Inorg. Chem. **1996,** *35,* 1701−1708 **1701**

1-Phenyl-1,2-dicarba-*closo*-dodecaborane, 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$. Synthesis, Characterization, and Structure As Determined in the Gas Phase by Electron Diffraction, in the Crystalline Phase at 199 K by X-ray Diffraction, and by *ab Initio* Computations

Paul T. Brain, Jill Cowie, David J. Donohoe, Drahomír Hnyk,[†] David W. H. Rankin, David Reed, Bruce D. Reid, Heather E. Robertson, and Alan J. Welch*

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, U.K.

Matthias Hofmann and Paul von Ragué Schleyer

Computer-Chemie-Centrum des Instituts für Organische Chemie, Universität Erlangen-Nürnberg,
Nägelbachstrasse 25, D-91052 Erlangen, Germany

Received August 24, 1995[⊗]

The compound 1-phenyl-1,2-dicarba-*closo*-dodecaborane(12), 1-C_6H_5-1,2-*closo*-$C_2B_{10}H_{11}$ (**1**), has been synthesized and characterized by a complete assignment of its ^{11}B NMR spectrum *via* $^{11}B\{^1H\}/^{11}B\{^1H\}$ (COSY), $^1H\{^{11}B_{selective}\}$ and $^1H\{^{11}B\}/^1H\{^{11}B\}$ (COSY) spectroscopy. An electron- and X-ray diffraction investigation of **1**, complemented by *ab initio* calculations, has been undertaken. The gas-phase electron-diffraction (GED) data can be fitted by several models describing conformations which differ in the position of the phenyl ring with respect to the carborane cage. Local symmetries of C_{2v} and D_{6h} for the 1,2-C_2B_{10} and C_6 moieties, respectively, were adopted in the GED model in order to simplify the problem. In addition, constraints among the close-lying C−C and B−B bonds were employed. However, even though such simplifications led to satisfactory refinements ($R_G = 0.069-0.071$), a unique, definitive solution could not be gained. The $(C-C)_{mean}$, $(C-B)_{mean}$ and $(B-B)_{mean}$ bond lengths, r_a, are *ca.* 1.44, 1.72, and 1.78 Å, respectively. The C_6 hexagon, with $r_a(C-C) =$ *ca.* 1.394 Å, either eclipses the C(1)−C(2) vector (overall C_s symmetry) or more or less eclipses the C(1)−B(4) cluster bond (overall C_1 symmetry). In contrast, in the solid at 199 K, the ring lies at a position intermediate between the two GED positions, as determined by X-ray crystallography [$C_8H_{16}B_{10}$, monoclinic $P2_1/a$: $a = 12.047(3)$ Å, $b = 18.627(4)$ Å, $c = 12.332(5)$ Å, $\beta = 110.09(4)°$, $Z = 8$]. The C−B distances span the range 1.681(6)−1.743(5) Å, and B−B lengths lie between 1.756(6) and 1.795(6) Å. A similar conformation was found for the theoretical (RHF/6-31G* level) structure which was fully optimized in C_1 symmetry. The r_e distances are consistent with the dimensions derived in the experimental studies. IGLO calculations of the ^{11}B chemical shifts, in addition to SCF single-point energies of the GED structures, further support these observations.

Introduction

1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ (henceforth referred to as monophenylcarborane, **1**) was one of the first carbon-substituted analogues of 1,2-*closo*-$C_2B_{10}H_{12}$ to be reported, more than 30 years ago.[1] Surprisingly, however, even though it can be regarded as the fusion of two fragments (phenyl and *closo*-carborane) each of which has an extensive chemistry, relatively little work on it or its derivatives has since been published. There are a few reports of derivatives of 1-Ph-2-X-1,2-*closo*-$C_2B_{10}H_{10}$, where X is an organic group,[2] an inorganic group,[3] or a transition metal fragment;[4] also, monophenylcarborane is readily deboronated [losing B(3) or B(6)] to afford the anion [7-Ph-7,8-*nido*-$C_2B_9H_{10}]^{2-}$ which can function as an η-ligand to a variety of metal-based fragments.[5]

In considering the structural chemistry of monophenylcarborane and its various derivatives, one important feature is the orientation of the phenyl ring relative to the C(1)−C(2) vector. This is described in terms of the angle θ', where $\theta' = 90° - [C(2)-C(1)-C(11)-C(16)]$, such that (a) when $\theta' = 90°$, C(2) lies in the plane of the phenyl ring (Figure 1a), and (b) when θ'

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* Author to whom correspondence should be addressed.

[†] On leave from the Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic, 250 68 Řež near Prague, Czech Republic.

[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1996.

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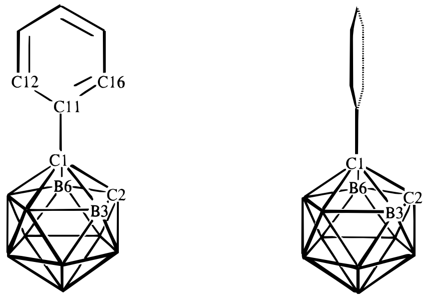

(a) θ' = 90° (b) θ' = 0°

Figure 1. (a) When $\theta' = 90°$, C(2) lies in the plane of the phenyl ring. (b) When $\theta' = 0°$, the ring is twisted about C(1)−C(11) such that C(2) lies in a plane perpendicular to it.

= 0°, the ring is twisted about C(1)−C(11) such that C(2) lies in a plane perpendicular to it (Figure 1b).[6]

Recently, extended Hückel molecular orbital (EHMO) calculations on an idealized model of monophenylcarborane have been reported.[2(a)] These suggested that the conformation with $\theta' = 90°$ occurred at the minimum on the potential energy surface, *ca.* 22 kJ mol^{-1} lower in energy than the conformation with $\theta' = 0°$. Interestingly, these calculations further suggested that both the C(1)−C(2) and C(1)−C(11) interactions should be strongest at $\theta' = 90°$, with, moreover, C(1)−C(2) stronger in this conformation (and weaker at $\theta' = 0°$) than in the parent compound $C_2B_{10}H_{12}$. However, as far as we are aware, the optimum conformation of monophenylcarborane, and the strength of preference for that conformation, have been explored neither experimentally nor by *ab initio* MO calculations.

The molecular structures of other large heteroboranes, *e.g.* 1,7-Cl_2-1,7-*closo*-$C_2B_{10}H_{10}$ and 1,2-*closo*-$C_2B_8H_{10}$,[7,8] have been determined recently in the gas-phase. In these studies, electron-diffraction data and *ab initio* geometry optimizations (MP2/6-31G* level) have been combined with ^{11}B IGLO (individual gauge for localized orbitals)[9] chemical-shift calculations in the so-called *ab initio*/IGLO/NMR/GED approach.[10] In such studies, constraints derived from geometries optimized *ab initio* are used in the GED refinements for parameters describing the boron cage. Such parameters, defining small differences in interatomic B−B and B-C distances, generally cannot be refined due to the effects of correlation between parameters.

In this paper, we report the results of studies of the molecular structure and the conformation of monophenylcarborane in both the gas phase (by electron diffraction) and the solid phase (by X-ray crystallography). In addition, the results of a theoretical study of the structure by *ab initio* and ^{11}B IGLO NMR[9] calculations are presented. Finally, we report the experimental ^{11}B NMR spectrum of monophenylcarborane and its complete assignment *via* $^{11}B\{^1H\}/^{11}B\{^1H\}$ (COSY), $^1H\{^{11}B_{selective}\}$ and $^1H\{^{11}B\}/^1H\{^{11}B\}$ (COSY) spectroscopy. These complement results of an $^{11}B\{^1H\}/^{11}B\{^1H\}$ (TOCSY; total correlation spectroscopy) experiment on 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ reported recently.[11]

Table 1. Nozzle-to-Plate Distances, Weighting Functions, Correlation Parameters, Scale Factors, and Electron Wavelengths Used in the Electron-Diffraction Study of **1**

Nozzle-to-plate dist/mm	weighting functions/nm^{-1}					corrln param	scale factor, k^a	electron wavelength^b/pm
	Δs	s_{min}	sw_1	sw_2	s_{max}			
258.7	2	30	50	140	164	0.489	0.655(8)	5.701
93.8	4	92	112	232	272	0.131	0.538(11)	5.698

[a] Figures in parentheses are the estimated standard deviations. [b] Determined by reference to the scattering pattern of benzene vapor.

Experimental Section

General Procedures. The synthesis of 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ was performed using standard Schlenk techniques with subsequent manipulation in the open atmosphere. Benzene, chloroform and pentane were dried over sodium wire prior to use. Acetonitrile, *N,N*-dimethylaniline, and $CDCl_3$ were predried over 4 Å molecular sieves. $B_{10}H_{14}$ (Callery) was recrystallized from Et_2O before use. PhCCH (Aldrich) was used as supplied. The IR spectrum was recorded from a $CHCl_3$ solution on a Perkin-Elmer 598 spectrophotometer using matched CaF_2 cells. NMR spectra (^{1}H at 600 MHz, ^{11}B at 192.5 MHz) were recorded from $CDCl_3$ solutions at 291 K on a Varian VXR600S spectrometer. Chemical shifts are referenced to external $SiMe_4$ (^{1}H) or $BF_3{\cdot}OEt_2$ (^{11}B) with positive shifts to high frequency. Techniques for recording $^{11}B\{^1H\}/^{11}B\{^1H\}$[12] and $^1H\{^{11}B\}/^1H\{^{11}B\}$[13] spectra have been reported previously.

Improved Synthesis of 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$. $B_{10}H_{14}$ (3.91 g, 32.1 mmol), PhCCH (3.47 g, 34.0 mmol), and MeCN (2.78 g, 67.8 mmol) were stirred for 1 h at room temperature in 45 mL of C_6H_6, and the reaction mixture heated subsequently to reflux for 72 h. After cooling, volatiles were removed *in vacuo*, leaving a yellow oil. The product was extracted into *n*-pentane (5 × 20 mL) and filtered, and the pentane was removed *in vacuo* to afford the crude product as a white, waxy solid. Crystallization from MeOH/H_2O (1:6) at room temperature produced 3.65 g (52% yield) of colorless needles of 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ which were analytically pure. Using *N,N*-dimethylaniline instead of MeCN afforded yields at least as high (60−65%). $^1H\{^{11}B\}$ NMR: δ 7.58−7.33 (5H, m, C_6H_5), 3.97 (1H, s, $C_{cage}H$), 2.62 (2H, s, B*H*), 2.53 (2H, s, B*H*), 2.46 (1H, s, B*H*), 2.35 (3H [2 + 1 coincidence], s, B*H*), 2.30 ppm (2H, s, B*H*). $^{11}B\{^1H\}$ NMR: δ −1.19 (1B, s), −3.49 (1B, s), −8.06 (2B, s), −9.88 (2B, s), −10.32 (2B, s), −11.85 ppm (2B, s). IR: 2595 cm^{-1} (broad, ν_{B-H}). Anal. Calcd for $C_8H_{16}B_{10}$: C, 43.6; H, 7.32. Found: C, 43.6; H, 7.44.

Electron Diffraction. Electron-scattering intensities were recorded on Kodak electron image plates using the Edinburgh gas-diffraction apparatus operating at *ca.* 44.5 kV (electron wavelength *ca.* 5.7 pm).[14] Nozzle-to-plate distances for the stainless steel inlet nozzle employed were *ca.* 94 and 259 mm, yielding data in the *s* range 30−272 nm^{-1}. The sample and nozzle were held at *ca.* 468 and 488 K respectively during the exposures.

The scattering patterns of benzene were also recorded for the purpose of calibration; these were analyzed in exactly the same way as those of the carborane so as to minimize systematic errors in the wavelengths and camera distances. Nozzle-to-plate distances, weighting functions used to set up the off-diagonal weight matrix, correlation parameters, final scale factors, and electron wavelengths for the measurements are collected together in Table 1.

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(6) This is slightly different from the definition θ = the modulus of the average $C_{cage}-C_{cage}-C_{ring}-C_{ring}$ used previously. See: Cowie, J.; Reid, B. D.; Watmough, J. M. S.; Welch, A. J. *J. Organomet. Chem.* **1994**, *481*, 283.

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Table 2. Crystallographic Data for 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$

$C_8H_{16}B_{10}$	fw = 220.23
$a = 12.047(3)$ Å	space group: $P2_1/a$ (monoclinic)
$b = 18.627(4)$ Å	T = 199 K
$c = 12.332(5)$ Å	$\lambda_{bar} = 0.71069$ Å
$\beta = 110.09(4)°$	$D_{calc} = 1.128$ g cm^{-3}
$V = 2595.3(14)$ Å^3	μ(Mo K_α) = 0.49 cm^{-1}
$Z = 8$	$R^a = 0.0831$
	$S^b = 1.073$

[a] $R = \sum||F_o| - |F_c||/\sum F_o$. [b] $S = (\sum w(|F_o| - |F_c|)^2/(n_o - n_v))^{1/2}$.

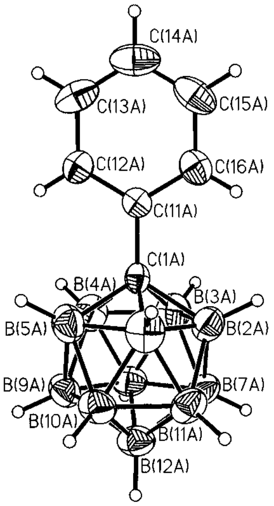

Figure 2. Perspective view of molecule A refined from the X-ray data (30% ellipsoids except for H atoms which have an artificial radius of 0.1 Å for clarity).

The electron-scattering patterns were converted into digital form using a computer-controlled Joyce-Loebl MDM6 microdensitometer with a scanning program described elsewhere.[15] The programs used for data reduction[15] and least-squares refinement[16] have been described previously; the complex scattering factors employed were those listed by Ross *et al.*[17]

X-ray Diffraction. Crystals suitable for X-ray diffraction were grown by very slow cooling (to room temperature) of a warm, concentrated, ethanolic solution. Crystallographic data were collected on an Enraf-Nonius CAD4 diffractometer operating with Mo-K_α X-radiation ($\lambda_{bar} = 0.71069$ Å), with the glass capillary containing the crystal held in a stream of nitrogen gas at 199 K. The unit cell was determined by the least-squares refinement of the setting angles of 25 reflections in the range $16 < 2\theta < 22°$. Intensity data in the range $2 < 2\theta < 50°$ were collected by the ω-2θ scan technique; ω-scan width ($0.8 + 0.34 \tan \theta$), ω-scan speeds in the range 0.235 to 0.782° min^{-1}. The intensities of 4572 unique reflections were measured (h, −14 to +14; k, 0 to 22; l, 0 to 14); of these, 2592 reflections had $F > 4\sigma(F)$. There was no decay or crystal movement during the 158 h of data collection (CADABS[18]). Crystallographic data are summarized in Table 2.

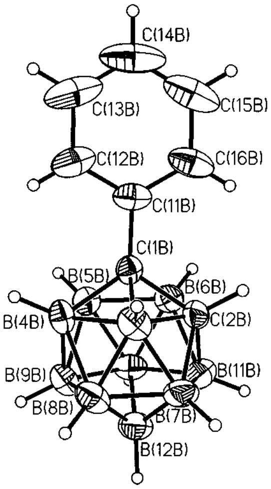

Figure 3. Perspective view of molecule B refined from the X-ray data (30% ellipsoids except for H atoms which have an artificial radius of 0.1 Å for clarity).

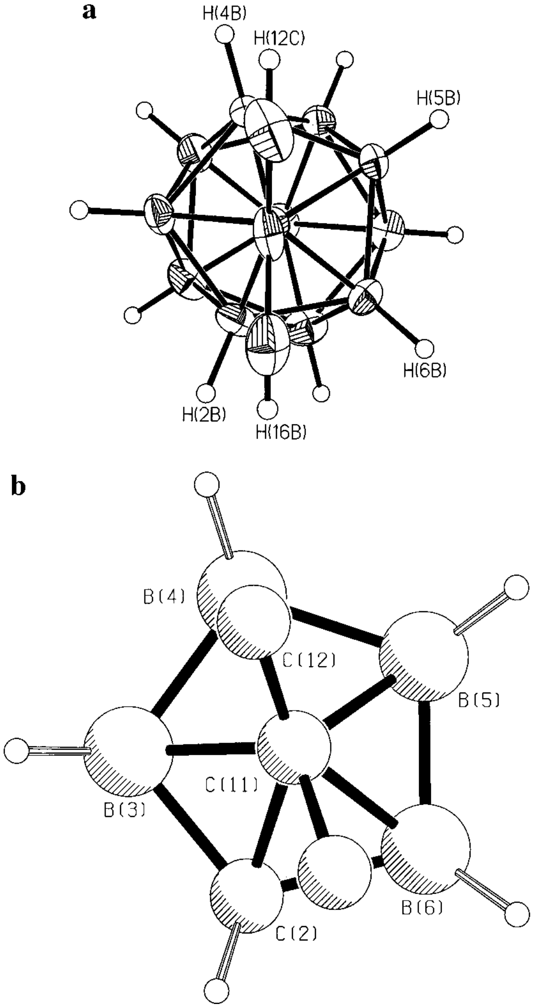

Figure 4. Views of **1** along C(11)−C(1): (a) molecule B from the X-ray study, with $\theta' = ca.$ 68°; (b) GED refinement B, with $\theta' = 54°$. Parts of the phenyl ring and carborane cage are omitted for clarity.

The structure was solved using direct methods (SHELXS86)[19] and developed by iterative full matrix least-squares refinement and difference Fourier syntheses (SHELXTL).[20] In molecule A (Figure 2), the cage carbon not carrying the phenyl substituent could not be unambiguously identified and consequently a disordered model was adopted in which all five boron atoms adjacent to C(1A) were given an occupancy of 1.04. In contrast, molecule B (Figures 3 and 4) was fully ordered and the position of C(2B) was clear. Phenyl rings were treated as planar hexagons (C−C = 1.390 Å) with phenyl-H atoms set in idealized positions (C−H = 0.93 Å). In the final stages of refinement, all non-H atoms were refined with anisotropic thermal parameters. Cage-H atoms were set 1.10 Å from C or B on a radial extension. All H atoms were

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Table 3. Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters[a] (Å^2 $\times$ 10^3) in 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$

	x	y	z	U_{eq}
C(12A)	462(2)	−45(1)	6913(2)	43(1)
C(13A)	1091(2)	−401(1)	6321(2)	58(1)
C(14A)	1758(2)	−13(2)	5803(2)	62(1)
C(15A)	1795(2)	732(2)	5877(2)	59(1)
C(16A)	1166(2)	1089(1)	6468(2)	43(1)
C(11A)	499(2)	700(1)	6986(2)	31(1)
C(1A)	−197(3)	1083(2)	7610(3)	30(1)
B(2A)	−160(3)	1985(2)	7745(3)	48(1)
B(3A)	560(4)	1458(2)	8944(3)	53(1)
B(4A)	−348(4)	712(2)	8787(3)	51(1)
B(5A)	−1557(3)	754(2)	7511(4)	53(1)
B(6A)	−1437(4)	1566(2)	6846(4)	56(1)
B(8A)	−422(4)	1390(3)	9734(4)	46(1)
B(9A)	−1720(4)	947(3)	8846(4)	49(1)
B(10A)	−2412(4)	1492(3)	7623(4)	51(1)
B(11A)	−1524(4)	2279(2)	7752(4)	50(1)
B(7A)	−298(4)	2209(2)	9059(4)	47(1)
B(12A)	−1713(4)	1893(3)	9001(4)	51(1)
C(12B)	−63(2)	5150(1)	2294(2)	60(1)
C(13B)	445(3)	5680(1)	1825(3)	85(2)
C(14B)	1213(3)	5493(2)	1252(3)	86(2)
C(15B)	1473(2)	4775(2)	1148(2)	79(2)
C(16B)	965(2)	4244(1)	1617(2)	59(1)
C(11B)	197(2)	4431(1)	2190(2)	41(1)
C(1B)	−406(3)	3872(2)	2669(3)	32(1)
C(2B)	175(3)	3067(2)	2949(3)	42(1)
B(3B)	274(4)	3605(2)	4102(3)	42(1)
B(4B)	−1081(3)	4069(2)	3650(3)	37(1)
B(5B)	−1911(3)	3813(2)	2199(3)	34(1)
B(6B)	−1073(4)	3177(2)	1757(3)	38(1)
B(10B)	−2225(4)	2872(2)	2210(4)	42(1)
B(9B)	−2234(4)	3431(2)	3377(4)	41(1)
B(8B)	−879(4)	3305(3)	4553(4)	46(1)
B(7B)	−36(4)	2678(3)	4094(4)	50(1)
B(11B)	−852(5)	2415(3)	2662(4)	53(1)
B(12B)	−1586(4)	2567(2)	3651(4)	47(1)

[a] $U_{eq} = \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

Table 4. Molecular Parameters (r_a/Å or $\angle$/deg)[a] for the GED Study of **1**

parameter[b]		refinement[c] A	refinement[c] B
p_1	$r(C-C)_{av}$, $^1/_8[(1-2) + 6(C-C)_{ring} + (1-11)]$	1.440(2)	1.436(2)
p_2	$r(C-B)_{av}$, $^1/_2[(1-3) + (1-4)]$	1.711(5)	1.720(6)
p_3	$r(B-B)_{av}$, $^1/_{15}[4(3-4) + 4(4-8) + 2(7-11) + (9-12) + 4(8-12)]$	1.788(4)	1.784(5)
p_4	$r(C-H)$	1.113(10)	1.120(12)
p_5	$r(B-H)$	1.179(8)	1.176(13)
p_6	C(2)C(1)B(4)	111.1(4)	110.6(4)
p_7	C(2)C(1)C(11)	126.3(7)	119.6(17)
p_8	BBH	120.0(f)	120.0(f)
p_9	C(1)C(2)H(2)	117.0(f)	117.0(f)
p_{10}	θ' [90° − C(2)C(1)C(11)C(16)]	90.0(f)	54.0(f)
p_{11}	Δ [C(1)−C(2)]−[$(C-C)_{ring}$]	0.238(7)	0.233(7)
p_{12}	Δ [C(1)−C(2)]−[C(1)−C(11)]	0.121(8)	0.126(8)
p_{13}	Δ [C(1)−B(3)]−[C(1)−B(4)]	−0.006(9)	−0.004(9)
p_{14}	Δ [B(3)−B(4)]−[B(4)−B(8)]	−0.004(8)	−0.001(9)
p_{15}	Δ [B(3)−B(4)]−[B(7)−B(11)]	0.005(8)	0.002(8)
p_{16}	Δ [B(3)−B(4)]−[B(9)−B(12)]	−0.007(10)	−0.008(10)
p_{17}	Δ [B(3)−B(4)]−[B(8)−B(12)]	−0.047(7)	−0.045(7)

[a] Figures in parentheses are the estimated standard deviations of the last digits: f = fixed. [b] For definitions, see text; for atom numbering see Figures 3 and 4. [c] For method of refinement, see text.

given isotropic displacement parameters riding at 1.2 times the equivalent isotropic parameter of their attached atom. Data were weighted such that $w^{-1} = [\sigma^2(F_o^2) + (0.1189P)^2 + 1.05P]$ where $P = [\max.(F_o^2 \text{ or } 0) + 2F_c^2]/3$. Using 2592 observed data, $R = 0.0831$ and $S = 1.073$ for 301 variable parameters. The maximum residue and minimum trough in a final Fourier synthesis were +0.34 and −0.26 e Å^{-3}, respectively. Atomic scattering factors were those inlaid in SHELXTL. The atomic fractional coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are listed in Table 3. Hydrogen atom fractional coordinates, non-hydrogen anisotropic thermal parameters, and a full listing of bond lengths and bond angles are available as Supporting Information.

***Ab Initio* Calculations.** The geometry was fully optimized in C_s and C_1 symmetry by standard *ab initio* methods[21] at the RHF/6-31G* level using the Gaussian 92[22] program package. Computations at a correlated level (*e.g.* MP2) were not possible due to the demands on CPU time and disk space for such a large, low symmetry molecule. ^{11}B chemical shieldings were computed with the IGLO (individual gauge for localized orbitals) program[9] using Huzinaga basis sets:[23] DZ; (7s3p) contracted to [4111, 21] for C,B and (3s) contracted to [21] for H; II″, (9s5p1d) contracted to [51111, 2111, 1] for C,B (cage atoms and C(11)), (7s3p) contracted to [4111, 21] for C(12−16) and (3s) contracted to [21] for H. Computations employing the DZ basis were obtained with an IGLO lobe version, while for the II″ basis the direct IGLO program (DIGLO)[9d] was used.

Molecular Model for the GED Refinement. Since 1-phenyl-1,2-dicarba-*closo*-dodecaborane(12), 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$, has either C_1 or, at most, C_s symmetry and a large number of different interatomic distances, it is a difficult system for investigation by electron-diffraction. Thus, in order to reduce the problem to a manageable dimension, local symmetries of C_{2v} and D_{6h} for the 1,2-C_2B_{10} cage and the C_6 hexagonal ring, respectively, were assumed. Such assumptions were based on the theoretically optimized geometry (HF/6-31G* level) in C_1 symmetry which predicted only small deviations from the idealized symmetries for these moieties (see below). However, even for this simplified model, in which only the weighted mean values of the C−C (p_1), C−B (p_2), and B−B (p_3) bonds were considered (see Table 4), seven parameters (p_{11}−p_{17}) defining differences between the close-lying C−B, B−B and C−C distances were also necessary. The initial values of such differences were derived from the HF/6-31G* optimization in C_1 symmetry. To complete the description of the C_2B_{10} framework, the C(2)C(1)B(4) bond angle (p_6) was used. The position of the phenyl ring with respect to the cage was defined by both the C(2)−C(1)−C(11) bond angle (p_7) and by the torsion angle, $\theta' = 90° - [C(2)-C(1)-C(11)-C(16)]$,($p_{10}$). The B−H bonds were assumed to be all of equal length (p_5), as were the six C−H bonds [five $(C-H)_{ring}$ and C(2)−H(2)] (p_4). For the angle parameters, the cluster hydrogens were located assuming a single value for the BBH angles (p_8) and the angle C(1)C(2)H(2) (p_9). Thus, the structure was defined by 17 refinable parameters in this model as listed in Table 4.

Results

Electron Diffraction. Electron-diffraction refinements for structures with a range of fixed θ' values were undertaken. The fit of data for the C_s structure with $\theta' = 0°$ was poorer ($R_G > 0.09$) than for either the C_s structure with $\theta' = 90°$ (refinement A, $R_G = 0.069$) or the optimum refinement in C_1 symmetry with $\theta' = 54°$, *i.e.* B(4)−C(1)−C(11)−C(12) = *ca.* 1° (refinement B, $R_G = 0.071$). In the original refinements, it was possible to refine five of the geometrical parameters (Table 4), *viz.* p_1−p_4 and p_7. Attempts to refine other parameters led to either unreasonable values or an unstable refinement. Consequently, the esd's for some of the independent and dependent parameters were likely to be underestimated, *e.g.* $r[C(1)-C(2)] = 1.629(2)$ Å. Subsequent refinements were therefore undertaken using the method of flexible parameter constraints.[24]

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(21) See: (a) Hehre, W.; Radom, L.; Schleyer, P. v.R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986. (b) Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methods*; Gaussian Inc.: Pittsburgh PA, 1993.

(22) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Schlegal, H. B.; Raghavachari, K.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Binkley, J. S.; Gonzalez, C.; Martin, R.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian Inc., Pittsburgh, PA, 1992.

(23) Huzinaga, S. *Approximate Atomic Wavefunctions*; University of Alberta: Edmonton, Canada, 1971.

Flexible parameter constraints may allow the refinement of parameters which would usually have to be fixed. Estimates of the values of these parameters and their uncertainties are used as additional observations in a combined analysis similar to those routinely carried out for electron-diffraction data combined with rotation constants and/or dipolar coupling constants. The starting values and uncertainties for the extra observations are derived from another method such as X-ray diffraction or theoretical computations. *All* parameters are then included in the refinements. Upon refinement, if the intensity pattern contains useful information concerning one of these parameters, it will refine with an esd less than the uncertainty in the corresponding additional observation. However, if there is little or no relevant information, the parameter will refine with an esd equal to the uncertainty of the extra observation. In this case, the parameter can simply be fixed, in the knowledge that doing this does not influence either the magnitudes or the esd's of other parameters. In some cases, increasing the number of refining parameters allows all effects of correlation to be considered, and so some esd's may actually increase. Overall, this approach utilizes all available data as fully as possible and returns more realistic esd's for parameters, *e.g.* r[C(1)−C(2)] = 1.627(8) Å.

Using the method of flexible constraints, it was possible to refine simultaneously 14 geometrical parameters (Table 4). Heavy-atom distance differences ($p_{11}-p_{17}$) were constrained with an uncertainty of 0.01 Å and r(B−H) with 0.02 Å. Additionally, eight amplitudes of vibration were refined simultaneously in the final refinements while the dependence of the final structure on other fixed amplitudes was also explored.

The parameters for refinements A and B are summarized in Table 4. Interatomic distances, vibrational amplitudes and angles as obtained in refinement B are listed in Table 5 and the most important elements of the least-squares correlation matrix are given in Table 6. Atomic coordinates of the HF/6-31G* and GED (refinement B) C_1 geometries are included as part of the Supporting Information. The radial-distribution curves and molecular-scattering intensities are shown in Figures 5 and 6, respectively.

***Ab Initio* and IGLO Computations.** IGLO ^{11}B chemical-shift calculations, performed for various HF/6-31G* optimized structures differing mainly in the phenyl ring position, indicated that the $\delta(^{11}\mathrm{B})$ values are sensitive to the phenyl-ring orientation, if only to a small degree. The HF/6-31G* level energy computations favor the structures in which the ring eclipses the C(1)-C(2) bond (C_s symmetry, $\theta' = 90°$), or more or less eclipses the C(1)-B(4) bond (C_1 symmetry, $\theta' = 65°$, B(4)−C(1)−C(11)−C(12) = *ca.* 14°), the latter being found as the minimum on the potential energy (p.e.) hypersurface, relative to the structure with the phenyl ring "perpendicular" to the C(1)−C(2) bond (C_s symmetry, $\theta' = 0°$). Selected geometrical parameters from the *ab initio* study are given in Table 7, and the results of the IGLO computations are shown in Table 8.

X-ray. There are two crystallographically-independent molecules of 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$ (molecules A and B) in the asymmetric fraction of the unit cell, and these are drawn in Figures 2 and 3, respectively. There are no significant contacts between molecules. Interatomic distances and selected interbond angles are given in Table 8; a full listing of geometrical parameters is included in the Supporting Information. In molecule A, the cage carbon atom not carrying the phenyl substituent, C(2), could not be distinguished with a sufficient degree of certainty [C(1A)−cage atom distances = 1.674(5)−1.728(5) Å], whereas in molecule B its location (based on a combination of interatomic distances and refined [as B] isotropic thermal parameters) was unambiguously established. Since the key feature of the structure of monophenylcarborane is the twist angle θ' which describes the conformation of the phenyl ring with respect to C(1)−C(2), only parameters for molecule B will be discussed.

Table 5. Final Interatomic Distances (r_a/Å)$^{a-c}$ and Mean Amplitudes of Vibration (u/Å) from the GED Refinement B of **1**

	distance	r_a	u
r_1	C(1)−C(2)	1.627(8)	0.045(f)
r_2	C(1)−B(3)	1.718(8)	0.054(f)
r_3	C(1)−B(4)	1.722(7)	0.054(f)
r_4	B(3)−B(4)	1.771(6)	0.062(4)
r_5	B(4)−B(5)	1.770(9)	
r_6	B(8)−B(12)	1.816(5)	
r_7	B(4)−B(8)	1.772(9)	
r_8	B(9)−B(12)	1.779(12)	
r_9	B(7)−B(12)	1.806(14)	
r_{10}	B(3)−B(8)	1.788(18)	
r_{11}	C(1)−C(11)	1.500(8)	0.042(f)
r_{12}	$(\mathrm{C-C})_{\mathrm{ring}}$	1.394(2)	0.042(f)
r_{13}	B−H	1.176(13)	0.108(f)
r_{14}	$(\mathrm{C-H})_{\mathrm{ring}}$	1.120(12)	0.078(f)
r_{15}	C(2)−H(2)	1.120(12)	0.085(f)
r_{16}	(C···B) [two bond]	2.752−2.831	0.075(5)
r_{17}	(B···B) [two bond]	2.837−2.925	
r_{18}	(C···B)^d	3.302(18)	0.084(f)
r_{19}	(B···B)^d	3.343−3.418	0.093(f)
r_{20}	C(12)···C(16)	2.414(3)	0.067(4)
r_{21}	C(11)···C(14)	2.788(3)	0.068(7)
r_{22}	($\mathrm{C_{ring}}$···B) [four/five bond]	4.470−5.071	0.152(30)
r_{23}	($\mathrm{C_{ring}}$···B) [four/five bond]	4.678−5.370	0.185(26)

^{a} Values in parentheses are the estimated standard deviations of the final digits: f = fixed. ^{b} For atom numbering scheme, see Figures 3 and 4. ^{c} All C(x)···C(1,2) and C(x)···B(N) distances (x = 11, 14, 15, 16; N = 3, ..., 12) with multiplicity 1 were included in the refinement but most are not shown here. Similarly, all the B···H, C···H, and H···H distances (cage and ring), with amplitudes fixed in the range 0.090−0.180 Å, were also included. ^{d} Cage body diagonals.

Table 6. Least Squares Correlation Matrix (×100) for GED Refinement B^a

p_6	p_{11}	p_{12}	u_7	u_{21}	u_{23}	
	65					p_1
			75			p_2
72						p_3
				66		p_7
		50				p_{11}
					55	u_{22}

^{a} Only elements with absolute values ≥ 50 are shown.

NMR. The ^{11}B{^{1}H} NMR spectrum of monophenylcarborane (Figure 7) reveals 6 resonances of relative integral 1:1:2:2:2:2 at −1.19, −3.49, −8.06, −9.88, −10.32, and −11.85 ppm respectively, all of which appear as doublets ($^1J_{\mathrm{BH}}$ = 148−170 Hz) in the proton-coupled spectrum.

In the ^{11}B{^{1}H}/^{11}B{^{1}H} COSY spectrum (Figure 8) the only integral-2 peak which couples to all other ^{11}B resonances is that at −8.06 ppm and is therefore assigned to B(8,10). The two highest frequency resonances (each integral-1) must be due to B(9) and B(12). They show, as expected, coupling to each other and to B(8,10). In addition, each couples to one other integral-2 resonance. The integral-2 resonance that does *not* couple to

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(24) Blake, A. J.; Brain, P. T.; McNab, H.; Miller, J.; Morrison, C. A.; Parsons, S.; Rankin, D. W. H.; Robertson, H. E.; Smart, B. A. *J. Phys. Chem.*, in press.

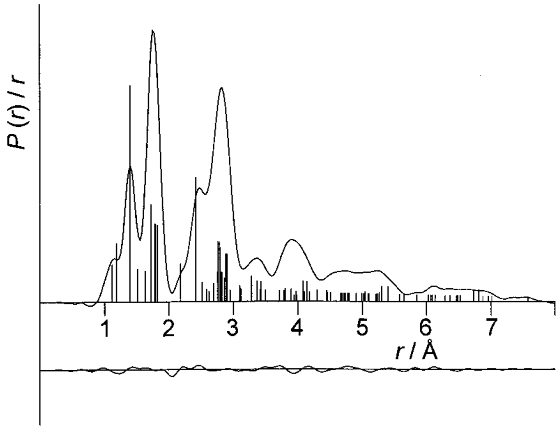

Figure 5. Observed and final weighted difference radial-distribution curves for the GED study of **1**. Before Fourier inversion the data were multiplied by $s \exp[(-0.00002s^2)/(Z_B - f_B)(Z_C - f_C)]$.

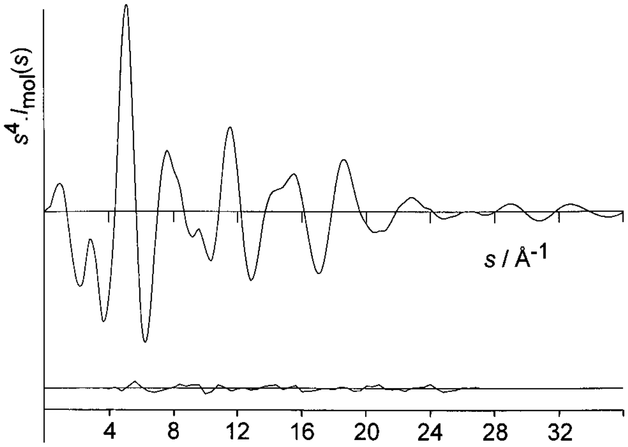

Figure 6. Observed and final weighted difference combined molecular-scattering intensity curves for the GED study of **1**. Theoretical data are shown for the regions 0−30 and 272−360 nm^{-1} for which no experimental data are available.

either B(9) or B(12) is that at −10.32 ppm, which must therefore arise from B(3,6).

In the ^{1}H{^{11}B} spectrum (Figure 9) there are five peaks in the B*H* region, of relative integral 2:2:1:$\underline{3}$:2 (high frequency to low frequency) the underlined resonance representing a 2 + 1 coincidence. In addition, the C(2)*H* proton (integral-1) resonates at a much higher frequency, 3.97 ppm. A series of ^{1}H-{^{11}B$_{\text{selective}}$} experiments, following the order of the ^{11}B resonances, revealed enhancement of the proton signals at 2.46, 2.35, 2.35, 2.53, 2.62 and 2.30 ppm, respectively. Clearly H(8,10) resonates at 2.35 ppm and H(3,6) at 2.62 ppm.

The ambiguities in the ^{11}B and ^{1}H assignments were resolved by a ^{1}H{^{11}B}/^{1}H{^{11}B} COSY spectrum (Figure 10). C(2)*H* showed two couplings, to the highest (2.62 ppm) and lowest (2.30 ppm) frequency B*H* resonances, and the last must therefore be due to H(7,11). Therefore B(7,11) resonates at −11.85 ppm. From the ^{11}B{^{1}H}/^{11}B{^{1}H} COSY spectrum the resonance at −3.49 ppm is now assigned to B(12), that at −1.19 ppm to B(9), and that at −9.88 ppm to B(4,5); from these, the remaining ^{1}H assignments were easily made.

Discussion

At the HF/6-31G* level, a conformation with the phenyl twist (θ') of *ca.* 65° is computed to be a minimum on the potential-energy hypersurface (Table 8). However, a conformation with C_s symmetry in which the phenyl ring eclipses the C−C cluster bond ($\theta' = 90°$) is predicted to lie only 0.3 kJ mol^{-1} higher in energy.

Table 7. Comparison of Theoretical and Experimental Geometrical Parameters for **1**$^{a-c}$

distance/angle	theoretical^d $\theta' = 65°$	GED^e $\theta' = 54°$(f)	X-ray^f $\theta' = 67.7(3)°$
C(1)−C(2)	1.626	1.627(8)	1.640(5)
C(1)−B(3)	1.733		1.743(5)
C(1)−B(6)	1.739	1.718(8)	1.719(5)
C(2)−B(3)	1.713		1.709(6)
C(2)−B(6)	1.708		1.711(6)
C(1)−B(4)	1.720		1.716(5)
C(1)−B(5)	1.722	1.722(7)	1.705(5)
C(2)−B(7)	1.701		1.683(5)
C(2)−B(11)	1.702		1.681(6)
B(3)−B(4)	1.780		1.758(6)
B(6)−B(5)	1.779	1.771(6)	1.761(6)
B(3)−B(7)	1.782		1.766(7)
B(6)−B(11)	1.785		1.768(6)
B(4)−B(8)	1.792		1.771(6)
B(5)−B(10)	1.785	1.772(9)	1.795(6)
B(7)−B(8)	1.787		1.764(7)
B(10)−B(11)	1.782		1.770(7)
B(4)−B(5)	1.785	1.770(9)	1.784(5)
B(7)−B(11)	1.785		1.767(7)
B(8)−B(12)	1.803		1.787(7)
B(10)−B(12)	1.803	1.816(5)	1.767(6)
B(8)−B(9)	1.799		1.783(6)
B(9)−B(10)	1.802		1.780(6)
B(9)−B(12)	1.791	1.779(12)	1.769(6)
B(7)−B(12)	1.784		1.766(6)
B(11)−B(12)	1.783	1.806(14)	1.761(7)
B(4)−B(9)	1.785		1.769(6)
B(5)−B(9)	1.781		1.778(6)
B(3)−B(8)	1.766	1.788(18)	1.756(6)
B(6)−B(10)	1.770		1.761(6)
C(1)−C(11)	1.516	1.500(8)	1.503(4)
(C−C)$_{\text{ring}}$	1.386^g	1.394(2)	1.39(f)
C(2)C(1)C(11)	118.3	119.6(17)	119.2(3)
C(2)C(1)B(4)	109.9	110.6(4)	108.6(3)
C(1)C(2)B(7)	113.5	110.6(4)	113.1(3)

^{a} For atom numbering scheme, see Figures 3 and 4. ^{b} $\theta' = 90° - [C(2)C(1)C(11)C(16)]$. ^{c} Figures in parentheses are the estimated standard deviations of the last digits: f = fixed. ^{d} HF/6-31G* level. ^{e} Model B, C_{2v} cage geometry. ^{f} Molecule B. ^{g} A mean value is given.

Refinements of the electron-diffraction data, assuming local C_{2v} symmetry for the C_2B_{10} cage and D_{6h} symmetry for the phenyl ring, are consistent equally with conformations in which $\theta' = 90°$ (refinement A) or $\theta' = 54°$ (refinement B). Both conformations exhibit geometrical parameters similar to those found in the *ab initio* optimization in C_1 symmetry (Table 7) with the exception of the bond angle C(2)C(1)C(11), which is considerably larger in refinement A [126.3(7)°] than in B [119.6(17)°], *cf.* HF/6-31G* 118.3°. Theoretical single-point SCF energies are computed lower for refinement B than for A, both with the DZ and II″ basis sets. Thus, considered in conjunction with the *ab initio* study, GED refinement B, with $\theta' = 54°$, is favored over refinement A.

At 488 K, the temperature of the vapor in the GED experiment, $RT = 4.1$ kJ mol^{-1}. The potential-energy barrier to rotation of the phenyl ring about C(1−C(11), assuming that the conformation with $\theta' = 90°$ lies at the maximum on the p.e. hypersurface (Table 8), is predicted to be 2.1 kJ mol^{-1} at the HF/6-31G* level. It thus seems likely that the gas-phase geometry of **1** is defined by almost unrestricted rotation of the phenyl ring, although the complexity of the GED analysis of such a dynamic motion precludes the possibility of confirming this experimentally.

Table 8. IGLO results for 1-Ph-1,2-$C_2B_{10}H_{11}$

	δ(^{11}B)[a]						
level of theory//geometry	B(3,6)	B(4,5)	B(7,11)	B(8,10)	B(9)	B(12)	relative energy[b]
DZ//HF/6-31G* (C_1, $\theta' = 65°$)	−11.9	−14.9	−16.9	−16.2	−3.8	−3.6	0.0
DZ//HF/6-31G* (C_s, $\theta' = 90°$)	−11.8	−14.5	−17.3	−16.0	−3.9	−3.7	0.3
DZ//HF/6-31G* (C_s, $\theta' = 0°$)	−14.5	−13.7	−16.4	−17.1	−2.1	−3.5	2.1
DZ//HF/6-31G* ("C_{2v}", $\theta' = 65°$)[c]	−12.2	−15.6	−16.7	−15.9	−2.9	−2.9	5.8
DZ//GED (C_s, $\theta' = 90°$)	−12.4	−11.4	−15.0	−12.6	4.7	2.1	60.7[d]
DZ//GED (C_1, $\theta' = 54°$)	−12.2	−13.9	−14.1	−13.1	3.8	1.8	53.1[d]
II″//HF/6-31G* (C_1, $\theta' = 65°$)	−11.4	−12.5	−15.0	−12.0	−2.2	−2.7	0.0
II″//GED (C_s, $\theta' = 90°$)	−11.8	−8.8	−13.2	−7.9	6.7	3.6	57.7[e]
II″//GED (C_1, $\theta' = 54°$)	−11.6	−11.4	−12.0	−8.4	5.7	3.3	50.6[e]
experimental[f]	−10.3	−9.9	−11.9	−8.1	−1.2	−3.5	

[a] Relative to $BF_3{\cdot}OEt_2$ (ppm); average values for effective C_s symmetry. [b] Energy (kJ mol^{-1}) of the structure relative to the HF/6-31G* fully optimized C_1 structure ($\theta' = 65°$, potential energy minimum). [c] C_{2v} symmetry for the C_2B_{10} cage is used. [d] HF/6-31G* single-point energy with respect to the HF/6-31G* fully optimized C_1 structure. [e] Relative energies at the HF/II″ level. [f] This work.

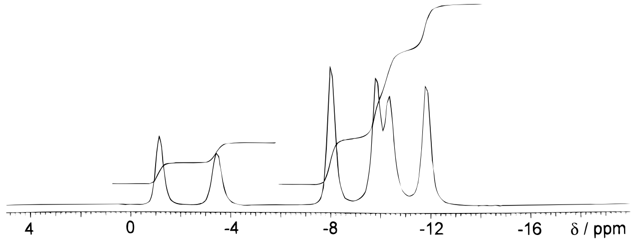

Figure 7. ^{11}B{^{1}H} NMR spectrum of **1**.

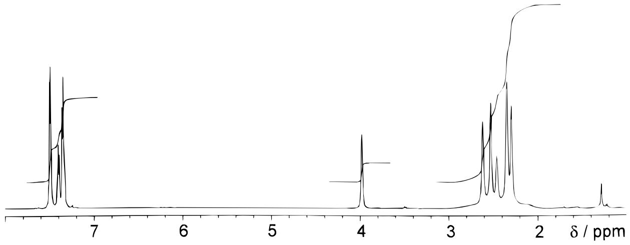

Figure 9. ^{1}H{^{11}B} NMR spectrum of **1**.

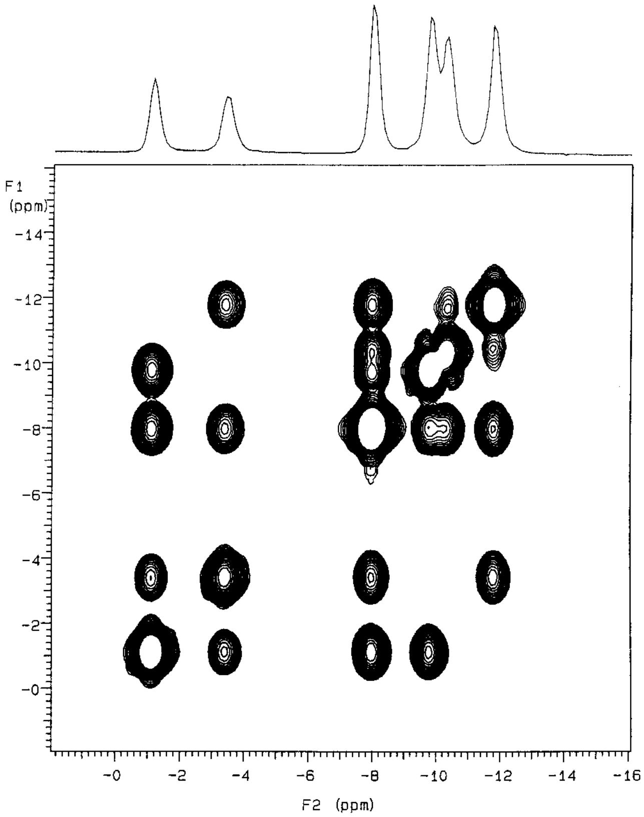

Figure 8. ^{11}B{^{1}H}/^{11}B{^{1}H} NMR COSY spectrum of **1**.

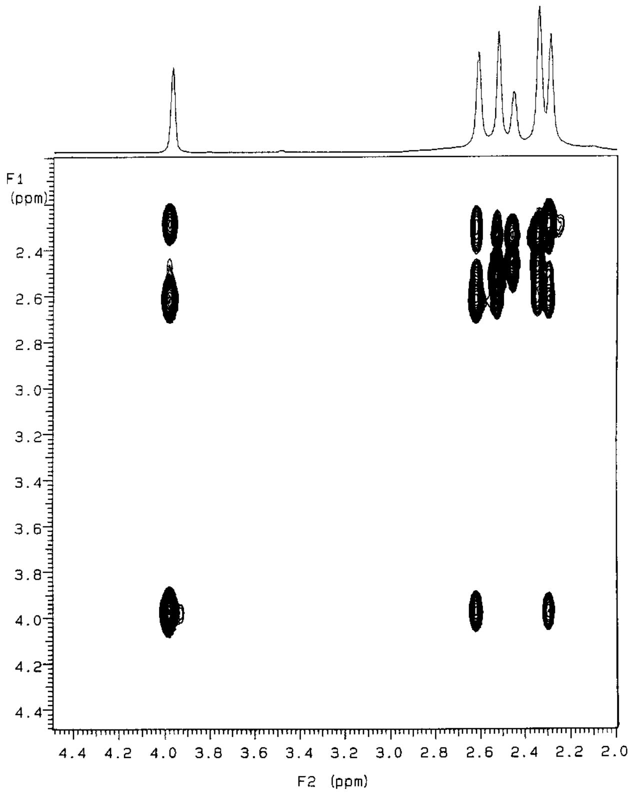

Figure 10. ^{1}H{^{11}B}/^{1}H{^{11}B} NMR COSY spectrum of **1**.

The fully assigned ^{1}H and ^{11}B chemical shifts for monophenylcarborane are listed in Table 9. Comparing the ^{11}B chemical shifts with those of the ubiquitous parent species 1,2-*closo*-$C_2B_{10}H_{12}$,[25] we note (a) a significant shift to high frequency of the resonances due to B(3,6) ($\Delta\delta$ = *ca.* 4 ppm) and B(4,5) ($\Delta\delta$ = *ca.* 3 ppm), atoms adjacent to C(1), the site of substitution, (b) relatively little difference ($\Delta\delta$ = 0−1 ppm) in the chemical shifts of B(9,8,10,7,11), and (c) a marked shift to low frequency ($\Delta\delta$ = *ca.* 2.7 ppm) of the resonance due to the antipodal atom B(12). Overall the pattern and values of ^{11}B resonances in monophenylcarborane are very similar to those recently reported[25] for the ether-substituted species 1-(CH_2OCH_3)-1,2-*closo*-$C_2B_{10}H_{11}$.

The experimental ^{11}B chemical shifts are reproduced well by the IGLO calculations, (see Table 8), with the exception of the δ(^{11}B) IGLO values of B(9) and B(12), antipodally coupled with C(2) and C(1), which are slightly overestimated (with both the

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(25) Shaw, K. F.; Welch, A. J. *Polyhedron* **1992**, *11*, 157.

Table 9. Assignment of the Experimental ^{11}B and ^{1}H NMR Chemical Shifts in 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$

position	$\delta(^{1}H)$	$\delta(^{11}B)$	$\delta(^{11}B, 1,2\text{-}C_2B_{10}H_{12})^{25}$
9	2.46	−1.19	−1.78
12	2.35	−3.49	−1.78
8, 10	2.35	−8.06	−8.59
4, 5	2.53	−9.88	−12.99
3, 6	2.62	−10.32	−14.10
7, 11	2.30	−11.85	−12.99

DZ and II″ basis sets) when employing the GED structures. For refinement B, the final experimental geometry of **1** is computed to lie 53.1 kJ mol^{-1} (6-31G* basis set) and 50.6 kJ mol^{-1} (II″ basis set) above the theoretical C_1 fully optimized structure. Such values are somewhat larger than usually observed for "excess energies" of GED structures.[7,8,10] However, considering the large number of relatively poorly defined geometrical parameters (including 16 hydrogen atoms), these values are not unreasonable.

In the solid-phase molecular structure, the angle θ' in molecule B is 67.7(3)°. The distance C(1B)−C(2B) is 1.640(5) Å (*cf.* GED 1.627(8) Å, *ab initio* 1.626 Å), significantly shorter than any other connectivity on the surface of the pseudoicosahedral carborane polyhedron including others to C(2B), 1.681(6)−1.711(6) Å.[26] We have already noted[2a] that a contribution to the short C(1)−C(2) connectivity derives from the orientation of the phenyl substituent. Thus, in derivatives 1-Ph-2-X-1,2-*closo*-$C_2B_{10}H_{10}$ (X = Me, Br), the 2-substituent is sufficiently bulky to ensure a conformation near $\theta' = 0°$ (experimentally 16.7 and 2.2°, respectively)[2e,3c] and results in C(1)-C(2) distances of 1.695(5) Å and 1.692(8) Å. Bulkier X groups, such as Ph,[2a] CCCPh,[2e] $SiMe_3$,[3d] and $SiMe_2{}^tBu$[3e] maintain or extend C(1)−C(2) and can additionally result in bending back of substituents and/or deformation of the cage.

In molecule B of 1-Ph-1,2-*closo*-$C_2B_{10}H_{11}$, C−B distances span the range 1.681(6)−1.743(5) Å, and B−B lengths lie between 1.756(6) and 1.795(6) Å. Inspection of the C(11B)−C(1B)−C/B angles reveals that the phenyl substituent is slightly tilted away from B(4B) and B(5B); however, there is a compensatory asymmetry in C(1B)−C(11B)−C angles, with that to C(12B) being measureably narrower than that to C(16B).

The conformation of molecule B is in excellent agreement with that determined by *ab initio* MO calculations (Table 7), as discussed above. We believe that this conformation is measureably different from that ($\theta' = 90°$) predicted by the earlier EHMO calculations[2a] because of steric crowding between cage- and *ortho*-phenyl-H atoms, poorly modeled in the former, low-level, calculation. In molecule B determined crystallographically, H(16B)···H(2B) = 2.21 Å, H(16B)···H(6B) = 2.81 Å, H(12B)···H(4B) = 2.30 Å and H(12B)···H(5B) = 3.03 Å. Figure 4 shows a view of the molecule from above (top half of the phenyl ring omitted for clarity), showing that the H(16B)···H(2B) repulsion would be more pronounced if the $\theta' = 90°$ conformation were adopted. Figure 11, a side view of the molecule, confirms that there are touching van der Waals' spheres on H(16B) and H(2B).

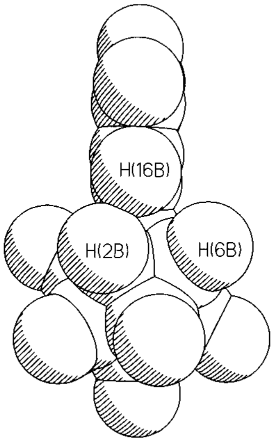

Figure 11. Space-filling plot of molecule B from the X-ray study. Sphere radii are proportional to the respective van der Waals' radii.

Acknowledgment. We acknowledge the Science and Engineering Research Council (now EPSRC) for support of the Edinburgh Electron-Diffraction Service (Grant No. GR/J59258), including provision of microdensitometer facilities at the Daresbury laboratory, the award of research fellowships to D.H., P.T.B., and H.E.R, and the award of research studentships to D.J.D. and B.D.R. We also thank the University of Edinburgh for the award of a studentship to J.C. D.H. thanks the Academy of Sciences of the Czech Republic (Grant No. 432402) and the Grant Agency of the Czech Republic (Grant No. 203/94/0984) for financial support. We thank Dr. M. Bühl for performing the IGLO calculations employing the II″ basis set. The calculations in Erlangen were performed on a Convex C220S computer and were supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Computer time was granted on a Cray YMP-8 of the Höchstleistungsrechenzentrum Jülich. We thank Professor W. Kutzelnigg, Dr. M. Schindler, Dr. U. Fleischer, and Dr. Ch. van Wüllen for the IGLO and DIGLO programs. A.J.W. acknowledges the Callery Chemical Co. for a generous gift of $B_{10}H_{14}$.

Supporting Information Available: Listings of (a) data pertinent to the crystal structure analysis, including (i) all bond distances and angles, (ii) fractional atomic coordinates and isotropic displacement parameters for the hydrogen atoms, and (iii) fractional atomic coordinates and anisotropic displacement parameters for the non-hydrogen atoms, and (b) atomic coordinates for the GED and theoretically optimized geometries is available (9 pages). Ordering information is given on any current masthead page.

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(26) Since submission of this manuscript, the crystal structure of a second polymorph of monophenylcarborane has been determined. In this new modification, $\theta' = 71.2(2)°$ and r[C(1)−C(2)] = 1.649(2) Å. See: Thomas, R. Ll.; Rosair, G. M.; Welch, A. J. *Acta Crystallogr.*, C, in press.