

Two isostructural carboranes: 3-phenyl-1,2-dicarba-*closo*- dodecaborane(12) and 1-phenyl- 1,7-dicarba-*closo*-dodecaborane(12)

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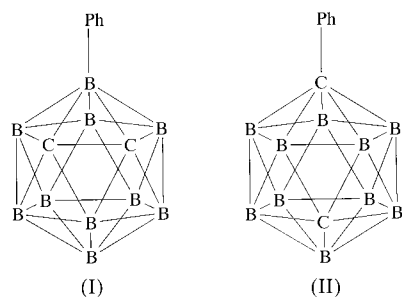
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Two phenyl-substituted carboranes, 3-phenyl-1,2-dicarba-*closo*-dodecaborane(12), $C_8H_{16}B_{10}$, (I), and 1-phenyl-1,7-dicarba-*closo*-dodecaborane(12), $C_8H_{16}B_{10}$, (II), were found to be isostructural. Comparison of the bond angles at the *ipso*-C atoms of the phenyl substituent for (I) and (II) [117.71 (3) and 118.45 (10)°, respectively] indicates that electron donation of the carborane cage for B- and C-substituted carboranes is different.

Comment

Carboranes are of great interest for the study of chemical bonding. In particular, they are interesting compounds for high-resolution X-ray analysis of electron-density distribution (Antipin *et al.*, 1997; Lyssenko *et al.*, 1998). The most attractive subjects for such investigation are isostructural compounds,



because in such a case most differences in the electron-density distribution may be attributed to intramolecular electronic effects. We found an interesting example of isostructural compounds in two monosubstituted carboranes, namely the title compounds, (I) and (II).

The molecular structures of (I) and (II) are shown in Figs. 1 and 2, respectively, and selected geometric parameters are

given in Tables 1 and 2. The X-ray investigation of (I) and (II) reveals that the two compounds are indeed isostructural and crystallize in the monoclinic space group $P2_1/c$ ($Z = 4$) with quite similar crystal packing. The crystal structures of (I) (Fig. 3) and (II) (Fig. 4) consist of layers of carborane molecules parallel to the bc plane. In both crystals, the arrangement of molecules in the layers is such that the phenyl group of each molecule is surrounded by four carborane cages of neighbouring molecules and *vice versa*, without formation

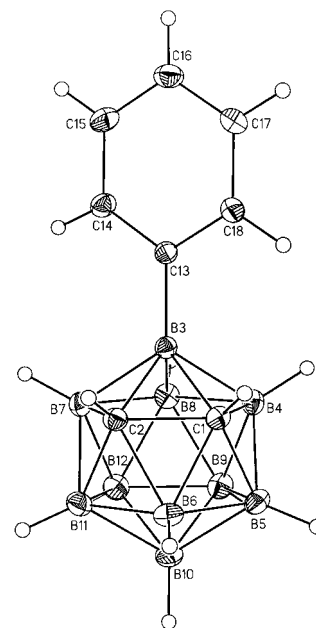


Figure 1
The molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

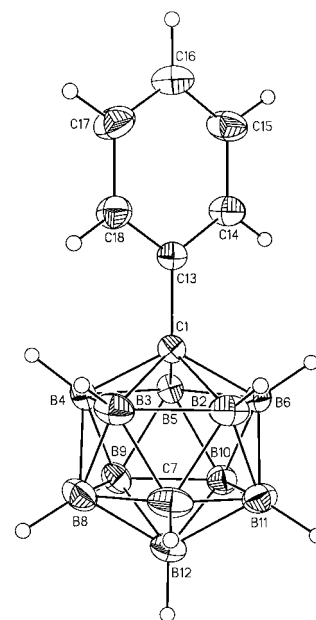


Figure 2
The molecular structure of (II) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

of intermolecular contacts within or between the layers. It is noteworthy that previously published structures of monophenyl-substituted carboranes, namely 1-Ph-1,2-C₂B₁₀H₁₁ (α form; Brain *et al.*, 1996), 1-Ph-1,2-C₂B₁₀H₁₁ (β form; Thomas *et al.*, 1996) and 9-Ph-1,7-C₂B₁₀H₁₁ (Kabachii *et al.*, 1985) are characterized by different crystal packing.

Consideration of the molecular geometry reveals that the carborane cages have near icosahedral architecture, with C–B distances in the range 1.6895 (5)–1.7345 (5) Å, B–B distances in the range 1.7683 (7)–1.7896 (6) Å and a C–C bond length of 1.6225 (5) Å in (I), and C–B distances in the range 1.6893 (18)–1.7297 (15) Å and B–B distances in the range 1.7622 (18)–1.787 (2) Å for (II).

The presence of the phenyl substituent in (I) and (II) has a marked influence on the geometry of the carborane cages. This is manifested in a lengthening of the B₃–B₄, B₃–B₈ and B₃–B₇ distances by approximately 0.01 Å with respect to the B₅–B₆, B₆–B₁₀ and B₁₀–B₁₁ bonds in (I), and of the C₁–B₂ and C₁–B₃ distances by 0.02 Å with respect to the C₇–B₂ and C₇–B₃ bonds in (II). Thus, the displacement of atom C₁ in (II) by 0.8305 (11) Å from the B₂/B₃/B₄/B₅/B₆ pentagonal plane results in a decrease of the deviation of atom C₇ to 0.7855 (13) Å from the corresponding B₂/B₃/B₈/B₁₁/B₁₂ plane.

In turn, the carborane cage affects the phenyl-ring geometry. Comparison of the bond angles at the *ipso*-C atoms of the phenyl substituent in (I) and (II) [117.71 (3) and 118.45 (10)°, respectively] indicates that electron donation of the carborane cage for B- and C-substituted carboranes is different (Domenicano & Hargittai, 1992). The increase in the *ipso*-angle in (II) means that the electron donation of the carborane cage in (I) is more pronounced than in (II). For comparison, the corresponding angles in 9-Ph-1,7-C₂B₁₀H₁₁

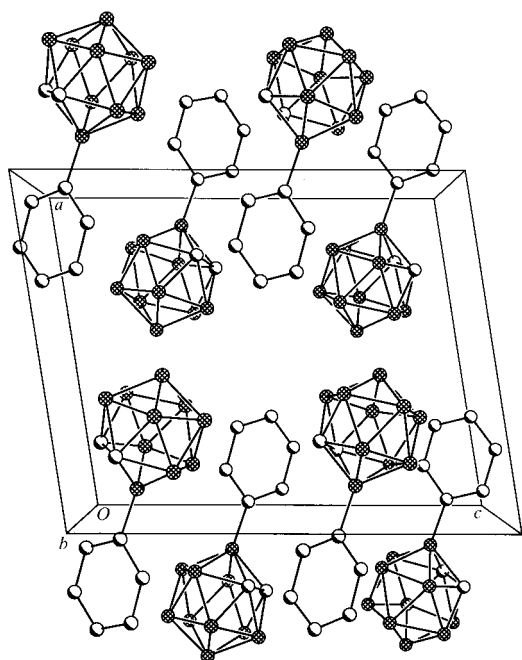


Figure 3
A view of the unit cell of (I) along the *b* direction.

and in the α and β forms of 1-Ph-1,2-C₂B₁₀H₁₁ are 117.1 (5), 119.14 (14) and 120.0 (3)°, respectively.

The orientation of the phenyl rings in phenyl-substituted carboranes may be described in terms of the minimal torsion angle between the plane of the phenyl and the edge of the carborane cage; the minimal torsion angles are B₇–B₃–C₁₃–C₁₄ of 18.16 (5)° in (I) and B₃–C₁–C₁₃–C₁₈ of 13.28 (14)° in (II).

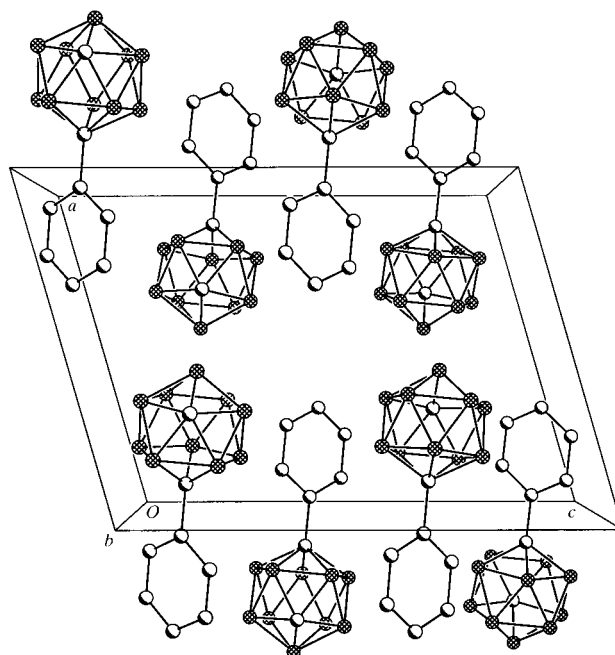


Figure 4
A view of the unit cell of (II) along the *b* direction.

Experimental

1-Ph-1,7-C₂B₁₀H₁₂ was prepared by thermal isomerization of 1-Ph-1,2-C₂B₁₀H₁₂ (Garrett *et al.*, 1964). 3-Ph-1,2-C₂B₁₀H₁₂ was synthesized from phenylboron dichloride and the C₂B₉H₁₁²⁻ anion (Hawthorne & Wegner, 1968). Single crystals of both compounds suitable for X-ray analysis were grown from a chloroform solution at room temperature by slow evaporation.

Compound (I)

Crystal data

C₈H₁₆B₁₀
M_r = 220.31
 Monoclinic, *P*2₁/*c*
a = 10.378 (2) Å
b = 9.725 (2) Å
c = 12.699 (3) Å
 β = 99.195 (7)°
V = 1265.2 (5) Å³
Z = 4

D_x = 1.157 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 890 reflections
 θ = 2–26°
 μ = 0.05 mm⁻¹
T = 110.0 (2) K
 Prism, colourless
 0.35 × 0.30 × 0.25 mm

Data collection

Bruker CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
T_{min} = 0.981, *T_{max}* = 0.987
 49 186 measured reflections

14 343 independent reflections
 9409 reflections with *I* > 2 σ (*I*)
R_{int} = 0.029
 θ_{max} = 52.8°
h = –22 → 22
k = –21 → 21
l = –28 → 28

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.142$
 $S = 0.96$
 14 343 reflections
 227 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.091P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.33 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

| | | | |
|-------------|------------|-------------|------------|
| C1—C2 | 1.6225 (5) | B4—B8 | 1.7734 (6) |
| C1—B4 | 1.6895 (5) | B5—B6 | 1.7778 (7) |
| C1—B5 | 1.7030 (6) | B5—B10 | 1.7833 (6) |
| C1—B6 | 1.7213 (6) | B6—B10 | 1.7683 (7) |
| C1—B3 | 1.7265 (5) | B6—B11 | 1.7785 (7) |
| C2—B7 | 1.6937 (6) | B7—B8 | 1.7782 (7) |
| C2—B11 | 1.7010 (6) | B10—B11 | 1.7825 (6) |
| C2—B6 | 1.7201 (6) | C13—C14 | 1.4019 (5) |
| C2—B3 | 1.7345 (5) | C13—C18 | 1.4020 (5) |
| B3—C13 | 1.5676 (5) | C14—C15 | 1.3967 (6) |
| B3—B8 | 1.7742 (6) | C15—C16 | 1.3895 (6) |
| B3—B4 | 1.7865 (6) | C16—C17 | 1.3898 (6) |
| B3—B7 | 1.7896 (6) | C17—C18 | 1.3975 (6) |
| C14—C13—C18 | 117.71 (3) | C16—C15—C14 | 120.17 (3) |
| C14—C13—B3 | 119.65 (3) | C17—C16—C15 | 119.54 (4) |
| C18—C13—B3 | 122.45 (3) | C16—C17—C18 | 120.23 (4) |
| C15—C14—C13 | 121.22 (4) | C17—C18—C13 | 121.12 (3) |

Compound (II)

Crystal data

$\text{C}_8\text{H}_{16}\text{B}_{10}$
 $M_r = 220.31$
 Monoclinic, $P2_1/c$
 $a = 10.350 (2) \text{ \AA}$
 $b = 9.449 (2) \text{ \AA}$
 $c = 13.763 (3) \text{ \AA}$
 $\beta = 106.07 (3)^\circ$
 $V = 1293.4 (5) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.131 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 24 reflections
 $\theta = 10\text{--}14^\circ$
 $\mu = 0.05 \text{ mm}^{-1}$
 $T = 163 (2) \text{ K}$
 Prism, colourless
 $0.30 \times 0.25 \times 0.20 \text{ mm}$

Data collection

Syntex $P2_1$ diffractometer
 $\theta/2\theta$ scans
 5094 measured reflections
 4872 independent reflections
 2765 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$
 $\theta_{\max} = 33.1^\circ$

$h = 0 \rightarrow 15$
 $k = 0 \rightarrow 14$
 $l = -21 \rightarrow 20$
 2 standard reflections every 98 reflections
 intensity decay: 2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.049$
 $wR(F^2) = 0.115$
 $S = 0.88$
 4872 reflections
 227 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0599P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.013$
 $\Delta\rho_{\max} = 0.24 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$

Table 2

Selected geometric parameters (\AA , $^\circ$) for (II).

| | | | |
|-------------|-------------|-------------|-------------|
| C1—C13 | 1.5095 (13) | B4—B5 | 1.7703 (16) |
| C1—B2 | 1.7100 (15) | B5—B6 | 1.7720 (15) |
| C1—B3 | 1.7170 (15) | C7—B12 | 1.7020 (16) |
| C1—B5 | 1.7212 (14) | C7—B11 | 1.7038 (19) |
| C1—B6 | 1.7254 (15) | C7—B8 | 1.7173 (18) |
| C1—B4 | 1.7297 (15) | B8—B12 | 1.7778 (19) |
| B2—C7 | 1.6961 (17) | B11—B12 | 1.7755 (18) |
| B2—B6 | 1.7622 (18) | C13—C18 | 1.3852 (14) |
| B2—B11 | 1.7699 (18) | C13—C14 | 1.3913 (14) |
| B2—B3 | 1.787 (2) | C14—C15 | 1.3872 (15) |
| B3—C7 | 1.6893 (18) | C15—C16 | 1.3762 (17) |
| B3—B8 | 1.7628 (18) | C16—C17 | 1.3775 (17) |
| B3—B4 | 1.7666 (17) | C17—C18 | 1.3905 (16) |
| C18—C13—C14 | 118.45 (10) | C16—C15—C14 | 120.92 (10) |
| C18—C13—C1 | 120.71 (9) | C15—C16—C17 | 119.15 (11) |
| C14—C13—C1 | 120.83 (9) | C16—C17—C18 | 120.38 (11) |
| C15—C14—C13 | 120.30 (11) | C13—C18—C17 | 120.80 (10) |

For compound (I), data collection: *SMART* (Bruker, 1998); cell refinement: *SMART* and *SAINT* (Bruker, 1998); data reduction: *SMART* and *SAINT*. For compound (II), data collection: *P3* (Siemens, 1989); cell refinement: *P3*; data reduction: *XDISK* (Siemens, 1991). For both compounds, program(s) used to solve structure: *SHELXTL* (Bruker, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1073). Services for accessing these data are described at the back of the journal.

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