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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Steric Effects in Heteroboranes. IV. 1-Ph-2-Br-1,2-*closo*-C$_2$B$_{10}$H$_{10}$

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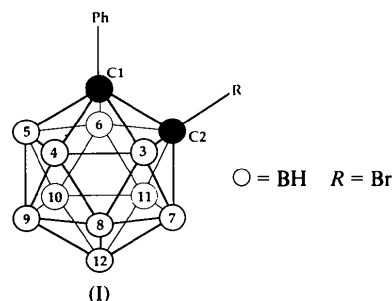
Abstract

The structure of 2-bromo-1-phenyl-1,2-dicarba-*closo*-dodecaborane(12), C$_8$H$_{15}$B$_{10}$Br, 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*-C$_2$B$_{10}$H$_{10}$, which was studied as a reference for a series of 1-Ph-2-*R*-1,2-*closo*-C$_2$B$_{10}$H$_{10}$ 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-carbaboranes 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*-C$_2$B$_{10}$H$_{10}$ species we herein describe the molecular structure of 1-Ph-2-Br-1,2-*closo*-C$_2$B$_{10}$H$_{10}$, (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.

(I)

The title compound (Fig. 1) displays approximate, although not crystallographically imposed, C_s symmetry (fully consistent with its ^{11}B 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*-C$_2$B$_{10}$H$_{10}$ (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*-C$_2$B$_{10}$H$_{10}$, 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
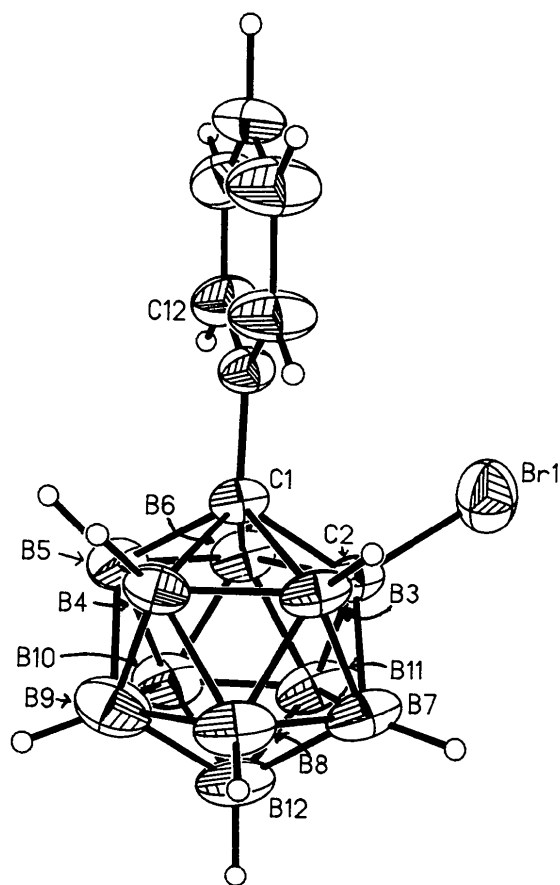
Fig. 1. Perspective view of 1-Ph-2-Br-1,2-*closo*-C₂B₁₀H₁₀ (50% displacement ellipsoids, except for H atoms which, for clarity, have artificial radii of 0.1 Å).

greater asymmetry in the Br(1)—C(2)—*Y* angles [*Y* = C(1), B(3), B(6), B(7), B(11)], with those to B(3), C(1) and B(6) [average 116.8 (6)°] being significantly narrower than those to B(7) and B(11) [average 120.7 (6)°]. Such an effect, although small, could be taken as evidence of a weak intramolecular interaction between the Br atom and the β-phenyl group. A similar small deformation is apparent in both crystallographically-independent molecules of 1,1-dibromo-2-phenyl-2-(2′-propenyl)cyclopropane (Kocharian, Nilssen, Pettersen, Rømming & Sydnes, 1988). It is possible that such an interaction could contribute to the very small θ value observed in the present case.

This structure, together with that of 1-Ph-2-Me-1,2-*closo*-C₂B₁₀H₁₀ (McGrath & Welch, 1995*a*), will subsequently be compared with those of more crowded analogues (McGrath & Welch, 1995*b,c*).

Experimental

The title compound was prepared by a variation of the method of Zakharkin & Podvisotskaya (1965) and recrystallized

from methanol. Found: 32.16% C; 5.36% H. Calculated for C₈H₁₅B₁₀Br: 32.11% C; 5.05% H. IR (CH₂Cl₂): ν_{BH} = 2605, 2630 cm^{-1}. NMR (298 K, CDCl₃): $\delta(^1H)$ 7.86–7.50 p.p.m. (C₆H₅); $\delta(^{11}B)$ −2.07 (1B), −3.07 (1B), −6.61 (2B), −7.30 (2B), −7.93 (2B), −8.60 (2B).

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å²)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Br(1)	0.05573 (8)	0.35618 (6)	0.11907 (4)	0.0670 (5)
C(1)	0.1014 (6)	0.0956 (5)	0.12567 (21)	0.030 (3)
C(2)	−0.0023 (6)	0.2060 (5)	0.13752 (24)	0.038 (4)
B(3)	−0.0349 (7)	0.1131 (6)	0.0849 (3)	0.040 (4)
B(4)	0.0111 (8)	−0.0252 (6)	0.1087 (3)	0.042 (4)
B(5)	0.0798 (7)	−0.0070 (6)	0.1760 (3)	0.044 (5)
B(6)	0.0732 (7)	0.1415 (6)	0.1928 (3)	0.043 (4)
B(7)	−0.1585 (8)	0.1677 (8)	0.1280 (3)	0.053 (5)
B(8)	−0.1510 (8)	0.0190 (7)	0.1105 (4)	0.053 (5)
B(9)	−0.0824 (9)	−0.0548 (8)	0.1676 (4)	0.061 (5)
B(10)	−0.0440 (8)	0.0470 (8)	0.2194 (3)	0.056 (5)
B(11)	−0.0921 (8)	0.1832 (8)	0.1965 (3)	0.052 (5)
B(12)	−0.1860 (8)	0.0612 (8)	0.1805 (4)	0.061 (6)
C(12)	0.3367 (4)	0.1410 (3)	0.13320 (13)	0.046 (4)
C(13)	0.4586 (4)	0.1547 (3)	0.10956 (13)	0.061 (5)
C(14)	0.4741 (4)	0.1438 (3)	0.05260 (13)	0.063 (5)
C(15)	0.3677 (4)	0.1193 (3)	0.01928 (13)	0.073 (6)
C(16)	0.2458 (4)	0.1056 (3)	0.04292 (13)	0.060 (4)
C(11)	0.2303 (4)	0.1165 (3)	0.09988 (13)	0.036 (4)

Table 2. *Selected geometric parameters* (Å, °)

Br(1)—C(2)	1.888 (6)	B(4)—B(9)	1.758 (12)
C(1)—C(2)	1.692 (8)	B(5)—B(6)	1.764 (10)
C(1)—B(3)	1.735 (9)	B(5)—B(9)	1.780 (12)
C(1)—B(4)	1.728 (9)	B(5)—B(10)	1.773 (11)
C(1)—B(5)	1.714 (9)	B(6)—B(10)	1.755 (11)
C(1)—B(6)	1.737 (9)	B(6)—B(11)	1.780 (11)
C(1)—C(11)	1.494 (7)	B(7)—B(8)	1.770 (12)
C(2)—B(3)	1.701 (9)	B(7)—B(11)	1.804 (12)
C(2)—B(6)	1.721 (9)	B(7)—B(12)	1.790 (12)
C(2)—B(7)	1.693 (10)	B(8)—B(9)	1.772 (12)
C(2)—B(11)	1.725 (10)	B(8)—B(12)	1.800 (12)
B(3)—B(4)	1.763 (11)	B(9)—B(10)	1.766 (12)
B(3)—B(7)	1.769 (11)	B(9)—B(12)	1.744 (13)
B(3)—B(8)	1.735 (11)	B(10)—B(11)	1.741 (12)
B(4)—B(5)	1.792 (11)	B(10)—B(12)	1.755 (12)
B(4)—B(8)	1.755 (11)	B(11)—B(12)	1.755 (12)
C(2)—C(1)—B(3)	59.5 (4)	C(1)—B(6)—B(5)	58.6 (4)
C(2)—C(1)—B(6)	60.3 (4)	C(2)—B(6)—B(11)	59.0 (4)
C(2)—C(1)—C(11)	121.1 (4)	B(5)—B(6)—B(10)	60.5 (4)
B(3)—C(1)—B(4)	61.2 (4)	B(10)—B(6)—B(11)	59.0 (5)
B(3)—C(1)—C(11)	118.0 (4)	C(2)—B(7)—B(3)	58.8 (4)
B(4)—C(1)—B(5)	62.8 (4)	C(2)—B(7)—B(11)	59.0 (4)
B(4)—C(1)—C(11)	120.9 (4)	B(3)—B(7)—B(8)	58.7 (4)
B(5)—C(1)—B(6)	61.5 (4)	B(8)—B(7)—B(12)	60.7 (5)
B(5)—C(1)—C(11)	121.7 (4)	B(11)—B(7)—B(12)	58.5 (5)
B(6)—C(1)—C(11)	119.5 (4)	B(3)—B(8)—B(4)	60.7 (4)
Br(1)—C(2)—C(1)	116.7 (4)	B(3)—B(8)—B(7)	60.6 (5)
Br(1)—C(2)—B(3)	117.7 (4)	B(4)—B(8)—B(9)	59.8 (5)
Br(1)—C(2)—B(6)	115.9 (4)	B(7)—B(8)—B(12)	60.2 (5)
Br(1)—C(2)—B(7)	120.8 (4)	B(9)—B(8)—B(12)	58.4 (5)
Br(1)—C(2)—B(11)	120.5 (4)	B(4)—B(9)—B(5)	60.9 (5)
C(1)—C(2)—B(3)	61.5 (4)	B(4)—B(9)—B(8)	59.6 (5)
C(1)—C(2)—B(6)	61.2 (4)	B(5)—B(9)—B(10)	60.0 (5)
B(3)—C(2)—B(7)	62.8 (4)	B(8)—B(9)—B(12)	61.6 (5)
B(6)—C(2)—B(11)	62.2 (4)	B(10)—B(9)—B(12)	60.0 (5)
B(7)—C(2)—B(11)	63.7 (4)	B(5)—B(10)—B(6)	60.0 (4)
C(1)—B(3)—C(2)	59.0 (4)	B(5)—B(10)—B(9)	60.4 (5)
C(1)—B(3)—B(4)	59.2 (4)	B(6)—B(10)—B(11)	61.2 (5)
C(2)—B(3)—B(7)	58.4 (4)	B(9)—B(10)—B(12)	59.4 (5)
B(4)—B(3)—B(8)	60.2 (4)	B(11)—B(10)—B(12)	60.3 (5)
B(7)—B(3)—B(8)	60.7 (5)	C(2)—B(11)—B(6)	58.8 (4)
C(1)—B(4)—B(3)	59.6 (4)	C(2)—B(11)—B(7)	57.3 (4)
C(1)—B(4)—B(5)	58.2 (4)	B(6)—B(11)—B(10)	59.8 (5)
B(3)—B(4)—B(8)	59.1 (4)	B(7)—B(11)—B(12)	60.4 (5)
B(5)—B(4)—B(9)	60.2 (4)	B(10)—B(11)—B(12)	60.3 (5)
B(8)—B(4)—B(9)	60.6 (5)	B(7)—B(12)—B(8)	59.1 (5)
C(1)—B(5)—B(4)	59.0 (4)	B(7)—B(12)—B(11)	61.2 (5)
C(1)—B(5)—B(6)	59.9 (4)	B(8)—B(12)—B(9)	60.0 (5)
B(4)—B(5)—B(9)	59.0 (4)	B(10)—B(12)—B(11)	59.5 (5)
B(6)—B(5)—B(10)	59.5 (4)	C(1)—C(11)—C(12)	119.8 (4)
B(9)—B(5)—B(10)	59.6 (5)	C(1)—C(11)—C(16)	120.1 (4)
C(1)—B(6)—C(2)	58.6 (4)		

The C atoms of the phenyl ring were constrained to form a regular hexagon (C—C = 1.395 Å); cage H atoms were allowed positional refinement subject to a common B—H distance of 1.11 (5) Å; phenyl H atoms were set in idealized positions. All H atoms were refined with a single group displacement parameter [0.060 (49) Å² at convergence].

Data reduction and corrections for Lorentz and polarization effects were performed using *CADABS* (Gould & Smith, 1986). *SHELX*76 (Sheldrick, 1976) was used to solve (Patterson synthesis for Br atom, difference Fourier syntheses for C, B and cage H atoms) and refine the structure. Fig. 1 was drawn using *SHELXTL/PC* (Sheldrick, 1990). Molecular geometry calculations were made using *CALC* (Gould & Taylor, 1986).

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Steric Effects in Heteroboranes. V. 1-Ph-2-Me₃Si-1,2-*closo*-C₂B₁₀H₁₀

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Abstract

The structure of 1-phenyl-2-trimethylsilyl-1,2-dicarba-*closo*-dodecaborane(12), $C_{11}H_{24}B_{10}Si$, has been determined crystallographically. The C_{cage}—C_{cage} distance is 1.708 (4) Å, only slightly longer than in the 2-methyl analogue. However, in contrast to the 2-methyl and 2-bromo analogues, relief from steric congestion is afforded by a mutual 'bend back' of both the phenyl and trimethylsilyl groups, the latter involving deformation of valency angles both at Si and the C_{cage} atom to which it is attached.

Comment

In the two preceding papers in the series (McGrath & Welch, 1995a,b) we described the molecular struc-

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