both 150 and 199 K. In other words, the π system of the phenyl ring adopted an almost bisected conformation in **3**. The preferred conformation of the cyclopropane ring in these *C*-cyclopropyl-*o*-carboranes was compared among the solid, the solution, and the gaseous states and was retained under the present conditions. Moreover, we found that the C−C bond length in the *o*-carborane cage not only varied along the rotation of the cyclopropyl group in **4** but also was longer than that in **3**, which bears a phenyl group at the dominant conformation. These phenomena may be related to homoconjugations between the caged *o*-carborane system that serves as an electron acceptor and the homoconjugative substituent that serves as an electron donor. In these *C*-cyclopropyl-*o*-carboranes, two types of homoconjugations would result in a slightly twisted perpendicular conformation and **4** would be more strongly stabilized than would the phenyl derivative **3**. On the basis of these studies, we propose the existence of a third type of strongly stabilizing interactive geometry for a cyclopropane ring in an *o*-carborane system.

Introduction

Due to their topology (*ortho*, *meta*, and *para* isomers), geometry (almost pure icosahedral architecture), high symmetry (both the *ortho* and the *meta* isomers have C_{2v} symmetry and the *para* isomer has D_{5d} symmetry), and stability (a three-center, two-electron interaction), carboranes have been regarded as a three-dimensional benzene (Chart 1).[1]

CHART 1. Three Topological Isomers of Icosahedral Dicarba-*closo*-dodecaborane(12)[a]



***o*-Carborane** ***m*-Carborane** ***p*-Carborane**

[a] Vertexes show the BH groups.

To study the electronic structure of carboranes, we have recently conducted attempts to generate carboranyl carbocations by using both *C*-carboranyl tosylates and triflates under solvolytic conditions, as well as treatment with superacids.[2] The anchimeric assistance of both homoconjugative and hyperconjugative substituents was also investigated, as demonstrated by a successful strategy devised for the solvolytic generation of a phenyl cation. In a previous study, we concluded that all of the topological isomers of carborane were not electronically similar to either cyclic alkane or aromatic benzene. In other words, it appeared that the extreme electron deficiency (in particular, at carbon atoms) rendered carborane systems extremely stable molecular species. All homoconjugative and hyperconjugative substituents failed to stabilize and/or generate the carboranyl carbocation under solvolytic conditions. However, in that study, we prepared a number of compounds of interest in terms of the electronic structure of the carborane cages; i.e., we obtained some *o*-carboranes bearing a cyclopropyl group at a caged carbon atom (Chart 2). Despite their simple and electronically interesting structures, which are similar to those of a cyclopropylbenzene, these *C*-cyclopropyl-*o*-carboranes have thus far not been described in the literature. In this study, we focused on the electronic structure of *C*-cyclopropyl-*o*-carboranes and investigated the crystal structures at 123 K. We provide here a detailed analysis of these crystal structures, as supported by the theoretical calculations. On the basis of these

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(1) Schleyer, P. v. R.; Najafian, K. *Inorg. Chem.* **1998**, *37*, 3454−3470.

(2) Tsuji, M. *J. Org. Chem.* **2003**, *68*, 9589−9597.

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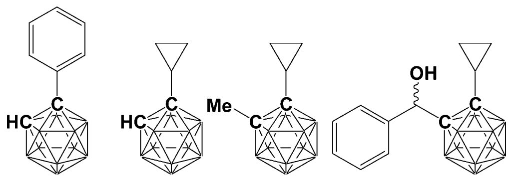
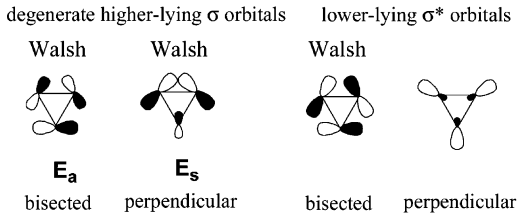
CHART 2. *C*-Cyclopropyl-*o*-carboranes and *C*-Phenyl-*o*-carborane



3 4 6 9

CHART 3. Homoconjugative Cyclopropane Walsh Orbitals and the Lower-Lying σ^* Orbital



experimental and theoretical investigations, we propose the existence of a third type of strongly stabilizing interactive geometry for the cyclopropane ring in an *o*-carborane system.

Structure of a Cyclopropane Ring Adjacent to a π (or p) System Conferred by Homoconjugation. It is already well-known that the conformation[3−5] and the distortion of each bond length (i.e., both vicinal and distal bonds)[6] of cyclopropane rings strongly depend on the neighboring systems.[7,8] These phenomena are thought to result in homoconjugative interactions between the neighboring system (as an electron acceptor or an electron donor) and cyclopropane (as an electron donor or an electron acceptor), whereby the properties of the cyclopropane are characterized by its higher-lying σ orbitals or its lower-lying σ^* orbital, that is, by a series of Walsh orbitals (Chart 3).[3]

Chart 4 depicts the two critical orbital interactions between a cyclopropane ring functioning as an electron donor and a π (or p) system functioning as an electron acceptor. The highest occupied molecular orbital (HOMO) of cyclopropane is a set of degenerate Walsh orbitals (see Chart 3); one such orbital ($\mathbf{E}_a$) is important for the bisected conformation,[9] and another ($\mathbf{E}_s$) is involved in the perpendicular conformation with respect to the π (or p) system.[4]

In the case involving the bisected conformation, both the vicinal bonds of the cyclopropane ring are maximally lengthened, since the substantial reduction[10] of the bonding nature at the cyclopropane vicinal bonds as compared with the original bonding nature of the Walsh orbital $\mathbf{e}_A$ is brought about due to homoconjugation via the π^* (or vacant p) orbital;[11,12] i.e., the reduction of the bonding nature is due to the orbital mixing of the cyclopropane Walsh* orbital ($\boldsymbol{\sigma}_A^*$) with the Walsh orbital ($\mathbf{e}_A$) via the π^* orbital ($\boldsymbol{\pi}^*$). In other words, the cyclopropane Walsh orbital $\mathbf{e}_A$ mixed primarily with the π orbital ($\boldsymbol{\pi}$) interacts (or homoconjugates) with the π^* orbital $\boldsymbol{\pi}^*$, which is primarily mixed with the cyclopropane Walsh* orbital $\boldsymbol{\sigma}_A^*$.[13] In addition, because of the substantial reduction of the antibonding nature at the cyclopropane distal bond by means of this homoconjugation, the distal bond of the cyclopropane ring is maximally shortened. This type of homoconjugation would also lead to the maximal stabilization of the entire system.[12] Cyclopropylcarbinyl cations,[14] cyclopropyl ketones,[14] cyclopropylbenzenes,[15,16] and homofulvenes[17] have been experimentally and theoretically investigated as models of this type of system (Chart 6). In contrast, in the case of the perpendicular conformation, none of the distal and the vicinal bond lengths are significantly distorted, because the Walsh orbital ($\mathbf{e}_S$) is slightly and orthogonally mixed with the lower-lying σ^* orbital ($\boldsymbol{\sigma}_S^*$), which does not cause significant changes of the σ-bonding nature of the Walsh orbital and subsequent significant distortion of the cyclopropane ring. The effect of this type of homoconjugation on the stabilization of the entire system would be expected to be considerably weaker than the effect of homoconjugation involving a bisected conformation.[18]

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(3) de Meijere, A. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 809−826.

(4) As another type of interactive geometry, a conformer with a synclinal (gauche) conformation (which has higher energy than the antiperiplanar conformation[9]) for the cyclopropane ring in vinylcyclopropanes has been observed as a minor conformer under solution and gaseous conditions. DeMare, G. R.; Martin, J. S. *J. Am. Chem. Soc.* **1966**, *88*, 5033−5034. Jorgenson, M. J.; Leung, T. *J. Am. Chem. Soc.* **1968**, *90*, 3769−3774. Günther, H.; Klose, H.; Wendlisch, D. *Tetrahedron* **1969**, *25*, 1531−1543. de Meijere, A.; Lüttke, W. *Tetrahedron* **1969**, *25*, 2047−2058.

(5) Schrumpf, G. *Tetrahedron Lett.* **1970**, 2571−2574. Klessinger, M.; Rademacher, P. *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 826−837. Eckert-Maksic, M.; Gleiter, R.; Zefirov, N. S.; Kozhushkov, S. I.; Kuznetsova, T. S. *Chem. Ber.* **1991**, *124*, 371−376.

(6) Tamagawa, K.; Hilderbrandt, R. L. *J. Phys. Chem.* **1983**, *87*, 3839−3844. Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3811−3819.

(7) Hoffmann, R. *Tetrahedron Lett.* **1970**, 2907−2909.

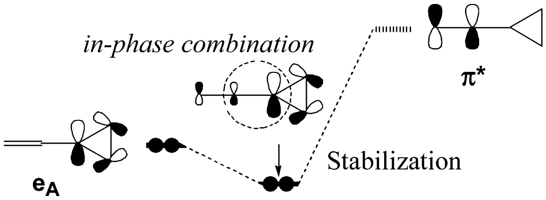
(8) Bischof, P.; Gleiter, R.; Heilbronner, E.; Hornung, V.; Schröder, G. *Helv. Chim. Acta* **1970**, *53*, 1645−1659.

(9) In this report, both antiperiplanar (*s-trans*) and synperiplanar (*s-cis*) conformations are represented as bisected conformations. See also ref 3.

(10) Since cyclopropane Walsh orbitals are σ orbitals, a perturbation of this orbital is directly reflected to the bond length.

(11) In this case, a homoconjugative interaction is possible, because the cyclopropane moiety is capable of assuming a three-center, two-electron interaction geometry.

(12) In this case, homoconjugation is depicted in general as primary orbital mixing between the Walsh orbital ($\mathbf{e}_A$) as an electron donor and the π^* orbital ($\boldsymbol{\pi}^*$) as an electron acceptor (as shown by the scheme). The resulting occupied molecular orbital, which contributes to the total energy of the entire system, is constructed mainly from $\mathbf{e}_A$ with a small contribution of $\boldsymbol{\pi}^*$ on the basis of their energy gap and adopts an in-phase combination at the junction between both fragments (referred to as a Walsh−π^* orbital interaction) due to a stabilization interaction. Charts 4 and 5 and the figures in the text simultaneously depict the secondary orbital mixing (refs 8 and 13).



(13) Secondary orbital mixing between the Walsh orbital ($\mathbf{e}_A$) and the Walsh* orbital ($\boldsymbol{\sigma}_A^*$) results in a homoconjugation between $\mathbf{e}_A$ and $\boldsymbol{\pi}^*$. See also ref 12.

(14) Childs, R. F.; Faggiani, R.; Lock, C. J. L.; Mahendran, M.; Zweep, S. D. *J. Am. Chem. Soc.* **1986**, *108*, 1692−1693.

(15) Shen, Q.; Wells, C.; Traetteberg, M.; Bohn, R. K.; Willis, A.; Knee, J. *J. Org. Chem.* **2001**, *66*, 5840−5845.

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(17) Gleiter, R.; Heilbronner, E.; de Meijere, A. *Helv. Chim. Acta* **1971**, *54*, 1029−1037. Harmony, M. D.; Mathur, S. N.; Choe, J.-I.; Kattija-Ari, M.; Howard, A. E.; Staley, S. W. *J. Am. Chem. Soc.* **1981**, *103*, 2961−2966. Haumann, T.; Boese, R.; Kozhushkov, S. I.; Rauch, K.; de Meijere, A. *Liebigs Ann.* **1997**, 2047−2053.

CHART 4. Stabilization Interactions of a π System Bearing a Cyclopropane Ring as an Electron Donor in a Given Conformation

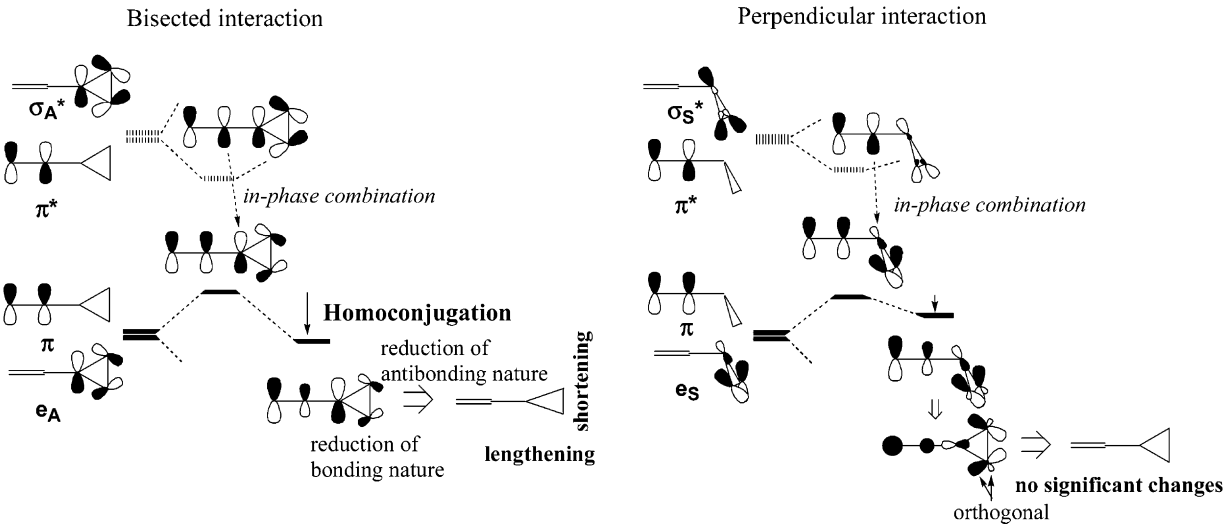


CHART 5. Stabilization Interactions of a π System Bearing a Cyclopropane Ring as an Electron Acceptor in a Given Conformation

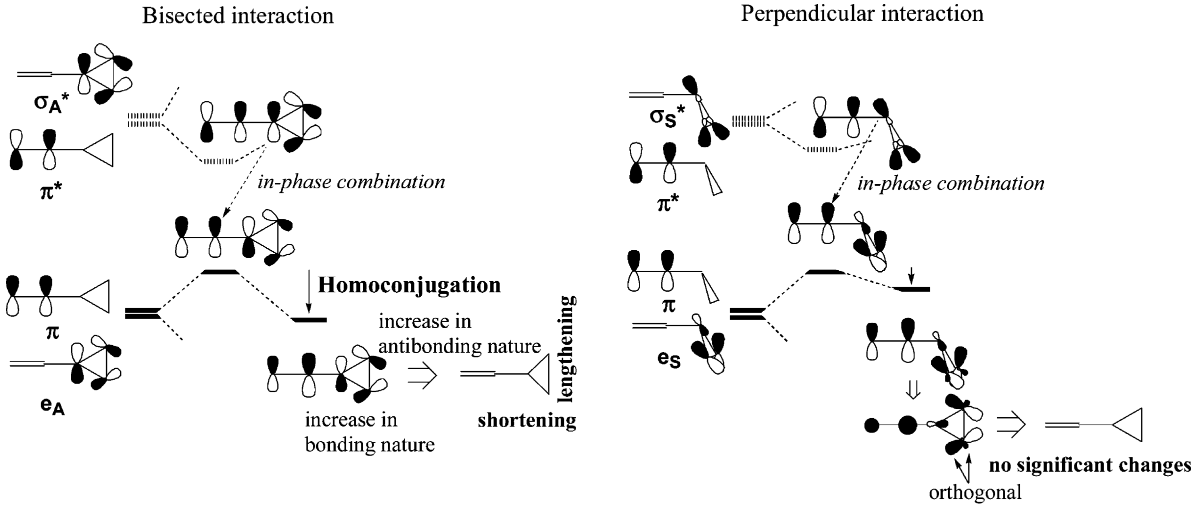
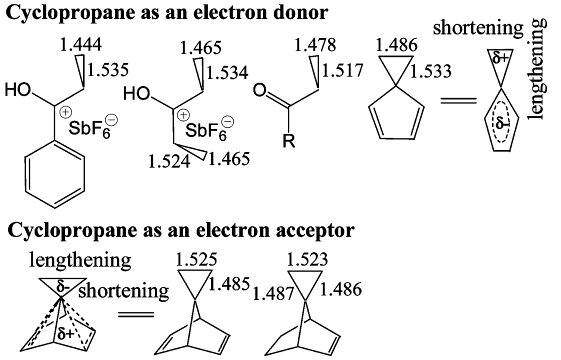


CHART 6. Cyclopropane Ring Distortion: Cyclopropyl Group as an Electron Donor or Acceptor[a]



[a] References 14, 17, and 19.

On the other hand, Chart 5 shows the two critical orbital interactions between a cyclopropane ring serving as an electron acceptor and a π system serving as an electron donor. In the case of the bisected conformation, both the vicinal and the distal bonds of the cyclopropane ring are maximally distorted in a manner opposite to that observed in the case of an electron-donating cyclopropane. In the bisected conformation, the ring distortion is also interpreted as being the result of homoconjugation between the cyclopropane Walsh* orbital ($\boldsymbol{\sigma}_\mathbf{A}$*****) and the π system ($\boldsymbol{\pi}$), but the relevant orbitals are in the relation opposite to those in the case of an electron-donating cyclopropane ring. Due to this type of homoconjugation, the entire system would be led to a state of maximal stabilization. The cyclopropylidenenorbornenes[19] and the cyclopropylidenenorbornadienes[19,20] have been experimentally and theoretically investigated as models of this type of system (Chart 6). In the case of the perpendicular conformation, interactions occur in the manner opposite to those that occur in the case of an electron-donating cyclopropane ring, whereas no additional significant

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(18) The homoconjugation could not be neglected, since there was a small interaction with the back-lobe orbital of cyclopropane ($\mathbf{e}_\mathbf{S}$).

(19) Haumann, T.; Benet-Buchholz, J.; Klärner, F.-G.; Boese, R. *Liebigs Ann.* **1997**, 1429–1435.

(20) Brogli, F.; Heilbronner, E.; Ipaktschi, J. *Helv. Chim. Acta* **1972**, *55*, 2447–2451.

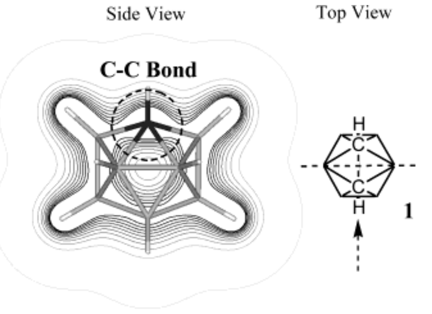

FIGURE 1. Electron density map calculated by the B3LYP/6-31G* method for *o*-carborane (**1**).

structural changes are brought about in terms of orthogonality. The effect of this type of homoconjugation on the stabilization of the system would also be considerably weak in comparison with that of the corresponding bisected conformation. A series of cyclopropylarenes, i.e., cyclopropylbenzene (in this compound, the cyclopropyl group acts as an electron donor with the bisected conformation), 1-cyclopropylnaphthalenes, and 9-cyclopropylanthrathenes, has been used for research on this type of compound.[16]

Results

Conformation of the Cyclopropane Ring Attached at a Carbon Atom in an *o*-Carborane Cage. In general, carborane cages are to a significant extent electron-deficient systems, and in particular, the electron density at the carbon atoms is the lowest in this type of caged system.[21] The triple-bonding nature of the C−C bond in an *o*-carborane cage is strongly reduced by the coordination of the vacant orbitals of a boron-cluster moiety.[22] However, as shown in Figure 1, the electron density map of the C−C bond of the *o*-carborane (**1**) sliced at a σ_v symmetry face strongly suggests that this bond retains its chemical bonding nature, as there is sufficient electron density at the midpoint of this C−C bond.

Our interest throughout the process of this study[2] was to more strongly stabilize the caged C−C bond by introducing homoconjugative and hyperconjugative substituents at a carbon atom of an *o*-carborane cage. Of these substituents, we noted the electronic effects of cyclopropyl and phenyl groups on an *o*-carborane system due to their strong homoconjugative effects.[3−8,14−20] On the basis of the cyclopropane chemistry, in *C*-cyclopropyl-*o*-carborane (**4**), it was expected that the cyclopropane moiety would give the bisected conformation with respect to the axis, including each carbon atom of the *o*-carborane cage (hereafter, the "C−C bond axis") and the entire system would be maximally stabilized, as is the case with cyclopropyl ketones or cyclopropylcarbinyl cations (Chart 6). In other words, on the basis of the explanations given above, it was assumed that the effect of the cyclopropane ring in this system corresponded to that of an electron donor. This conclusion was supported by the experimental results showing that, in the corresponding *C*-phenyl derivative (**3**), the phenyl group was almost parallel with respect to this C−C bond axis (18.3 and 22.3°) in the solid state at both 150 and 199 K (Figure 2);[23] i.e., the π system of the phenyl ring adopted an almost bisected conformation.

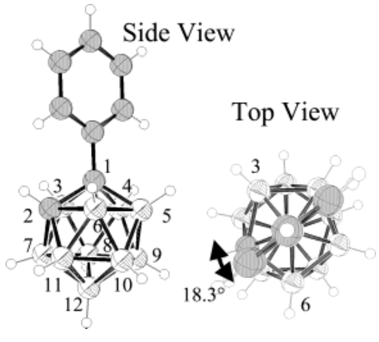

FIGURE 2. X-ray crystal structure of *C*-phenyl-*o*-carboranes (**3**) at 150 K, as reported by Thomas et al. Ellipsoids show carbon (gray) and boron (white) atoms.[23b,24]

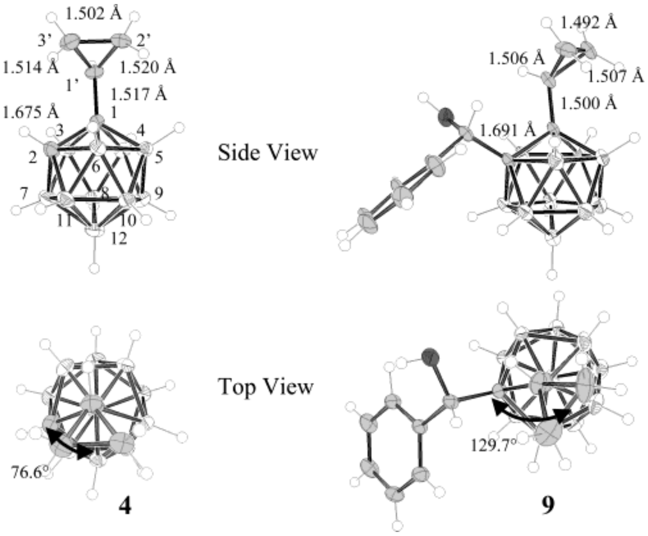

FIGURE 3. Structural views of the *C*-cyclopropyl-*o*-carboranes (**4** and **9**) as determined by X-ray crystal analysis at 123 K. Ellipsoids show carbon (gray), boron (white), and oxygen (dark gray) atoms.[24]

However, the crystal structures suggest that, with respect to this electron-deficient C−C bond, the bisected conformation was not the most stable conformation for the cyclopropane ring at a carbon atom of an *o*-carborane cage. Figure 3 shows the crystal structures of the *C*-cyclopropyl-*o*-carboranes (**4** and **9**) obtained at 123 K. The cyclopropyl group in the crystal structure of both **4** and **9** predominantly adopted a single respective conformation. In **4**, the cyclopropane ring was slightly twisted from a truly perpendicular conformation. The midpoint of the cyclopropane distal bond was twisted away from the C−C bond axis by 76.6° and was located on the adjacent C−B bond (71.5°). In **9**, on the other hand, due

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[21] Bregadze, V. I. *Chem. Rev.* **1992**, *92*, 209−223.

[22] The antibonding σ orbital of the C−C bond of the *o*-carborane cage is lowered in energy to the occupied orbital level via bonding interactions with a vacant boron-cluster orbital. It appears that this type of occupied orbital renders the length of the C−C bond of an *o*-carborane unusual (1.625 Å).

[23] (a) Brain, P. T.; Cowie, J.; Donohoe, D. J.; Hnyk, D.; Rankin, D. W. H.; Reed, D.; Reid, B. D.; Robertoson, H. E.; Welch, A. J. Hofmann, M.; Schleyer, P. v. R. *Inorg. Chem.* **1996**, *35*, 1701−1708. (b) Thomas, R. Ll.; Rosair, G. M.; Welch, A. J. *Acta Crystallogr.* **1996**, *C52*, 1024−1026.

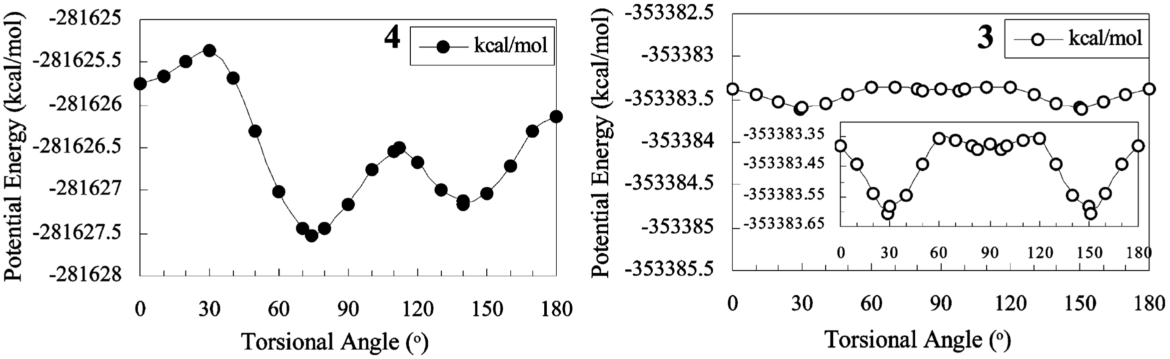

FIGURE 4. Relaxed potential energy surface scan of the cyclopropane ring for **4** (left) and of the benzene ring for **3** (right).

to steric repulsion with the *C*′-substituent (i.e., the rotation of the 1-hydroxy-1-phenylmethyl moiety), the midpoint of the cyclopropane distal bond was twisted by 129.7° (122.8° at 297 K; data not shown) and the cyclopropyl group was located on another C−B bond (143.8°) toward the C−C bond side of the *o*-carborane cage.

To evaluate the crystal structures obtained, we carried out a relaxed potential energy surface scan using the hybrid density functional theory (B3LYP) together with the 6-31G* basis set for the phenyl **3** and the cyclopropyl **4** derivatives. These theoretical calculations predicted some local minima on the potential energy surface which accompanied the rotation of the torsional bond between the substituent and the *o*-carborane moieties, as shown in Figure 4. Three local minima (at 0, 74.3, and 139.4°) were found in the case of **4**. Among these minima, the total energy of the corresponding minimum structure with the truly bisected conformation was considerably higher than that of the other corresponding minimum structures (1.767 and 1.373 kcal/mol, respectively). As a result, we found that each of the conformations, which were fixed in **4** and **9** in the solid state, were quite similar to those of the two deeper-minimum structures on the calculated potential energy surface of **4** in the gas phase. In other words, by introducing a substituent at the other carbon atom of the *o*-carborane cage in **4** (i.e., **9**), we were able to fix the cyclopropyl group at the second local minimum position on the potential energy surface of **4**.

In the gas phase, the conformer with the slightly twisted perpendicular conformation was the most stable in energy, and the other twisted conformer was estimated to be slightly higher in energy (0.394 kcal/mol). Although the peripheral constituents and arrangements (B−H, C−H, and B−H bonds for the bisected conformer vs C−H, B−H, and B−H bonds for the deepest-minimum conformer vs B−H, B−H, and B−H bonds for the second minimum conformer)[25] of the cyclopropane ring differ among each of the local minimum structures, this energetic advantage of the slightly twisted perpendicular conformation of **4** in the gas phase (and in the solid state as well) would result in the contribution of an electronic effect of the cyclopropane ring in this conformation.

In contrast, the corresponding minimum to the conformer, being truly parallel (0°; the bisected conformation in terms of the π system of the phenyl ring) with respect to the C−C bond axis, could not be obtained for *C*-phenyl derivative **3**,[23] due to the steric repulsion between the phenyl proton at the *ortho* position and the proton attached at the other carbon atom of the *o*-carborane cage. Thus, in **3**, the phenyl group (29.0°) of the most stable conformer was somewhat twisted away from the C−C bond axis under gas-phase conditions, although the rotation barrier for **3** was only in the range of 0.253 kcal/mol using the B3LYP/6-31G* method. The other minimum (82.4°) was found to be slightly twisted away from the orthogonality, since both phenyl protons at the *ortho* positions made contact with the protons at both the 3 and the 6 positions of the *o*-carborane cage as well (Figure 2).

Of especial interest in this context was the finding that the difference between the rotation barriers of **3**[23a] and **4** (0.253 kcal/mol vs 2.091 kcal/mol; about 10-fold energy) was not predicted by the effects of steric repulsion alone, since the steric repulsion between the cyclopropyl protons and the protons at both the carbon and the boron atoms of the *o*-carborane cage in **4** was roughly estimated to be less than twice (0.253 × 2 kcal/mol) the steric repulsion of those in **3**.[25] Therefore, we expected that the energetic advantage of **4**, i.e., the subtracted energy difference of $1.26 = 1.767 - (0.253 \times 2)$ kcal/mol at the B3LYP/6-31G* level, would be deduced from the electronic effect of the cyclopropane ring with the slightly twisted perpendicular conformation.[26] Regardless of the nearly perpendicular conformation, **4** would be homoconjugated by the strong electron-donating effect of the cyclopropyl group, in comparison with that of the phenyl group; therefore, this electronic effect would stabilize the entire molecule.

Conformation of *C*-Cyclopropyl-*o*-carboranes among Solid, Solution, and Gaseous States. As mentioned above, the conformation of the cyclopropane ring of **4** and **9** in the solid state at 123 K (at 297 K for **9** as well) was quite similar to those of two deeper-minimum structures of **4** at the B3LYP/6-31G* level. Since it was difficult to operate **9** theoretically, we evaluated the structure of the

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(24) Ortep-3, version 1.05: Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(25) In the *o*-carborane (**1**), the C−H bond length and the H−C−C bond angle were estimated at 1.0831 Å and 116.19°, respectively, using the B3LYP/6-31G* method, whereas the CB−H bond length and the H−B−C bond angle were estimated at 1.1827 Å (or 1.1849 Å) and 117.53° (or 117.92°), respectively.

(26) This is the energy difference between the total energies at the truly bisected conformation (at this conformation, some electronic effects of the cyclopropyl group would be expected to occur) and at the slightly twisted perpendicular conformation. Since the steric environments of both conformations are almost identical,[25] this energy difference would reflect the difference between the electronic effects of the cyclopropyl groups between these conformations (and not the total electronic effect of the cyclopropyl group).

TABLE 1. Experimental and Theoretical (GIAO) NMR Chemical Shifts for 4 and 9

$\delta(^{11}\mathrm{B})$[a] or $\delta(^{13}\mathrm{C})$[b] for **4**				$\delta(^{11}\mathrm{B})$[a] or $\delta(^{13}\mathrm{C})$[b]		
posn[c]	calcd[d] $\theta = 74.3°$	calcd[d] $\theta = 0°$	expt	posn[c]	calcd for **6**[d,e] $\theta = 136.1°$	expt for **9**
C1	63.3 (73.7)[f]	61.4 (71.7)[f]	77.8	C1	66.5 (77.3)[f]	84.4[h]
C2	51.0(59.9)[f]	41.4 (49.2)[f]	62.1	C2	60.9(71.1)[f]	83.2[h]
B7,11	−14.85[g]	−14.35	−13.45[h]	B8,10	−13.02[g]	−12.56[h]
B3,6	−14.08[g]	−12.64	−12.79[h]	B4,5	−12.91[g]	−12.13[h]
B4,5	−11.39[g]	−11.68	−11.69[h]	B7,11	−11.13[g]	−11.59[h]
B8,10	−11.30[g]	−11.59	−9.75[h]	B3,6	−8.71[g]	−10.72[h]
B12	−3.94	−3.89	−6.13[h]	B9	−3.88	−5.36[h]
B9	−2.35	−0.60	−2.79[h]	B12	−3.01	−3.24[h]
C1′	13.8	13.6	18.0	C1′	12.4	15.9
C2′,3′	8.0[g]	7.0	8.9	C2′	7.2	9.1[h]
				C3′	8.2	9.5[h]

[a] Relative to $BF_3 \cdot OEt_2$ (ppm). [b] Relative to TMS (ppm). [c] For the atom numbering scheme, see Figure 3. [d] Model chemistry (HF/6-31G*//B3LYP/6-31G*) at C_1 symmetry. [e] Model compound for **9**. [f] The numbers in parentheses show the scaled chemical shift ($(\mathrm{ppm}_{\mathrm{calcd}} + 2.554)/0.893$).[28] [g] Average value. [h] A chemical shift assignment was not performed.

corresponding model compound **6**, based on the potential energy surface scan of **4** (see Computational Methods for details). Selected geometrical parameters from the X-ray and theoretical studies are given in Supporting Information section. (Atom coordinates, anisotropic thermal parameters, and a full listing of bond lengths are also available as Supporting Information.) As a result, the structures of both **4** and **9** in the solid state were in good agreement with the deepest minimum structures of **4** and **6** at the B3LYP/6-31G* level. Particularly, the geometries of the cyclopropane moieties in the theoretical structures (**4** and **6**) were in excellent agreement with the corresponding crystal structures (**4** and **9**) at 123 K, respectively. For the *o*-carborane moiety of **4** at the B3LYP/6-31G* level, certain underestimations were observed as compared with the geometrical parameters of the crystal structure. However, the trend in the B−B bond lengths was well reproduced; for example, the B3−B8 bond length was the shortest in both the crystal and the theoretical structures and the B8−B12 bond length was the longest in both the crystal and the theoretical structures (see Supporting Information). For **6**, the geometry of the *o*-carborane moiety, as well as that of the cyclopropane moiety, was in excellent agreement with the crystal structure of **9** at 123 K.

We then investigated a preferred conformation for the cyclopropane ring attached at a carbon atom of an *o*-carborane cage in solution. It has been reported that the ^{11}B NMR chemical shifts of **3** are very sensitive to the phenyl-ring orientation and are thus useful for predicting the preferred conformation in solution.[23a] The GIAO[27] calculation using HF/6-31G*//B3LYP/6-31G* model chemistry was carried out for the above theoretical structures. Table 1 shows the experimental and the theoretically predicted chemical shifts of both ^{13}C and ^{11}B nuclei for **4**, **6**, and **9**. In the case of **4**, it appeared that the cyclopropyl group freely rotated around the C_1 axis of the molecule in solution, as indicated by the potential energy surface scan analysis (Figure 4) as well as by the ^{1}H NMR chemical shifts, which revealed single respective peaks in $CDCl_3$ solution at 298 K (see the Experimental Section). However, when the torsional angle (θ) was 0°, the calculated B9 and B12 chemical shifts of **4** significantly deviated from the experimental values. In contrast, at $\theta = 74.3°$, these deviations were reduced and the calculated B9 chemical shift was in excellent agreement with the experimental value in $CDCl_3$ solution. Similarly, in the ^{13}C NMR chemical shifts of the caged carbon atoms[28] in **4**, the predicted chemical shifts at $\theta = 74.3°$ were in good agreement with the experimental values obtained in $CDCl_3$ solution, while those at $\theta = 0°$ were in poor agreement. This finding implies that the preferred conformation of **4** in solution was similar to that of the crystal structure at 123 K, as well as being similar to that of the deepest-minimum structure in the gaseous state.[29] Moreover, in the case of **6**, the ^{11}B NMR chemical shifts were in good agreement with those of **9** in $CDCl_3$ solution.[30] This result strongly suggested that the rotation of the cyclopropane moiety in **9** was highly constrained by the substituent at the other carbon atom of the *o*-carborane cage, thus biasing to a large extent its equilibrium toward the conformation similar to that of the crystal structure. Therefore, we concluded that the preferred conformation of the cyclopropane moieties in both **4** and **9** under solution conditions was quite similar to the conformation of their crystal and theoretical structures, respectively.

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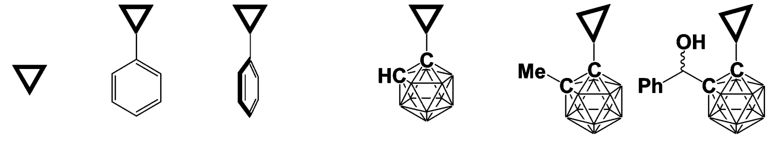
[27] Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251. Dodds, J. L.; McWeeny, R.; Sadlej, A. J. *Mol. Phys.* **1980**, *41*, 1419. Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789. McWeeny, R. **1962**, *126*, 1028. London, F. *J. Phys. Radium* **1937**, *8*, 397.

[28] Diaz, M.; Jaballas, J.; Arias, J.; Lee, H.; Onak, T. *J. Am. Chem. Soc.* **1996**, *118*, 4405−4410.

[29] We preliminarily estimated the free energies of the three local minimum structures and the three transition structures of the rotation for **4** using a frequency analysis at the B3LYP/6-31G* level with a scale factor[36] of 0.9804 at 298.15 K. The free energy differences to the deepest minimum ($\theta = 74.3°$) were 0.20 kcal/mol for the second deepest minimum ($\theta = 139.4°$) and 1.37 kcal/mol for another minimum ($\theta = 0°$) corresponding to the bisected conformation of the cyclopropane ring, respectively. These free energy differences corresponded to the existence ratio of 10:7:1 in solution at 298.15 K, according to the Eyrin equation. The free energies of activation were 1.32 kcal/mol for the pass to $\theta = 74.3°$ from $\theta = 0°$ through $\theta = 29.8°$ (corresponding to the highest-energy transition state), 0.88 kcal/mol for the pass to $\theta = 74.3°$ from $\theta = 139.4°$ through $\theta = 111.8°$ (corresponding to the lowest-energy transition state), and 1.67 kcal/mol for the pass to $\theta = 139.4°$ from $\theta = -139.4°$ through $\theta = 180°$ (corresponding to the second highest-energy transition state), respectively. The predicted ^{11}B and ^{13}C NMR chemical shifts for the second deepest-minimum structure were in good agreement with the corresponding experimental values in $CDCl_3$ solution. Therefore, it appears that the conformation of the cyclopropane ring in **4** was in a rapid equilibrium (biased slightly toward the deepest-minimum conformation) between those of the deepest and the second deepest-minimum structures in solution at 298.15 K.

[30] The ^{13}C NMR chemical shifts of the caged carbon atoms could not be compared in terms of the experimental and the theoretical values, due to differences between the directly attached substituents.

TABLE 2. Effects of an Electron-Withdrawing Bisected π System, an Electron-Donating Perpendicular π System, and an Electron-Withdrawing Caged *o*-Carborane System on Cyclopropane Ring Distortion[a–c]



		10'	10	4		6	9
C-C bond	calcd	calcd	calcd	calcd	exp.	calcd	exp.
vicinal		1.5110	1.5186	1.5104	1.520	1.5124	1.507
(Δ)		(+0.0030)	(+0.0106)	(+0.0024)	(+0.012)	(+0.0044)	(-0.001)
				1.5147	1.514	1.5136	1.506
	1.5080			(+0.0067)	(+0.006)	(+0.0056)	(-0.002)
distal		1.5098	1.5009	1.5035	1.502	1.5028	1.492
(Δ)		(+0.0018)	(-0.0071)	(-0.0045)	(-0.006)	(-0.0052)	(-0.016)
distortion (%)	-	0	100	50	85	56	66

[a] The calculations were performed using the B3LYP/6-31G* method under a constraint symmetry (D_{3h} for the cyclopropane, C_1 for **4** and **6**, and C_s for the rotamers **10** and **10′**). [b] The numbers in parentheses show the differences (Å) between the bond lengths in the cyclopropane molecules. [c] The experimental values represented the geometrical parameters for **4** and **9** in the solid state at 123 K.

Distortion of the Cyclopropane Ring Connecting at a Carbon Atom of an *o*-Carborane Cage. In the solid state, both the vicinal and the distal bonds of the cyclopropane ring of the *C*-cyclopropyl-*o*-carboranes (**4** and **9**) seemed to be distorted in the same manner as had been observed in the electron-donating cyclopropane ring with the bisected conformation; i.e., both the vicinal bonds were lengthened and the distal bond was shortened, although the distortion was very small in magnitude (see Chart 6 and Figure 3). Otherwise, it is also possible that significant distortion did not occur, due to the perpendicular-like conformation of the cyclopropane ring.

To investigate the distortion of the cyclopropane ring in **4** obtained here, we carried out the theoretical calculations in the gas phase. Table 2 shows the calculated bond lengths for the cyclopropane (D_{3h} symmetry), the cyclopropylbenzene (**10** and **10′**; C_s symmetry, respectively), **4** (C_1 symmetry), and **6** (C_1 symmetry) as a model compound for **9**, using the B3LYP/6-31G* method together with the experimental parameters for **4** and **9** at 123 K. On the basis of the above-mentioned structure of this type of cyclopropane ring, and since significant bond distortion does not occur in cyclopropane rings adopting a truly perpendicular conformation, a rotamer (**10′**) of cyclopropylbenzene was used as the standard reference.[16] To confirm our considerations, we carried out the theoretical calculations for the rotamer **10′** using the B3LYP/6-31G* method. As shown in Table 2, the cyclopropane ring distortion of the rotamer **10′** was minimized, when the C−C bond lengths of the rotamer **10′** were compared with those of the parent cyclopropane molecule. In the dominant conformer **10** of cyclopropylbenzene, the cyclopropane ring distortion was reproduced by the theoretical calculation, when the C−C bond lengths were compared with the respective C−C bond lengths of the cyclopropane rings of both the rotamer **10′** and the parent cyclopropane molecules. Therefore, we were able to confirm that the rotamer **10′** would be the best reference for our considerations that were based on an electron-donating cyclopropane ring with the bisected conformation.[15] That is, in conformer **10**, both the vicinal bonds were apparently lengthened (more than 3-fold) as compared with the corresponding cyclopropyl bonds of the reference **10′** and the distal bond was considerably shortened (about 4-fold) as compared with reference **10′**. On the basis of these results, we found that the distortion of the cyclopropane rings in **4** and **6** (at the B3LYP/6-31G* level) was estimated as being on the order of 50% of that observed in conformer **10**, in which the cyclopropane ring acts as an electron-donating group. Somewhat larger distortions were also observed in the crystal structures for **4** (85%) and **9** (66%) in the same manner as being expected in the case with an electron-donating cyclopropane ring. These results strongly supported our expectation that the effect of a cyclopropane ring attached at a carbon atom of an *o*-carborane cage would correspond to that of an electron-donating group.

The Electron-Donating Property of a Cyclopropyl Group Is Stronger Than That of a Phenyl Group in an *o*-Carborane System. Additionally, as shown in Figure 5, we found that the C−C bond length of an *o*-carborane cage varied according to the rotation of the cyclopropyl group in **4**, as well as according to the rotation of the phenyl group in **3**.[23a,31] In the phenyl substituent (**3**), the C−C bond length (in the range of 0.0335 Å) was the longest when the phenyl group was orthogonal with respect to the C−C bond axis of an *o*-carborane cage (the π system of this phenyl ring corresponded to the perpendicular conformation of the cyclopropane ring) and the C−C bond length was the shortest when the phenyl group was parallel with respect to this C−C bond axis (the π system of this phenyl ring

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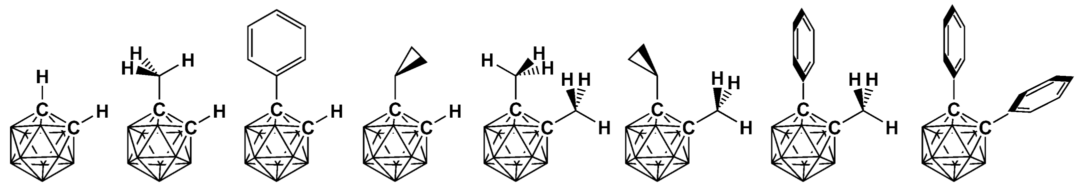
(31) Alekseyeva, E. S.; Fox, M. A.; Howard, J. A. K.; MacBride, J. A. H.; Wade, K. *Appl. Organomet. Chem.* **2003**, *17*, 499−508.

TABLE 3. Calculated and Experimentally Averaged C−C Bond Lengths[a]



Model (Symmetry)	**1** (C_{2v})	**2** (C_s)	**3** (C_1)	**4** (C_1)	**5** (C_{2v})	**6** (C_1)	**7** (C_s)	**8** (C_2)
averaged X-ray (Å)	1.625	1.645	1.655 (15.1)	1.675 (76.6)[c]	1.677	1.691 (129.7)[c]	1.700 (77.1)	1.729 (82.0)
B3LYP/6-31G* (Å)	1.624	1.645	1.646 (29.0)	1.656 (74.3)	1.663	1.679 (136.1)	1.687 (91.6)[d]	1.764 (85.7)
Δ (%)[b]	-0.06	0.00	-0.54	-1.13	-0.83	-0.71	-0.76	+2.02
HF/6-31G* (Å)	1.609	1.626	1.626 (24.8)	1.630 (74.9)	1.637	1.650 (138.7)	1.664 (91.5)[d]	1.699 (87.3)
Δ (%)[b]	-0.98	-1.16	-1.75	-2.69	-2.39	-2.42	-2.12	-1.74

[a] The numbers in parentheses indicate the torsional angle (deg). [b] Δ is shown as a percentage, obtained by dividing the difference between the calculated length and the averaged length by the averaged length. [c] Only one example was obtained in this study. [d] The local minimum structure had C_s symmetry, and therefore the benzene ring was distorted out of the plane.

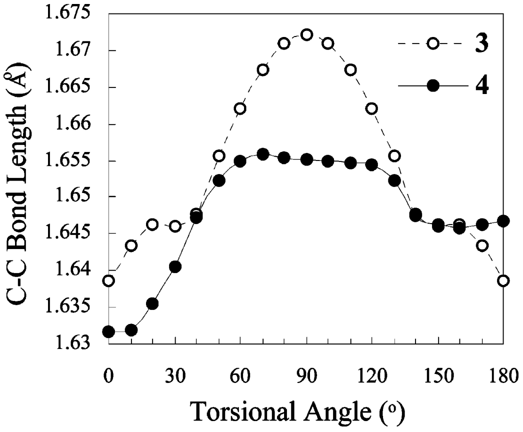


FIGURE 5. Lengthening of the C−C bond accompanying the rotation of the cyclopropane ring in **4** and the benzene ring in **3**.

corresponded to the bisected conformation of the cyclopropane ring). The point (ca. 30°) of inflection regarding the C−C bond length in **3** was found at the potential energy surface corresponding to the deepest local minimum (Figures 4 (right) and 5). Similarly, in the cyclopropyl substituent (**4**), the C−C bond length (in the range of 0.0243 Å) was the longest at the slightly twisted perpendicular conformer corresponding to the deepest local minimum and the C−C bond length was the shortest at the bisected conformation (Figures 4 (left) and 5). These results indicated that the lengthening of the caged C−C bond strongly depended on the directionality of the π system of the phenyl ring in **3**, although the lengthening in **4** was complex.

To obtain experimental evidence for this phenomenon, we carried out a statistical analysis of the C−C bond lengths in *o*-carboranes employing a Cambridge Structural Database (CSD) search.[32] Table 3 shows the C−C bond lengths of the calculated model compounds (**1**−**8**) and the averaged C−C bond lengths of the corresponding derivatives, which have been registered in the CSD database. As the result of the classification of *o*-carboranes into six categories, i.e., unsubstituted, *C*-alkyl, *C*-aryl, *C*,*C*′-dialkyl, *C*-alkyl-*C*′-aryl, and *C*,*C*′-diaryl derivatives, we noted the tendency of the C−C bond length to lengthen in association with the order of the electron-donating properties of the *C*(,*C*′)-(di)substituent(s): *C*-H-*C*′-H- < *C*-alkyl-*C*′-H- < *C*-aryl-*C*′-H- < *C*,*C*′-dialkyl- < *C*-alkyl-*C*′-aryl- < *C*,*C*′-diaryl-*o*-carboranes. The lengthening of the C−C bond[31,33] in association with the order of the electron-donating properties of the *C*(*C*′)-(di)substituent(s) was also reproduced by higher-level calculations using the B3LYP/6-31G* method and our model compounds (**1**−**8**). This tendency was also observed by calculations using the HF/6-31G* method, but all cases were underestimated to a larger degree than they had been when assessed by the B3LYP/6-31G* method, although even with the B3LYP/6-31G* method, the obtained C−C bond lengths were still underestimated, with the exception of those of the model compounds (**2** and **8**).

In the solid state, the C−C bond lengths (1.675 Å for **4** and 1.691 Å for **9**) of the *o*-carborane cage for each of the *C*-cyclopropyl-*o*-carboranes corresponded to the averaged lengths of *C*,*C*′-dialkyl-*o*-carboranes (1.677 Å) and *C*-alkyl-*C*′-aryl-*o*-carboranes (1.700 Å), respectively. Despite the underestimation, the C−C bond length (1.656 Å) of **4** was also similar to that (1.663 Å) of **5** (a model compound for *C*,*C*′-dialkyl-*o*-carboranes) and also the C−C bond length (1.679 Å) of **6** (a model compound for **9**) was similar to that (1.687 Å) of **7** (a model compound

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(32) Cambridge Structural Database: Allen, F. H.; Motherwell, W. D. S. *Acta Crystallogr.* **2002**, *B58*, 407−422.

(33) The lengthening of the C−C bond of an *o*-carborane cage has been discussed by Kivekäs et al. in terms of both the electronic and the steric properties of the substituent(s): Kivekäs, R.; Sillanpää, R.; Teixidor, F.; Vinas, C.; Nunez, R. *Acta Crystallogr.* **1994**, *C50*, 2027−2030. Kivekäs, R.; Sillanpää, R.; Teixidor, F.; Vinas, C.; Nunez, R.; Abad, M. *Acta Crystallogr.* **1995**, *C51*, 1864−1868. Kivekäs, R.; Teixidor, F.; Vinas, C.; Nunez, R. *Acta Crystallogr.* **1995**, *C51*, 1868−1870.

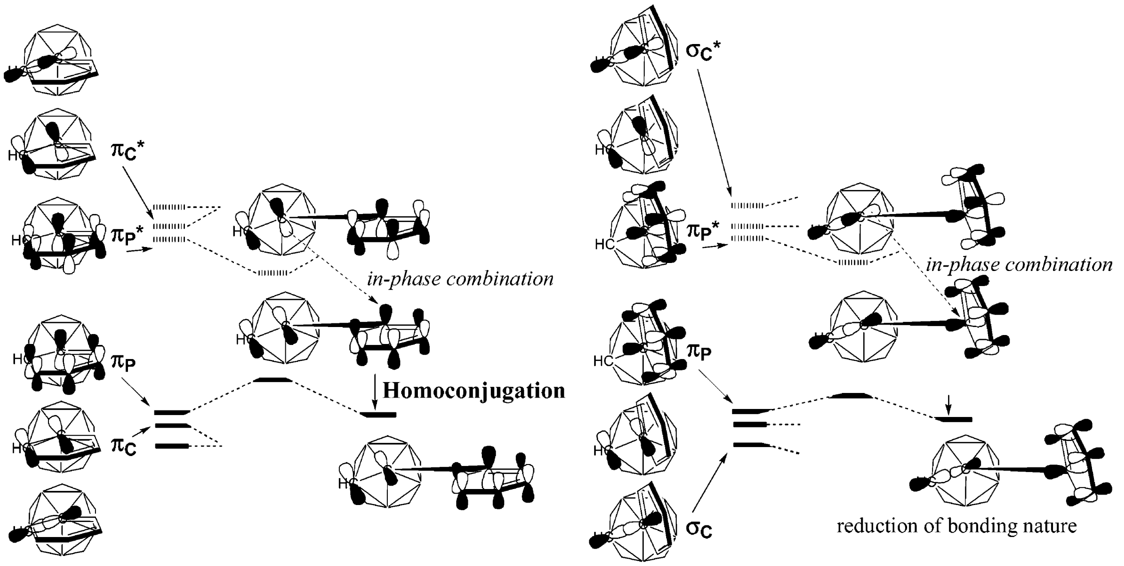

FIGURE 6. Orbital interactions between the C−C bond of an *o*-carborane and the phenyl π system in the bisected (left) and the perpendicular (right) conformations.

for *C*-alkyl-*C*′-aryl-*o*-carboranes) at the B3LYP/6-31G* level in the gaseous state. Interestingly, the caged C−C bond length of **4** was clearly longer than that of **3** in both the solid and the gaseous states. Thus, the caged C−C bond lengths of the cyclopropyl derivatives (**4** and **9**) were long or were of the same length, as compared with those of the corresponding phenyl derivatives (**3** and **7**). Moreover, in **7** and **8** (a model compound for *C,C*′-diaryl-*o*-carboranes), the phenyl group was constrained to be almost orthogonal with respect to the C−C bond axis due to steric repulsion between the substituents at both caged carbon atoms, thus making the C−C bond length of the *o*-carborane longer.[23a] In other words, it is likely that, in both **7** and **8**, the long C−C bond lengths were related to the orthogonality (the π system of the phenyl group was almost perpendicular) of one (or two) phenyl group(s) with respect to the C−C bond axis, as was also observed in the phenyl ring rotation in **3** (see Figure 5).[31] Therefore, although the caged C−C bond length in **7** represented a unique case, we concluded that the electron-donating properties of the cyclopropyl group were stronger than those of the phenyl group in the *o*-carborane system; this conclusion was based on the tendency observed here, namely, that increases in the strength of the electron-donating properties of the *C*-substituent correlated with increases in the length of the C−C bond of *o*-carborane cages.

Discussion

Orbital Interactions with Respect to the Conformation and the C−C Bond Length of *C*-Substituted *o*-Carboranes. In **4**, the cyclopropane ring adopted a slightly twisted perpendicular conformation with respect to the electron-deficient C−C bond axis of the *o*-carborane cage. On the basis of the general explanation for the structure of cyclopropane rings, we did not expect that both the cyclopropane ring distortion and the homoconjugative stabilization would occur to any significant extent, since the cyclopropane ring of **4** would behave as an electron donor with the perpendicular conformation. However, this interpretation may not account for the structures (weak distortion of the cyclopropane ring) of **4**, **6**, and **9** obtained in both the solid and the gaseous states. Moreover, when we considered the results obtained from the relaxed potential energy surface scan, which indicated the participation of additional electronic effects (1.26 kcal/mol at the B3LYP/6-31G* level), together with the above general explanations of conformation, distortion, and stabilization, then we were unable to account for these experimental results.

Fortunately, however, when considering these complex experimental results, we found that the tendency of the lengthening of the caged C−C bond was closely related among the conformation of the *C*-substituents, the cyclopropane ring distortion of *C*-cyclopropyl-*o*-carboranes, and the stabilization of the *C*-substituted *o*-carboranes. That is, we succeeded in deriving a consistent explanation of the experimental results by considering the contributions of the σ (sp−sp) orbital of the caged C−C bond.

Figure 6 shows the orbital interactions between the C−C bond of an *o*-carborane cage and the phenyl ring in bisected and perpendicular conformations in terms of the phenyl π system of **3**.

On the basis of the generally accepted explanations for these structures, in the preferred conformation of the phenyl ring, the π* orbital (π_C*) of the caged C−C bond would be expected to be mixed with its π orbital (π_C) by homoconjugation; i.e., the π* orbital (π_C*) of the caged C−C bond would mix with the phenyl π orbital (π_P).[34] In other words, the phenyl π orbital (π_P) mixed primarily with the π orbital (π_C) of the caged C−C bond interacts (or homoconjugates) with the caged C−C π* orbital (π_C*), which is primarily mixed with the phenyl π* orbital (π_P*). The orbital interaction relevant for the lengthening of the caged C−C bond would not occur in this conformation, because of the lower-lying σ and the higher-lying

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[34] The significant structural changes in the phenyl ring did not occur in the same manner as the changes in the electron-donating cyclopropane ring with the bisected conformation, because of the nonbonding electron (π electron) perturbation.

σ^* orbitals of the phenyl ring (note that these orbitals were omitted in Figure 6). Thus, the C−C bond length of the *o*-carborane cage was minimized, as demonstrated in the previous section (Figures 4 and 5). This type of homoconjugation would lead to the stabilization of **3**. Due to the steric repulsion between the phenyl proton at the *ortho* position and the proton at the other carbon atom of the *o*-carborane moiety, the phenyl ring would be slightly twisted, therefore leading to the observed conformation. In contrast, when the phenyl group was orthogonal in **3**,[31] another type of homoconjugation would become dominant (Figure 6 (right)). That is, since the π system of the phenyl group adopts the perpendicular conformation, the σ^* orbital ($\boldsymbol{\sigma_C^*}$) of the caged C−C bond is mixed with its σ orbital ($\boldsymbol{\sigma_C}$) by this homoconjugation; thus, the σ^* orbital ($\boldsymbol{\sigma_C^*}$) of the caged C−C bond is mixed with the phenyl π orbital ($\boldsymbol{\pi_P}$). In other words, the phenyl π orbital ($\boldsymbol{\pi_P}$) mixed primarily with the σ orbital ($\boldsymbol{\sigma_C}$) of the caged C−C bond interacts (or homoconjugates) with the caged C−C σ^* orbital ($\boldsymbol{\sigma_C^*}$), which is primarily mixed with the phenyl π^* orbital ($\boldsymbol{\pi_P^*}$). The σ orbital of the caged C−C bond interacts with the phenyl π system most likely due to the p character of this σ type (sp−sp) of orbital and the high instability of this C−C bond resulting from the coordination of a boron-cluster moiety. As a result, the bonding nature of the caged C−C σ orbital would be reduced and the C−C bond of the *o*-carborane cage would be lengthened (Figure 5) and maximized in this conformation. This line of reasoning enabled us to account for the changes in the C−C bond length along the rotation of the phenyl ring in **3** in terms of the contributions of this type of homoconjugation. However, this type of homoconjugation would not be expected to contribute significantly to the stabilization of the entire system (Figure 4 (right)), since the phenyl π orbital ($\boldsymbol{\pi_P}$) interacts more weakly with the σ orbital ($\boldsymbol{\sigma_C}$) than with the π orbital ($\boldsymbol{\pi_C}$) of the caged C−C bond. Moreover, no significant interaction between the π orbital of the *o*-carborane cage and the σ orbitals of the phenyl ring would be expected to occur, because the lower-lying σ and the higher-lying σ^* orbitals of the phenyl ring would not contribute to a significant stabilization of the entire system.

In contrast, in **4**, the C−C bond length hardly changed within the range of 60−120° (Figure 5). Thus, we concluded that, in **4**, the participation of more than two types of interactions, dependent on directionality, would be needed to explain this phenomenon, whereas the C−C bond length of **3** could simply be related to the directionality of the phenyl π system. We then considered that these interactions of **4** might reflect the four possible types of homoconjugation involved in the two types of Walsh orbitals in cyclopropane; moreover, the Walsh orbital ($\mathbf{e_A}$ and $\boldsymbol{\sigma_A^*}$) would be related to the phenyl π system ($\boldsymbol{\pi_P}$ and $\boldsymbol{\pi_P^*}$) involved in the two types of homoconjugation at both the bisected and the perpendicular conformations in **3**. As a result, in **4**, the cooperation of these homoconjugations in this region (60−120°) would render the determination of the C−C bond length more complicated and would lead to the two deeper local minimum structures (74.3 and 139.4° in the gas phase, respectively) around this periphery. This line of reasoning would then suggest the following underlying interactions as being involved in determining the structural parameters of **4** (i.e., weak cyclopropane ring distortion, three minimum conformations of the cyclopropane ring, and the lengthening of the caged C−C bond).

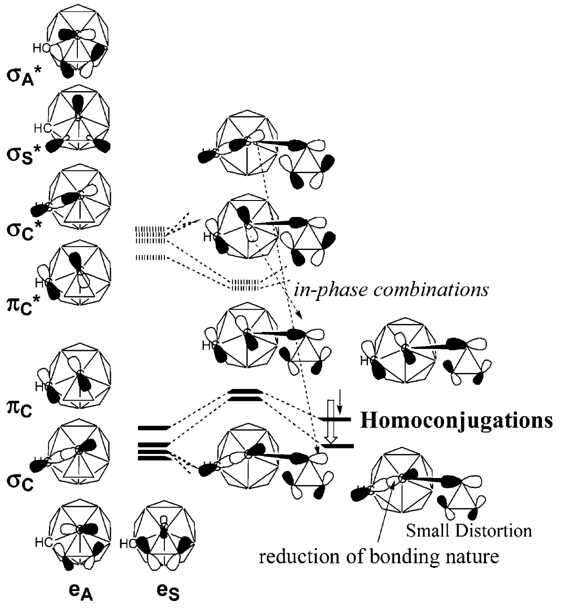

FIGURE 7. Orbital interactions relevant to the C−C bond of an *o*-carborane at the dominant conformation in **4**. Orbital interactions relevant to the cyclopropane $\mathbf{e_S}$ orbital were omitted.

Figure 7 shows the orbital interactions between the C−C bond of an *o*-carborane cage and the cyclopropane ring in the case of the dominant conformation of **4**. Using the analogy of the relevant orbital interaction for the C−C bond length in **3**, the σ orbitals ($\boldsymbol{\sigma_C}$ and $\boldsymbol{\sigma_C^*}$) of the C−C bond of an *o*-carborane moiety would mainly interact with the Walsh orbitals ($\mathbf{e_A}$ and $\boldsymbol{\sigma_A}$*) of the cyclopropane. And also, the π orbitals ($\boldsymbol{\pi_C}$ and $\boldsymbol{\pi_C^*}$) of the C−C bond of an *o*-carborane moiety would mainly interact with these cyclopropane Walsh orbitals ($\mathbf{e_A}$ and $\boldsymbol{\sigma_A}$*). Although the latter orbital interactions did not significantly contribute to the stabilization of **3**, they may have significantly contributed to stability in the case of **4**, as demonstrated below.

A Conceptualization of the Most Strongly Stabilizing Interactive Geometry of the Cyclopropane Ring in an *o*-Carborane System. To interpret the results, we investigated a combination of the possible four interactions between the two types of C−C bond orbitals ($\boldsymbol{\pi_C}$ and $\boldsymbol{\sigma_C}$) and the two types of Walsh orbitals ($\mathbf{e_A}$ and $\mathbf{e_S}$) as a function of directionality in **4** (Figure 8).

In Figure 8, the diagram at left shows the energy levels of the C−C bond orbitals ($\boldsymbol{\pi_C}$ and $\boldsymbol{\sigma_C}$) and the cyclopropane Walsh orbitals ($\mathbf{e_A}$ and $\mathbf{e_S}$). The diagram also shows the interactions between these orbitals at a certain angle θ (in the range of 0−90°). Each component ($\mathbf{a}_x$) of the Walsh orbital ($\mathbf{e_S}$) and each component ($\mathbf{b}_x$) of the Walsh orbital ($\mathbf{e_A}$) is a horizontal component, and these horizontal components are parallel with respect to the $\boldsymbol{\pi_C}$ orbital (the horizontal component of the $\boldsymbol{\pi_C}$ orbital is identical with **B**) of the caged C−C bond. On the other hand, each component ($\mathbf{a}_y$) of the Walsh orbital ($\mathbf{e_S}$) and each component ($\mathbf{b}_y$) of the Walsh orbital ($\mathbf{e_A}$) is a vertical component, and these vertical components are parallel with respect to the $\boldsymbol{\sigma_C}$ orbital (the vertical component of

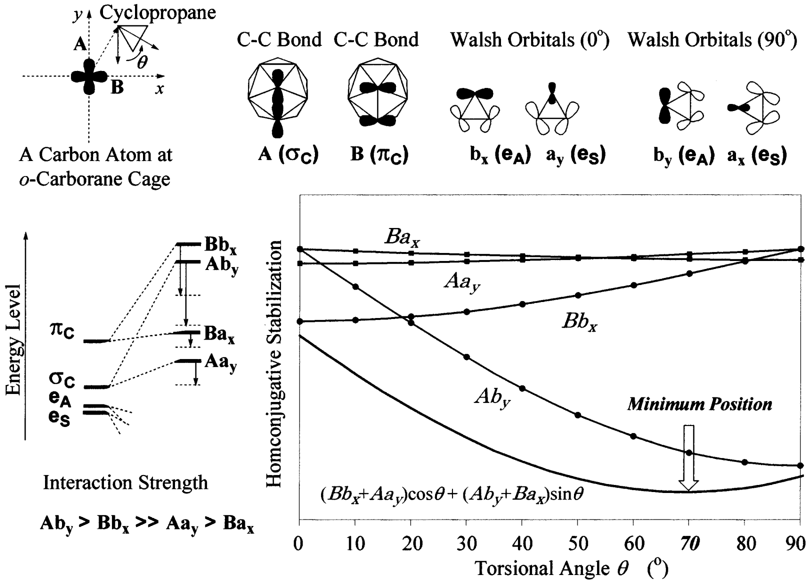

FIGURE 8. Combination of interactions depending on torsional angle.

the $\boldsymbol{\sigma}_\mathrm{C}$ orbital is identical with **A**) of the caged C−C bond. Thus, when angle θ (i.e., the torsional angle between the C−C bond of an *o*-carborane moiety and the midpoint of the cyclopropane distal bond) is 0° (i.e., the bisected conformation), each interaction (**Aa**$_y$) between $\boldsymbol{\sigma}_\mathrm{C}$ and $\mathbf{e}_\mathrm{S}$ and each interaction (**Bb**$_x$) between $\boldsymbol{\pi}_\mathrm{C}$ and $\mathbf{e}_\mathrm{A}$ reaches a maximum, whereas neither of the interactions **Ab**$_x$ and **Ba**$_y$ occur in terms of orthogonality. In this case, the magnitude of interaction **Bb**$_x$ is considerably stronger than that of **Aa**$_y$, because of the back-lobe interaction of **Aa**$_y$.[18] On the other hand, when the angle θ is 90° (i.e., the perpendicular conformation), each interaction **Ab**$_y$ between $\boldsymbol{\sigma}_\mathrm{C}$ and $\mathbf{e}_\mathrm{A}$ and each interaction **Ba**$_x$ between $\boldsymbol{\pi}_\mathrm{C}$ and $\mathbf{e}_\mathrm{S}$ reaches a maximum, whereas neither of the interactions **Aa**$_x$ and **Bb**$_y$ occur in terms of orthogonality. In this case, the magnitude of interaction **Ab**$_y$ is considerably stronger than that of **Ba**$_x$, also because of the back-lobe interaction of **Ba**$_x$. Moreover, the magnitude of interaction **Ab**$_y$ is stronger than that of **Bb**$_x$, because the energy separation between $\boldsymbol{\sigma}_\mathrm{C}$ and $\mathbf{e}_\mathrm{A}$ is significantly smaller than that between $\boldsymbol{\pi}_\mathrm{C}$ and $\mathbf{e}_\mathrm{A}$ (see the diagram in Figure 8). The more strongly the donor- and the acceptor-occupied orbitals interact, the more strongly the resulting orbital will homoconjugate via the vacant acceptor orbital (see Chart 4), because the overlap between the occupied orbital of the donor moiety and the unoccupied orbital of the acceptor moiety reaches a maximum, and the energy gap between them reaches a minimum. Therefore, each type of stabilization (Aa_y, Bb_x, Ab_y, and Ba_x) resulting from the corresponding homoconjugation is able to approximate the relative strength of each of these four types of interactions. As a result, we were easily able to identify many conditions to account for the experimental results. The right-hand side of Figure 8 shows one of the best conditions in this context. Both **Aa**$_y$ and **Bb**$_x$ interactions are related to a function of the cosine θ, and both **Ab**$_y$ and **Ba**$_x$ interactions are related to a function of the sine θ. Thus, we would identify the coefficients of the linear equation, $f(\theta) = C_1 \cos\theta + C_2 \sin\theta$. In this case, $C_1 = (-|Aa_y + Bb_x|)$ and $C_2 = (-|Ab_y + Ba_x|)$, on the basis of the energy levels of the orbitals. Here, the equation $|Aa_y + Bb_x|$ is inversely proportional to $|\boldsymbol{\sigma}_\mathrm{C} - \mathbf{e}_\mathrm{S}|$ and $|\boldsymbol{\pi}_\mathrm{C} - \mathbf{e}_\mathrm{A}|$, and the equation $|Ab_y + Ba_x|$ is inversely proportional to $|\boldsymbol{\sigma}_\mathrm{C} - \mathbf{e}_\mathrm{A}|$ and $|\boldsymbol{\pi}_\mathrm{C} - \mathbf{e}_\mathrm{S}|$. As shown on the right-hand side of Figure 8, the interactions (**Aa**$_y$ and **Ba**$_x$) involved in the cyclopropane Walsh orbital $\mathbf{e}_\mathrm{S}$ would not significantly affect the stabilization of the system, as expected.

Due to the combination of these two types of major homoconjugation (corresponding to both **Ab**$_y$ and **Bb**$_x$), the stabilization of the entire system is maximized at a slightly twisted perpendicular conformation (ca. 70°), and **4** would be stabilized more strongly than **3**, because of the strong homoconjugation involved in interaction **Ab**$_y$. The strong homoconjugative stabilization involved in **Ab**$_y$ in the case of **4** would be caused by the small energy gap between the Walsh orbital $\mathbf{e}_\mathrm{A}$ of cyclopropane and the caged C−C σ orbital $\boldsymbol{\sigma}_\mathrm{C}$; in contrast, in **3**, the energy gap between the phenyl π orbital $\boldsymbol{\pi}_\mathrm{P}$ and $\boldsymbol{\sigma}_\mathrm{C}$ orbital would be significantly larger. Therefore, we concluded that a complicated C−C bond length pattern (60−120°) would result in these four types of homoconjugation in the case of this conformation. The second local minimum structure would then be accounted for by the same interactions, although the stabilization by homoconjugation was weaker in magnitude than that achieved at the deepest local minimum.

Conclusions

On the basis of the current explanations for cyclopropane ring structure (and for homoconjugation as well), we concluded that the conformation of the cyclopropane ring observed by both experimental and theoretical assessments would result in the electronic effect of the cyclopropane ring adjacent to a carbon atom of an *o*-carborane cage. This type of the electronic effect would result in two types of major homoconjugation. These major homoconjugations were found to depend greatly on directionality, wherein the Walsh orbital ($\mathbf{E}_\mathbf{a}$) interacted with both the σ and the π orbitals of the multicoordinated triple bond of the *o*-carborane cage. As a result, the homoconjugative stabilization of the cyclopropyl group was stronger than that of the phenyl group in this caged *o*-carborane system.

In this report, we proposed a conceptualization of the most strongly stabilizing interactive geometry for a cyclopropane ring occurring adjacent to a highly electron-deficient system, wherein the system is stabilized by a slightly twisted perpendicular conformation of the cyclopropane ring. These phenomena were attributed to the specific character of cyclopropane, which has degenerate, higher-lying occupied, lower-lying unoccupied, bent, and direction-dependent Walsh orbitals; in addition, the present results suggested that the specific bonding nature of the multicoordinated triple bond of the *o*-carborane cage contributes to these phenomena.

Experimental Section

General Procedure. The melting point is uncorrected. The ^{1}H, ^{11}B, and ^{13}C NMR spectra were measured at 400, 160.35, and 100 MHz, respectively. The NMR spectra referenced the peak of $CHCl_3$ (7.25 ppm, ^{1}H), the peak of $BF_3{\cdot}OEt_2$ (0.0 ppm, ^{11}B) (15% (v/v)) in $CDCl_3$ solution (external reference), and the middle peak of $CDCl_3$ (77.0 ppm, ^{13}C), respectively. The low-resolution mass spectrum (LRMS) was measured by tuning with both N_2 and perfluoro kerosene (PFK). The high-resolution mass spectrum (HRMS) was calibrated with PFK. The infrared spectum was measured by KBr tablet.

1-Cyclopropyl-1,2-dicarba-*closo*-dodecaborane(12) (4). The preparation of this compound (colorless prism (mp 30−31 °C)) was given in the Supporting Information of ref 2. ^{1}H NMR ($CDCl_3$ at +25 °C): δ 0.61−0.81 (4H, m), 1.25−3.00 (11H, m, br), 3.59 (1H, s). ^{13}C NMR ($CDCl_3$ at +30 °C): δ 8.9, 18.0, 62.1, 77.8. ^{13}C NMR ($CDCl_3$ at −60 °C): δ 9.1, 17.6, 62.1, 77.8. ^{11}B NMR ($CDCl_3$ at +30 °C): δ −13.45 (2B, d, 152.5), −12.79 (2B, d, 166.0), −11.69 (2B, d, 165.6), −9.75 (2B, d, 148.2), −6.13 (1B, d, 151.0), −2.79 (1B, d, 151.0). LRMS: *m/e* 184 (M^+). HRMS: calcd for $C_5H_{16}(^{10}B)_2(^{11}B)_8$ *m/e* 184.2255, found *m/e* 184.2249 (−0.6 mmu). The prismatic crystal was subjected to X-ray crystal structure analysis at 123 ± 1 K.

(2-Cyclopropyl-1,2-dicarba-*closo*-dodecaborane(12)-1-yl)phenylmethanol (9). This material (recrystallized from *n*-hexane; colorless prism (mp 134 °C)) was obtained as a byproduct in the synthesis of 2-cyclopropyl-1,2-dicarba-*closo*-dodecaborane(12)-1-alcohol from **4** with benzoyl peroxide, as described in ref 2. ^{1}H NMR ($CDCl_3$ at +25 °C): δ 0.80−1.00 (4H, m), 1.20−3.20 (11H, m, br), 2.47 (1H, d, 4.2), 5.33 (1H, d, 4.2), 7.40 (5H, s). ^{13}C NMR ($CDCl_3$ at +30 °C): δ 9.1, 9.5, 15.9, 73.3, 83.2, 84.4, 127.0, 128.6, 129.3, 139.6. ^{13}C NMR ($CDCl_3$ at −60 °C): δ 9.0, 9.6, 15.8, 72.6, 82.9, 83.4, 126.7, 128.5, 129.2, 139.2. ^{11}B NMR ($CDCl_3$ at +30 °C): δ −12.56 (2B, d, overlap), −12.13 (2B, d, overlap), −11.59 (2B, d, 145.1), −10.72 (2B, d, 148.2), −5.36 (1B, d, 142.2), −3.24 (1B, d, 153.9). IR (ν_{max}, KBr): 3500, 2550, 1450, 1130, 1055, 1030, 730, 700 cm^{-1}. LRMS: *m/e* 290 (M^+). HRMS: calcd for $C_{12}H_{22}O(^{10}B)_2(^{11}B)_8$ *m/e* 290.2674, found *m/e* 290.2654 (−2.0 mmu). The prismatic crystal was subjected to X-ray crystal structure analysis at both 123 ± 1 and 297 ± 1 K (data not shown).

Computational Methods. Calculations were performed using the Gaussian98 program.[35] The geometry of the molecules was optimized with the ab initio Hartree−Fock (HF) and the hybrid density functional (B3LYP) theory, using the 6-31G* basis set. The local minimum structures of **1**, **2**, and **5** were obtained under constrained symmetry (C_s symmetry for **2** and C_{2v} symmetry for **1** and **5**) conditions. The orientation of the methyl group in **2** and **5**−**7** was determined on the basis of the total energies calculated using the HF/6-31G* method; **2** had two possible conformations with the C_s symmetry, **5** had two possible conformations with the C_{2v} symmetry and one possible conformation with the C_s symmetry, and **6** and **7** each had two possible conformations with the C_s symmetry (wherein the cyclopropane or benzene ring was constrained to the C_s symmetry). The conformation of the cyclopropyl group of **6** with the C_1 symmetry was based on the relaxed potential energy surface scan of the parent molecule, **4**. In the same manner as that used for **6**, the structure of **8** was obtained with the C_2 symmetry using both the HF/6-31G* and the B3LYP/6-31G* methods. **7** had a local minimum with C_s symmetry rather than with C_1 symmetry. Both the total energies and the carbon−carbon bond lengths (varying the torsional angle) of **3** and **4** were obtained by a relaxed potential energy surface scan. This partial optimization was carried out using the B3LYP/6-31G* method. The gauge-independent atomic orbital (GIAO) method[27] was used for the comparisons between the experimental and the theoretical chemical shifts (^{11}B and ^{13}C nuclei). Model chemistry (HF/6-31G*//B3LYP/6-31G*) was carried out for the GIAO calculation of **4** and **6**. The calculated ^{13}C NMR chemical shifts of the caged carbon atoms were scaled according to the following equation: $\delta(\text{ppm}_{\text{calcd}}) = \delta(\text{ppm}_{\text{exp}}) \times 0.893 - 2.554$.[28]

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Supporting Information Available: Part of the Experimental Section, the X-ray structural information, the calculated geometries and total energies for all molecules, and the ^{13}C NMR spectrum obtained from this work, as well as the CSD codes used for the statistical analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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