

C(10)—C(5)—C(6)	117.3 (4)	C(9)—C(10)—C(1)	114.1 (3)
C(11)—C(1)—C(10)	108.2 (3)	C(9)—C(8)—C(7)	116.8 (4)
C(12)—C(9)—C(10)	107.8 (2)	C(5)—C(10)—C(1)	123.7 (3)
C(13)—C(11)—C(1)	113.4 (2)	C(9)—C(10)—C(5)	122.3 (3)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O(1)—H(O1)...O(3 ⁱ)	1.12 (4)	1.55 (4)	2.610 (4)	155 (1)
O(4)—H(O4)...O(2 ⁱⁱ)	1.01 (4)	1.65 (4)	2.655 (3)	175 (3)

Symmetry codes: (i) $\frac{1}{2} - x, y - \frac{1}{2}, 2 - z$; (ii) $\frac{1}{2} - x, \frac{1}{2} + y, 2 - z$.

Based on the systematic absences (*h*00: *h* ≠ 2*n* and 0*k*0: *k* ≠ 2*n*), the space group was uniquely determined to be *P*2₁2₁2. Lorentz-polarization and empirical absorption corrections were applied. The structure was solved by direct methods using *SAPI*91 (Fan, 1991) and refined by full-matrix least-squares calculations with the non-H atoms anisotropic. Allowance was made for anomalous dispersion (Cromer & Liberman, 1970). H atoms were located from a ΔF map and were included in the refinement cycles allowing an overall isotropic temperature factor to refine [final value 0.074 (3) Å²]. Reflections were collected in two quadrants (*hkl* and $-hkl$) and were not merged. At the final stages of refinement, parallel and independent calculations on the two stereoisomers of the molecule converged with *R* = 0.0414 and 0.0438 and *wR* = 0.0457 and 0.0587. A statistical test on the *wR*-factor ratio (Hamilton, 1965) indicated that the latter stereoisomer could be rejected at the 0.005 significance level as being the configuration present in this crystal. Accordingly, all coordinates reported in this paper refer to the statistically favoured configuration. Computer programs used in this study were *TEXSAN* (Molecular Structure Corporation, 1993) and *SHELX*76 (Sheldrick, 1976). The figures were drawn using *ORTEP*II (Johnson, 1976).

The authors wish to thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving H atoms and least-squares-planes data have been deposited with the IUCr (Reference: FG1008). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 646–649

Steric Effects in Heteroboranes. III.

1-Ph-2-Me-1,2-*closo*-C₂B₁₀H₁₀

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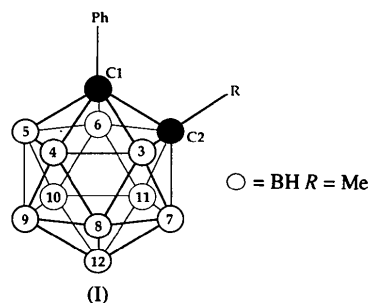
(Received 20 December 1993; accepted 24 May 1994)

Abstract

The crystallographically determined structure of 2-methyl-1-phenyl-1,2-dicarba-*closo*-dodecaborane(12), C₉H₁₈B₁₀, is reported. The 12-vertex polyhedron is relatively undistorted although the phenyl substituent is twisted by *ca* 73° from its electronically preferred orientation by steric pressure from the methyl group, resulting in a C—C(cage) separation of 1.695 (5) Å.

Comment

In the first two papers in this series (Lewis & Welch, 1993; Baghurst *et al.*, 1993) we have demonstrated that unusual polyhedral structures and unusually facile polyhedral isomerizations can result as a consequence of intramolecular crowding in carbametalaboranes. These findings have prompted us to study the stereochemical consequences of systematically varying the amount of crowding within a homologous series of heteroboranes. In this and subsequent papers we report the molecular structures of a series of *closo* carbaboranes 1-Ph-2-*R*-1,2-C₂B₁₀H₁₀, in which the steric demand of the changing group *R* is gradually increased. In the present contribution *R* = Me.



The title compound, (I), has been synthesized in good yield by direct reaction between MeC≡CPh and B₁₀H₁₄ in the presence of *N,N*-dimethylaniline.

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As far as we are aware, this is the first reported synthesis of the target material by this route and it represents a considerable improvement in terms of overall yield and ease of procedure and work-up over the previous synthesis (Hawthorne, Young, Garrett, Owen, Schwerin, Tebbe & Wegner, 1968). In a typical preparation, $B_{10}H_{14}$ (0.500 g, 4.09 mmol), *N,N*-dimethylaniline (0.496 g, 4.09 mmol) and $MeC\equiv CPh$ (0.475 g, 4.09 mmol) were dissolved in toluene (50 ml) and the resulting solution refluxed for 3 h. Evaporation of the mixture *in vacuo* yielded a yellow oily solid. Addition of small amounts (1–2 ml) of ice-cold MeOH to this residue and decantation of the resulting supernatant liquid afforded the title compound as a white microcrystalline solid (the combined methanolic washings were evaporated *in vacuo* and treated with MeOH as before to yield further crops of product). Total yield: 0.647 g (0.276 mmol, 67.5%). Found: 46.14% C; 7.80% H. Calculated for $C_9H_{18}B_{10}$: 46.13% C; 7.74% H. IR (CH_2Cl_2): $\nu_{BH} = 2590\text{ cm}^{-1}$. NMR (298 K, $CDCl_3$): $\delta(^1H)$ 7.66–7.33 (5H, C_6H_5), 1.68

(br, 3H, CH_3) p.p.m.; $\delta(^{11}B)$ –2.36 (1B), –3.76 (1B), –8.53 (4B), –9.37 (4B) p.p.m.

Fig. 1 shows a perspective view of a single molecule and the atomic numbering scheme adopted. Note that for ease of comparison, we have chosen in this and the following contributions (McGrath & Welch, 1995*a,b,c*) to label the aryl-bearing C_{cage} atom consistently as C(1). The compound crystallizes with no close intermolecular contacts.

The conformational preferences of *C*-phenyl *closo*-carbaboranes are conveniently discussed in terms of the angle θ (the modulus of the average $C_{cage}-C_{cage}-C-C$ torsion angle) and we (Lewis & Welch, 1993) have predicted previously [extended Hückel molecular-orbital (MO) calculations] that in 1-Ph-1,2-*closo*- $C_2B_{10}H_{11}$, the optimum θ value would be 90° ; this conformation results in a short C(1)–C(2) distance. These predictions have now been strengthened by *ab initio* MO calculations and confirmed experimentally (Brain *et al.*, 1994) by a low-temperature crystallographic study which afforded a large θ value (68.8°) and a C(1)–C(2) separation of $1.646(8)\text{ \AA}$ in the one crystallographically ordered molecule in the asymmetric fraction of the unit cell. In 1,2-Ph₂-1,2-*closo*- $C_2B_{10}H_{10}$, the corresponding parameters are 5.5° and $1.727\text{ \AA}$, averaged over two crystallographically independent molecules (Lewis & Welch, 1993). In the case of the present compound, the presence of the cage-bound methyl group would be expected to prohibit the phenyl group from attaining its electronically preferred conformation and, indeed, it is found here that $\theta = 16.7^\circ$, more than 70° from its desired value. As a direct consequence of this twist of the phenyl group, in the title compound C(1)–C(2) is $1.696(5)\text{ \AA}$, significantly longer than in 1-Ph-1,2-*closo*- $C_2B_{10}H_{11}$.

Although the pendant methyl group has clearly influenced the conformation of the phenyl substituent, in the structure adopted there is no significant intramolecular contact between them. Thus, analysis of the C(11)–C(1)–*X* [*X* = C(2), B(3), B(4), B(5), B(6)] and C(21)–C(2)–*Y* [*Y* = B(3), B(6), B(7), B(11), C(1)] angles reveals no mutual ‘bend-back’ of the exopolyhedral groups, nor is there a measurable twist of the phenyl and methyl substituents about the C(1)–C(2) vector [C(11)–C(1)–C(2)–C(21) torsion angle $0.6(5)^\circ$].

In conclusion, this structural study reveals that 1-Ph-2-Me-1,2-*closo*- $C_2B_{10}H_{10}$ is almost an ideal reference against which to compare more crowded 1,2-*closo*-dicarbaboranes. Since we wish to extend our studies by increasing the steric demand of the group bound to C(2) (where we anticipate θ values closer to 0°) and since the length of the C(1)–C(2) connectivity has been shown to be dependent on θ , we have sought an alternative reference (McGrath & Welch, 1995*a*).

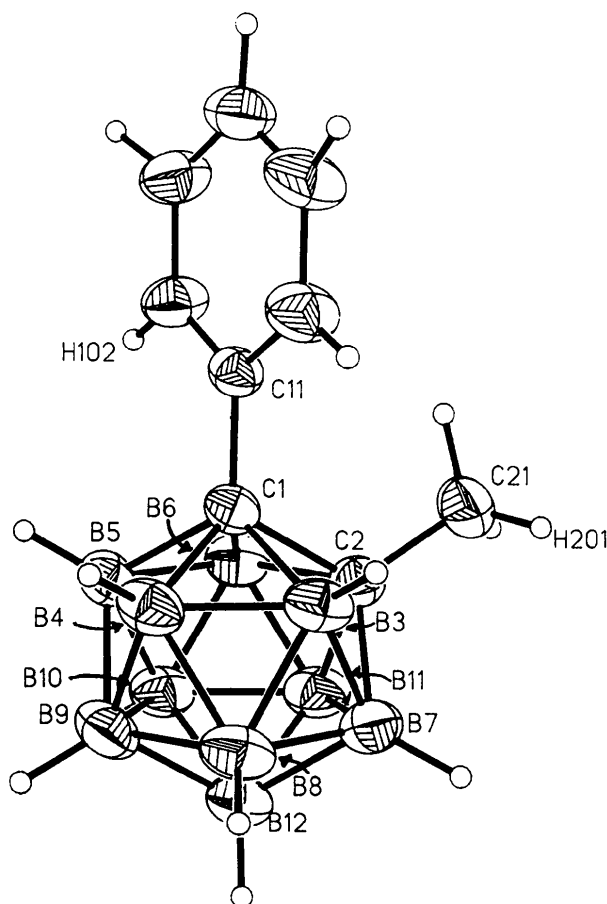


Fig. 1. Perspective view of 1-Ph-2-Me-1,2-*closo*- $C_2B_{10}H_{10}$ (50% displacement ellipsoids, except for H atoms which, for clarity, have artificial radii of $0.1\text{ \AA}$).

Experimental

Crystal data

C₉H₁₈B₁₀ $M_r = 234.34$

Monoclinic

 $P2_1/n$ $a = 7.3931 (19) \text{ \AA}$ $b = 24.113 (5) \text{ \AA}$ $c = 7.8245 (13) \text{ \AA}$ $\beta = 94.100 (17)^\circ$ $V = 1391.3 \text{ \AA}^3$ $Z = 4$ $D_x = 1.119 \text{ Mg m}^{-3}$ Mo $K\alpha$ radiation $\lambda = 0.71069 \text{ \AA}$

Cell parameters from 25

reflections

 $\theta = 11\text{--}13^\circ$ $\mu = 0.049 \text{ mm}^{-1}$ $T = 293 (1) \text{ K}$

Plate

 $0.4 \times 0.2 \times 0.15 \text{ mm}$

Colourless

Data collection

CAD-4 diffractometer

 ω - 2θ scans

Absorption correction:

refined from ΔF

(DIFABS; Walker &

Stuart, 1983)

2705 measured reflections

2443 independent reflections

1660 observed reflections

 $[F \geq 2.0\sigma(F)]$ $R_{\text{int}} = 0.0292$ $\theta_{\text{max}} = 25^\circ$ $h = -8 \rightarrow 8$ $k = 0 \rightarrow 28$ $l = 0 \rightarrow 9$

2 standard reflections

frequency: 480 min

intensity decay: <3%

Refinement

Refinement on F $R = 0.0849$ $wR = 0.1160$ $S = 1.152$

1660 reflections

191 parameters

 $w = 1/[\sigma^2(F) + 0.003541F^2]$ $(\Delta/\sigma)_{\text{max}} = 0.001$ $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$

Extinction correction: none

Atomic scattering fac-

tors from *SHELX76*

(Sheldrick, 1976)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
C(1)	0.2045 (4)	0.61598 (15)	0.8239 (4)	0.0344 (19)
C(2)	0.0784 (5)	0.67343 (16)	0.8542 (4)	0.0394 (22)
B(3)	0.2687 (6)	0.67840 (19)	0.7424 (6)	0.0430 (25)
B(4)	0.2771 (6)	0.61638 (21)	0.6226 (5)	0.045 (3)
B(5)	0.0915 (6)	0.57424 (20)	0.6735 (6)	0.043 (3)
B(6)	-0.0290 (5)	0.61097 (20)	0.8249 (6)	0.0425 (25)
B(7)	0.0664 (7)	0.71400 (21)	0.6756 (6)	0.048 (3)
B(8)	0.1902 (7)	0.67775 (21)	0.5225 (6)	0.051 (3)
B(9)	0.0805 (7)	0.61368 (23)	0.4815 (6)	0.052 (3)
B(10)	-0.1099 (6)	0.60921 (20)	0.6097 (6)	0.046 (3)
B(11)	-0.1182 (6)	0.67175 (22)	0.7265 (6)	0.049 (3)
B(12)	-0.0512 (7)	0.67309 (21)	0.5126 (6)	0.049 (3)
C(11)	0.3151 (5)	0.59119 (16)	0.9755 (4)	0.0359 (20)
C(12)	0.2607 (5)	0.54215 (18)	1.0460 (5)	0.0478 (24)
C(13)	0.3611 (6)	0.51811 (20)	1.1822 (6)	0.055 (3)
C(14)	0.5172 (6)	0.54384 (22)	1.2521 (5)	0.055 (3)
C(15)	0.5718 (7)	0.59275 (23)	1.1822 (6)	0.063 (3)
C(16)	0.4728 (6)	0.61647 (20)	1.0433 (5)	0.053 (3)
C(21)	0.0830 (6)	0.69819 (19)	1.0329 (5)	0.057 (3)

Table 2. Selected geometric parameters ($\text{\AA}$, $^\circ$)

C(1)—C(2)	1.696 (5)	B(5)—B(10)	1.752 (7)
C(1)—B(3)	1.715 (6)	B(6)—B(10)	1.747 (6)
C(1)—B(4)	1.700 (6)	B(6)—B(11)	1.762 (7)
C(1)—B(5)	1.720 (6)	B(7)—B(8)	1.787 (7)
C(1)—B(6)	1.732 (6)	B(7)—B(11)	1.771 (7)

C(1)—C(11)	1.514 (5)	B(7)—B(12)	1.788 (7)
C(2)—B(3)	1.713 (6)	B(8)—B(9)	1.764 (7)
C(2)—B(6)	1.710 (6)	B(8)—B(12)	1.784 (7)
C(2)—B(7)	1.703 (6)	B(9)—B(10)	1.789 (7)
C(2)—B(11)	1.704 (6)	B(9)—B(12)	1.759 (7)
C(2)—C(21)	1.518 (6)	B(10)—B(11)	1.766 (7)
B(3)—B(4)	1.769 (6)	B(10)—B(12)	1.785 (7)
B(3)—B(7)	1.771 (7)	B(11)—B(12)	1.779 (7)
B(3)—B(8)	1.776 (7)	C(11)—C(12)	1.377 (5)
B(4)—B(5)	1.775 (7)	C(11)—C(16)	1.388 (6)
B(4)—B(8)	1.773 (7)	C(12)—C(13)	1.381 (6)
B(4)—B(9)	1.762 (7)	C(13)—C(14)	1.388 (7)
B(5)—B(6)	1.770 (6)	C(14)—C(15)	1.373 (7)
B(5)—B(9)	1.775 (7)		
C(2)—C(1)—B(3)	60.29 (22)	B(4)—B(8)—B(9)	59.8 (3)
C(2)—C(1)—B(6)	59.86 (22)	B(7)—B(8)—B(12)	60.1 (3)
C(2)—C(1)—C(11)	119.0 (3)	B(9)—B(8)—B(12)	59.4 (3)
B(3)—C(1)—B(4)	62.38 (25)	B(4)—B(9)—B(5)	60.3 (3)
B(3)—C(1)—C(11)	119.3 (3)	B(4)—B(9)—B(8)	60.4 (3)
B(4)—C(1)—B(5)	62.55 (25)	B(5)—B(9)—B(10)	58.9 (3)
B(4)—C(1)—C(11)	122.7 (3)	B(8)—B(9)—B(12)	60.9 (3)
B(5)—C(1)—B(6)	61.71 (24)	B(10)—B(9)—B(12)	60.4 (3)
B(5)—C(1)—C(11)	120.9 (3)	B(5)—B(10)—B(6)	60.8 (3)
B(6)—C(1)—C(11)	116.8 (3)	B(5)—B(10)—B(9)	60.1 (3)
C(1)—C(2)—B(3)	60.40 (22)	B(6)—B(10)—B(11)	60.2 (3)
C(1)—C(2)—B(6)	61.10 (23)	B(9)—B(10)—B(12)	59.0 (3)
C(1)—C(2)—C(21)	118.3 (3)	B(11)—B(10)—B(12)	60.1 (3)
B(3)—C(2)—B(7)	62.4 (3)	C(2)—B(11)—B(6)	59.12 (5)
B(3)—C(2)—C(21)	118.5 (3)	C(2)—B(11)—B(7)	58.6 (3)
B(6)—C(2)—B(11)	62.1 (3)	B(6)—B(11)—B(10)	59.3 (3)
B(6)—C(2)—C(21)	116.7 (3)	B(7)—B(11)—B(12)	60.5 (3)
B(7)—C(2)—B(11)	62.6 (3)	B(10)—B(11)—B(12)	60.5 (3)
B(7)—C(2)—C(21)	121.7 (3)	B(7)—B(12)—B(8)	60.0 (3)
B(11)—C(2)—C(21)	120.8 (3)	B(7)—B(12)—B(11)	59.5 (3)
C(1)—B(3)—C(2)	59.31 (22)	B(8)—B(12)—B(9)	59.7 (3)
C(1)—B(3)—B(4)	58.40 (23)	B(9)—B(12)—B(10)	60.6 (3)
C(2)—B(3)—B(7)	58.50 (25)	B(10)—B(12)—B(11)	59.4 (3)
B(4)—B(3)—B(8)	60.0 (3)	C(1)—B(5)—B(6)	59.48 (24)
B(7)—B(3)—B(8)	60.5 (3)	B(4)—B(5)—B(9)	59.5 (03)
C(1)—B(4)—B(3)	59.22 (24)	B(6)—B(5)—B(10)	59.4 (03)
C(1)—B(4)—B(5)	59.26 (24)	B(9)—B(5)—B(10)	61.0 (03)
B(3)—B(4)—B(8)	60.2 (3)	C(1)—B(6)—C(2)	59.04 (22)
B(5)—B(4)—B(9)	60.2 (3)	C(1)—B(6)—B(5)	58.81 (23)
B(8)—B(4)—B(9)	59.8 (3)	C(2)—B(6)—B(11)	58.77 (25)
C(1)—B(5)—B(4)	58.19 (24)	B(5)—B(6)—B(10)	59.8 (03)
B(10)—B(6)—B(11)	60.5 (3)	C(1)—C(11)—C(12)	119.8 (3)
C(2)—B(7)—B(3)	59.06 (25)	C(1)—C(11)—C(16)	121.2 (3)
C(2)—B(7)—B(11)	58.7 (3)	C(12)—C(11)—C(16)	119.0 (4)
B(3)—B(7)—B(8)	59.9 (3)	C(11)—C(12)—C(13)	120.9 (4)
B(8)—B(7)—B(12)	59.9 (3)	C(12)—C(13)—C(14)	120.1 (4)
B(11)—B(7)—B(12)	60.0 (3)	C(13)—C(14)—C(15)	119.1 (4)
B(3)—B(8)—B(4)	59.8 (3)	C(14)—C(15)—C(16)	120.8 (5)
B(3)—B(8)—B(7)	59.6 (3)		

Cage H atoms were fixed in idealized positions 1.10 $\text{\AA}$ from the corresponding B atoms, methyl H atoms were set in idealized positions (C—H 1.08 $\text{\AA}$) and phenyl H atoms were allowed positional refinement. All H atoms were refined with a single group displacement parameter: 0.080 (36) $\text{\AA}^2$ at convergence.

Data reduction and corrections for Lorentz and polarization effects were performed using *CADABS* (Gould & Smith, 1986). *SHELXS86* (Sheldrick, 1985) was used to solve the structure (direct methods for C and B atoms). *SHELX76* (Sheldrick, 1976) was used to locate the phenyl H atoms (difference Fourier syntheses) and refine the structure. Fig. 1 was drawn using *SHELXTL/PC* (Sheldrick, 1990) and molecular-geometry calculations were made with *CALC* (Gould & Taylor, 1986).

We thank the SERC for support (TDM) and the Callery Chemical Company for a generous gift of B₁₀H₁₄.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1110). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). **C51**, 649–651

Steric Effects in Heteroboranes. IV. 1-Ph-2-Br-1,2-closo-C₂B₁₀H₁₀

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(Received 20 December 1993; accepted 24 May 1994)

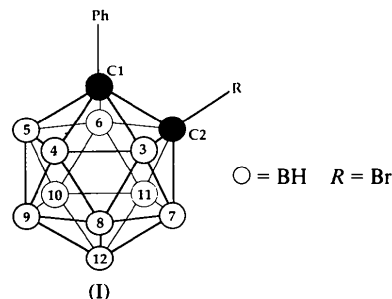
Abstract

The structure of 2-bromo-1-phenyl-1,2-dicarba-closo-dodecaborane(12), C₈H₁₅B₁₀Br, has been determined crystallographically. The phenyl substituent is oriented orthogonally to the effective molecular mirror plane and there is tentative evidence for a weak intramolecular Ph...Br interaction. C(1)—C(2) is 1.692 (8) Å.

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Comment

The preceding paper (McGrath & Welch, 1995a) describes the molecular structure of 1-Ph-2-Me-1,2-closo-C₂B₁₀H₁₀, which was studied as a reference for a series of 1-Ph-2-*R*-1,2-closo-C₂B₁₀H₁₀ compounds with gradually more sterically demanding substituents *R*. We have already shown that the length of the C(1)—C(2) connectivity in *C*-phenyl-1,2-carboranes is sensitive to θ , the twist angle of the phenyl group (Lewis & Welch, 1993), and we aimed to structurally characterize a series of compounds with differing *R* groups and with θ approximately zero. We hoped to monitor the influence on molecular structure of changing *R* alone. However, when *R* = Me, θ was found to be 16.7°. Seeking another relatively uncrowded 1-Ph-2-*R*-1,2-closo-C₂B₁₀H₁₀ species we herein describe the molecular structure of 1-Ph-2-Br-1,2-closo-C₂B₁₀H₁₀, (I). The van der Waals radii of a methyl group and a Br atom are both ca 2.0 Å, but since C(2)—Br is expected to be longer than C(2)—Me, the present compound could be considered less crowded than the 2-methyl analogue.



The title compound (Fig. 1) displays approximate, although not crystallographically imposed, *C_s* symmetry (fully consistent with its ¹¹B NMR spectrum) and crystallizes with no close contacts between molecules. The C(1)—C(11) bond length is 1.494 (7) Å, 0.020 (9) Å shorter than in 1-Ph-2-Me-1,2-closo-C₂B₁₀H₁₀ (McGrath & Welch, 1995a). However, C(1)—C(2) in the present compound [1.692 (8) Å], is identical with that observed in the 2-methyl analogue and the difference between the C(2)—Br(1) bond length here and C(2)—C(21) in the 2-methyl compound exactly matches the difference in covalent radii between an *sp*³-C atom and a Br atom (Purcell & Kotz, 1977).

In 1-Ph-2-Br-1,2-closo-C₂B₁₀H₁₀, the measured θ value is only 2.2°, *i.e.* the plane of the phenyl group lies essentially perpendicular to the non-crystallographic mirror plane which bisects the molecule. No significant twist is observed about C(1)—C(2), the torsion angle C(11)—C(1)—C(2)—Br(1) being only –2.2 (6)°. Although the five angles C(11)—C(1)—*X* [*X* = C(2), B(3), B(4), B(5), B(6)] do not vary much [118.0 (4)–121.7 (4)°], there is some evidence for