1,2-Ph$_2$-9-I-1,2-*closo*-C$_2$B$_{10}$H$_9$[1]

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The title compound, 9-iodo-1,2-diphenyl-1,2-dicarba-*closo*-dodecaborane(9), C$_{14}$H$_{19}$B$_{10}$I, has the expected pseudo-icosahedral cluster geometry, with a cage C—C distance of 1.724 (4) Å, comparable to that in the non-iodinated parent. However, the twist angles, θ, of the phenyl rings are 2.1 (6) and 27.6 (5)°, the latter being unusually large.

Comment

We are currently investigating the mechanism of the isomerization of *closo*-12-vertex dicarbametallaboranes (3,1,2-*closo*-MC$_2$B$_9$), wherein we exploit steric crowding to facilitate isomerization at reduced temperatures. This process models the well known thermal rearrangement (450°) of the parent *ortho*-carborane to *meta*-carborane (Grafstein & Dvorak, 1963).

Our recent isolation and structural characterization of an intermediate in this process (Dunn *et al.*, 1997) combine with our present vertex-labelling studies (Dunn *et al.*, 1998, 1999) to provide evidence whereby a reliable picture of the rearrangement pathway may ultimately be built up.

As part of these labelling experiments we have prepared the title compound, (I), and are embarking upon studies of its metal complexes. However, the structure of the parent carborane reported here serves as a useful reference and

(I)
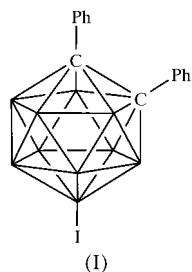
provides confirmation both of the position and of the structural 'innocence' of the iodine substituent. [In fact, (I) was briefly reported over 20 years ago (Vasil'eva & Khalfina, 1976), but detailed structural and spectroscopic characterization are only now presented herein.]

[1] *Steric effects in heteroboranes*. Part 24. For Part 23, see Dunn *et al.* (1999).

A view of a molecule of (I) is shown in Fig. 1, along with the atomic numbering scheme. The carborane skeleton clearly has the anticipated pseudo-icosahedral architecture, with the two adjacent C$_{cage}$ atoms C1 and C2 bearing phenyl substituents, and the molecule overall having the approximate molecular C$_s$ symmetry mirrored in the solution NMR data. The boron atom B9, antipodal to one of the C$_{cage}$ atoms, has undergone electrophilic substitution and bears the iodine atom I1 [B9—I1 2.178 (4) Å]. Cluster B—B and C—B distances are unremarkable, whilst the C$_{cage}$—C$_{cage}$ separation, 1.724 (4) Å, is comparable to that in parent 1,2-Ph$_2$-1,2-*closo*-C$_2$B$_{10}$H$_{10}$ (Lewis & Welch, 1993) where the corresponding parameter is 1.733 (4) (molecule *A*) and 1.720 (4) Å (molecule *B*).

The major deviation from molecular mirror symmetry in the structure of (I) lies in the twisting of the planes of the aryl substituents away from orthogonality with the notional molecular mirror plane. This twisting may be described by the angle θ, the modulus of the average C$_{cage}$—C$_{cage}$—C$_{Ph(ipso)}$—C$_{Ph(ortho)}$ torsion angles (Cowie *et al.*, 1994). In (I), the phenyl ring bound to C1 has θ = 2.1 (6)° and that at C2 has θ = 27.6 (5)°. The former value compares well with θ values in the parent compound [2.3 and 2.4° (molecule *A*), and 9.2 and 8.0° (molecule *B*); Lewis & Welch, 1993]; whereas the latter is unusually large. In such compounds, the magnitude of θ appears to be a consequence of weak intermolecular Ph···Ph interactions and/or packing in the solid state. In (I), the phenyl ring bound at C1 has a closest interplanar approach of over 3.3 Å to a neighbouring parallel ring, related to it by an inversion centre; whilst the ring bound at C2 is approximately orthogonal to the phenyl ring at C1 in a neighbouring molecule, with H103 and H104 within 3.0 Å of the plane of the former ring. It has in any case been shown previously that at lower θ different conformations are very similar in energy (Brain *et al.*, 1996), and that in 1,2-Ph$_2$-1,2-*closo*-C$_2$B$_{10}$H$_{10}$, θ values of up to *ca* 40° can be tolerated without any destabilizing intramolecular Ph···Ph interaction (Lewis & Welch, 1993).
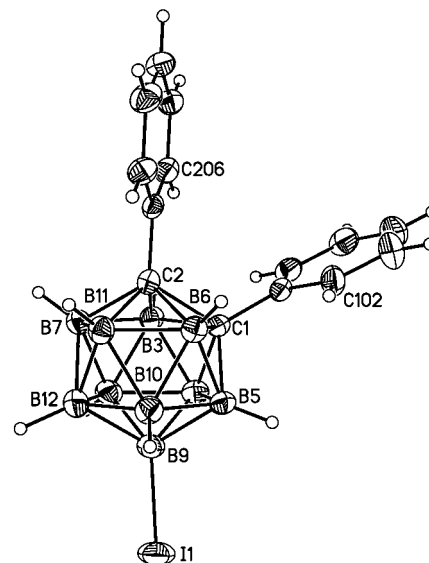

Figure 1
Perspective view of (I) with displacement ellipsoids shown at the 50% probability level for non-H atoms. H atoms are drawn as small circles of arbitrary radii.

Another molecular feature of interest is that the B9—I1 vector is not symmetrically disposed with respect to the five B atoms to which B9 is bound, but 'bends' slightly towards C1. Thus B4—B9—I1 and B5—B9—I1 are both 119.1 (2)° whilst the other three B—B9—I1 angles lie in the range 121.7 (3) to 123.7 (2)°. (A similar effect can be seen, albeit less reliably, in a bending of the B12—H12 vector towards C2.) This perhaps reveals an interesting structural–electronic effect of the mutual steric crowding between the two phenyl groups. In the unsubstituted parent compound 1,2-$closo$-$C_2B_{10}H_{12}$, the C_{cage}—C_{cage} distance is typically 1.629 (5) Å (Davidson $et\ al.$, 1996). Thus, as the C···C connectivity extends in compounds such as (I) or its non-halogenated parent, the directions of the exo-radial orbitals forming the C_{cage}—C_{Ph} bonds mutually diverge and this is mirrored in the bending of the antipodal B9—X or B12—X vectors.

Experimental

Compound (I) was prepared by an improvement upon the method of Vasil'eva & Khalfina (1976). Typically, 1,2-Ph_2-1,2-$closo$-$C_2B_{10}H_{10}$ (2.96 g, 10 mmol) and sublimed I_2 (1.27 g, 5 mmol) were dissolved in glacial acetic acid (40 ml) at 313 K. A mixture of concentrated nitric acid and concentrated sulfuric acid (1:1 volume ratio, 20 ml) was added very slowly to the mixture (1 ml min^{-1}). A brown vapour was observed above the purple solution and within 90 min the solution became pale brown and then decolourized. The colourless mixture was poured into a beaker containing distilled water (300 ml), resulting in a white precipitate which was isolated by filtration, washed with distilled water, dissolved in diethyl ether and dried over $MgSO_4$. The dried ethereal solution was evaporated and the resulting off-white residue recrystallized from hexane to give the title compound (3.02 g, 7.15 mmol, 71.5%). Found: C 39.3, H 4.3%; $C_{14}H_{19}B_{10}I$ requires: C 39.8, H 4.5%; IR (KBr disc): 3060 (w, ν_{CH}) and 2597 (s, ν_{BH}) cm^{-1}; MS (EI): $(m/z)_{max}$ 424 ($^{12}C_{14}{}^{1}H_{19}{}^{11}B_{10}{}^{127}I$); NMR (CDCl$_3$, 298 K): δ(^{11}B) −0.9 (1B, B12), −8.6 (6B, B4,5,7,11,8,10), −11.0 (2B, B3,6), −15.2 (1B, B9); δ(^{1}H) 7.39 (4H, m; $ortho$- or $meta$-C_6H_5), 7.26 (2H, m; $para$-C_6H_5), 7.15 (4H, m; $meta$- or $ortho$-C_6H_5), 3.33 (2H, H3,6), 3.00 (3H, H12 and H4,5 or H7,11 or H8,10), 2.83 (2H, H8,10 or H7,11 or H4,5), 2.62 (2H, H7,11 or H8,10 or H4,5); δ(^{13}C) 130.8 (2 $para$-C, $ortho$-C), 130.7 ($ortho$-C), 130.2 ($ipso$-C), 129.8 ($ipso$-C), 128.7 (2 $meta$-C), 86.1 (carboranyl C), 82.2 (carboranyl C). Diffraction-quality single crystals were obtained by slow mutual diffusion of a dichloromethane solution and petroleum ether (333–353 K) at 243 K.

Crystal data

$C_{14}H_{19}B_{10}I$	$D_x = 1.497$ Mg m^{-3}
$M_r = 422.29$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 32
$a = 9.0913$ (9) Å	reflections
$b = 11.4168$ (11) Å	$\theta = 4.84$–12.51°
$c = 18.0817$ (17) Å	$\mu = 1.702$ mm^{-1}
$\beta = 93.460$ (7)°	$T = 160$ (2) K
$V = 1873.3$ (3) Å^3	Block, colourless
$Z = 4$	$0.40 \times 0.15 \times 0.12$ mm

Data collection

Bruker $P4$ diffractometer	$R_{int} = 0.033$
ω scans	$\theta_{max} = 24.99°$
Absorption correction: empirical	$h = -1 \rightarrow 10$
($SHELXTL$; Sheldrick, 1999)	$k = -13 \rightarrow 1$
$T_{min} = 0.746$, $T_{max} = 0.815$	$l = -21 \rightarrow 21$
4407 measured reflections	3 standard reflections
3304 independent reflections	every 97 reflections
2628 reflections with $I > 2\sigma(I)$	intensity decay: 1.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0259P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$+ 1.7031P]$
$wR(F^2) = 0.085$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.022$	$(\Delta/\sigma)_{max} = 0.001$
3304 reflections	$\Delta\rho_{max} = 0.77$ e Å^{-3}
253 parameters	$\Delta\rho_{min} = -0.58$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å, °).

C1—C101	1.514 (4)	C2—C201	1.506 (5)
C1—C2	1.724 (4)	B9—I1	2.178 (4)
B5—B9—I1	119.1 (2)	B8—B9—I1	122.1 (2)
B12—B9—I1	123.7 (2)	B10—B9—I1	121.7 (3)
B4—B9—I1	119.1 (2)		
C1—C2—C201—C202	−117.3 (3)	C2—C1—C101—C102	94.3 (4)
C1—C2—C201—C206	62.1 (4)	C2—C1—C101—C106	−90.2 (4)

Phenyl-H atoms were set riding with C—H = 0.95 Å and with $U_{iso} = 1.2U_{eq}$(C). Cluster H atoms were allowed free positional refinement, but were assigned isotropic displacement parameters equal to 1.2U_{eq}(B). The refined B—H distances are in the range 1.03 (4)–1.19 (4) Å.

Data collection: $XSCANS$ (Bruker, 1996); cell refinement: $XSCANS$; data reduction: $SHELXTL$ (Sheldrick, 1999); program(s) used to solve structure: $SHELXTL$; program(s) used to refine structure: $SHELXTL$; molecular graphics: $SHELXTL$; software used to prepare material for publication: $SHELXTL$.

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