Tetra-*n*-butylammonium 7-phenylethynyl-8-phenyl-7,8-*nido*-dicarbadecahydroundecaborate(1−)

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Key indicators

The $[NBu_4]^+$ salt of 7-phenylethynyl-8-phenyl-7,8-*nido*-dicarbadecahydroundecaborate(1−), $C_{16}H_{36}N^+ \cdot C_{16}H_{20}B_9^-$, has been prepared and studied crystallographically. The carborane cage is ordered, unlike that which crystallizes as the $[PPh_4]^+$ salt.

Comment

In the preceding article (Rosair *et al.*, 2001), we describe the structure of the anion $[7\text{-}PhC_2\text{-}8\text{-}Ph\text{-}7,8\text{-}nido\text{-}C_2B_9H_{10}]^-$ as its $[PPh_4]^+$ salt. Whilst the Ph group directly bound to C8 of the cage subtends a relatively low θ value of 15.8{15.1}° (two crystallographically independent cages), that of the PhCC substituent bound to C7 has a relatively high θ value, 57.6{52.2}°. The parameter θ is defined as the modulus of the average C_{cage}—C_{cage}—C_{Ph}—C_{Ph} torsion angle (Cowie *et al.*, 1994).
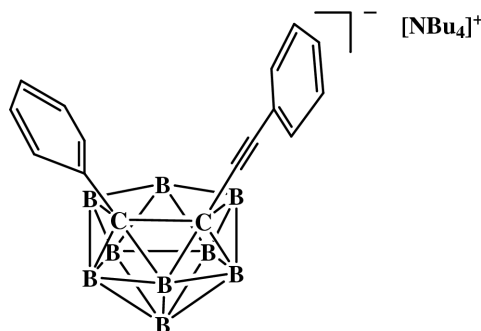
(I)

In the $[NBu_4]^+$ salt described herein, there is only one crystallographically independent cage, with θ values of 24.3 and 67.4°, respectively. Moreover, the present cage is ordered, unlike those of the $[PPh_4]^+$ salt; this may reflect the relatively discoidal shape of the $[NBu_4]^+$ cation compared with the more spherical $[PPh_4]^+$ cation.

Experimental

A 5 ml solution of 46.22 mg NBu$_4$Br (143.38 mmol) in water was added slowly to 50 mg K[7-CCPh-8-Ph-7,8-C$_2$B$_9$H$_{10}$] (143.38 mmol) dissolved in 10 ml water, producing a white precipitate. After filtration and washing with water, the white solid was dissolved in CH$_2$Cl$_2$ and dried over MgSO$_4$. Recrystallization from 333–353 K light petroleum/CH$_2$Cl$_2$ gave 56.0 mg (73.5%) of the product as white microcrystals. ^{11}B {^{1}H} FT–NMR data: (128.4 MHz, BF$_3$·Et$_2$O in d_6 acetone): δ/p.p.m. = −32.0 (1*B*), −29.6 (1*B*), −17.1 (1*B*), −15.9 (1*B*), −13.9 (1*B*), −12.8 (1*B*), −8.2 (1*B*), −4.2 (2*B*). NMR spectra were recorded on a Bruker DPX400 spectrometer at 293 K.
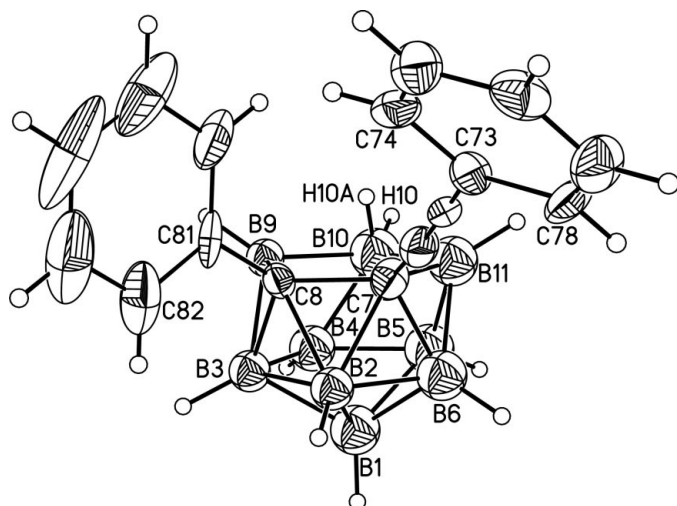
Figure 1
The molecular structure of the title anion showing 40% probability displacement ellipsoids.

Crystal data

$C_{16}H_{36}N^{+}·C_{16}H_{20}B_{9}^{-}$
$M_r = 552.07$
Orthorhombic, $Pna2_1$
$a = 20.626 (4)$ Å
$b = 10.099 (2)$ Å
$c = 17.183 (3)$ Å
$V = 3579.3 (12)$ Å^3
$Z = 4$
$D_x = 1.024$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 59
  reflections
$\theta = 3.9$–$22.2°$
$\mu = 0.05$ mm^{-1}
$T = 293 (2)$ K
Plate, colourless
$0.74 \times 0.42 \times 0.26$ mm

Data collection

Bruker $P4$ diffractometer
ω scans
Absorption correction: none
3381 measured reflections
2457 independent reflections
1104 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$

$\theta_{max} = 24.9°$
$h = -1 \rightarrow 23$
$k = -1 \rightarrow 10$
$l = -20 \rightarrow 1$
3 standard reflections
  every 97 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.102$
$wR(F^2) = 0.302$
$S = 1.02$
2457 reflections
228 parameters
H atoms treated by a mixture of
  independent and constrained
  refinement

$w = 1/[\sigma^2(F_o^2) + (0.1216P)^2 + 6.0328P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

B1—B2	1.77 (2)	B5—B10	1.69 (3)
B1—B3	1.81 (2)	B5—B11	1.72 (3)
B1—B4	1.80 (2)	B6—B11	1.78 (2)
B1—B5	1.79 (3)	C7—C8	1.608 (15)
B1—B6	1.77 (2)	C7—B2	1.75 (2)
B2—B3	1.77 (2)	C7—B6	1.71 (2)
B2—B6	1.71 (2)	C7—B11	1.62 (2)
B3—B4	1.80 (2)	C8—B2	1.737 (18)
B3—B9	1.79 (2)	C8—B3	1.676 (18)
B4—B5	1.82 (2)	C8—B9	1.605 (17)
B4—B9	1.78 (2)	B9—B10	1.83 (2)
B4—B10	1.74 (3)	B10—B11	1.80 (3)
B5—B6	1.75 (3)		

Friedel pairs have been merged and the absolute configuration could not be determined from the experiment because of the lack of any significant anomalous scattering. Beyond 45° in 2θ very little diffraction was observed and, with a sequential detector, it was thought that little would be gained by collecting data at a higher angle. This was the biggest single crystal present in the sample. The study is of limited precision because the crystal was relatively weakly diffracting and data were collected at room temperature. Data collection at low temperature and with a more sensitive detector would have improved the result.

The *exo*-cage-H atoms were constrained to idealized positions (B—H 1.10 Å), as were the phenyl-H atoms (C—H 0.98 Å), methylene (C—H 0.97 Å) and methyl-H atoms (C—H 0.96 Å). The *endo*-cage-H atom was restrained to B—H = 1.10 (2) Å. The isotropic displacement parameters of the cage-H atoms were defined as $1.2U_{iso}$ of the attached cage atom. The U_{iso} parameters of the phenyl, methylene and methyl H atoms were defined as 1.2, 1.2 and $1.5U_{iso}$ of the attached C atom, respectively. The phenyl rings were constrained to idealized hexagons. Only the cage-C and phenyl-C atoms were refined anisotropically.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

References

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