

$$\gamma = \frac{1}{\kappa\nu_i^0} \left[ \frac{d\nu}{dP} \right] \quad (1)$$

of a molecule is therefore directly proportional to  $d\nu/dP$ . From our vibrational data, it appears that the low-pressure, disordered phase of  $o\text{-C}_2\text{B}_{10}\text{H}_{12}$  is more compressible than the ordered, high-pressure phase.

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## New Syntheses of 1,2-Ethano-*o*-carborane and the Structure of 9-Chloro-1,2-ethano-*o*-carborane<sup>†</sup>

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Two new routes to 1,2-ethano-*o*-carborane (**1**) are described. Both depend on the intramolecular displacement of a leaving group by a cage carbanion. The X-ray structure of the 9-chloro derivative (**5**) was determined. Crystals of **5** are monoclinic, space group  $P2_1/c$ , with  $a = 11.456$  (4) Å,  $b = 8.120$  (2) Å,  $c = 12.333$  (5) Å,  $\beta = 105.18$  (3)°,  $Z = 4$ , and  $D_{\text{calcd}} = 1.23$  g/cm<sup>3</sup>. The structure was solved by direct methods and refined by blocked-cascade least squares to an  $R$  value of 0.057 for 1326 independent reflections.

### Introduction

Among the myriad known 1,2-disubstituted *o*-carboranes are several molecules in which the framework carbon atoms are also members of a five- or six-membered exo-cage bridge.<sup>1</sup> However, there is but one compound (**1**) in which the two framework carbons are members of a four-membered ring as well as the cage.<sup>2</sup> Our earlier synthesis of **1** was impractical, as it involved several steps, the last of which produced a number of products in comparable amounts. Accordingly, it is not surprising that no X-ray structural determination of **1** has been reported. Here we report two related new and efficient syntheses of **1** as well as the structural data on the 9-chloro derivative.

### Experimental Section

**General Remarks.** <sup>1</sup>H NMR spectra were recorded on a General Electric QE 300 spectrometer at 300 MHz in CDCl<sub>3</sub>, with signals referenced to Me<sub>4</sub>Si. Analytical gas chromatography was performed on a Hewlett-Packard 5890A gas chromatograph with helium as carrier gas, using 2-mm-i.d. stainless steel columns packed with 3% OV 17 on Chromosorb W-HP. GC/MS runs were conducted on a Hewlett-Packard 5992B instrument, using 2-mm-i.d. glass columns packed with 3% OV 17 on Chromosorb W-HP. Preparative gas chromatography was performed on a Varian A90P gas chromatograph with helium as carrier gas. Mass spectra were obtained on a KRATOS MS 50 RFA high-resolution mass spectrometer. In general, reactions were conducted under argon. All solvents were purified and dried by using standard procedures. Melting points were determined on a Thomas-Hoover Uni-Melt or an Electrothermal Digital Melting Point Apparatus and are uncorrected.

**1-(*o*-Carboranyl)-ethan-2-ol Tosylate (**2**).** Into a 250-mL three-neck round-bottomed flask was placed 4 g (32.7 mmol) of decarborane in 50 mL of CH<sub>3</sub>CN. The solution was refluxed under an atmosphere of argon for 2 h. The CH<sub>3</sub>CN was removed by distillation to yield the B<sub>10</sub>H<sub>10</sub>·2CH<sub>3</sub>CN complex. This was dissolved in 50 mL of toluene and 10.5 g (46.8 mmol) of 4-tosyl-1-butyne<sup>3</sup> was added. The reaction mixture was refluxed under argon for 2 h. The toluene was removed by distillation to leave a gummy yellow solid. This material was placed in a Soxhlet apparatus and extracted with hexane followed by CH<sub>2</sub>Cl<sub>2</sub>. The organic solutions were combined, and the solvent was removed on a rotary evaporator to leave a whitish solid. This solid was purified by column chromatography on silica gel (CHCl<sub>3</sub>) to give 4.5 g (40%) of a white solid, mp 112–114 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  7.78, 7.40 (AA'BB', 4 H), 4.11 (t, 2 H,  $J = 6.1$  Hz), 3.69 (br s, 1 H), 2.63 (t, 2 H,  $J = 6.1$  Hz), 2.49 (s, 3 H), 1.4–3.0 (br m, 10 H, B–H). IR (KBr): 3058, 2577, 1597, 1426, 1355, 1190, 1173, 815 cm<sup>-1</sup>. Precise mass: calcd for C<sub>11</sub>H<sub>22</sub><sup>11</sup>B<sub>8</sub><sup>10</sup>B<sub>2</sub>SO<sub>3</sub> 342.2292, found 342.2246.

**1,2-Ethano-*o*-carborane (**1**).** Into a 100-mL three-neck round-bottomed flask was placed 1.5 g (4.4 mmol) of tosylate **2** in 50 mL of benzene. The flask was placed under an argon atmosphere, and 2.1 mL of 2.5 M *n*-BuLi in hexanes was added all at once. The solution was allowed to stir for 14.5 h at room temperature. The reaction mixture was poured into 25 mL of 5% HCl, and the layers were separated. The aqueous layer was extracted with 2 × 10 mL ether. The combined organic layers were washed with saturated NaHCO<sub>3</sub> solution and dried over MgSO<sub>4</sub>. The solvent was removed on a rotary evaporator to leave a white solid. This material was purified by column chromatography on silica gel (hexanes) to give 0.3 g (40%) of a white waxy solid, mp 274–275 °C (sealed) (lit.<sup>2</sup> mp 261 °C (sealed)). Suitable crystals for X-ray analysis could not be obtained.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  2.85 (s, 4 H), 1.4–3.6 (br m, 10 H, B–H).

**9-Chloro-1,2-ethano-*o*-carborane (**5**).** Into a 25-mL round-bottomed flask was placed 100 mg (0.6 mmol) of **1** and 17 mg of AlCl<sub>3</sub> in 5 mL of CCl<sub>4</sub>. The reaction mixture was refluxed overnight. GC analysis showed the mixture to be mostly starting material. An additional 60 mg of AlCl<sub>3</sub> was added, and the mixture was refluxed for 15 min, after which time it turned dark brown. The solution was allowed to cool to room temperature and poured into 15 mL of brine. The layers were separated, the organic layer was dried over MgSO<sub>4</sub>, and the solvent was removed on a rotary evaporator. GC/MS analysis showed the crude material to be a mixture of monochloro- and dichloro-substituted carboranes. The mixture was purified by preparative GC (0.25 in. × 10 ft 10% OV17 column; oven temp 160 °C), and 17 mg (14%) of a white solid, mp 192–194 °C (sealed), was obtained. Suitable crystals were obtained by slow evaporation of a heptane solution.

**1-(*o*-Carboranyl)-2-bromoethane (**4**).** A solution of 2.5 g of 1-(*o*-carboranyl)-2-hydroxyethane<sup>4</sup> was dissolved in 5 mL of phosphorus tribromide and stirred at room temperature for 10 h. The mixture was then dissolved in 50 mL of ether and washed with sodium bicarbonate and brine solutions. The ether was removed by rotary evaporation. The crude oil was distilled by using a Kugelrohr apparatus at 120 °C (oven)/0.1 mmHg. A yield of 2.3 g of product (69%) was obtained, mp 108–110 °C (sealed) (lit.<sup>5</sup> mp 114–115 °C).

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  3.72 (s, 1 H, H–C, cage), 3.40 (t,  $J = 9.0$  Hz, 2 H), 2.79 (t,  $J = 9.0$  Hz, 2 H). Precise mass: calcd for

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<sup>†</sup> Dedicated to Professor E. C. Taylor on the occasion of his 65th birthday.

**Table I.** Relative Ratios of **1** and **3**

reacn conditions	% <b>1</b>	% <b>3</b>
<i>n</i> -BuLi/THF; 0°C	45	55
<i>n</i> -BuLi/THF; 27 °C	63	37
<i>n</i> -BuLi/benzene; 27 °C	99	1
LiN[Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> ; THF; -76 °C	45	55
DBU/benzene; 27 °C	0	100

C<sub>4</sub>H<sub>15</sub><sup>79</sup>Br<sup>11</sup>B<sub>8</sub><sup>10</sup>B<sub>2</sub> 250.1360, found 250.1238; calcd for C<sub>4</sub>H<sub>15</sub><sup>81</sup>Br<sup>11</sup>B<sub>8</sub><sup>10</sup>B<sub>2</sub> 252.1340, found 252.1237.

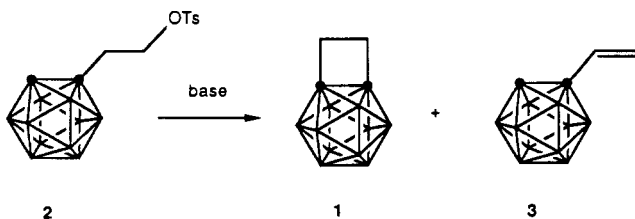
**Gas-Phase Synthesis of 1,2-Ethano-*o*-carborane.** A U-shaped Pyrex tube (12 in. long) was wrapped with heating wire and insulating tape. An 8.5-in. section of the tube was filled with quartz chips that were coated with *n*-butyllithium. The chips were coated by adding 15 mL of a 2.5 M *n*-butyllithium/*n*-hexane solution to dry quartz chips under argon. The chips were then dried by removing the solvent under vacuum. The coated chips were transferred to the U-tube under argon by using a glovebag. The apparatus was connected at one end to a solids addition funnel and at the other to a trap cooled with liquid nitrogen. The system was evaporated to 0.005 Torr at room temperature. The temperature of the U-tube was raised slowly to 140 °C. After 10 min equilibration, 2–5 mg of **4** was added. The pressure would rise to 0.01–0.025 Torr. In about 5 min the pressure would return to 0.005 Torr and another 2–5 mg of solid was then added. The reaction was repeated at 50-, 100-, and 200-mg scales. The average ratio of **1**/**3** was the same despite the scale change. Among the recovered products in the trap there were 94.3% **1** (64%), 1.1% **3**, and 2.5% starting material. Yields were determined by analytical gas chromatography using known amounts of **1** as standard. The mass balance was nearly quantitative.

**X-ray Data and Structure Determination for 5.** A clear platelike crystal of **5** with dimensions 0.05 mm × 0.25 mm × 0.028 mm was used in the X-ray structure determination. All data were collected on a Nicolet R3m diffractometer at room temperature using graphite-monochromated Cu Kα radiation (λ = 1.541 78 Å) and an ω-scan technique with a variable scan rate. Background counts were taken for half the scan time at each extreme of the scan range. Crystal decomposition was monitored throughout data collection by remeasuring two standard reflections after every 50 data measurements; a 10% linear decline in intensity was observed. The intensities were reduced by applying Lorentz, polarization, and decay corrections. Details of X-ray data are given in Table II.

The structure was solved by direct methods using the SHELXTL software.<sup>6</sup> Carbon and boron atoms were refined with anisotropic temperature factors. All hydrogen atoms were located on a difference Fourier map. The carborane hydrogens were fixed at the observed positions; the methylene hydrogens were included in refinement at idealized positions (C–H = 0.96 Å, CCH = 109°) and were varied by using a riding model. Refinement converged (shift/error ≤ 0.10) at *R* = 0.057, *R*<sub>w</sub> = 0.067.<sup>7</sup> The largest peaks in the final difference map (max e/Å<sup>3</sup> = 0.35) were in the vicinity of the chlorine atom. The quantity minimized by the least-squares program was Σw(|F<sub>o</sub>| - |F<sub>c</sub>|)<sup>2</sup>, where *w* is the weight of a given observation.<sup>8</sup> The analytical forms for the scattering factors of the neutral atoms were used.<sup>9</sup>

## Results and Discussion

The new syntheses of **1** derive from the observation that the elimination of *p*-toluenesulfonic acid from tosylate **2** was accompanied by varying amounts of **1**, depending upon the solvent. In



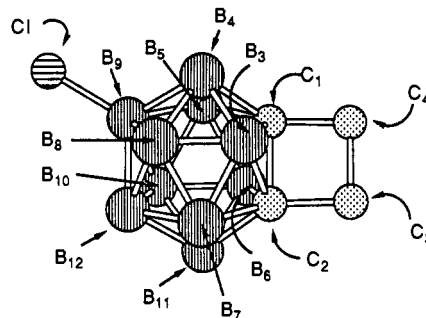
benzene/*n*-BuLi, the optimal solvent/base combination, the iso-

(6) Sheldrick, G. M. "SHELXTL. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffusion Data", University of Göttingen, Göttingen, 1980.

(7)  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $R_w = \sum [w(|F_o| - |F_c|)]^{1/2} / \sum (w|F_o|)^{1/2}$ .

(8)  $w^{-1} = \sigma^2(|F_o|) + g|F_o|^2$ ; final value of *g* = 0.0031.

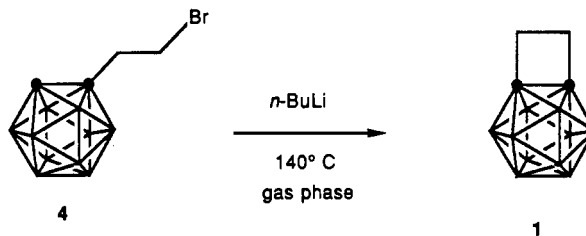
(9) *International Tables of X-ray Crystallography*; Kynoch: Birmingham, England, 1975; pp 99, 149.

**Figure 1.** X-ray-derived structure and numbering for **1**.**Table II.** Crystallographic Data

molecular formula	C <sub>4</sub> H <sub>13</sub> B <sub>10</sub> Cl	diffractometer radiation	Nicolet R3m Cu Kα
fw	204.7	monochromator	graphite
cryst color	clear		single cryst
cryst size	0.03 × 0.25 × 0.28 mm	2θ range	3–114°
<i>a</i>	11.456 (4) Å	reflens measd	± <i>h</i> , ± <i>k</i> , ± <i>l</i>
<i>b</i>	8.120 (2) Å	no. of unique reflcns	1504
<i>c</i>	12.333 (5) Å	no. of obsd reflcns	1326 ( F <sub>o</sub>   ≥ 3σ F <sub>o</sub>  )
β	105.18 (3)°	no. of params	136
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>R</i>	0.057
<i>D</i> (calcd)	1.23 g/cm <sup>3</sup>	<i>R</i> <sub>w</sub>	0.067
<i>F</i> (000)	416 e	GOF	1.36
μ(Cu Kα)	25.5 cm <sup>-1</sup>		

lated yield of **1** was 40% and the ratio of **1** to 1-vinyl-*o*-carborane (**3**) was as high as 99/1. Table I gives the ratio of **1**/**3** as a function of a few solvent/base systems.

An even better route to **1** in which 1-(1-*o*-carboranyl)-2-bromoethane (**4**) was decomposed over *n*-butyllithium in the gas phase at 140 °C maintained the **1**/**3** ratio at 99/1 but increased the yield to 56–64% based upon unrecovered starting material.



Although the amount of recovered starting material varied from run to run, the amount was always small, typically about 2.5%. This route is especially convenient, and **4** can be decomposed on a 200-mg scale.

Thus, **1** can be obtained in reasonable amounts, and the way seemed open for a straightforward determination of structure by X-ray diffraction. Unfortunately, our best efforts failed to yield usable crystals of **1**. Accordingly, a solid derivative was sought in which it seemed likely that there would be minimal disruption of the critical area around the four-membered ring.

Treatment of **1** with CCl<sub>4</sub> and AlCl<sub>3</sub> led to a mixture of 9-chloro-1,2-ethano-*o*-carborane (**5**) and a dichlorinated isomer, which could be separated by preparative gas chromatography to give 14% of **5**. This molecule gave crystals of a quality suitable for X-ray analysis.

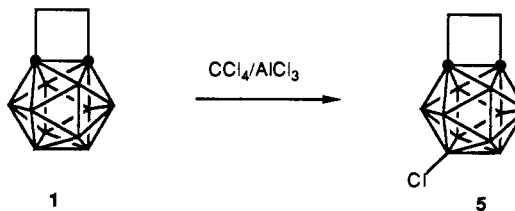
**Figure 1** shows a view of the X-ray-derived structure<sup>10</sup> along

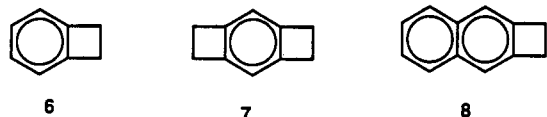
Table III. Bond Lengths (Å)

C(1)–C(2)	1.621 (4)	C(1)–B(3)	1.720 (4)
C(1)–B(4)	1.684 (5)	C(1)–B(5)	1.692 (4)
C(1)–B(6)	1.717 (5)	C(1)–C(4)	1.533 (5)
C(2)–B(3)	1.710 (5)	C(2)–B(6)	1.729 (4)
C(2)–B(7)	1.705 (5)	C(2)–B(11)	1.689 (5)
C(2)–C(3)	1.544 (5)	B(3)–B(4)	1.752 (5)
B(3)–B(8)	1.708 (5)	B(3)–B(11)	1.770 (6)
B(4)–B(5)	1.780 (5)	B(4)–B(8)	1.797 (5)
B(4)–B(9)	1.781 (5)	B(5)–B(6)	1.762 (5)
B(5)–B(9)	1.765 (5)	B(5)–B(10)	1.802 (5)
B(6)–B(7)	1.763 (5)	B(6)–B(10)	1.709 (5)
B(7)–B(10)	1.783 (4)	B(7)–B(11)	1.779 (5)
B(7)–B(12)	1.764 (5)	B(8)–B(9)	1.786 (4)
B(8)–B(11)	1.771 (5)	B(8)–B(12)	1.787 (5)
B(9)–B(10)	1.780 (5)	B(9)–B(12)	1.792 (5)
B(9)–C1	1.784 (3)	B(10)–B(12)	1.777 (4)
B(11)–B(12)	1.770 (5)	C(3)–C(4)	1.564 (5)

with the numbering for **1**, and Tables II–IV give the crystallographic data and the bond lengths and bond angles for **1**.<sup>11</sup>

As was the case for a pair of carbon-to-boron bridged carboranes,<sup>12</sup> the boron–boron cage bonds have normal bond lengths, ranging from 1.708 (5) to 1.802 (5) Å, with the average distance, 1.770 Å, exactly the same as that for tetrabromo-1,2-dimethyl-*o*-carborane.<sup>13</sup> Similarly, the carbon–boron bonds are quite normal, with the average C–B bond distance being 1.692 Å. In the pair of carbon-to-boron bridged compounds mentioned earlier<sup>12</sup> the average C–B distance is 1.705 Å, and the calculated value for *o*-carborane itself is 1.700 Å.<sup>14</sup>

Not surprisingly, the carbon–carbon cage distance of 1.621 (4) Å is the shortest measured for an *o*-carborane, although a distance of 1.63 Å has been found for 9,12-dibromo-*o*-carborane,<sup>15</sup> and the calculated value for the parent *o*-carborane is 1.634 Å.<sup>14</sup> The four-membered ring is nearly a square, with no internal angle deviating from the ideal 90° by more than 1.3°, and the dihedral angle between the carbon–hydrogen bonds is measured at 0°. Substituents on dihalobenzocyclobutenes are similarly eclipsed,<sup>16</sup> as the four-membered rings are flat or only very slightly buckled.<sup>17</sup> The C(3)–C(4) bond distance of 1.564 (5) Å is slightly shorter than the analogous bonds in benzocyclobutene (**6**, 1.576 Å<sup>18</sup>) and



1,2,4,5-tetrahydrodicyclobuta[*a,d*]benzene (**7**, 1.575 Å<sup>18</sup>) and nearly identical with that in naphtho[*b*]cyclobutene (**8**, 1.565 Å<sup>17</sup>). It is shorter than that in halogenated benzocyclobutenes (1.582 Å,<sup>19</sup> 1.584 Å<sup>16</sup>). The four-membered rings in benzocyclobutenes are more trapezoidal than that in **1**, with the short side being the bond between the fusion positions. In **1** this bond is lengthened by the requirements of the cage, and the result is a nearly square arrangement.

Similarities also appear when comparison is made to aliphatic cyclobutanes or cyclobutenes. The C(3)–C(4) bond distance of

Table IV. Bond Angles (deg)

C(2)–C(1)–B(3)	61.5 (2)	C(2)–C(1)–B(4)	112.0 (2)
C(2)–C(1)–B(5)	112.7 (2)	C(2)–C(1)–B(6)	62.3 (2)
C(2)–C(1)–C(4)	89.2 (2)	B(4)–C(1)–B(3)	61.9 (2)
B(3)–C(1)–B(5e)	114.7 (2)	B(6)–C(1)–B(3)	114.3 (2)
B(3)–C(1)–C(4)	104.9 (2)	B(4)–C(1)–B(5)	63.7 (2)
B(4)–C(1)–B(6)	114.8 (2)	B(4)–C(1)–C(4)	139.5 (3)
B(6)–C(1)–B(5)	62.2 (2)	B(5)–C(1)–C(4)	140.2 (2)
B(6)–C(1)–C(4)	105.6 (2)	C(1)–C(2)–B(3)	62.1 (2)
C(1)–C(2)–B(6)	61.6 (2)	C(1)–C(2)–B(7)	112.0 (2)
C(1)–C(2)–B(11)	112.7 (2)	C(1)–C(2)–C(3)	88.7 (2)
B(6)–C(2)–B(3)	114.2 (2)	B(3)–C(2)–B(7)	114.9 (2)
B(3)–C(2)–B(11)	62.8 (2)	B(3)–C(2)–C(3)	104.9 (3)
B(6)–C(2)–B(7)	61.8 (2)	B(6)–C(2)–B(11)	114.1 (2)
B(6)–C(2)–C(3)	105.0 (2)	B(7)–C(2)–B(11)	63.2 (2)
B(7)–C(2)–C(3)	140.1 (3)	B(11)–C(2)–C(3)	140.8 (2)
C(1)–B(3)–C(2)	56.4 (2)	C(1)–B(3)–B(4)	58.0 (2)
C(1)–B(3)–B(8)	105.5 (2)	C(1)–B(3)–B(11)	104.3 (2)
C(2)–B(3)–B(4)	104.7 (2)	C(2)–B(3)–B(8)	105.0 (3)
C(2)–B(3)–B(11)	58.1 (2)	B(4)–B(3)–B(8)	62.6 (2)
B(4)–B(3)–B(11)	111.1 (2)	B(8)–B(3)–B(11)	61.2 (2)
C(1)–B(4)–B(3)	60.0 (2)	C(1)–B(4)–B(5)	58.4 (2)
C(1)–B(4)–B(8)	103.1 (2)	C(1)–B(4)–B(9)	102.8 (3)
B(3)–B(4)–B(5)	108.8 (3)	B(3)–B(4)–B(8)	57.5 (2)
B(9)–B(4)–B(3)	105.9 (3)	B(8)–B(4)–B(5)	107.6 (3)
B(9)–B(4)–B(5)	59.4 (2)	B(9)–B(4)–B(8)	59.9 (2)
C(1)–B(5)–B(4)	57.9 (2)	C(1)–B(5)–B(6)	59.6 (2)
C(1)–B(5)–B(9)	103.2 (2)	C(1)–B(5)–B(10)	103.1 (2)
B(4)–B(5)–B(6)	107.9 (2)	B(4)–B(5)–B(9)	60.3 (2)
B(4)–B(5)–B(10)	108.1 (2)	B(9)–B(5)–B(6)	105.5 (2)
B(10)–B(5)–B(6)	57.3 (2)	B(9)–B(5)–B(10)	59.8 (2)
C(1)–B(6)–C(2)	56.1 (2)	C(1)–B(6)–B(5)	58.2 (2)
C(1)–B(6)–B(7)	104.8 (2)	C(1)–B(6)–B(10)	106.1 (2)
C(2)–B(6)–B(5)	104.4 (2)	C(2)–B(6)–B(7)	58.4 (2)
C(2)–B(6)–B(10)	105.6 (2)	B(7)–B(6)–B(5)	111.4 (2)
B(10)–B(6)–B(7)	61.8 (2)	B(10)–B(6)–B(5)	62.5 (2)
C(2)–B(7)–B(6)	59.8 (2)	C(2)–B(7)–B(10)	103.5 (2)
C(2)–B(7)–B(11)	58.0 (2)	C(2)–B(7)–B(12)	103.2 (2)
B(10)–B(7)–B(6)	57.6 (2)	B(6)–B(7)–B(11)	108.1 (3)
B(6)–B(7)–B(12)	106.0 (2)	B(10)–B(7)–B(11)	108.1 (2)
B(10)–B(7)–B(12)	60.1 (2)	B(12)–B(7)–B(11)	60.0 (2)
B(4)–B(8)–B(3)	59.9 (2)	B(9)–B(8)–B(3)	107.6 (2)
B(3)–B(8)–B(11)	61.1 (2)	B(3)–B(8)–B(12)	108.5 (3)
B(9)–B(8)–B(1)	59.6 (2)	B(4)–B(8)–B(11)	108.9 (2)
B(4)–B(8)–B(12)	108.2 (2)	B(9)–B(8)–B(11)	108.0 (2)
B(9)–B(8)–B(12)	60.2 (2)	B(12)–B(8)–B(11)	59.7 (2)
B(4)–B(9)–B(5)	60.3 (2)	B(4)–B(9)–B(8)	60.5 (2)
B(4)–B(9)–B(10)	109.1 (2)	B(4)–B(9)–B(12)	108.7 (2)
B(4)–B(9)–C1	121.1 (2)	B(8)–B(9)–B(5)	108.8 (2)
B(10)–B(9)–B(5)	61.1 (2)	B(12)–B(9)–B(5)	109.0 (2)
B(5)–B(9)–C1	120.7 (2)	B(10)–B(9)–B(8)	108.0 (2)
B(8)–B(9)–B(12)	59.9 (2)	B(8)–B(9)–C1	121.8 (2)
B(10)–B(9)–B(12)	59.7 (2)	B(10)–B(9)–C1	121.3 (2)
B(12)–B(9)–C1	121.6 (2)	B(6)–B(10)–B(5)	60.2 (2)
B(7)–B(10)–B(5)	108.7 (2)	B(9)–B(10)–B(5)	59.0 (2)
B(12)–B(10)–B(5)	108.0 (2)	B(6)–B(10)–B(7)	60.6 (2)
B(9)–B(10)–B(6)	107.1 (3)	B(6)–B(10)–B(12)	107.8 (2)
B(9)–B(10)–B(7)	107.8 (2)	B(12)–B(10)–B(7)	59.4 (2)
B(9)–B(10)–B(12)	60.5 (2)	C(2)–B(11)–B(3)	59.2 (2)
C(2)–B(11)–B(7)	58.8 (2)	C(2)–B(11)–B(8)	103.2 (2)
C(2)–B(11)–B(12)	103.6 (2)	B(3)–B(11)–B(7)	108.4 (2)
B(3)–B(11)–B(8)	57.7 (2)	B(3)–B(11)–B(12)	106.5 (2)
B(8)–B(11)–B(7)	108.2 (2)	B(12)–B(11)–B(7)	59.6 (2)
B(8)–B(11)–B(12)	60.6 (2)	B(8)–B(12)–B(7)	108.1 (2)
B(9)–B(12)–B(7)	108.1 (2)	B(10)–B(12)–B(7)	60.5 (2)
B(7)–B(12)–B(11)	60.4 (2)	B(9)–B(12)–B(8)	59.9 (2)
B(10)–B(12)–B(8)	108.1 (2)	B(8)–B(12)–B(11)	59.7 (2)
B(9)–B(12)–B(10)	59.8 (2)	B(9)–B(12)–B(11)	107.7 (3)
B(10)–B(12)–B(11)	108.7 (2)	C(2)–C(3)–C(4)	90.9 (2)
C(1)–C(4)–C(3)	91.2 (3)		

**1** [1.564 (5) Å] slightly more closely resembles the sp<sup>3</sup>–sp<sup>3</sup> bond of cyclobutene [1.566 (3) Å]<sup>19</sup> than that of cyclobutane [1.554 (1) Å].<sup>20</sup> A collection of 17 planar cyclobutenes gave an average bond distance of 1.558 (3) Å.<sup>21</sup> The conclusion that neither an

(10) A copy of the Chem3D file used to create Figure 1 from the crystal coordinates can be obtained from the authors if a 3.5-in. disk is supplied. "Chem3D" is a trade mark of Cambridge Scientific Computing, Inc., P.O. Box 2123, Cambridge, MA 02238.

(11) Atomic coordinates, H atom coordinates and thermal parameters, anisotropic thermal parameters, and observed and calculated structure factors can be found in the supplemental material.

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opposite long bond (carborane) nor short bond (cyclobutene, benzocyclobutenes) generates much distortion in the  $sp^3$ – $sp^3$  bond of the four-membered ring is inescapable.

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**Supplementary Material Available:** Tables of atomic coordinates, H atom coordinates and thermal parameters, and anisotropic thermal parameters (2 pages); a table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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## Low-Temperature X-ray Absorption Spectroscopy of Plastocyanin: Evidence for Copper-Site Photoreduction at Cryogenic Temperatures

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X-ray absorption spectra for copper(II) plastocyanin have been measured at low temperature. These data confirm our previous observation (based on room-temperature measurements) that the methionine sulfur in plastocyanin makes no significant contribution to the Cu EXAFS and that the Cu–S(Met) interaction must therefore be extremely weak. We report both preliminary data, having a very poor signal/noise ratio, and subsequent measurements with much higher quality data. Analysis of the preliminary data provides a cautionary example of the dangers of deriving structural results from noisy EXAFS data, at least in cases where the scatterer is weakly contributing to the signal. Analysis of the near-edge structure gives direct evidence for X-ray-induced photoreduction of Cu(II) when extremely intense X-rays from synchrotron sources are used. The rate of photoreduction decreases by approximately a factor of 2 between 190 and 4 K, but it is still significant even at the lower temperatures studied.

### Introduction

Plastocyanin is a copper-containing electron-transfer protein. The copper atom is in a "type 1" or "blue" site characterized by an intense electronic absorption band at  $\sim 600$  nm, an unusually small hyperfine splitting in the  $g_{\parallel}$  region of the EPR spectrum, and an unusually high reduction potential.<sup>1</sup> The molecular structures of four "blue" Cu proteins—plastocyanin from poplar leaves,<sup>2</sup> two azurins (from *Pseudomonas aeruginosa*<sup>3a,b</sup> and *Alcaligenes denitrificans*<sup>3c,d</sup>), and the "basic blue protein" from cucumbers<sup>4</sup>—are now known from X-ray crystallographic studies. In the oxidized [Cu(II)] state of all four proteins the Cu atom is coordinated by the N atoms of two histidine residues, a cysteine S atom, and a methionine S atom. A refinement of the poplar plastocyanin crystal structure at 1.6 Å resolution has shown that the metal–ligand distances in this protein are Cu–N(His) = 2.04 and 2.10 Å, Cu–S(Cys) = 2.13 Å, and Cu–S(Met) = 2.90 Å, respectively, with esd's of  $\sim 0.05$  Å.<sup>5</sup>

Although the unique features of blue Cu proteins have been substantially rationalized in terms of the X-ray structural results, the significance of the extremely long Cu–S(Met) bond remains a subject for speculation and study.<sup>6</sup> Polarized electronic absorption spectra and EPR spectra of oriented single crystals have shown that the S(Met) atom has at best a small effect on the ligand field at the Cu atoms.<sup>7</sup> Further, the S(Met) atom makes no significant contribution to the Cu extended X-ray absorption fine structure (EXAFS) of either plastocyanin<sup>8</sup> or azurin<sup>9</sup> in solution at room temperature. Understanding this result is important, in view of the widespread use of EXAFS spectroscopy in investigations of metalloprotein structure.<sup>10</sup>

Previously we reported EXAFS measurements on oriented single crystals of plastocyanin.<sup>11</sup> The orientations of the four symmetry-related molecules in the unit cell (Figure 1) are such that all the Cu–S(Met) bonds may be aligned parallel to the polarization vector ( $e\parallel\hat{e}$ ) or perpendicular to it ( $b\parallel\hat{e}$ ). In the  $c\parallel\hat{e}$  orientation, the contribution of Cu–S(Met) to the EXAFS is expected to be enhanced by a factor of approximately 3. In the  $b\parallel\hat{e}$  orientation, the contribution of the S(Met) to the Cu EXAFS

is essentially zero.<sup>10f</sup> The single-crystal study confirmed, with greater sensitivity than was possible in the solution measurements, that the S(Met) makes no detectable contribution to the Cu EXAFS spectrum at room temperature.

The failure of the EXAFS measurements to detect a ligand of Cu whose presence had been demonstrated by the crystal structure analysis was explained in terms of thermal disorder.<sup>11</sup> Since the temperature parameters of the Cu and S(Met) atoms as determined by X-ray diffraction are relatively small,<sup>5</sup> the hypothesis of large thermal disorder in the EXAFS can be correct only if the vibrations of the Cu and S(Met) atoms are effectively uncorrelated.<sup>11</sup> If this is the case, then it should be possible to reduce the vibrational effects, and thus to enhance the EXAFS contribution of the S(Met) atom, by lowering the temperature

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