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Haloaryl Carboranes. I. 1,4-Bis[2-phenyl-1,2-dicarba-*closo*-dodecaboran(12)-1-yl]-2,3,5,6-tetrafluorobenzene

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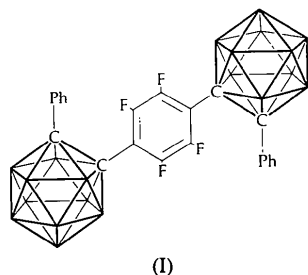
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Abstract

The title molecule, $C_{22}H_{30}B_{20}F_4$, has a crystallographically imposed inversion centre. The twist angle (θ) of the phenyl ring is $15.6(3)^\circ$, and that of the haloaryl ring is $3.7(3)^\circ$. These low values are presumably a consequence of the mutual steric crowding of the rings. The $C_{\text{cage}}-C_{\text{cage}}$ distance is $1.730(3) \text{ \AA}$, in good agreement with that found in similar molecules.

Comment

In the course of recent studies of the chemistry of haloaryl carboranes, the title molecule, (I), has been synthesized. It had been reported previously (Zakharkin & Lebedev, 1970), but was not conclusively identified. Herein we report the full characterization of (I), including the results of a single crystal X-ray diffraction study.



These haloaryl carboranes, particularly fluoroaryl carboranes, have been studied to establish the structural consequences of modifying the steric and electronic properties of the phenyl ring in carboranes by substitution. Structural studies of a series of phenyl carboranes, 1-Ph-2-*R*-1,2- $C_2B_{10}H_{10}$, have been reported previously (Lewis & Welch, 1993; McGrath & Welch, 1995*a,b*); these provide useful reference compounds and structures for the haloaryl carboranes. It might be anticipated that fluoroaryl carboranes are of particular interest, since these may have the largest difference in the electronic properties of the ring, simply due to the strong electron-withdrawing ability of fluorine. Steric effects

are expected to be much smaller, fluorine being almost isosteric with hydrogen. Moreover, it is important to establish structural parameters for molecules containing an aryl function bridging between two carborane moieties because of the potential importance of such units in new carborane-containing polymeric materials. An archetypal example of such a molecule is 1,4-(1'-*closo*-2'-Me-1',2'- $C_2B_{10}H_{10}$)₂-2,3,5,6- C_6H_4 (Henly, Knobler & Hawthorne, 1992).

The title molecule possesses a crystallographically imposed centre of symmetry at the centre of the fluoroaryl ring. The asymmetric unit thus comprises half a molecule. Fig. 1 shows a complete molecule and the atomic numbering scheme.

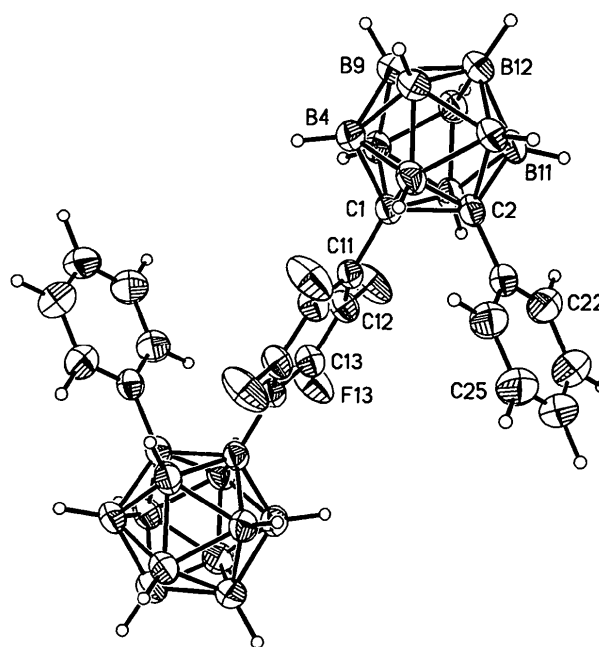


Fig. 1. View of the title compound with displacement ellipsoids shown at the 50% probability level for non-H atoms. H atoms are drawn as small circles of arbitrary radii. Only one half of the molecule is labelled, this being the asymmetric unit.

In discussing the conformation of aryl rings in aryl carboranes, the angle θ , defined as the modulus of the average $C_{\text{cage}}-C_{\text{cage}}-C_{\text{aryl}}-C_{\text{aryl}}$ torsion angles (Cowie, Reid, Watmough & Welch, 1994) is useful. The electronically preferred conformation for a phenyl ring in the absence of intersubstituent steric interactions has been calculated to be 65° (Brain *et al.*, 1996), and shown experimentally to be 68.8° (Brain *et al.*, 1996) and 71.2° (Thomas, Rosair & Welch, 1996). In the present case, the presence of the haloaryl ring causes θ_{phenyl} to be reduced by *ca.* 50° to $15.6(3)^\circ$, and θ_{haloaryl} is even less, $3.7(3)^\circ$. These low θ values are fully consistent with

those found in related monocarborane species: $\theta_{\text{phenyl}} = 5.5^\circ$ (average) in 1,2-Ph₂-1,2-C₂B₁₀H₁₀ (Lewis & Welch, 1993), $\theta_{\text{phenyl}} = 4.7^\circ$ (average) and $\theta_{\text{haloaryl}} = 6.3^\circ$ (average) in 1-Ph-2-(4'-BrC₆F₄)-1,2-C₂B₁₀H₁₀ (Thomas & Welch, 1996). In these diaryl carboranes, the C1—C2 distances are substantially longer than in PhC₂B₁₀H₁₁ (Brain *et al.*, 1996; Thomas, Rosair & Welch, 1996) and in 1-Ph-2-*R*-1,2-C₂B₁₀H₁₀ analogues with small C2 substituents (McGrath & Welch, 1995a). It is believed that there are two contributory factors: steric crowding between the two aryl groups and weakening of the C1—C2 connectivity, which is itself a consequence of the low θ_{aryl} value thereby necessitated. In 1-Ph-2-(4'-BrC₆F₄)-1,2-C₂B₁₀H₁₀, the average C1—C2 bond length [1.739 (10) Å] is not significantly different from that in 1,2-Ph₂-1,2-C₂B₁₀H₁₀ [1.726 (6) Å], showing that the substitution of C₆F₄Br for Ph has little structural effect. In the present molecule, C1—C2 is 1.732 (3) Å, in excellent agreement with the values cited above.

Experimental

The title compound was synthesized by an improvement upon the method of Zakharkin & Lebedev (1970). Typically, a solution of 1-Ph-C₂B₁₀H₁₁ (0.72 g, 3.3 mmol) (Reid, 1992) in diethyl ether was treated with ⁿBuLi solution (3.5 mmol) at 273 K and stirred for 30 min. To this was added C₆F₆ (0.31 g, 1.7 mmol), and the mixture stirred for 15 h at 293 K. The ether solvent was removed from the resultant yellow solution under reduced pressure, giving an oily solid. Pentane extraction (3 × 10 ml) of this gave a colourless solution that left a waxy white solid after removal of solvent. Washing with cold methanol (5 ml) gave the product as a white powder (0.67 g, 69%). Found: C 44.47, H 5.69%. Calculated for C₂₂H₃₀B₂₀F₄: C 45.04, H 5.15%. IR: ν_{BH} 2545 cm⁻¹. NMR (298 K, CDCl₃): δ [¹B(1H)] 2.11 (2B), -2.61 (4B) -8.29 (14B) p.p.m., δ (¹⁹F) -129.31 p.p.m. (broad, *s*, 4F), δ (¹H) 7.08–7.42 p.p.m. (*m*, 10H, C₆H₅). Crystals were grown by slow diffusion of hexane into a chloroform solution at 240 K. The crystals tend to shatter on attempts to cleave them.

Crystal data

C₂₂H₃₀B₂₀F₄
 $M_r = 586.66$
 Monoclinic
 $P2_1/c$
 $a = 8.710$ (3) Å
 $b = 12.988$ (2) Å
 $c = 14.069$ (3) Å
 $\beta = 102.44$ (4)^o
 $V = 1554.2$ (7) Å³
 $Z = 2$
 $D_x = 1.254$ Mg m⁻³
 D_m not measured

Data collection

Enraf–Nonius CAD-4
 diffractometer

Mo $K\alpha$ radiation
 $\lambda = 0.71069$ Å
 Cell parameters from 25
 reflections
 $\theta = 8$ –11^o
 $\mu = 0.078$ mm⁻¹
 $T = 293$ (2) K
 Needle
 $0.65 \times 0.40 \times 0.30$ mm
 Colourless

$R_{\text{int}} = 0.013$
 $\theta_{\text{max}} = 24.96^\circ$

ω -2 θ scans

Absorption correction:
 none

2929 measured reflections
 2738 independent reflections
 2151 observed reflections
 $[I > 2\sigma(I)]$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.0463$
 $wR(F^2) = 0.1361$
 $S = 1.110$

2738 reflections
 228 parameters
 Only coordinates of H atoms
 refined
 $w = 1/[\sigma^2(F_o^2) + (0.0825P)^2 + 0.1663P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$h = -10 \rightarrow 10$

$k = 0 \rightarrow 15$

$l = 0 \rightarrow 16$

2 standard reflections
 frequency: 480 min
 intensity decay: 2.1%

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.193$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.191$ e Å⁻³

Extinction correction: none

Atomic scattering factors

from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

	x	y	z	U_{eq}
C11	0.3651 (2)	0.05379 (11)	0.44136 (11)	0.0329 (4)
C12	0.4875 (2)	0.01308 (13)	0.40384 (11)	0.0390 (4)
C13	0.6155 (2)	-0.03630 (13)	0.45942 (12)	0.0388 (4)
F12	0.48556 (14)	0.01763 (10)	0.30859 (7)	0.0650 (4)
F13	0.72295 (13)	-0.06660 (10)	0.41038 (8)	0.0656 (4)
C22	0.4664 (2)	0.33576 (11)	0.36287 (7)	0.0574 (5)
C23	0.60400 (14)	0.38545 (12)	0.40831 (10)	0.0687 (6)
C24	0.64017 (13)	0.39647 (12)	0.50895 (10)	0.0678 (6)
C25	0.5387 (2)	0.35780 (12)	0.56414 (7)	0.0682 (6)
C26	0.40107 (14)	0.30811 (11)	0.51870 (8)	0.0558 (5)
C21	0.36490 (12)	0.29709 (9)	0.41807 (8)	0.0418 (4)
C1	0.2231 (2)	0.10596 (12)	0.37936 (11)	0.0341 (4)
C2	0.2196 (2)	0.23872 (12)	0.36755 (12)	0.0383 (4)
B3	0.1019 (2)	0.1800 (2)	0.43629 (15)	0.0407 (5)
B4	0.0393 (2)	0.0612 (2)	0.37677 (15)	0.0408 (5)
B5	0.1246 (2)	0.0511 (2)	0.27346 (14)	0.0412 (5)
B6	0.2414 (2)	0.16290 (15)	0.27022 (13)	0.0396 (5)
B7	0.0311 (3)	0.2822 (2)	0.3562 (2)	0.0473 (5)
B8	-0.0868 (2)	0.1708 (2)	0.3608 (2)	0.0500 (5)
B9	-0.0739 (3)	0.0918 (2)	0.2593 (2)	0.0492 (5)
B10	0.0538 (3)	0.1541 (2)	0.19325 (15)	0.0476 (5)
B11	0.1160 (3)	0.2717 (2)	0.25373 (15)	0.0452 (5)
B12	-0.0788 (3)	0.2278 (2)	0.2469 (2)	0.0522 (6)

Table 2. Selected geometric parameters (Å, °)

C11—C13'	1.388 (2)	B3—B4	1.784 (3)
C11—C12	1.392 (2)	B4—B5	1.774 (3)
C11—C1	1.511 (2)	B4—B9	1.777 (3)
C12—F12	1.338 (2)	B4—B8	1.782 (3)
C12—C13	1.375 (2)	B5—B10	1.774 (3)
C13—F13	1.336 (2)	B5—B9	1.778 (3)
C13—C11'	1.388 (2)	B5—B6	1.780 (3)
C21—C2	1.515 (2)	B6—B10	1.759 (3)
C1—B4	1.697 (3)	B6—B11	1.770 (3)
C1—B5	1.707 (2)	B7—B11	1.761 (3)
C1—C2	1.732 (2)	B7—B12	1.773 (3)
C1—B6	1.742 (2)	B7—B8	1.783 (3)
C1—B3	1.745 (2)	B8—B12	1.780 (3)
C2—B7	1.711 (3)	B8—B9	1.782 (3)
C2—B11	1.714 (2)	B9—B12	1.775 (3)
C2—B6	1.730 (3)	B9—B10	1.789 (3)
C2—B3	1.730 (3)	B10—B11	1.775 (3)
B3—B8	1.758 (3)	B10—B12	1.787 (3)
B3—B7	1.765 (3)	B11—B12	1.772 (3)

C13 ¹ —C11—C12	112.47 (14)	B4—C1—B3	62.42 (11)
C13 ¹ —C11—C1	124.10 (14)	C2—C1—B3	59.69 (10)
C12—C11—C1	123.35 (14)	C21—C2—B7	124.53 (14)
F12—C12—C13	115.08 (14)	C21—C2—B11	122.13 (13)
F12—C12—C11	121.18 (14)	B7—C2—B11	61.88 (12)
C13—C12—C11	123.72 (14)	C21—C2—B6	115.65 (13)
F13—C13—C12	114.59 (14)	B7—C2—B6	112.38 (14)
F13—C13—C11 ¹	121.63 (15)	B11—C2—B6	61.86 (11)
C12—C13—C11 ¹	123.78 (14)	C21—C2—B3	119.61 (13)
C26—C21—C2	120.83 (10)	B7—C2—B3	61.70 (11)
C22—C21—C2	119.10 (10)	C21—C2—C1	117.22 (12)
C11—C1—B4	120.65 (13)	B6—C2—C1	60.43 (9)
C11—C1—B5	120.76 (13)	B3—C2—C1	60.53 (10)
B4—C1—B5	62.83 (12)	B12—B8—B9	59.77 (13)
B5—C1—B6	62.13 (11)	B5—B9—B10	59.63 (11)
C2—C1—B6	59.74 (10)	B11—B12—B10	59.81 (12)

Symmetry code: (i) $1 - x, -y, 1 - z$.

The C atoms of the phenyl ring were constrained to form a regular hexagon ($C-C = 1.395 \text{ \AA}$), whilst those of the haloaryl ring were refined freely. The H atoms of the phenyl ring were set in idealized positions ($C-H = 1.08 \text{ \AA}$) with a common displacement parameter ($U_{iso} = 0.089 \text{ \AA}^2$). The positions of the cage H atoms were allowed to refine with a separate common displacement parameter ($U_{iso} = 0.059 \text{ \AA}^2$ at convergence).

Data reduction: *CADABS* (Gould & Smith, 1986). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1994).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1305). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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p-Nitrobenzaldehyde

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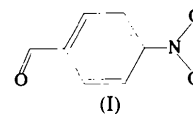
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Abstract

The title compound, $C_7H_5NO_3$, constitutes the simplest aromatic nitrocarbonyl system whose class of structures is commonly investigated for photochromic behavior. The nitro and aldehyde groups of *p*-nitrobenzaldehyde are coplanar with the plane of the arene ring.

Comment

As part of our continuing interest in the intramolecular interaction of carbonyl groups with nitro-substituted aromatic systems (King & Bryant, 1990; Bryant & King, 1995), *p*-nitrobenzaldehyde, (I), was examined at low temperature by single-crystal X-ray diffraction. The *para* data was compared with that of *o*-nitrobenzaldehyde (Coppens & Schmidt, 1964) in order to contrast steric effects for ground-state modeling work. The modeling work was initiated, in part, in order to gain a better understanding of the geometrical limitations involved in photochromism for this class of compounds (Margerum & Miller, 1971). The *para* isomer was necessary for this structural comparison.



The nitro and aldehyde groups of *p*-nitrobenzaldehyde are coplanar with the plane of the arene ring. The carbonyl bond length is $1.197(6) \text{ \AA}$ and the $O(3)-N-O(2)$ bond angle is $120.0(7)^\circ$. The aldehyde group of *p*-nitrobenzaldehyde was disordered. The general structure is unexceptional. A comparison of bond lengths and angles between the *ortho* and *para* isomers is given in Table 1. In contrast to the *para* isomer, the functional groups in *o*-nitrobenzaldehyde (Coppens & Schmidt, 1964) exhibit a slight canting of the nitro and aldehyde groups from coplanarity with the arene ring; the torsional angles are $C(6)-C(1)-N(1)-O(1) = -151.1(1)$, $C(7)-C(2)-C(1)-N(1) = 9.5(1)$

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