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Synthesis and characterization of a protected amino alcohol containing *ortho*-carborane

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Abstract—The reaction between the alkyne, N-(5-Benzyloxy-2-pentynyl)phthalimide and decaborane (14) in the presence of dimethyl sulfide resulted in the isolation of 1-$C_6H_4(CO)_2NCH_2$-2-$C_6H_5CH_2OCH_2CH_2$-1, 2-$C_2B_{10}H_{10}$ **(5)**, 1-methylphthalimido-2-ethylbenzyl ether-*o*-carborane, in moderate yield. Compound **5** was characterized by single crystal X-ray diffraction study. Compound **5** crystallizes in the $P\bar{1}$ space group, a = 10.5328 (5) Å, b = 11.9209 (6) Å, c = 10.3451 (3) Å, $\alpha = 110.492$ (3)°, $\beta = 102.868$ (3)°, $\gamma = 87.279$ (2)°, Z = 2, $D_{calc} = 1.226$ g/cm^3, $R = 0.0491$ for 3521 reflections with $F > 4.0\sigma$. Deprotection of the ether linkage of **5** results in the formation of 1-$C_6H_4(CO)_2NCH_2$-2-$HOCH_2CH_2$-1, 2-$C_2B_{10}H_{10}$ **(6)**, 1-methylphthalimido-2-ethylalcohol-*o*-carborane. The transformation is accomplished by hydrogenation of **(5)** over a Pd/C catalyst and resulted in the efficient conversion of **(5)** into **(6)** (83% yield). Experimental details and analytical data leading to the identification of the reported compounds is provided.

Keywords: carborane; synthesis; amino; alcohol; reactivity; crystallography.

INTRODUCTION

The recent report by Hawthorne and coworkers and that of Kahl and Kasar regarding the high-yield synthesis of polyhedral carborane amino acids are significant steps in the field of boron neutron capture therapy [1–3]. There is definitely a need for the synthesis and characterization of a wide variety of these compounds if progress is to be made in this field. Our approach relies in the introduction of a protected amine and a protected alcohol into the carborane cage, using the well established synthetic route for the preparation of substituted *ortho*-carboranes, relying on the reaction of an alkyne with decaborane (14) [4–10].

The scope of the presented work is the synthesis of compounds that might be suitable for use in boron neutron capture therapy (BNCT). Although in recent years there is an apparent acceptance of this technique as a viable option for the treatment of certain tumors, specifically malignant melanoma and glioblastoma multiforme, there are too few compounds that are sufficiently selective to perform this task. The two compounds currently under clinical trials, $Na_2B_{12}H_{11}SH$ (BSH) and boronophenylalanine (BPA) exhibit a tumor to normal brain ratio of 1.69:1 and 3:1 respectively [11, 12]. Another problem is the low solubility of these compounds at physiological pH, this is especially true for BPA. Therefore, synthetic methodology for the synthesis of bifunctional carboranes is highly desirable.

The introduction of bifunctional alkynes into the decaborane (14) framework to produce heterobifunctional *o*-carboranes is not unprecedented in the literature [4–10, 13, 14]. This methodology is simple and efficient. The main obstacle is choosing the appropriate bifunctional alkyne needed to perform the reaction. Our objective was to find the appropriate alkyne containing a protected amine and a protected alcohol precursor that could be reacted with decaborane (14). Given the fact that this type of compound is not commercially available, one of the tasks for this study

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was the synthesis of such a compound. We chose $C_6H_4(CO)_2NCH_2C{\equiv}CCH_2CH_2OC_6H_5$ as our precursor, since it contained a protected amine and a protected alcohol. In this communication we describe the synthesis of this alkyne from its precursors and its subsequent transformation to the heterobifunctional *ortho*-carborane. The synthesis of this carborane could open the door for the preparation of other bifunctional carboranes needed for BNCT. The key to successful BNCT is the delivery of ^{10}B-containing compounds to the malignant tumor cell selectively. The necessary tumor/normal tissue and tumor/blood ratios must be at least two [15, 16].

Common strategies used to achieve the above indicated objective include the attachment of boron containing residues to existing compounds known to accumulate in tumor tissues [17] and to a variety of recognition elements, such as amino acids [18, 19], peptides [15], antibodies [20], nucleosides [21–24], liposomes [25] and other regulatory biomolecules [26]. The most commonly used boron containing residues are carborane clusters, such as *ortho*-carborane and derivatives. These clusters have the advantage over monoboronated compounds, since they contain up to ten boron atoms and naturally abundant ^{10}B may be used [27]. Also these clusters are stable at physiological pH. The main task is the design and combination of the boron clusters with the recognition elements or derivative thereof. This communication intends to address this strategy.

EXPERIMENTAL

All manipulations were carried out using standard high vacuum or inert atmosphere techniques, when warranted, as described by Shriver [28].

Materials

3-butynyl-1-ol, benzyl bromide, sodium hydride, tetrahydrofuran, dimethylformamide, paraformaldehyde, n-butyllithium (2.0 M in cyclohexane), magnesium sulfate, chloroform, acetonitrile, methanol, ethanol, potassium phthalimide, hexanes, silica gel, acetone-d_6, CD_3CN and $CDCl_3$ were purchased form Aldrich. All solvents were dried prior to use. Decaborane (14) was obtained from Strem Chemicals.

Physical measurements

The 128.4 MHz boron-11 and 400.0 MHz proton spectra were obtained on a Varian Unity-400 Fourier transform spectrometer. All boron-11 chemical shifts were referenced to $BF_3{\cdot}O(C_2H_5)_2 = 0.0$ ppm with a negative sign indicating an upfield shift. Proton NMR at 200 MHz and carbon-13 NMR at 50.0 MHz were obtained on Varian Gemini-200 Fourier transform spectrometer. Proton chemical shifts and carbon-13 chemical shifts were referenced to TMS = 0.00 ppm with positive values indicating downfield shifts. Infrared spectra were recorded on a Perkin-Elmer 337 grating infrared spectrophotometer and on Perkin Elmer 1720 Fourier transform spectrophotometer. Low resolution mass spectrometry data was obtained in a HP GC/MS system, model 5995.

X-ray crystallography

X-ray intensity data were collected on a Rigaku R-AXIS IIc area detector employing graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) at a temperature of 223 K for compound **5**. Indexing was performed from a series of 1° oscillations with exposures of 8 minutes per frame. A hemisphere of data was collected using 6° oscillations with exposures of 4 minutes per frame. The crystal to detector distance was 82 mm. Oscillation images were processed using bioteX [29], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the teXsan [30] program package for further processing and structure solution on a Silicon Graphics Indigo R4000 computer. A total of 9100 reflections were measured over the ranges: $5.18 \leqslant 2\theta \leqslant 50.70°$, $-12 \leqslant h \leqslant 12$, $-14 \leqslant k \leqslant 12$, $-12 \leqslant l \leqslant 12$, yielding 3949 unique reflections ($R_{int} = 0.0176$). Other relevant crystallographic data are given in Table 1. The intensity data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods (SIR92) [31]. The refinement was full-matrix least squares based on F^2 using SHELXL-93 [32]. All reflections were used during refinement (F^2's that were experimentally negative were replaced by $F^2 = 0$). The weighting scheme was $w = 1/[\sigma^2(F_o^2) + 0.0586P^2 + 0.3395P]$ where $P = (F_o^2 + 2F_c^2)/3$.

Non-hydrogen atoms were refined anisotropically; cage hydrogens were refined isotropically; all other hydrogen atoms were refined using a 'riding' model which the positions of the hydrogen atoms were re-idealized before each least squares cycle by applying the coordinate shifts of the atom to which each hydrogen atom is attached. Refinement converged to $R_1 = 0.0491$ and $wR_2 = 0.1215$ for 3521 reflections for which $F > 4\sigma(F)$ and $R_1 = 0.0556$, $wR_2 = 0.1270$ and GOF = 1.070 for all 3949 unique, non-zero reflections and 348 variables. The maximum Δ/σ in the final cycle of least squares was 0.000 and the two most prominent peaks in the final Fourier were +0.191 and −0.176 e/Å^3.

Selected bond distances and angles are given in Table 2 and Table 3 respectively. Final atomic positions for non Hydrogen atoms and their isotropic parameters, Hydrogen atom coordinates and displacement parameters, non-hydrogen atom thermal parameters, full listing of interatomic distances and bond angles are available as supplementary material.

Table 1. Summary of Structure Determination of 1-$C_6H_4(CO)_2NCH_2$-2-$C_6H_5CH_2OCH_2CH_2$-1, 2-$C_2B_{10}H_{10}$ (5)

Formula:	$C_{20}B_{10}H_{27}NO_3$
Formula weight:	437.54
Crystal class:	triclinic
Space group:	$P\bar{1}$ (#2)
Z	2
Cell constants:	
a	10.5328(5) Å
b	11.9209(6) Å
c	10.3451(3) Å
α	110.492(3)°
β	102.868(3)°
γ	87.279(2)°
V	1185.52(9) Å^3
μ	0.72 cm^{-1}
crystal size, mm	$0.50 \times 0.35 \times 0.22$
D_{calc}	1.226 g/cm^3
$F(000)$	456
Radiation:	Mo-K_α ($\lambda = 0.71069$ Å)
2θ range	5.18–50.70°
hkl collected:	$-12 \leqslant h \leqslant 12$; $-14 \leqslant k \leqslant 12$; $-12 \leqslant l \leqslant 12$
No. reflections measured:	9100
No. unique reflections:	3949 ($R_{int} = 0.0176$)
No. observed reflections	3521 ($F > 4\sigma$)
No. reflections used in refinement	3949
No. parameters	348
R indices ($F > 4\sigma$)	$R_1 = 0.0491$, w$R_2 = 0.1215$
R indices (all data)	$R_1 = 0.0556$, w$R_2 = 0.1270$
GOF:	1.070
Final Difference Peaks, e/Å^3	+0.191, −0.176

Table 2. Selected Bond Distances in 1-$C_6H_4(CO)_2NCH_2$-2-$C_6H_5CH_2OCH_2CH_2$-1, 2-$C_2B_{10}H_{10}$ (5), Å

Bond		Bond		Bond	
O23–C15	1.209(2)	O24–C22	1.211(2)	O27–C28	1.413(3)
O27–C26	1.421(2)	N14–C22	1.395(2)	N14–C15	1.399(2)
N14–C13	1.452(2)	C1–C13	1.528(2)	C1–C2	1.684(2)
C1–B5	1.707(3)	C1–B9	1.709(3)	C1–B6	1.722(2)
C1–B8	1.727(2)	C2–C25	1.527(3)	C2–B3	1.706(3)
C2–B7	1.711(3)	C2–B8	1.722(3)	C2–B6	1.732(2)
C15–C16	1.484(2)	C16–C17	1.383(3)	C16–C21	1.387(2)
C17–C18	1.383(3)	C18–C19	1.378(4)	C19–C20	1.389(3)
C20–C21	1.382(2)	C21–C22	1.486(2)	C25–C26	1.505(3)
C29–C30	1.364(3)	C29–C34	1.369(3)	C30–C31	1.378(5)
C31–C32	1.367(6)	C32–C33	1.341(6)	C33–C34	1.345(4)
B3–B7	1.772(3)	B3–B11	1.773(3)	B3–B4	1.774(3)
B3–B6	1.779(3)	B4–B6	1.767(3)	B4–B5	1.775(3)
B4–B11	1.779(3)	B4–B10	1.782(3)	B5–B10	1.766(3)
B5–B9	1.772(3)	B5–B6	1.776(3)	B7–B11	1.765(3)
B7–B12	1.766(4)	B7–B8	1.772(3)	B8–B12	1.770(3)
B8–B9	1.777(3)	B9–B12	1.773(3)	B9–B10	1.779(3)
B10–B11	1.776(3)	B10–B12	1.784(4)	B11–B12	1.787(3)

Table 3. Selected Bond Angles in 1-$C_6H_4(CO)_2NCH_2$-2-$C_6H_5CH_2OCH_2CH_2$-1, 2-$C_2B_{10}H_{10}$ (5), °

Bond	Angle	Bond	Angle
C28–O27–C26	111.4(2)	C22–N14–C15	111.79(13)
C22–N14–C13	123.88(14)	C15–N14–C13	123.54(13)
C13–C1–C2	118.74(14)	C13–C1–B5	118.69(13)
C2–C1–B5	110.58(13)	C13–C1–B9	123.16(14)
C2–C1–B9	110.43(13)	B5–C1–B9	62.51(12)
C13–C1–B6	113.72(13)	C2–C1–B6	61.14(10)
B5–C1–B6	62.40(11)	B9–C1–B6	113.89(14)
C13–C1–B8	121.11(14)	C2–C1–B8	60.64(11)
B5–C1–B8	113.54(14)	B9–C1–B8	62.32(13)
B6–C1–B8	113.17(13)	C25–C2–C1	120.75(14)
C25–C2–B3	121.1(2)	C1–C2–B3	110.17(13)
C25–C2–B7	118.5(2)	C1–C2–B7	110.00(14)
B3–C2–B7	62.46(12)	C25–C2–B8	115.7(2)
C1–C2–B8	60.92(10)	B3–C2–B8	113.7(2)
B7–C2–B8	62.16(12)	C25–C2–B6	120.6(2)
C1–C2–B6	60.51(10)	B3–C2–B6	62.31(11)
B7–C2–B6	113.3(2)	B8–C2–B6	112.87(14)
N14–C13–C1	114.40(13)	O23–C15–N14	124.7(2)
O23–C15–C16	129.4(2)	N14–C15–C16	105.89(14)
C17–C16–C21	121.4(2)	C17–C16–C15	130.4(2)
C21–C16–C15	108.2(2)	C18–C17–C16	117.2(2)
C19–C18–C17	121.6(2)	C18–C19–C20	121.2(2)
C21–C20–C19	117.3(2)	C20–C21–C16	121.2(2)
C20–C21–C22	130.6(2)	C16–C21–C22	108.2(2)
O24–C22–N14	124.7(2)	O24–C22–C21	129.4(2)
N14–C22–C21	105.89(14)	C26–C25–C2	117.2(2)
O27–C26–C25	108.9(2)	O27–C28–C29	109.9(2)
C30–C29–C34	118.6(2)	C30–C29–C28	120.7(3)
C34–C29–C28	120.7(3)	C29–C30–C31	119.8(3)
C32–C31–C30	119.6(3)	C33–C32–C31	120.4(3)
C32–C33–C34	120.0(3)	C33–C34–C29	121.6(3)
C2–B3–B7	58.91(11)	C2–B3–B11	105.4(2)
B7–B3–B11	59.72(13)	C2–B3–B4	105.76(14)
B7–B3–B4	107.9(2)	B11–B3–B4	60.20(13)
C2–B3–B6	59.57(11)	B7–B3–B6	108.17(14)
B11–B3–B6	107.9(2)	B4–B3–B6	59.65(12)
B6–B4–B3	60.32(11)	B6–B4–B5	60.19(11)
B3–B4–B5	108.0(2)	B6–B4–B11	108.2(2)
B3–B4–B11	59.89(13)	B5–B4–B11	107.5(2)
B6–B4–B10	107.93(14)	B3–B4–B10	107.7(2)
B5–B4–B10	59.53(12)	B11–B4–B10	59.83(13)
C1–B5–B10	105.6(2)	C1–B5–B9	58.79(11)
B10–B5–B9	60.38(12)	C1–B5–B4	105.43(14)
B10–B5–B4	60.43(12)	B9–B5–B4	108.6(2)
C1–B5–B6	59.20(11)	B10–B5–B6	108.2(2)
B9–B5–B6	108.2(2)	B4–B5–B6	59.67(12)
C1–B6–C2	58.34(10)	C1–B6–B4	105.18(14)
C2–B6–B4	104.92(14)	C1–B6–B5	58.39(10)
C2–B6–B5	105.20(14)	B4–B6–B5	60.14(12)
C1–B6–B3	105.11(13)	C2–B6–B3	58.12(11)
B4–B6–B3	60.03(12)	B5–B6–B3	107.8(2)
C2–B7–B11	105.6(2)	C2–B7–B12	105.9(2)
B11–B7–B12	60.81(14)	C2–B7–B3	58.63(12)
B11–B7–B3	60.19(13)	B12–B7–B3	108.8(2)
C2–B7–B8	59.23(11)	B11–B7–B8	108.7(2)
B12–B7–B8	60.04(13)	B3–B7–B8	108.14(14)
C2–B8–C1	58.44(10)	C2–B8–B12	105.2(2)
C1–B8–B12	104.9(2)	C2–B8–B7	58.61(12)
C1–B8–B7	105.25(14)	B12–B8–B7	59.81(13)
C2–B8–B9	105.52(14)	C1–B8–B9	58.35(11)
B12–B8–B9	59.98(13)	B7–B8–B9	107.6(2)

(*continued on next page*)

Table 3 (continued)

Bond	Angle	Bond	Angle
C1–B9–B5	58.70(11)	C1–B9–B12	105.6(2)
B5–B9–B12	108.0(2)	C1–B9–B8	59.34(11)
B5–B9–B8	108.0(2)	B12–B9–B8	59.81(13)
C1–B9–B10	105.0(2)	B5–B9–B10	59.64(12)
B12–B9–B10	60.28(13)	B8–B9–B10	107.9(2)
B5–B10–B11	108.1(2)	B5–B10–B9	59.98(12)
B11–B10–B9	108.0(2)	B5–B10–B4	60.04(12)
B11–B10–B4	59.99(13)	B9–B10–B4	108.0(2)
B5–B10–B12	107.8(2)	B11–B10–B12	60.26(14)
B9–B10–B12	59.70(13)	B4–B10–B12	108.1(2)
B7–B11–B3	60.09(13)	B7–B11–B10	107.8(2)
B3–B11–B10	108.0(2)	B7–B11–B4	108.0(2)
B3–B11–B4	59.91(12)	B10–B11–B4	60.18(13)
B7–B11–B12	59.63(14)	B3–B11–B12	107.8(2)
B10–B11–B12	60.08(14)	B4–B11–B12	108.1(2)
B7–B12–B8	60.15(13)	B7–B12–B9	108.1(2)
B8–B12–B9	60.22(12)	B7–B12–B10	107.4(2)
B8–B12–B10	108.0(2)	B9–B12–B10	60.03(13)
B7–B12–B11	59.57(14)	B8–B12–B11	107.8(2)
B9–B12–B11	107.8(2)	B10–B12–B11	59.66(13)

Synthesis of $HC{\equiv}CCH_2CH_2OCH_2C_6H_5$ (**1**)

In a 250 cm^3 round bottom flask were placed 7.0 g (0.10 mol) of 3-butyn-1-ol and 100 cm^3 of anhydrous THF. To the resulting suspension, 2.8 g (0.11 mol) of sodium hydride were added slowly. After gas evolution had ceased, 19.0 g (0.11 mol) of benzyl bromide were added to the solution and stirred at room temperature overnight. After 12 hrs, a voluminous precipitate had formed. The precipitate was filtered and the solvent removed by rotary evaporation. The resulting residue was distilled under reduced pressure, resulting in the isolation of a colorless oil which was identified as benzyl-3-butynyl ether (12.3 g, 0.077 mol, 77% yield, bp 66–68°C/0.6 mm Hg). ^{1}H NMR: ($CDCl_3$), 1.98 (1H, t, $J=2.64$ Hz), 2.47 (2H, d of t, $J_{AB}=2.64$ Hz, $J_{AX}=6.96$ Hz), 3.58 (2H, t, $J=6.96$ Hz), 4.54 (2H, s), 7.32 (5H, m), ^{13}C NMR: ($CDCl_3$), 19.66 (CH_2), 67.90 (CH_2O), 69.21 (OCH_2), 72.71 (≡C), 81.04 (HC≡), 127.47 (C_6H_5), 128.19 (C_6H_5), 137.82 (C_6H_5), IR (cm^{-1}): 3296 (s), 3028 (m), 2868 (s), 2220 (w), 1720 (m), 1496 (m), 1456 (m), 1364 (m), 1275 (w), 1204 (w), 1100 (s), 1028 (m), 795 (w), 740 (m), 700 (m), 648 (m). MS (EI): *m*/*z* relative intensity 159 (M^+-H, 100), 107 (M^+-$HC{\equiv}CCH_2CH_2$, 9.1), 83 (M^+-C_6H_5, 22.7).

Synthesis of $HOCH_2C{\equiv}CCH_2CH_2OCH_2C_6H_5$ (**2**)

To a solution containing 9.6 g (0.060 mol) of benzyl-3-butynyl ether in 90 cm^3 of dry THF kept at −20°C, 31 cm^3 (0.061 mol) of a 2.0 M solution n-BuLi in cyclohexane were added slowly. The mixture was allowed to warm to room temperature and stirred for one hour. To this solution, 2.0 g (0.066 mol) of paraformaldehyde were added and stirring of the resulting solution was continued for an additional 2 hrs. The THF was removed by rotary evaporation and to the resulting residue, 25 cm^3 of distilled water were added. This solution was extracted with three 20 cm^3 of anhydrous ether. The ethereal solution was dried over $MgSO_4$. The ether was then removed by rotary evaporation. The resulting oil was distilled and a colorless oil (8.2 g, 0.043 mol, 72% yield, bp 130–132°C/0.5 mm Hg) was obtained and identified as 5-benzylox-2-pentyn-1-ol. ^{1}H NMR: ($CDCl_3$), 2.31 (1H, t, $J=5.94$ Hz), 2.52 (2H, m), 3.57 (2H, t, $J=6.88$ Hz), 4.20 (2H, m), 4.54 (2H, s), 7.33 (5H, m). ^{13}C NMR: ($CDCl_3$), 19.84 (CH_2), 50.86 ($HOCH_2$), 67.90 (CH_2O), 72.69 (OCH_2), 79.34 (C≡), 82.61 (C≡), 127.27 (C_6H_5), 128.20 (C_6H_5), 137.66 (C_6H_5). IR (cm^{-1}): 3444 (s, br), 2872 (s), 2240 (m), 1716 (m), 1680 (sh), 1480 (w), 1456 (m), 1310 (m), 1272 (m), 1096 (m), 975 (m), 750 (m), 700 (m). MS (EI): *m*/*z* relative intensity 189 (M^+-H, 3.6), 159 (M^+-$HOCH_2$, 3.6), 121 (M^+-$HOCH_2C{\equiv}CCH_2$, 92.6), 113 (M^+-C_6H_5, 7.1), 107 (M^+-$HOCH_2C{\equiv}CCH_2CH_2$, 3.6), 83 (M^+-$OCH_2C_6H_5$, 3.6).

Synthesis of $BrCH_2C{\equiv}CCH_2CH_2OCH_2C_6H_5$ (**3**)

In a 250 cm^3 round bottom flask were placed 7.0 g (0.037 mol) of $HOCH_2C{\equiv}CCH_2CH_2OCH_2C_6H_5$ and 10.0 g (0.046 mol) of $(CH_3)_2NCHBr_2$, which was prepared according to the literature procedure [33]. To this mixture, 100 cm^3 of dry acetonitrile was added

and the resulting solution was heated to reflux for 2 hrs. The acetonitrile was removed *in vacuo* and the resulting residue extracted with ether. After evaporation of the ether from the solution, the extract was separated on a silica gel column chromatography using a 2:1 mixture of hexanes/methylene chloride. The resulting oil obtained was identified as benzyl-5-bromo-2-pentynyl ether. (8.0 g, 0.031 mol, 85% yield). ^{1}H NMR ($CDCl_3$), 2.56 (2H, m), 3.58 (2H, t, $J=6.88$ HZ), 3.91 (2H, t, $J=2.24$ Hz), 4.55 (2H, s), 7.34 (5H, m). ^{13}C NMR ($CDCl_3$), 15.03 ($BrCH_2$), 20.13 (CH_2), 67.61 (CH_2O), 72.71 (OCH_2), 77.37 (C≡), 84.49 (C≡), 127.43 (C_6H_5), 128.16 (C_6H_5), 137.68 (C_6H_5). IR (cm^{-1}): 3028 (m), 2868 (s), 2236 (m), 1720, 1648 (w), 1496 (w), 1456 (s), 1364 (s), 1212 (s), 1100 (s), 740 (s), 700 (s), 608 (s). MS (EI, ^{81}Br) *m/z* relative intensity 255 ($M^+ + H$, 5.3), 254 (M^+, 4.1), 252 (M-2^+, 1.2), 173 (M^+-Br, 35.8), 159 (M^+-$BrCH_2$, 2.6), 147 (M^+-$BrCH_2C$, 3.0), 143 (M-2^+-$HOCH_2C_6H_5$, 100), 121 (M^+-$BrCH_2C{\equiv}CCH_2$, 4.7), 108 (M^+-$BrCH_2C{\equiv}CCH_2CH_2$, 2.1), 77 (M^+-$BrCH_2C{\equiv}CCH_2CH_2O$, 15.9).

Synthesis of $C_6H_4(CO)_2NCH_2C{\equiv}CCH_2CH_2OCH_2C_6H_5$ (**4**).

A solution consisting of 2.53 g (0.010 mol) of $BrCH_2C{\equiv}CCH_2CH_2OCH_2C_6H_5$ dissolved in 15 cm^3 of DMF was added to 2.04 g (0.011 mol) of potassium phthalimide and stirred at room temperature overnight. After that time, 50 cm^3 of distilled water was added to the solution and the mixture extracted with three 20 cm^3 portions of chloroform. This solution was dried over $MgSO_4$ and the chloroform stripped off *in vacuo*. The residue was dissolved in a minimal amount of methylene chloride and separated via silica gel column chromatography. This resulted in the isolation of a viscous oil which was identified as N-(5-benzyloxy-2-pentynyl)phthalimide (3.05 g, 0.0096 mol, 96% yield). ^{1}H NMR: ($CD_3C(O)CD_3$), 2.45 (2H, m), 3.53 (2H, t, $J=7.12$ Hz), 4.41 (2H, t, $J=2.24$ Hz), 4.50 (2H, s), 7.30 (5H, m), 7.86 (4H, m). ^{13}C NMR: ($CD_3C(O)CD_3$), 20.08 (CH_2), 27.36 (CH_2), 68.50 (CH_2O), 72.67 (OCH_2), 75.44 (C≡), 80.54 (C≡), 123.65 (C_6H_5), 127.86 (C_6H_5), 128.67 (C_6H_5), 132.57 (C_6H_5), 134.86 (C_6H_5), 139.23 (C_6H_5), 167.22 (C═O). IR (cm^{-1}): 3020 (m), 2872 (m), 2245 (w), 1772 (s), 1716 (s), 1650 (m), 1550 (w), 1520 (w), 1420 (m), 1392 (m), 1320 (m), 1116 (s), 944 (m), 724 (s), 628 (m), 532 (m). MS (EI), *m/z* relative intensity 320 ($M^+ + H$, 5.9), 212 (M^+-$OCH_2C_6H_5$, 3.0), 198 (M^+-$CH_2OCH_2C_6H_5$, 5.3), 173 (M^+-$C_6H_4(CO)_2N$, 8.3), 172 (M^+-$CH_2CH_2OCH_2C_6H_5$, 21.6), 160 (M^+-$C{\equiv}CCH_2CH_2OCH_2C_6H_5$, 42.4), 159 ($M^+$-$C_6H_4(CO)_2NCH_2$, 83.2), 131 ($M^+$-CO and $HC{\equiv}CCH_2CH_2OCH_2C_6H_5$, 3.5), 104 ($M^+$-CO and $NCH_2C{\equiv}CCH_2CH_2OCH_2C_6H_5$, 15.1), ($M^+$-91($M^+$-$C_6H_4(CO)_2NCH_2C{\equiv}CCH_2CH_2$, 100), 77 ($M^+$-$C_6H_4(CO)_2NCH_2C{\equiv}CCH_2CH_2OCH_2$, 12.8).

Synthesis of 1-$C_6H_4(CO)_2NCH_2$-2-$C_6H_5CH_2OCH_2CH_2$-1, 2-$C_2B_{10}H_{10}$ (**5**)

In a 100 cm^3 round bottom flask, 0.400 g (0.0033 mol) of decaborane (14) and 0.60 cm^3 (0.008 mol) of dimethyl sulfide were dissolved in 35.0 cm^3 of dry benzene. The solution was stirred to reflux for 4 hrs. After allowing the solution to cool to room temperature, 1.03 g (0.0033 mol) of N-(5-benzyloxy-2-pentynyl)phthalimide were added quickly and stirred at room temperature for 10 min., to ensure complete dissolution of the alkyne. The resulting solution was then heated to reflux for 10 hrs. The benzene was removed *in vacuo* and to the resulting solid, 2.5 cm^3 of methanol were added and stirred at room temperature for 4 hrs. The suspension was filtered, resulting in a white solid which was washed with three portions of 5.0 cm^3 of cold ethanol. The white solid was dissolved in a 1:1 mixture of CH_3CN/CH_2Cl_2 and recrystallized from this solution, resulting in the isolation of 1-methylphthalimido-2-ethylbenzyl ether-*o*-carborane (0.70 g, 50% yield, mp 1175–177°C). The identity of this compound was confirmed by a single crystal X-ray diffraction study. ^{1}H NMR: ($CD_3C(O)CD_3$), 3.04 (2H, t, $J=5.86$ Hz), 3.77 (2H, t, $J=5.86$ Hz), 4.56 (2H, s), 4.57 (2H, s), 7.35 (5H, m), 7.89 (4H, m). ^{13}C NMR ($CD_3C(O)CD_3$), 35.68 (CH_2), 40.49 (CH_2), 68.79 (CH_2O), 73.26 (OCH_2), 78.16 (carborane C), 80.89 (carborane C), 124.20 (C_6H_5), 128.16 (C_6H_5), 128.76 (C_6H_5), 131.95 (C_6H_5), 135.30 (C_6H_5), 138.36 (C_6H_5), 167.36 (C═O). ^{11}B NMR: ($CD_3C(O)CD_3$), −0.48 (2B), −5.49 (8B). The coupling constants for this compound could not be reliably determined due to coincidental overlap of signals. IR (cm^{-1}): 2996 (m), 2888 (m), 2580 (s), 1776 (s), 1724 (s), 1612 (w), 1484 (m), 1468 (w), 1456 (w), 1420 (m), 1400 (s), 1364 (s), 1288 (m), 1136 (m), 1104 (s), 1080 (s), 1036 (m), 960 (m), 864 (w), 848 (w), 824 (w), 792 (w), 752 (m), 716 (s), 700 (m), 646 (w), 608 (w), 528 (m). MS (EI), *m/z* relative intensity 439 (M^+, 6.5), 348 (M^+-$CH_2C_6H_5$, 7.6), 332 (M^+-$OCH_2C_6H_5$, 42.7), 303 (M^+-H and $CH_2CH_2OCH_2C_6H_5$, 7.8), 160 (M^+-$C_2B_{10}H_{10}CH_2CH_2OC_6H_5$, 14.4), 107 ($M^+$-$C_6H_4(CO)_2NCH_2C_2B_{10}H_{10}CH_2CH_2$, 39.7), 91 ($M^+$-$C_6H_4(CO)_2NCH_2C_2B_{10}H_{10}CH_2CH_2O$, 100), 77 ($M^+$-$C_6H_4(CO)_2NCH_2C_2B_{10}H_{10}CH_2CH_2OCH_2$, 15.9).

Synthesis of 1-$C_6H_4(CO)_2NCH_2$-2-$HOCH_2CH_2$-1, 2-$C_2B_{10}H_{10}$ (**6**)

In a 5.0 cm^3 round bottom flask, 0.045 g (0.10 mmol) of 1-methylphthalimido-2-ethylbenzyl ether-*o*-carborane were placed and 0.50 cm^3 of $CHCl_3$ added. To the resulting solution, 0.50 cm^3 of ethanol and 30 mg of Pd/C were added. The flask was then attached to a three-way vacuum stopcock, the contents frozen and degassed. A balloon filled with H_2 gas was then attached to the three-way vacuum stopcock and opened to fill the flask with an atmosphere

of hydrogen. The solution was then stirred at room temperature overnight. The solution was then filtered to remove the catalyst and the solvent was removed *in vacuo*. The resulting residue was dissolved in CH_2Cl_2 and purified via column chromatography (packed with silica gel). The elutant used was a 2% CH_3OH mixture in CH_2Cl_2. This resulted in the isolation of 29 mg of a white solid, which was identified as 1-methylphthalimido-2-ethylalcohol-*o*-carborane (0.029 g, 0.083 mmol, 83% yield, mp 137–139°C). ^{1}H NMR: (CD_3CN), 2.83 (2H, t, $J = 6.50$ Hz), 3.10 (1H, t, $J = 5.20$ Hz), 3.75 (2H, m, $J_{AB} = 6.50$ Hz, $J_{AX} = 5.20$ Hz), 4.47 (2H, s), 7.86 (4H, m). ^{13}C NMR: (CD_3CN), 38.24 (CH_2), 41.18 (CH_2), 61.15 (CH_2O), 78.89 (carborane C), 81.53 (carborane C), 124.65 (C_6H_5), 132.52 (C_6H_5), 135.90 (C_6H_5), 168.55 (C═O). ^{11}B NMR: (CD_3CN), 0.89 (1B, $J_{BH} = 129$ Hz), −0.89 (1B, $J_{BH} = 129$ Hz), −4.76 (4B, the coupling constant for this peak could not be reliably be calculated due to coincidental overlap of signals), −5.44 (4B, $J_{BH} = 128$ Hz). IR (cm^{-1}): 3536 (s), 3444 (br), 2956 (w) 2596 (s), 1776 (m), 1716 (s), 1488 (m), 1420 (m), 1400 (s), 1360 (m), 1140 (w), 1088 (w), 1054 (w), 960 (w), 716 (m), 532 (w). MS (EI), *m*/*z* relative intensity, 349 (M^+, 87.8), 348 (M^+-H, 41.1), 331 (M^+-H_2O, 87.6), 130 (M^+-$HOCH_2CH_2C_2B_{10}H_{10}$, H_2 and CO, 100).

RESULTS AND DISCUSSION

In order to prepare the desired precursor, it was necessary to first synthesize the corresponding alkyne needed for the reaction with decaborane (14). This procedure was a multistep synthesis starting from 3-butyn-1-ol, which is the commercially available alkyne needed for the synthesis of the desired alkyne. The synthesis of **1** was accomplished by adapting the reported literature procedure [33]. The isolation of benzyl-3-butynyl ether in significant yield (77%) allowed for the continuation of the proposed synthetic scheme, shown in Fig. 1. The identity of this compound was determined by ^{1}H and ^{13}C NMR, mass spectrometry, as well as IR spectroscopy. The nature of **1**, an air stable colorless oil, allowed for the easy handling of this compound. The ^{1}H NMR data shows an interesting pattern of resonances. The proton assigned to the terminal hydrogen of the alkyne appears at δ 1.98 ppm, as a triplet. Obviously there is coupling between this proton and the CH_2 group next to the β-carbon of the alkyne, even though they are separated by four bonds. This is confirmed by the splitting of resonances arising from the CH_2 group of protons bonded directly to the alkylinic carbon, these protons show a resonance at δ 2.47 ppm, as a doublet of triplets. The coupling constant of the doublets is 2.64 Hz, which corresponds to the coupling constant obtained for the triplet at δ 1.98 ppm. Furthermore, the downfield triplet at δ 3.58 ppm, assigned to the CH_2 group bonded to that CH_2 group and to the $OCH_2C_6H_5$ group, exhibits a coupling constant of 6.96 Hz, matching that of the triplets of the resonance at δ 2.47 ppm. The benzylic hydrogens appear as a singlet at 4.54 ppm, typical of benzylic protons. The IR spectra also shows the typical peaks, especially the C≡C triple bond stretch, which is found at 2220 cm^{-1}, also typical for this class of compounds. The ^{13}C NMR consists of eight resonances, at the typical shifts for the type of functional groups present in compound **1**.

The next step in the synthesis of the alkyne precursor is the preparation of the amino end of the molecule. Care had to be taken in choosing an appropriate procedure that would carry the protected alcoholic part of the alkyne intact. For this reason, the reaction of **1** with n-BuLi, followed by the addition of paraformaldehyde was chosen. The method is simple and does not result in deprotection of the benzylic group to form the corresponding alcohol. Compound **2** was isolated in reasonable yield (72%), as a colorless air stable oil. The identification of this compound was not as straightforward as that of **1**. The presence of multiplets at δ 2.52 ppm and δ 4.20 ppm, each due to two set of protons, prevents an analysis based on coupling constants as that performed for **1**. Nonetheless, the peak as δ 2.31 ppm, is due to the OH group and the resonance at δ 3.57 ppm is due to the CH_2O group. The other two resonances, δ 2.52 and δ 4.20 ppm respectively are assigned to the CH_2 groups bonded to the C≡C bond. The downfield resonance is that of the CH_2 group bonded to the OH and the other one corresponds to the other CH_2 group. The fact that the obtained coupling constants are similar in value, resulted in the observed multiplets for these resonances. The benzylic protons were assigned to the resonance at δ 4.54 ppm, again typical for these type of protons. The ^{13}C NMR showed nine resonances, which is the expected number of resonances for compound **2**. The IR spectra was more informative, the presence of a broad peak at 3440 cm^{-1}, typical of a OH group, coupled with a resonance at 2240 cm^{-1} assignable to the C≡C triple bond, indicated the formation of **2**. Based on this information, the fact that the benzylic group was left intact, as indicated by the ^{1}H and ^{13}C NMR data, the task of continuing toward the formation of the alkyne precursor could be continued.

Compound **3** was prepared by the reaction of **2** with $(CH_3)_2NCHBr_2$. This procedure resulted in the bromination of the CH_2 group carrying the alcohol, while keeping the protected alcohol on the other side of the alkyne unaffected. The isolated yield (85%) of the colorless oil, which was purified by column chromatography was high enough to allow the continuation of the synthetic strategy proposed. The ^{1}H and ^{13}C NMR data agrees with the formulation of compound **3**. The IR spectra also showed the presence of the C≡C triple bond, which is of paramount importance for the synthesis of the sought carborane. The mildness of the bromination method and the ease of synthesis of **3** in high yield is an attractive feature of

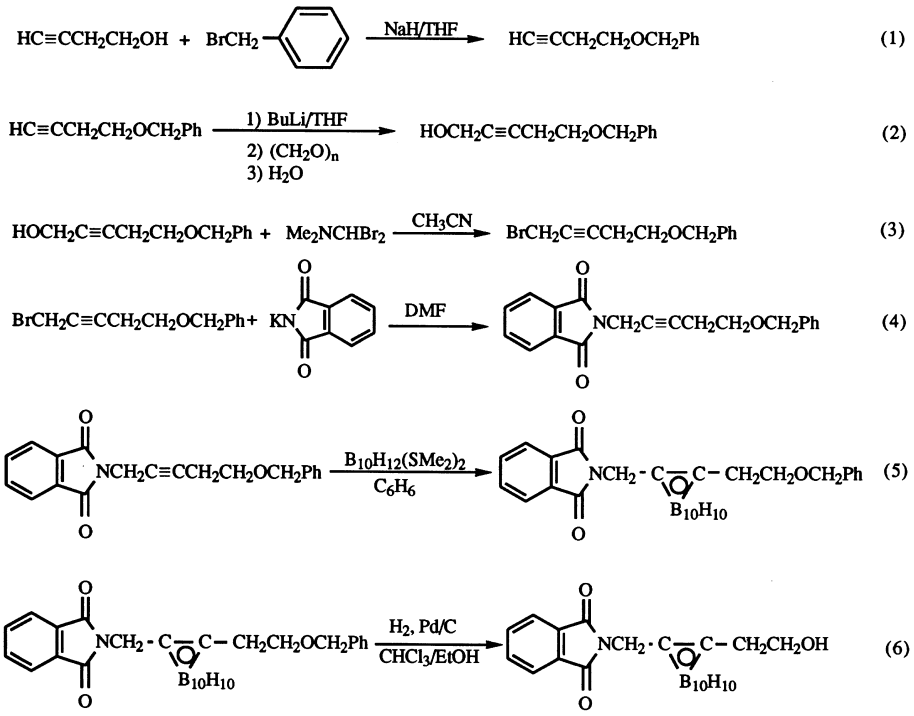

Fig. 1. Reaction sequence leading to the synthesis of heterodisubstituted *ortho*-carboranes.

this synthetic strategy. Compound **3** is the immediate precursor to the protected amino alcohol alkyne sought for the preparation of carborane **5**.

The preparation of compound **4** was accomplished by using Gabriel's reagent, potassium phthalimide, this allowed for the convenient preparation of the protected amine in high yield (96%). Compound **4** was isolated as a viscous oil. The ^{1}H NMR showed a multiplet at δ 2.45 ppm, assignable to CH_2 protons bonded to the β-carbon of the alkyne, a triplet at δ 3.53 ppm, corresponding to the NCH_2 group, a triplet at δ 4.41 ppm, due to the CH_2O group, a singlet at δ 4.50 ppm, for the benzylic protons of the protected alcohol, an two different sets of aromatic multiplets at δ 7.30 and δ 7.84 ppm, respectively, due to the $OCH_2C_6H_5$ and $C_6H_4(CO)_2N$ groups. The ^{13}C NMR of **4** should consist of thirteen peaks, which were observed. The C=O resonance was found at δ 167.22 ppm, typical for an amide group. The IR spectra of **4** also indicated its identity. The weak resonance at 2245 cm^{-1} coupled with the strong carbonyl stretch at 1716 cm^{-1} clearly indicated that compound **4** was formed. The high yield of this reaction indicates that this is a convenient method to prepare the desired precursor. The next step is simply the reaction of decaborane (14) in the presence of dimethyl sulfide with **4**, in order to produce the sought compound.

The identities of compounds **1** through **4** were further confirmed by mass spectrometric experiments and the synthesis and characterization of compound **5**. The single crystal X-ray structure determination of **5** is ample evidence of the identity of every intermediate leading to its formation.

The identity of **5** is supported by the ^{1}H, ^{11}B, and ^{13}C NMR data, as well as the IR spectra, mass spectrometry and the single crystal X-ray diffraction study of this compound. An ORTEP diagram for this compound is shown in Fig. 2.

The ^{1}H NMR data shows the expected peaks for a compound of this type. The triplet at δ 3.04 ppm is due to the CH_2 group of the ethylene unit in the carborane, which is coupled to the CH_2 group of the ether moiety and the CH_2 group of the phthalimide unit. The triplet at δ 3.77 ppm is due to the other CH_2 of the ethylene group in this carborane. The coupling constants were found to be identical for these protons, indicating that they are neighbors. The singlets at δ 4.56 and δ 4.57 ppm respectively are the result of the protons in the CH_2 group linked to the oxygen atom of the ether unit and the CH_2 group in the phthalimide unit. The expected multiplets, consisting of 4 protons and 5 protons respectively, are due to the benzene groups present in this molecule. The ^{13}C NMR data shows the expected thirteen peaks. The presence of the carbonyl resonance at δ 167.36 ppm clearly indicates that the alkyne incorporated into the cage. This fact coupled to the resonances are δ 78.16 and δ 80.89 ppm, assignable to the carborane carbons showed that the expected product was indeed synthesized.

The IR data for **5** further supports the identity of this compound. Peaks at 2558 cm^{-1}, typical of B–H

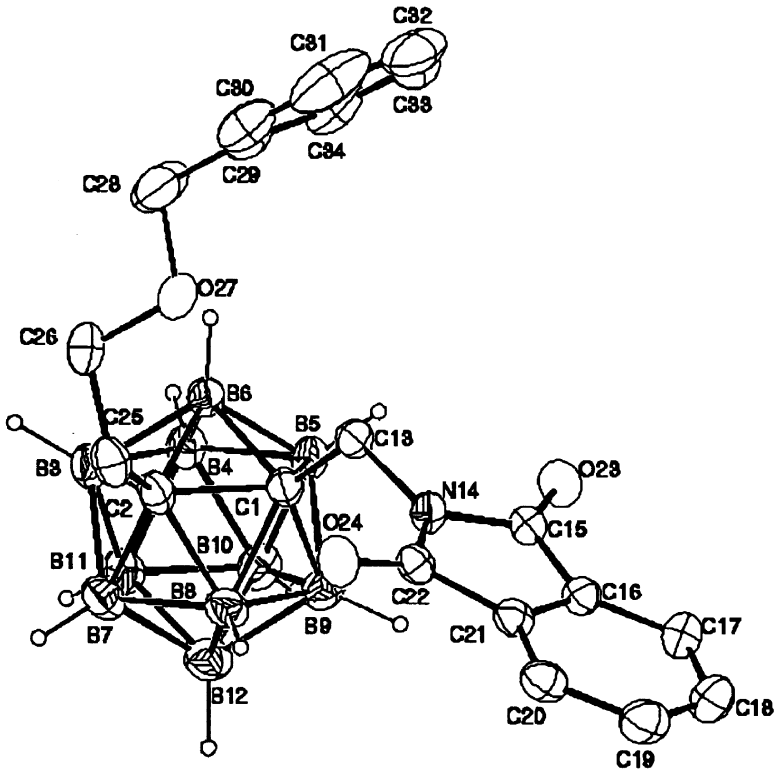

Fig. 2. ORTEP drawing of 1-$C_6H_4(CO)_2NCH_2$-2-$C_6H_5CH_2OCH_2CH_2$-1, 2-$C_2B_{10}H_{10}$ (5) with 30% probability thermal ellipsoids.

stretches, coupled with peaks at 1776 and 1724 cm^{-1} respectively, due to the carbonyl groups of the phthalimide unit are indicative of the incorporation of the alkyne into the decaborane (14) framework.

The single X-ray data shows the expected bond distances for a compound of this type. The boron-boron distances are within the expected range, 1.765 to 1.787 Å, typical of these type of compounds. The carbon-carbon in the cage and the boron-carbon distances are also typical, 1.684 to 1.732 Å. This clearly indicates that the steric effects imposed by the substituent groups are minimal, since in systems like 1-diphenylphosphino-2-methyl-1, 2-dicarba-*closo*-dodecaborane (12) [34], 1-diphenylphosphino-2-phenyl-1, 2-dicarba-*closo*-dodecaborane (12) [35], 1-phenyl-2-(*tert*-butyldimethylsilyl)-1, 2-dicarba-*closo*-dodecaborane (12) [36], 1-phenyl-2-trimethylsilyl-1, 2-dicarba-*closo*-dodecaborane (12) [37], 1-diisopropylphosphino-2-methyl-1, 2-dicarba-*closo*-dodecaborane (12) [38], 1, 2-Bis(diisopropylphosphino)-1, 2-dicarba-*closo*-dodecaborane (12) [38], 2-bromo-1-phenyl-1, 2-dicarba-*closo*-dodecaborane (12) [39], 1-diisopropylphosphino-2-phenyl-1, 2-dicarba-*closo*-dodecaborane (12) [40], and 1-phenyl-2-methyl-1, 2-dicarba-*closo*-dodecaborane (12) [41] the carbon-carbon bond length is significantly lengthened due to the steric constraints placed by the exopolyhedral groups in the cage. The values obtained in these compounds for the carbon-carbon bond length range from a minimum of 1.692 (8) Å for 2-bromo-1-phenyl-1, 2-dicarba-*closo*-dodecaborane (12) [39], which could be argued to be the less sterically demanding of these compounds and therefore closer in electronic structure to that of **5** to a maximum of 1.769 (4) Å in 1-diisopropylphosphino-2-phenyl-1, 2-dicarba-*closo*-dodecaborane (12) [40], which would be more sterically demanding and dissimilar to the electronic structure of **5**. The argument used for the lengthening of the carbon-carbon bond in these compounds is the partial overlap of tangentially oriented p orbitals of the cluster carbon with orbitals having the appropriate symmetry in the exopolyhedral group. When the overlap is between a sp^3 hybridized carbon and the cluster carbon, no significant effect should be observed, as is the case in compound **5**.

The relative importance of the characterization of **5** lies in the fact that a viable precursor to an amino acid containing carborane has been isolated. The exploration of its chemistry could potentially lead to the synthesis of such a compound, which could prove useful in BNCT.

The identity of compound **6** is based on the ^1H, ^{11}B, ^{13}C NMR, IR spectral and mass spectrometric data obtained. The ^1H NMR consists of two triplets at δ 2.83 and δ 3.10 ppm of relative intensities two and one respectively. The first triplet is due to the CH_2 group

bonded directly to the cluster carbon. Its coupling constant of 6.50 Hz, which corresponds to one of the coupling constants found in the resonance at δ 3.75 ppm, allows for the identification of these protons, as well as those at δ 3.75 ppm, which is a triplet of doublets. The coupling constant of the doublets is 5.20 Hz, which corresponds to the coupling constant found for the resonance at δ 3.10 ppm, assigned to the alcoholic proton. The singlet at δ 4.47 ppm is due to the CH_2 group in the phthalimide unit. The downfield multiplet of area four is due to the phenyl group in the compound. The ^{13}C NMR shows a total of nine peaks, which the number of resonances expected for compound **6**.

The IR spectral data shows the expected OH stretch at 3444 cm^{-1}, as well as the expected BH and C═O stretches in the normal regions.

The ^{11}B NMR data, as mentioned earlier consists of four peaks, of relative intensities 1:1:4:4. The signals observed are not the expected pattern of signals for a compound of this type, but similarly heterodisubstituted compounds had shown the same type of pattern in the ^{11}B NMR spectra [42, 43]. The coincidental overlap of resonances in the ^{11}B NMR time scale is not unprecedented, a relevant example for the observation of this type of pattern in the ^{11}B NMR spectrum is 1-phenyl-2-methyl-1, 2-dicarba-*closo*-dodecaborane (12) [41], which is also a bifunctionally substituted *ortho*-carborane.

With the isolation of compound **6**, the goal of preparing an amino acid *ortho*-carborane derivative is in principle possible. Unfortunately, all attempts to isolate this compound have proven unsuccessful at this time. Although there is some evidence that upon deprotection of the phthalimide group and oxidation of the alcohol, a compound that could possibly be the amino acid carborane is formed, its isolation has not been possible. The conditions upon which the deprotection is being carried out might be too harsh and unwanted side reactions could be taking place. We are continuing to investigate alternate routes for the preparation of the amino acid carborane and the results from this effort will be reported in the future.

Supporting information available—Tables of bond lengths and angles, atomic coordinates and thermal parameters (10 pages) are available. Order information is available on any current masthead page.

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Table 4. Refined Positional Parameters for 1-$C_6H_4(CO)_2NCH_2$-2- $C_6H_5CH_2OCH_2CH_2$-1, 2-$C_2B_{10}H_{10}$ (5)[1]

Atom	*x*	*y*	*z*	U_{eq}, Å^2
O23	0.36158(13)	−0.07683(11)	0.06008(13)	0.0528(3)
O24	0.42218(14)	0.23720(11)	0.47923(13)	0.0583(4)
O27	0.65719(12)	0.38849(11)	0.3092(2)	0.0555(4)
N14	0.39435(13)	0.10015(12)	0.25185(14)	0.0394(3)
C1	0.3464(2)	0.23644(14)	0.1108(2)	0.0406(4)
C2	0.3500(2)	0.3873(2)	0.1699(2)	0.0449(4)
C13	0.4481(2)	0.1728(2)	0.1885(2)	0.0421(4)
C15	0.3599(2)	−0.02155(14)	0.1824(2)	0.0407(4)
C16	0.3257(2)	−0.0639(2)	0.2896(2)	0.0435(4)
C17	0.2832(2)	−0.1758(2)	0.2778(2)	0.0604(5)
C18	0.2616(2)	−0.1891(2)	0.3988(3)	0.0729(7)
C19	0.2809(2)	−0.0949(2)	0.5260(3)	0.0688(6)
C20	0.3237(2)	0.0175(2)	0.5379(2)	0.0556(5)
C21	0.3453(2)	0.0311(2)	0.4172(2)	0.0426(4)
C22	0.3912(2)	0.1375(2)	0.3948(2)	0.0424(4)
C25	0.4419(2)	0.4594(2)	0.3086(2)	0.0545(5)
C26	0.5777(2)	0.4867(2)	0.3015(2)	0.0581(5)
C28	0.7846(2)	0.4066(3)	0.2958(4)	0.1147(13)
C29	0.8716(2)	0.3150(2)	0.3325(2)	0.0584(5)
C30	0.9459(2)	0.3394(2)	0.4658(3)	0.0773(7)
C31	1.0250(3)	0.2530(5)	0.4981(4)	0.121(2)
C32	1.0273(3)	0.1432(5)	0.3962(7)	0.135(2)
C33	0.9547(4)	0.1197(3)	0.2649(5)	0.1106(12)
C34	0.8785(3)	0.2044(2)	0.2332(3)	0.0789(7)
B3	0.3131(2)	0.4374(2)	0.0309(2)	0.0493(5)
B4	0.2825(2)	0.3071(2)	−0.1234(2)	0.0487(5)
B5	0.3059(2)	0.1801(2)	−0.0697(2)	0.0447(5)
B6	0.4100(2)	0.3096(2)	0.0214(2)	0.0422(4)
B7	0.1965(2)	0.4377(2)	0.1307(3)	0.0557(6)
B8	0.2221(2)	0.3120(2)	0.1861(3)	0.0509(5)
B9	0.1907(2)	0.1811(2)	0.0320(2)	0.0513(5)
B10	0.1464(2)	0.2271(2)	−0.1176(3)	0.0557(5)
B11	0.1504(2)	0.3862(2)	−0.0557(3)	0.0565(6)
B12	0.0938(2)	0.3083(2)	0.0411(3)	0.0598(6)

$U_{eq} = {}^1/_3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha]$

Table 5. Refined Positional Parameters of Hydrogen Atoms for 1-$C_6H_4(CO)_2NCH_2$-2-$C_6H_5CH_2OCH_2CH_2$-1, 2-$C_2B_{10}H_{10}$ (5)[2]

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H13a	0.4972(2)	0.1219(2)	0.1224(2)	0.056
H13b	0.5084(2)	0.2326(2)	0.2623(2)	0.056
H17	0.2696(2)	−0.2395(2)	0.1921(2)	0.080
H18	0.2333(2)	−0.2633(2)	0.3944(3)	0.097
H19	0.2650(2)	−0.1068(2)	0.6052(3)	0.091
H20	0.3371(2)	0.0811(2)	0.6237(2)	0.074
H25a	0.4020(2)	0.5349(2)	0.3491(2)	0.073
H25b	0.4487(2)	0.4162(2)	0.3735(2)	0.073
H26a	0.5760(2)	0.4997(2)	0.2137(2)	0.077
H26b	0.6131(2)	0.5589(2)	0.3795(2)	0.077
H28a	0.8177(2)	0.4861(3)	0.3584(4)	0.153
H28b	0.7828(2)	0.4007(3)	0.1995(4)	0.153
H30	0.9433(2)	0.4141(2)	0.5348(3)	0.103
H31	1.0764(3)	0.2694(5)	0.5886(4)	0.160
H32	1.0796(3)	0.0843(5)	0.4180(7)	0.179
H33	0.9571(4)	0.0450(3)	0.1959(5)	0.147
H34	0.8292(3)	0.1874(2)	0.1416(3)	0.105
H3	0.363(2)	0.522(2)	0.043(2)	0.057(5)
H4	0.306(2)	0.306(2)	−0.221(2)	0.055(5)
H5	0.351(2)	0.096(2)	−0.119(2)	0.047(5)
H6	0.514(2)	0.307(2)	0.032(2)	0.041(4)
H7	0.173(2)	0.521(2)	0.210(2)	0.066(6)
H8	0.221(2)	0.314(2)	0.291(2)	0.061(6)
H9	0.162(2)	0.097(2)	0.044(2)	0.062(6)
H10	0.076(2)	0.173(2)	−0.215(2)	0.066(6)
H11	0.087(2)	0.439(2)	−0.107(2)	0.066(6)
H12	−0.008(2)	0.310(2)	0.054(2)	0.069(6)

$$U_{eq} = {}^1/_3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha]$$

Table 6. Refined Thermal Parameters (U's) for 1-$C_6H_4(CO)_2NCH_2$-2- $C_6H_5CH_2OCH_2CH_2$-1, 2-$C_2B_{10}H_{10}$ (5)[3]

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O23	0.0638(8)	0.0492(7)	0.0402(7)	0.0077(6)	0.0141(6)	0.0030(6)
O24	0.0807(9)	0.0450(7)	0.0428(8)	0.0074(6)	0.0142(6)	0.0039(6)
O27	0.0525(7)	0.0483(7)	0.0680(9)	0.0258(6)	0.0070(6)	−0.0068(6)
N14	0.0492(8)	0.0366(7)	0.0339(8)	0.0127(6)	0.0114(6)	0.0019(6)
C1	0.0454(9)	0.0401(9)	0.0398(10)	0.0155(7)	0.0143(7)	0.0045(7)
C2	0.0547(10)	0.0401(9)	0.0429(10)	0.0152(7)	0.0170(8)	0.0093(7)
C13	0.0467(9)	0.0438(9)	0.0417(10)	0.0201(7)	0.0135(7)	0.0050(7)
C15	0.0403(9)	0.0394(9)	0.0406(10)	0.0123(7)	0.0090(7)	0.0046(7)
C16	0.0418(9)	0.0441(9)	0.0484(11)	0.0198(8)	0.0125(7)	0.0054(7)
C17	0.0646(12)	0.0474(11)	0.075(2)	0.0232(10)	0.0221(10)	−0.0007(9)
C18	0.0752(14)	0.0664(14)	0.101(2)	0.0480(14)	0.0369(13)	0.0058(11)
C19	0.0687(13)	0.086(2)	0.084(2)	0.0578(14)	0.0376(12)	0.0203(11)
C20	0.0570(11)	0.0705(13)	0.0519(12)	0.0323(10)	0.0225(9)	0.0183(9)
C21	0.0425(9)	0.0495(10)	0.0423(10)	0.0225(8)	0.0139(7)	0.0114(7)
C22	0.0473(9)	0.0419(9)	0.0368(9)	0.0124(7)	0.0104(7)	0.0075(7)
C25	0.0709(12)	0.0427(10)	0.0432(11)	0.0069(8)	0.0136(9)	0.0087(9)
C26	0.0716(13)	0.0380(10)	0.0583(13)	0.0131(8)	0.0061(10)	−0.0050(9)
C28	0.0550(14)	0.123(2)	0.214(4)	0.121(3)	0.024(2)	−0.0007(14)
C29	0.0440(10)	0.0672(13)	0.0706(14)	0.0353(11)	0.0034(9)	−0.0154(9)
C30	0.078(2)	0.093(2)	0.0580(14)	0.0230(12)	0.0064(12)	−0.0368(14)
C31	0.072(2)	0.205(4)	0.109(3)	0.112(3)	−0.038(2)	−0.063(2)
C32	0.045(2)	0.163(4)	0.259(6)	0.151(4)	0.034(2)	0.014(2)
C33	0.108(3)	0.077(2)	0.172(4)	0.042(2)	0.083(3)	0.007(2)
C34	0.088(2)	0.090(2)	0.0568(14)	0.0226(13)	0.0057(12)	−0.042(2)
B3	0.0609(12)	0.0422(11)	0.0500(13)	0.0207(9)	0.0164(10)	0.0075(9)
B4	0.0609(12)	0.0478(11)	0.0418(12)	0.0215(9)	0.0111(9)	0.0036(9)
B5	0.0545(11)	0.0421(11)	0.0386(11)	0.0161(8)	0.0087(8)	0.0005(9)
B6	0.0518(11)	0.0385(10)	0.0393(11)	0.0146(8)	0.0148(8)	0.0033(8)
B7	0.0591(13)	0.0570(13)	0.0588(14)	0.0268(11)	0.0214(11)	0.0197(10)
B8	0.0521(12)	0.0582(13)	0.0534(14)	0.0277(10)	0.0225(10)	0.0139(10)
B9	0.0469(11)	0.0569(13)	0.0562(14)	0.0287(10)	0.0081(9)	−0.0004(9)
B10	0.0568(13)	0.0588(13)	0.0547(14)	0.0290(11)	0.0031(10)	−0.0017(10)
B11	0.0577(13)	0.0588(13)	0.061(2)	0.0330(11)	0.0123(11)	0.0117(10)
B12	0.0474(12)	0.074(2)	0.071(2)	0.0415(13)	0.0162(11)	0.0123(11)

The form of the anisotropic displacement parameter is: $\exp[-2p^2(a^{*2}U_{11}h^2+b^{*2}U_{22}k^2+c^{*2}U_{33}l^2+2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)]$.

Table 7. Bond Distances in Compound 1-$C_6H_4(CO)_2NCH_2$-2-$C_6H_5CH_2OCH_2CH_2$-1, 2-$C_2B_{10}H_{10}$ (5), Å

O23–C15	1.209(2)	O24–C22	1.211(2)	O27–C28	1.413(3)
O27–C26	1.421(2)	N14–C22	1.395(2)	N14–C15	1.399(2)
N14–C13	1.452(2)	C1–C13	1.528(2)	C1–C2	1.684(2)
C1–B5	1.707(3)	C1–B9	1.709(3)	C1–B6	1.722(2)
C1–B8	1.727(2)	C2–C25	1.527(3)	C2–B3	1.706(3)
C2–B7	1.711(3)	C2–B8	1.722(3)	C2–B6	1.732(2)
C13–H13a	0.97	C13–H13b	0.97	C15–C16	1.484(2)
C16–C17	1.383(3)	C16–C21	1.387(2)	C17–C18	1.383(3)
C17–H17	0.93	C18–C19	1.378(4)	C18–H18	0.93
C19–C20	1.389(3)	C19–H19	0.93	C20–C21	1.382(2)
C20–H20	0.93	C21–C22	1.486(2)	C25–C26	1.505(3)
C25–H25a	0.97	C25–H25b	0.97	C26–H26a	0.97
C26–H26b	0.97	C28–C29	1.488(3)	C28–H28a	0.97
C28–H28b	0.97	C29–C30	1.364(3)	C29–C34	1.369(3)
C30–C31	1.378(5)	C30–H30	0.93	C31–C32	1.367(6)
C31–H31	0.93	C32–C33	1.341(6)	C32–H32	0.93
C33–C34	1.345(4)	C33–H33	0.93	C34–H34	0.93
B3–B7	1.772(3)	B3–B11	1.773(3)	B3–B4	1.774(3)
B3–B6	1.779(3)	B3–H3	1.11(2)	B4–B6	1.767(3)
B4–B5	1.775(3)	B4–B11	1.779(3)	B4–B10	1.782(3)
B4–H4	1.09(2)	B5–B10	1.766(3)	B5–B9	1.772(3)
B5–B6	1.776(3)	B5–H5	1.10(2)	B6–H6	1.08(2)
B7–B11	1.765(3)	B7–B12	1.766(4)	B7–B8	1.772(3)
B7–H7	1.10(2)	B8–B12	1.770(3)	B8–B9	1.777(3)
B8–H8	1.08(2)	B9–B12	1.773(3)	B9–B10	1.779(3)
B9–H9	1.11(2)	B10–B11	1.776(3)	B10–B12	1.784(4)
B10–H10	1.11(2)	B11–B12	1.787(3)	B11–H11	1.08(2)
B12–H12	1.11(2)				

Table 8. Bond Angles in 1-$C_6H_4(CO)_2NCH_2$-2-$C_6H_5CH_2OCH_2CH_2$-1, 2-$C_2B_{10}H_{10}$ (5), Å

C28–O27–C26	111.4(2)	C22–N14–C15	111.79(13)	C22–N14–C13	123.88(14)
C15–N14–C13	123.54(13)	C13–C1–C2	118.74(14)	C13–C1–B5	118.69(13)
C2–C1–B5	110.58(13)	C13–C1–B9	123.16(14)	C2–C1–B9	110.43(13)
B5–C1–B9	62.51(12)	C13–C1–B6	113.72(13)	C2–C1–B6	61.14(10)
B5–C1–B6	62.40(11)	B9–C1–B6	113.89(14)	C13–C1–B8	121.11(14)
C2–C1–B8	60.64(11)	B5–C1–B8	113.54(14)	B9–C1–B8	62.32(13)
B6–C1–B8	113.17(13)	C25–C2–C1	120.75(14)	C25–C2–B3	121.1(2)
C1–C2–B3	110.17(13)	C25–C2–B7	118.5(2)	C1–C2–B7	110.00(14)
B3–C2–B7	62.46(12)	C25–C2–B8	115.7(2)	C1–C2–B8	60.92(10)
B3–C2–B8	113.7(2)	B7–C2–B8	62.16(12)	C25–C2–B6	120.6(2)
C1–C2–B6	60.51(10)	B3–C2–B6	62.31(11)	B7–C2–B6	113.3(2)
B8–C2–B6	112.87(14)	N14–C13–C1	114.40(13)	N14–C13–H13a	108.66(8)
C1–C13–H13a	108.66(8)	N14–C13–H13b	108.66(9)	C1–C13–H13b	108.66(9)
H13a–C13–H13b	107.6	O23–C15–N14	124.7(2)	O23–C15–C16	129.4(2)
N14–C15–C16	105.89(14)	C17–C16–C21	121.4(2)	C17–C16–C15	130.4(2)
C21–C16–C15	108.2(2)	C18–C17–C16	117.2(2)	C18–C17–H17	121.41(14)
C16–C17–H17	121.41(12)	C19–C18–C17	121.6(2)	C19–C18–H18	119.18(12)
C17–C18–H18	119.18(14)	C18–C19–C20	121.2(2)	C18–C19–H19	119.39(12)
C20–C19–H19	119.39(13)	C21–C20–C19	117.3(2)	C21–C20–H20	121.35(12)
C19–C20–H20	121.35(13)	C20–C21–C16	121.2(2)	C20–C21–C22	130.6(2)
C16–C21–C22	108.2(2)	O24–C22–N14	124.7(2)	O24–C22–C21	129.4(2)
N14–C22–C21	105.89(14)	C26–C25–C2	117.2(2)	C26–C25–H25a	107.99(10)
C2–C25–H25a	107.99(9)	C26–C25–H25b	107.99(11)	C2–C25–H25b	107.99(10)
H25a–C25–H25b	107.2	O27–C26–C25	108.9(2)	O27–C26–H26a	109.90(10)
C25–C26–H26a	109.90(11)	O27–C26–H26b	109.90(10)	C25–C26–H26b	109.90(10)
H26a–C26–H26b	108.3	O27–C28–C29	109.9(2)	O27–C28–H28a	109.7(2)
C29–C28–H28a	109.7(2)	O27–C28–H28b	109.7(2)	C29–C28–H28b	109.7(2)
H28a–C28–H28a	108.2	C30–C29–C34	118.6(2)	C30–C29–C28	120.7(3)
C34–C29–C28	120.7(3)	C29–C30–C31	119.8(3)	C29–C30–H30	120.1(2)
C31–C30–H30	120.1(2)	C32–C31–C30	119.6(3)	C32–C31–H31	120.2(3)
C30–C31–H31	120.2(2)	C33–C32–C31	120.4(3)	C33–C32–H32	119.8(3)
C31–C32–H32	119.8(3)	C32–C33–C34	120.0(3)	C32–C33–H33	120.0(3)
C34–C33–H33	120.0(2)	C33–C34–C29	121.6(3)	C33–C34–H34	119.2(2)
C29–C34–H34	119.2(2)	C2–B3–B7	58.91(11)	C2–B3–B11	105.4(2)
B7–B3–B11	59.72(13)	C2–B3–B4	105.76(14)	B7–B3–B4	107.9(2)
B11–B3–B4	60.20(13)	C2–B3–B6	59.57(11)	B7–B3–B6	108.17(14)
B11–B3–B6	107.9(2)	B4–B3–B6	59.65(12)	C2–B3–H3	117.4(10)
B7–B3–H3	121.5(10)	B11–B3–H3	128.7(10)	B4–B3–H3	125.8(10)
B6–B3–H3	117.2(10)	B6–B4–B3	60.32(11)	B6–B4–B5	60.19(11)
B3–B4–B5	108.0(2)	B6–B4–B11	108.2(2)	B3–B4–B11	59.89(13)
B5–B4–B11	107.5(2)	B6–B4–B10	107.93(14)	B3–B4–B10	107.7(2)
B5–B4–B10	59.53(12)	B11–B4–B10	59.83(13)	B6–B4–H4	119.4(10)
B3–B4–H4	120.9(10)	B5–B4–H4	121.5(10)	B11–B4–H4	123.4(10)
B10–B4–H4	123.7(10)	C1–B5–B10	105.6(2)	C1–B5–B9	58.79(11)
B10–B5–B9	60.38(12)	C1–B5–B4	105.43(14)	B10–B5–B4	60.43(12)
B9–B5–B4	108.6(2)	C1–B5–B6	59.20(11)	B10–B5–B6	108.2(2)
B9–B5–B6	108.2(2)	B4–B5–B6	59.67(12)	C1–B5–H5	115.5(9)
B10–B5–H5	129.4(9)	B9–B5–H5	119.3(9)	B4–B5–H5	128.1(9)
B6–B5–H5	117.4(9)	C1–B6–C2	58.34(10)	C1–B6–B4	105.18(14)
C2–B6–B4	104.92(14)	C1–B6–B5	58.39(10)	C2–B6–B5	105.20(14)
B4–B6–B5	60.14(12)	C1–B6–B3	105.11(13)	C2–B6–B3	58.12(11)
B4–B6–B3	60.03(12)	B5–B6–B3	107.8(2)	C1–B6–H6	116.0(9)
C2–B6–H6	118.1(9)	B4–B6–H6	131.3(9)	B5–B6–H6	122.6(9)
B3–B6–H6	126.2(9)	C2–B7–B11	105.6(2)	C2–B7–B12	105.9(2)
B11–B7–B12	60.81(14)	C2–B7–B3	58.63(12)	B11–B7–B3	60.19(13)
B12–B7–B3	108.8(2)	C2–B7–B8	59.23(11)	B11–B7–B8	108.7(2)
B12–B7–B8	60.04(13)	B3–B7–B8	108.14(14)	C2–B7–H7	115.8(11)
B11–B7–H7	130.2(11)	B12–B7–H7	126.2(11)	B3–B7–H7	121.2(11)
B8–B7–H7	115.7(11)	C2–B8–C1	58.44(10)	C2–B8–B12	105.2(2)
C1–B8–B12	104.9(2)	C2–B8–B7	58.61(12)	C1–B8–B7	105.25(14)
B12–B8–B7	59.81(13)	C2–B8–B9	105.52(14)	C1–B8–B9	58.35(11)
B12–B8–B9	59.98(13)	B7–B8–B9	107.6(2)	C2–B8–H8	116.9(11)
C1–B8–H8	117.0(10)	B12–B8–H8	131.3(10)	B7–B8–H8	124.7(10)

(*continued on next page*)

Table 8 (continued)

B9–B8–H8	124.1(10)	C1–B9–B5	58.70(11)	C1–B9–B12	105.6(2)
B5–B9–B12	108.0(2)	C1–B9–B8	59.34(11)	B5–B9–B8	108.0(2)
B12–B9–B8	59.81(13)	C1–B9–B10	105.0(2)	B5–B9–B10	59.64(12)
B12–B9–B10	60.28(13)	B8–B9–B10	107.9(2)	C1–B9–H9	117.1(11)
B5–B9–H9	120.9(10)	B12–B9–H9	126.5(10)	B8–B9–H9	117.3(11)
B10–B9–H9	129.1(11)	B5–B10–B11	108.1(2)	B5–B10–B9	59.98(12)
B11–B10–B9	108.0(2)	B5–B10–B4	60.04(12)	B11–B10–B4	59.99(13)
B9–B10–B4	108.0(2)	B5–B10–B12	107.8(2)	B11–B10–B12	60.26(14)
B9–B10–B12	59.70(13)	B4–B10–B12	108.1(2)	B5–B10–H10	121.9(11)
B11–B10–H10	121.8(11)	B9–B10–H10	121.4(11)	B4–B10–H10	122.2(11)
B12–B10–H10	121.3(11)	B7–B11–B3	60.09(13)	B7–B11–B10	107.8(2)
B3–B11–B10	108.0(2)	B7–B11–B4	108.0(2)	B3–B11–B4	59.91(12)
B10–B11–B4	60.18(13)	B7–B11–B12	59.63(14)	B3–B11–B12	107.8(2)
B10–B11–B12	60.08(14)	B4–B11–B12	108.1(2)	B7–B11–H11	119.4(11)
B3–B11–H11	119.6(11)	B10–B11–H11	124.5(11)	B4–B11–H11	122.7(11)
B12–B11–H11	122.4(11)	B7–B12–B8	60.15(13)	B7–B12–B9	108.1(2)
B8–B12–B9	60.22(12)	B7–B12–B10	107.4(2)	B8–B12–B10	108.0(2)
B9–B12–B10	60.03(13)	B7–B12–B11	59.57(14)	B8–B12–B11	107.8(2)
B9–B12–B11	107.8(2)	B10–B12–B11	59.66(13)	B7–B12–H12	119.7(11)
B8–B12–H12	118.7(11)	B9–B12–H12	121.9(11)	B10–B12–H12	125.1(11)
B11–B12–H12	123.6(11)				