Refinement

Refinement on F^2
$R(F) = 0.040$
$wR(F^2) = 0.091$
$S = 1.024$
1699 reflections
178 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0482P)^2 + 0.0374P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.014$
$\Delta\rho_{\max} = 0.169$ e Å^{-3}
$\Delta\rho_{\min} = -0.244$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C9	1.322 (3)	C3—C4	1.381 (3)
O1—H9	0.87 (3)	C3—H3	0.94 (2)
O2—C9	1.227 (3)	C4—C5	1.389 (3)
O3—N1	1.232 (2)	C4—N2	1.473 (3)
O4—N1	1.229 (2)	C5—C6	1.386 (3)
O5—N2	1.232 (2)	C5—H5	0.96 (2)
O6—N2	1.233 (2)	C6—H6	0.98 (2)
C1—C2	1.405 (3)	C7—C8	1.330 (3)
C1—C6	1.409 (3)	C7—H7	0.92 (2)
C1—C7	1.472 (3)	C8—C9	1.477 (3)
C2—C3	1.383 (3)	C8—H8	0.96 (2)
C2—N1	1.477 (3)		
C9—O1—H9	109.1 (18)	C5—C6—H6	119.0 (14)
C2—C1—C6	116.5 (2)	C1—C6—H6	119.4 (14)
C2—C1—C7	124.5 (2)	C8—C7—C1	123.2 (2)
C6—C1—C7	119.0 (2)	C8—C7—H7	120.6 (13)
C3—C2—C1	123.4 (2)	C1—C7—H7	116.1 (13)
C3—C2—N1	116.2 (2)	C7—C8—C9	120.2 (2)
C1—C2—N1	120.4 (2)	C7—C8—H8	122.5 (12)
C4—C3—C2	117.3 (2)	C9—C8—H8	117.2 (12)
C4—C3—H3	121.6 (14)	O2—C9—O1	124.0 (2)
C2—C3—H3	121.1 (14)	O2—C9—C8	123.0 (2)
C3—C4—C5	122.6 (2)	O1—C9—C8	113.0 (2)
C3—C4—N2	118.3 (2)	O4—N1—O3	124.0 (2)
C5—C4—N2	119.0 (2)	O4—N1—C2	117.7 (2)
C6—C5—C4	118.6 (2)	O3—N1—C2	118.3 (2)
C6—C5—H5	122.4 (13)	O5—N2—O6	124.2 (2)
C4—C5—H5	119.0 (13)	O5—N2—C4	117.6 (2)
C5—C6—C1	121.6 (2)	O6—N2—C4	118.2 (2)

Data collection: Nicolet system software. Cell refinement: Nicolet system software. Data reduction: Nicolet system software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: BK1250). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$[Ph_3PH][\textit{nido}\text{-}B_{11}H_{14}]$

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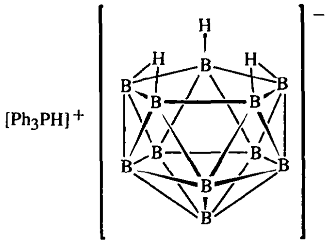
Abstract

The structure of the tetradecahydro-*nido*-undecaborate(1−) anion, as its triphenylphosphonium salt, is reported ($C_{18}H_{16}P^+.B_{11}H_{14}^-$). The borane anion has the expected icosahedral fragment geometry, with crystallographically-imposed mirror symmetry.

Comment

In the course of our synthetic and structural studies of metalla(hetero)boranes, we have isolated and structurally characterized the title salt, (I).



(I) B = B—H

Although the borane anion, $[B_{11}H_{14}]^-$, has been known for over 30 years (Aftandilian, Miller, Parshall & Muetterties, 1962), its structure determination was only reported relatively recently (Getman, Krause & Shore, 1988) and the species continues to be the subject of

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some considerable theoretical interest (see, for example, Maitre *et al.*, 1993).

Perspective views of the cation and borane anion of (I), showing the atomic numbering schemes, are given in Fig. 1. Both the cation and anion possess crystallographically-imposed C_s symmetry. Such mirror symmetry in this cation, rather than a C_3-type 'propeller' geometry, is not unprecedented; the same symmetry is found, for example, in the simple bromide salt of this cation (Bricklebank, Godfrey, McAuliffe & Pritchard, 1993). The Ph_3PH^+ moiety is otherwise structurally unremarkable.

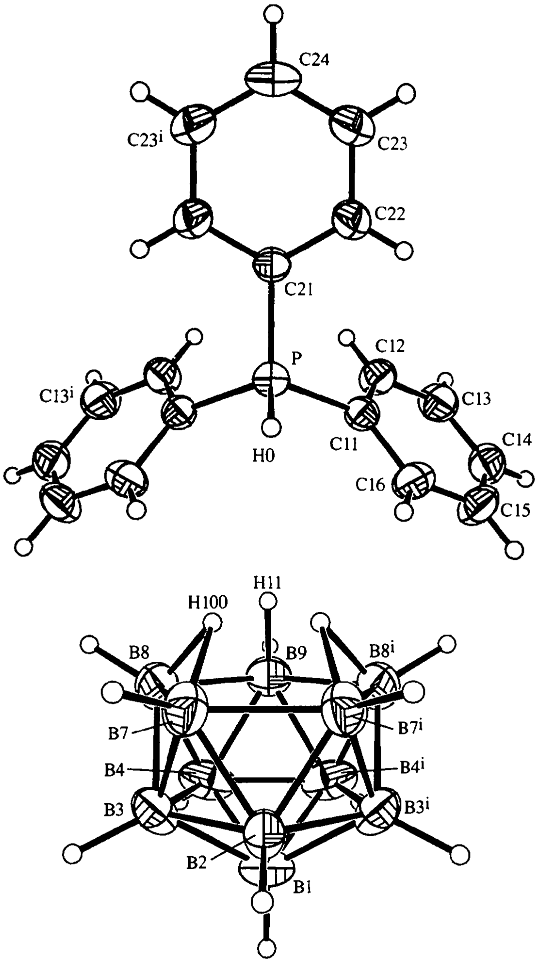

Fig. 1. Perspective views of a whole cation (top) and a whole anion of (I) showing the atomic numbering scheme. Displacement ellipsoids are shown at the 40% probability level and H atoms are shown as small circles with artificial radii for clarity. [Symmetry code: (i) x, $\frac{3}{2}-y$, z.]

The atoms B1, B2 and B9 (and their terminal H atoms) lie on a crystallographic mirror plane, as does the *endo*-H11 atom (also bound to B9). Although peaks apparently corresponding to H11 and to the (facial) bridging H100 atom could readily be observed in difference maps, the positions of these H atoms were not refined (see *Experimental*) and distances involving them are perhaps rather longer than may be reasonable [*endo*-B9—H11 1.32, bridging B7—H100 1.50 and B8—H100 1.38 Å; *cf.* *endo*-B—H 1.13 and bridging B—H 1.19–1.38 Å in the Me_3PH^+ salt (Getman *et al.*, 1988), where these H atoms were located]. Indeed, the identification of these atoms is far from certain. We found no evidence, however, of positional disorder in these (probably) facially bonded H atoms, or any B-atom disorder of the kind often seen in 11-vertex *nido*-carbaboranes (see, for example, Cowie, Donohoe, Douek & Welch, 1993), where a partial B atom appears to 'cap' the open cluster face. Otherwise, the borane skeleton has a structure very similar to that found in its Me_3PH^+ salt (Getman *et al.*, 1988); B—B distances around the open face are in the range 1.856 (6)–1.895 (8) Å in (I) and 1.875 (6)–1.895 (6) Å in the Me_3PH^+ salt, while B—B distances within the borane cage lie between 1.741 (8) and 1.780 (6) Å in (I) and between 1.747 (6) and 1.775 (6) Å in the Me_3PH^+ salt. The structure of (I) is likewise similar to that determined for the [*nido*-$B_{11}H_{13}]^{2-}$ ion (Fritchie, 1967) and for the related species $Me_2S.B_{11}H_{13}$ (Keller, Kester, Huffman & Todd, 1993).

Experimental

The title salt [Ph_3PH][*nido*-$B_{11}H_{14}$] was isolated (filtration and evaporation) from the reaction between equimolar amounts of Na[*nido*-$B_{11}H_{14}$].$nC_4H_8O_2$ (Aftandilian *et al.*, 1962; Miller & Muetterties, 1967) and $[HgCl_2(PPh_3)]_2$ (Evans, Mann, Peiser & Purdie, 1940) in CH_2Cl_2. Recrystallization was by slow diffusion of *n*-hexane into a dichloromethane solution at 243 K.

Crystal data

$C_{18}H_{16}P^+.B_{11}H_{14}^-$
$M_r = 396.30$
Monoclinic
$P2_1/m$
$a = 8.641\ (3)$ Å
$b = 13.064\ (2)$ Å
$c = 10.945\ (3)$ Å
$\beta = 106.861\ (2)°$
$V = 1182.5\ (6)$ Å^3
$Z = 2$
$D_x = 1.113$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12$–$14°$
$\mu = 0.120$ mm^{-1}
$T = 293\ (2)$ K
Block
0.40 × 0.30 × 0.25 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2326 measured reflections
2175 independent reflections
1334 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0207$
$\theta_{\rm max} = 24.97°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 15$
$l = -13 \rightarrow 12$
2 standard reflections every 250 reflections intensity decay: 0.3%

Refinement

Refinement on F^2
$R(F) = 0.0594$
$wR(F^2) = 0.1653$
$S = 1.028$
2174 reflections
155 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0888P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.37$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.28$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

P—C11	1.7722 (15)	B3—B4	1.763 (6)
P—C21	1.777 (4)	B3—B8	1.780 (6)
B1—B2	1.741 (8)	B4—B8	1.758 (7)
B1—B3	1.758 (6)	B4—B9	1.764 (6)
B1—B4	1.763 (7)	B4—B4$^{\rm i}$	1.776 (10)
B2—B3	1.751 (5)	B7—B8	1.856 (6)
B2—B7	1.761 (6)	B7—B7$^{\rm i}$	1.895 (8)
B3—B7	1.751 (6)	B8—B9	1.883 (6)
C11$^{\rm i}$—P—C11	112.5 (2)	B8—B4—B9	64.6 (3)
C11—P—C21	110.29 (9)	B1—B4—B4$^{\rm i}$	59.8 (2)
B2—B1—B3	60.1 (2)	B9—B4—B4$^{\rm i}$	59.8 (2)
B3—B1—B4	60.1 (2)	B3—B7—B2	59.8 (2)
B4$^{\rm i}$—B1—B4	60.5 (4)	B3—B7—B8	59.0 (2)
B1—B2—B3	60.5 (2)	B2—B7—B7$^{\rm i}$	57.4 (2)
B3—B2—B7	59.8 (2)	B8—B7—B7$^{\rm i}$	107.4 (2)
B7$^{\rm i}$—B2—B7	65.1 (3)	B4—B8—B3	59.8 (2)
B2—B3—B7	60.4 (3)	B3—B8—B7	57.6 (2)
B2—B3—B1	59.5 (3)	B4—B8—B9	57.9 (3)
B1—B3—B4	60.1 (3)	B7—B8—B9	109.6 (3)
B7—B3—B8	63.4 (2)	B4—B9—B4$^{\rm i}$	60.4 (4)
B4—B3—B8	59.5 (2)	B4—B9—B8	57.5 (2)
B8—B4—B3	60.7 (2)	B8$^{\rm i}$—B9—B8	105.9 (4)
B1—B4—B3	59.8 (2)		

Symmetry code: (i) $x, \frac{3}{2} - y, z$.

The structure was solved by Patterson methods (*SHELX*76; Sheldrick, 1976) for the P atom and by difference Fourier syntheses (*SHELXL*93; Sheldrick, 1993) for B and C atoms, and for the phosphonium and borane H atoms. The C atoms of the wholly crystallographically-independent phenyl ring were constrained to be a rigid planar hexagon (C—C 1.39 Å) and all phenyl H atoms were set riding in idealized positions (C—H 0.93 Å), with an isotropic displacement parameter equal to 1.5 times the equivalent isotropic displacement parameter of the corresponding C atom. Terminal borane H atoms were positionally refined subject to a common B—H distance [1.15 (3) Å at convergence]; the positions of the *endo* and bridging borane H atoms H11 and H100 were fixed after their location. [Attempts to refine the positions of H11 and H100 were unsuccessful, resulting in their migration to chemically non-sensible positions away from the borane face (with B···H > 2 Å) and the reappearance of electron-density peaks in the difference Fourier map close to the original apparent positions of these atoms.] The parameters of the phosphonium H atom were successfully refined to a final P—H distance of 1.37 (4) Å. All non-H atoms were ultimately refined with anisotropic displacement parameters; all non-phenyl H atoms were assigned a common (refined) isotropic displacement parameter [$U_{\rm iso} = 0.081$ (4) Å^2 at convergence].

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CADABS* (Gould & Smith, 1986). Program used to refine structure: *SHELXL*93. Molecular graphics: *ORTEX* (McArdle, 1994).

The authors thank the EPSRC for support (TDM) and the Callery Chemical Company for a generous gift of decaborane.

Lists of structure factors, anisotropic displacement parameters, atomic coordinates and complete geometry have been deposited with the IUCr (Reference: MU1262). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetrakis(*p*-dimethylaminophenyl)ethylene Hemibenzene Solvate

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Abstract

The crystal structure of the title compound, ethylenetetrayltetrakis[dimethyl(4-phenyl)amine] hemibenzene solvate, $C_{34}H_{40}N_4.0.5C_6H_6$, has been determined by X-ray diffraction at 200 K. The molecular halves of the tetrasubstituted ethylene subunit are twisted by 12.0 (2)°