A Conformational Comparison of 1,2-Bis(phenylthio)-o-carborane, $C_{14}H_{20}B_{10}S_2$, by X-Ray Diffraction Method and Molecular Orbital Calculation

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Abstract

The reaction of dilithio-o-carborane with dipenyl disulfide produces a phenyl thiolated o-carborane and it has been confirmed that there is conformational similarity between the structure of the compound elucidated by X-ray crystallography and that calculated by ab initio and density functional theory.

抄　　錄

Dilithio-o-carborane과 dipenyl disulfide를 反應하여 a phenyl thiolated o-carborane compound 가 얻어 졌으며 X-ray crystallography로 밝혀진 이 compound의 構造와 ab initio 및 density functional theory로 計算한 이 compound의 構造間에 conformational similarity가 있음을 確認하였다.

1. Introduction

o-Carboranes are "superaromatic" systems,[1] which can undergo electrophilic and nucleophilic substitution. The o-carborane has icosahedral geometry to be idealized mm2 (C_{2v}) symmetry.[2] To develop the chemistry of dilithio-o-carborane ($Li_2C_2B_{10}H_{10}$), we have examined its reactions with diphenyl disulfide which is capable of binding substrates such as palladium (II) complex.[3]

The structure of the title compound (I) was already elucidated by Vinas, *et al.*[4] by means of X-ray crystallography in 2002. We now report its slightly better structural result than the previous one from the viewpoint of the number of intensity data and the reliability index and besides the calculated result carried out using the ab initio Hartree-Fock level of theory with self-consistent reaction field method in the gas phase.

2. Experimental Section

2-1. Synthesis

All experiments were performed under a nitrogen atmosphere by standard Schlenk techniques. A stirred THF solution (10 mL) of o-carborane (0.15 g, 1.04 mmol) was lithiated using 1.6 M n-BuLi (1.43 mL, 2.29 mmol) at −78°C. The reaction mixture was stirred continuously. After 2 hours at −78°C, diphenyldisulfide (0.25 g, 1.14 mmol) was dropwised. The mixture was slowly warmed to room temperature and stirred for additional 4 hours. The solution was extracted with ether, washed with saturated aqueous NaCl, and dried over anhydrous $MgSO_4$. All volatiles were evaporated in vacuo.

The pure product was obtained by chromatography on silica gel using benzene/hexane (1:10) as an eluent, and recrystallized from benzene/hexane solution as colorless crystals in 94% yield. mp: 186°C.

^{1}H NMR (CDCl$_3$): δ 7.48 (d, 4H, J = 8.0 Hz), 7.24 (m, 6H). IR (KBr pellet: cm^{-1}): 2552 (ν(B-H)).

2-2. Collection and reduction of X-ray diffraction data

The X-ray diffraction data were collected on a Bruker SMART diffractometer[5] with 1 K CCD area detector using graphite-monochromated MoKα radiation (0.71073 Å) at room temperature. The processes for the collection and reduction of X-ray data were same as those by Kim and others[5-7] and only difference was that 1850 frames by the command MULTIRUN were collected because the title compound belonged to the monoclinic system. All crystal data and structure refinement for (I) are given in Table 1.

2-3. Structure solution and refinement

The structure was solved by direct methods and subsequent Fourier synthesis with the space group $C2/c$(15); it was refined by full-matrix least-squares on F^2 using reflections with I > 2σ(I).[8] Scattering factors for neutral atoms and dispersion corrections were taken from the internal library of SHELXL97.[8]

Table 2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for (I). U(eq) is defined as one third of the trace of the orthogonalized U$_{ij}$ tensor

	x	y	z	U(eq)
S	604(1)	10173(1)	4013(1)	31(1)
C(1)	341(1)	8392(1)	3253(1)	24(1)
C(2)	1368(1)	10726(1)	3671(1)	29(1)
C(3)	2052(1)	10281(2)	4441(2)	43(1)
C(4)	2643(1)	10794(2)	4191(2)	55(1)
C(5)	2556(1)	11744(2)	3205(2)	54(1)
C(6)	1878(1)	12196(2)	2450(2)	47(1)
C(7)	1281(1)	11694(2)	2685(1)	35(1)
B(1)	−535(1)	7925(1)	3027(1)	25(1)
B(2)	888(1)	6875(2)	3392(1)	28(1)
B(3)	212(1)	6871(2)	4052(1)	28(1)
B(4)	−549(1)	5892(2)	3037(1)	29(1)
B(5)	335(1)	5235(2)	3248(1)	30(1)

Table 1. Crystal data and structure refinement for (I)

Identification code	(I)
Empirical formula	$C_{14}H_{20}B_{10}S_2$
Formula weight	360.52
Temperature	233(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, C2/c
Unit cell dimensions	a = 19.956(4) Å alpha = 90°
	b = 8.7533(18) Å beta = 111.17(3)^o
	c = 11.598(2) Å gamma = 90°
Volume	1889.2(7) Å^3
Z, Calculated density	4, 1.268 Mg/m^3
Absorption coefficient	0.276 mm^{-1}
F(000)	744
Crystal size	0.34 × 0.25 × 0.23 mm
Theta range for data collection	2.19 to 28.37^o
Limiting indices	−26<=h<=26, −11<=k<=11, −15<=l<=15
Reflections collected/unique	9512/2357 [R(int) = 0.0177]
Completeness to theta = 28.37	99.3%
Max. and min. transmission	0.9392 and 0.9118
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2357/0/124
Goodness-of-fit on F^2	1.080
Final R indices [I>2sigma(I)]	R1 = 0.0313, wR2 = 0.0886
R indices (all data)	R1 = 0.0347, wR2 = 0.0925
Extinction coefficient	0.0014(7)
Largest diff. peak and hole	0.293 and −0.214 e.Å^{-3}

Table 3. Bond lengths [Å] and angles [deg] for (I)

S-C(1)	1.7749(11)	C(1)#1-B(1)-B(4)	104.63(8)
S-C(2)	1.7754(12)	C(1)-B(1)-B(4)	104.69(8)
C(1)-B(2)	1.6897(17)	C(1)#1-B(1)-B(3)	107.66(8)
C(1)-B(3)	1.6937(17)	C(1)-B(1)-B(3)	57.65(7)
C(1)-B(1)#1	1.7135(16)	B(4)-B(1)-B(3)	59.44(7)
C(1)-B(1)	1.7203(16)	C(1)#1-B(1)-B(2)#1	57.58(7)
C(1)-C(1)#1	1.784(2)	C(1)-B(1)-B(2)#1	107.62(9)
C(2)-C(7)	1.3828(18)	B(4)-B(1)-B(2)#1	59.41(7)
C(2)-C(3)	1.3894(18)	B(3)-B(1)-B(2)#1	107.60(9)
C(3)-C(4)	1.387(2)	C(1)-B(2)-B(4)#1	106.08(9)
C(4)-C(5)	1.374(3)	C(1)-B(2)-B(3)	58.46(7)
C(5)-C(6)	1.378(2)	B(4)#1-B(2)-B(3)	107.97(9)
C(6)-C(7)	1.3848(19)	C(1)-B(2)-B(5)	105.49(9)
B(1)-B(4)	1.7802(19)	B(4)#1-B(2)-B(5)	60.36(8)
B(1)-B(3)	1.7905(19)	B(3)-B(2)-B(5)	59.82(7)
B(1)-B(2)#1	1.7921(18)	C(1)-B(2)-B(1)#1	58.87(7)
B(2)-B(4)#1	1.7703(19)	B(4)#1-B(2)-B(1)#1	59.96(7)
B(2)-B(3)	1.7755(19)	B(3)-B(2)-B(1)#1	106.77(9)
B(2)-B(5)	1.7815(19)	B(5)-B(2)-B(1)#1	107.59(9)
B(3)-B(4)	1.7703(19)	C(1)-B(3)-B(4)	106.26(9)
B(3)-B(5)	1.7736(19)	C(1)-B(3)-B(5)	105.66(9)
B(4)-B(5)#1	1.7857(19)	B(4)-B(3)-B(5)	60.51(8)
B(4)-B(5)	1.7857(19)	C(1)-B(3)-B(2)	58.24(7)
B(5)-B(5)#1	1.767(3)	B(4)-B(3)-B(2)	108.48(9)
C(1)-S-C(2)	104.65(5)	B(5)-B(3)-B(2)	60.26(7)
B(2)-C(1)-B(3)	63.30(8)	C(1)-B(3)-B(1)	59.10(7)
B(2)-C(1)-B(1)#1	63.54(7)	B(4)-B(3)-B(1)	59.99(7)
B(3)-C(1)-B(1)#1	114.38(9)	B(5)-B(3)-B(1)	107.91(9)
B(2)-C(1)-B(1)	114.46(9)	B(2)-B(3)-B(1)	107.05(8)
B(3)-C(1)-B(1)	63.26(7)	B(2)#1-B(4)-B(3)	109.47(9)
B(1)#1-C(1)-B(1)	110.28(8)	B(2)#1-B(4)-B(1)	60.63(7)
B(2)-C(1)-S	125.27(8)	B(3)-B(4)-B(1)	60.57(7)
B(3)-C(1)-S	119.68(7)	B(2)#1-B(4)-B(5)#1	60.13(8)
B(1)#1-C(1)-S	121.38(7)	B(3)-B(4)-B(5)#1	107.77(9)
B(1)-C(1)-S	112.77(7)	B(1)-B(4)-B(5)#1	107.93(9)
B(2)-C(1)-C(1)#1	109.35(7)	B(2)#1-B(4)-B(5)	108.08(9)
B(3)-C(1)-C(1)#1	108.82(7)	B(3)-B(4)-B(5)	59.83(8)
B(1)#1-C(1)-C(1)#1	58.87(7)	B(1)-B(4)-B(5)	107.83(9)
B(1)-C(1)-C(1)#1	58.50(7)	B(5)#1-B(4)-B(5)	59.32(9)
S-C(1)-C(1)#1	118.07(4)	B(5)#1-B(5)-B(3)	108.45(8)
C(7)-C(2)-C(3)	120.28(12)	B(5)#1-B(5)-B(2)	108.41(8)
C(7)-C(2)-S	119.34(9)	B(3)-B(5)-B(2)	59.92(7)
C(3)-C(2)-S	120.21(11)	B(5)#1-B(5)-B(4)#1	60.34(9)
C(4)-C(3)-C(2)	119.14(14)	B(3)-B(5)-B(4)#1	107.38(9)
C(5)-C(4)-C(3)	120.51(14)	B(2)-B(5)-B(4)#1	59.51(7)
C(4)-C(5)-C(6)	120.23(14)	B(5)#1-B(5)-B(4)	60.34(9)
C(5)-C(6)-C(7)	120.04(15)	B(3)-B(5)-B(4)	59.65(8)
C(2)-C(7)-C(6)	119.78(13)	B(2)-B(5)-B(4)	107.53(9)
C(1)#1-B(1)-C(1)	62.62(8)	B(4)#1-B(5)-B(4)	107.65(9)

Symmetry transformations used to generate equivalent atoms: #1 −x, y, −z + 1/2.

Anisotropic displacement parameters were assigned to all non-hydrogen atoms. The positional parameters of all H-atoms were constrained to ride on their attached atoms with isotropic displacement parameters fixed at 1.2 times the equivalent isotropic displacement parameter of their parent atoms. The highest peak and deepest holes in the final difference density map are 0.293 $e/\text{Å}^3$ at 0.76 Å from C5 and -0.214 $e/\text{Å}^3$ at 1.21 Å from C1, respectively.

The crystallographic data, final conventional agreement indexes and other structure refinement parameters are listed in Table 1. Final atomic coordinates and the equivalent isotropic thermal parameters are given in Table 2. Table 3 shows selected bond lengths and angles. All average value given in this paper are calculated by the program AVERESD.[9]

3. Discussion

In the title compound (I), a half molecule belongs to an asymmetric unit and a molecule is completed by another half molecule obtained by twofold symmetry along b-axis at $x = 0$ and $z = 1/4$ [symmetry code (i) $-x$, y, $-z + 1/2$] (see Fig. 1).

The aromatic C_{sp2}-C_{sp2} distances in the phenyl ring, which is planar within $0.007(1)$ Å, vary from $1.374(3)$ to $1.3894(18)$ Å with a mean value of $1.3827(9)$ Å and the average C-C-C angle is $120.00(6)°$. These values are very similar to those
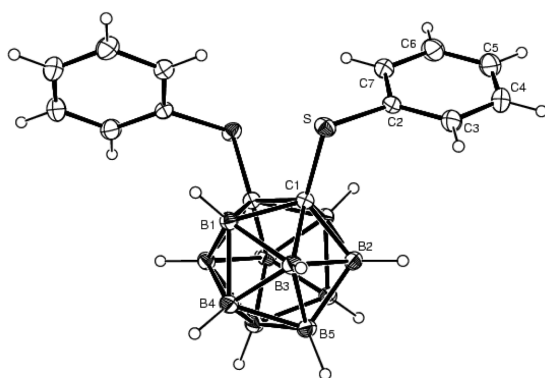

Fig. 1. An ORTEP diagram[10] (20% probability ellipsoids) of (I). H atoms are drawn as small circles of arbitrary radii. Only half molecule (an asymmetric unit) is labelled and another half molecule is obtained by symmetry element −x, y, −z + 1/2.

of 25,27:26,28-bis(3,9-dioxa-6-aza-undecane-1,11-dioxy)calix[4]arene tetrahydrate.[11] The dihedral angle between the phenyl ring in an asymmetric unit and another one by the symmetry element [code (i)] is $74.70(5)°$.

The average S-C distance is $1.7752(8)$ Å, which is slightly shorter than $1.818(8)$ Å found in the molecular structure of $1,2\text{-Ph}_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}(3)$[4] but similar to $1.772(4)$ Å in the molecular structure of $1,2\text{-(SPh)}_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}(5)$.[4] The angle of C1-S-C2 $104.65(5)°$, which is very close to the tetrahedral angle, denotes that there is two lone pairs at the sulfur atom. S ... S [code (i)] distance is $3.467(1)$ Å.

In icosahedral $B_{12}H_{12}^{-2}$, the three center bond theory in boron hydride provides a useful description for understanding the structure and the electronic distributions. Carbon has one more electron than boron, so the C-H moiety is isoelectronic with the B-H$^-$ moiety. Replacing the two B-H$^-$ moieties, icosahedral carborane can be represented as $C_2B_{10}H_{12}$.[2]

In the carborane moiety of (I), B-B distances range from $1.7703(19)$ Å of B3-B4 to $1.7921(18)$ Å of B1-B2 [code (i)] with the average B-B distance $1.78000(52)$ Å. B-B-B angles are divided into two kinds: acute angles with a mean $60.00(1)$ Å and obtuse angles with a mean $107.98(2)$ Å as shown in Table 3.

As shown in Fig. 1, the carborane forms an icosahedron consisting of twenty nearly regular triangles with a side $1.78000(52)$ Å on the average (see Table 3). All these conformational values are similar to those found in $1,2\text{-(SPh)}_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}(5)$.[4]

It is, however, noteworthy that the C1-C1 [code (i)] distance $1.784(2)$ Å is considerably longer than 1.629 Å in $1,2\text{-C}_2\text{B}_{10}\text{H}_{10}(1)$,[4] 1.64 Å in $o\text{-B}_{10}\text{Br}_2\text{H}_8\text{C}_2\text{H}_2$,[12] $1.67(4)$ Å in $\text{B}_{10}\text{Br}_2\text{H}_8\text{C}_2\text{H}_2$,[12] $1.733(4)$ Å in $1,2\text{-Ph}_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}(3)$,[4] but shorter than $1.798(3)$ Å in $1,2\text{-(SPh)}_2\text{-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}(5)$[4] and $1.858(5)$ Å in $1,2\text{-}\mu\text{-SCH}_2(\text{CH}_2\text{OCH}_2)\text{CH}_2\text{S-}1,2\text{-C}_2\text{B}_{10}\text{H}_{10}(7)$,[4] and the C1-C1 [code (i)] distance is slightly longer than B5-B5 [code (i)] = $1.767(3)$ Å, which is the shortest one among B-B bond lengths (see Table 3), even though the covalent radius 0.77 Å for carbon is shorter than 0.83 Å for boron. This phenomenon appears to be attributable to the steric repulsion between the freely moveable two phenyl

sulfides related by symmetry code (i), and so it could be said that the C-C distance in the carborane cluster may vary depending on substituent.

The closest intermolecular distance 3.0613 Å between S and H1 [code (i)] suggests that the molecular packing is governed only by Van der Waals forces.

4. Molecular Orbital Calculation

The molecular orbital calculation was performed using Gaussian 98 W revision A. 7.[14] The geometries obtained from X-ray analysis were optimized by Hartree Fork theory (HF), # RHF/3-21G(d) and the optimized geometry was used in the input file

Table 4. Selected bond lengths, bond angles, HOMO, LUMO and total energy obtained from X-ray analysis and Gaussian 98 W are tabulated and no information on the energy is available from X-ray analysis. Only the minimum and maximum values for the acute and obtuse angles in the *o*-carborane are listed.

	X-Ray Analysis (Å, °)	Gaussian 98 W (Å, °)
C1-C1#1	1.784(2)	1.7045
C1-B1	1.7203(16)	1.7175
C1-B2	1.6897(17)	1.7065
C1-B3	1.6937(17)	1.7155
C1-B1#1	1.7135(16)	1.7215
S-C1	1.7749(11)	1.8020
S-C2	1.7755(12)	1.7851
Shortest B-B	B3-B4, 1.7703(19)	B1-B4, 1.7773
Longest B-B	B1-B2#1, 1.7921(18)	B4-B5, 1.8024
Shortest C-C in Ph	C4-C5, 1.364(3)	C6-C7, 1.3846
Longest C-C in Ph	C2-C3, 1.3894(18)	C2-C3, 1.3901
B-H	1.1100 (constrain)	1.1732~1.1827
C-H	0.9400 (constrain)	1.0733~1.0752
<B2#1-B4-B3 (max)	109.47(9)	108.7806
<C1#1-B1-B2#1 (min)	57.58(7)	57.9704
<C1-S-C2	104.65(5)	106.4008
<S-C1-C1#1	118.07(4)	119.5347
<S-C1-C1#1-S#1	10.73	12.4561
HOMO		−0.25146 Ha = −6.8425 eV
LUMO		−0.04240 Ha = −1.1538 eV
Total energy		−1590.554 Ha = −43280.565 eV

where the total energy is HF = E(E-E) + E(N-N) + E(E-N) + KE.
1 Hartree = 27.211 eV. Symmetry code #1: −x, y, −z + 1/2.

(a)   (b)
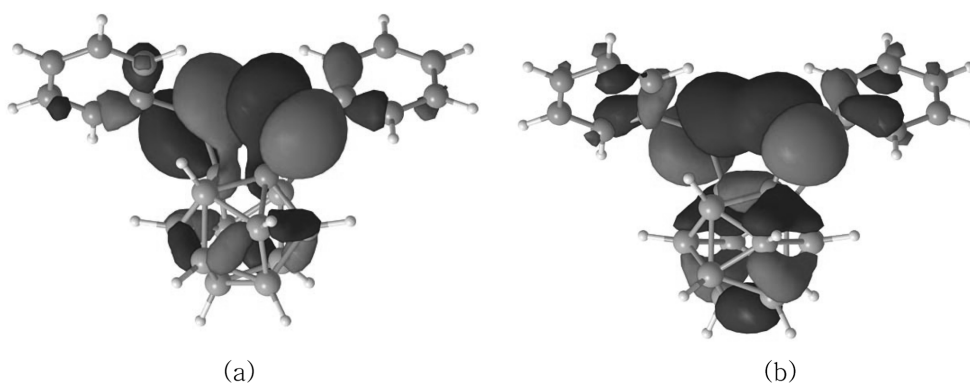
Fig. 2. Orbital shape for (I). (a) LUMO: −1.1538 eV, (b) HOMO: −6.8425 eV.

for the calculation of HOMO, LUMO and total energy. The calculation was carried out using # RB3LYP/6-31G(d).

The selected bond lengths and bond angles obtained from both X-ray analysis are compared with those from Gaussian 98W, and the HOMO, LUMO and total energies are also listed in Table 4. As can be seen in Table 4, the atomic bond lengths from the Gaussian 98W data are slightly longer on the whole than those including the calculated C-H = 0.94 Å and B-H = 1.11 Å in the carborane cluster from the X-ray analysis, but the valence angles are very similar to each other. Fig. 2 shows the LUMO and HOMO are mainly situated in the vicinity of sulphur atoms and their energy gap 5.6887 eV indicates the compound (I) is close to an insulator rather than a conductor. The UV absorption edge for (I) has not been measured.

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