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# Structures of $[HNEt_3]^+$ and $[Me_3NCH_2C_6H_5]^+$ Salts of [7,8-$Ph_2$-7,8-*nido*-$C_2B_9H_{10}]^-$

By Jill Cowie, David J. Donohoe, Natalia L. Douek and Alan J. Welch
*Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, Scotland*

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**Abstract.** Triethylammonium 7,8-diphenyl-7,8-dicarba-*nido*-decahydroundecaborate(1−), $C_6H_{16}N^+.C_{14}H_{20}B_9^-$, $M_r = 387.80$, triclinic, $P\bar{1}$, $a = 11.014$ (4), $b = 11.030$ (7), $c = 12.333$ (6) Å, $\alpha = 67.83$ (5), $\beta = 80.78$ (4), $\gamma = 60.20$ (5)°, $V = 1203.3$ Å$^3$, $Z = 2$, $D_x = 1.070$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.052$ mm$^{-1}$, $F(000) = 416$, $T = 291$ (1) K, $R = 0.1074$ for 3289 independent observed reflections. Benzyltrimethylammonium 7,8-diphenyl-7,8-dicarba-*nido*-decahydroundecaborate(1−), $C_{10}H_{16}N^+.C_{14}H_{20}B_9^-$, $M_r = 435.85$, monoclinic, $P2_1/n$, $a = 10.751$ (4), $b = 21.662$ (4), $c = 11.9745$ (25) Å, $\beta = 106.592$ (23)°, $V = 2672.5$ Å$^3$, $Z = 4$, $D_x = 1.083$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.053$ mm$^{-1}$, $F(000) = 928$, $T = 185$ (1) K, $R = 0.0637$ for 3857 independent observed reflections. In both determinations, the phenyl substituents lie very roughly orthogonal to the open $C_2B_3$ face of the anion, pairs of rings being twisted (in a conrotatory manner) by an average of 7.8° for the $[HNEt_3]^+$ salt, and 19.0° for the $[Me_3NCH_2C_6H_5]^+$ salt, from this extreme. In the latter case, this twist is traced to interion contacts. The C(cage)—C(cage) distances, 1.590 (5) and 1.602 (3) Å, respectively, and the mean facial B—B and facial B—C distances are discussed in relation to the equivalent distances in 1,2-$Ph_2$-1,2-*closo*-$C_2B_{10}H_{10}$.

**Introduction.** The preceding paper (Lewis & Welch, 1993*a*) reports the molecular structure of 1,2-$Ph_2$-1,2-*closo*-$C_2B_{10}H_{10}$, noting the relatively long C(1)—C(2) connectivity [1.727 (6) Å averaged over the two crystallographically independent molecules] and the low $\theta$ values [$\theta$ is the average difference between 90° and the moduli of the C(cage)—C(cage)—C—C torsion angles] that describe the molecular conformation.

Our interest in diphenylcarbaborane rests primarily in its use as a ligand to *d*- and *f*-block metals, predominantly in the partially degraded form [7,8-$Ph_2$-7,8-*nido*-$C_2B_9H_9]^{2-}$ [note the change in conventional numbering between related *closo* and *nido* polyhedra (Casey, Evans & Powell, 1983)]. We have already shown (Lewis & Welch, 1992) that unusual structure deformation can arise when the phenyl

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rings are twisted into positions described by high $\theta$ values on ligation to a sterically demanding metal fragment such as Rh($\eta$-$C_5Me_5$).

In this context, we considered it important to have full stereochemical information on diphenylcarbaborane in its ligand form. As is the case with the parent compound [7,8-*nido*-$C_2B_9H_{11}$]$^{2-}$ and related derivatives, it is convenient to study such species as the partially protonated monoanion, in which the additional H atom occupies an *endo* position on B(10) (Buchanan, Hamilton, Reed & Welch, 1990; Shaw & Welch, 1992). Thus the present studies were undertaken.

**Experimental.** K[7,8-$Ph_2$-7,8-*nido*-$C_2B_9H_{10}$], a light yellow solid, was prepared from 1,2-$Ph_2$-1,2-*closo*-$C_2B_{10}H_{10}$ by an analogous method to that which affords K[7,8-*nido*-$C_2B_9H_{12}$] from $C_2B_{10}H_{12}$ (Hawthorne, Young, Garrett, Owen, Schwerin, Tebbe & Wegner, 1968). The title salts were each isolated as fine white precipitates by addition of aqueous solutions of excess [$HNEt_3$]Cl or [$Me_3NCH_2C_6H_5$]Br to an aqueous solution of K[7,8-$Ph_2$-7,8-*nido*-$C_2B_9H_{10}$], and recrystallized from $CH_2Cl_2$–*n*-hexane (1/3) at 243 K. $^1H$ NMR spectroscopy in $(CD_3)_2CO$ showed each to be a 1:1 salt and $^{11}B$ and $^{11}B$-{$^1H$} NMR spectroscopies revealed signals very similar to those (fully assigned) of 7,8-*nido*-$C_2B_9H_{12}$]$^-$ (Buchanan, Hamilton, Reed & Welch, 1990). Thus, for the [$HNEt_3$]$^+$ salt, $^{11}B$-{$^1H$} $\delta$ −6.49 (2B), −12.77 (1B), −14.80 (2B), −17.30 (2B), −31.49 (1B) and −33.84 p.p.m. (1B), all signals showing doublet coupling [$^1J_{BH(exo)}$ 137–160 Hz] with that at −31.49 showing additional doublet coupling [$^1J_{BH(endo)}$ 49.5 Hz] in the $^{11}B$ spectrum. Crystals of both salts were mounted on an Enraf–Nonius CAD-4 diffractometer (graphite monochromator). Experimental details in curly brackets, {}, represent differences in respect of the [$Me_3NCH_2C_6H_5$]$^+$ salt. Crystal size 0.3 × 0.2 × 0.2 mm {0.2 × 0.15 × 0.15 mm}; cell parameters and orientation matrix from least-squares refinement of the setting angles (9{12} < $\theta$ < 13°) of 25 centred reflections; data collection by $\omega$–2$\theta$ scans in 96 steps with $\omega$-scan width (0.8 + 0.34tan$\theta$)°; data (*h* 0 to 13, *k* −13 to 13, *l* −14 to 14 {*h* 0 to 12, *k* 0 to 25, *l* −13 to 13}) measured for $1 \leq \theta \leq 25°$ at room temperature {185 (1) K, ULT-1 low-temperature attachment} over 96 {115} X-ray hours with *ca* 2% decay subsequently corrected {no appreciable decay or movement}; corrections for Lorentz and polarization effects applied (Gould & Smith, 1986); of 4462 {5118} data measured, 3289 {3857} [$F \geq 2.0\sigma(F)$] used to solve [direct methods for most non-H atoms (Sheldrick, 1986), difference Fourier syntheses for all others (Sheldrick, 1976)] and refine (least squares on *F*) the structure.

In the case of the [$HNEt_3$]$^+$ salt, the ethyl groups of the cation were found to be involved in disorder, the best model of which involves six methylene C atoms and four methyl C atoms with 0.5 occupancy, only one methyl C atom, C(12), being essentially ordered; all cation atoms were refined with isotropic thermal parameters and no cation H atoms were included; cage H atoms were allowed positional refinement [except H(12), the *endo* H atom bound to B(10), which was included in an idealized position (Buchanan, Hamilton, Reed & Welch, 1990) but not thereafter refined] and phenyl H atoms were set in idealized positions (C—H 1.08 Å); non-H atoms of the anion were refined with anisotropic thermal parameters but cage and phenyl H atoms were refined with a single group isotropic thermal parameter, 0.085 (3) Å$^2$ at convergence; weights were assigned according to $w^{-1} = [\sigma^2(F) + 0.000306F^2]$; $R = 0.1074$, $wR = 0.1206$, $S = 2.165$; max. shift/e.s.d. in final cycle < 0.15; max. and min. residues in final $\Delta F$ synthesis 0.64 and −0.42 e Å$^{-3}$, respectively; the former of these essentially caps the *nido* polyhedral face, 1.73–1.80 Å from atoms C(7)—B(11), and is presumably due to partial boron disorder. Such a phenomenon is fairly frequently met in structural studies of *nido* icosahedral (hetero)boranes; scattering factors for N, C, B and H inlaid in *SHELX76*; Fig. 1 drawn using *EASYORTEP* (Mallinson & Muir, 1985); molecular geometry calculations *via* *CALC* (Gould & Taylor, 1986); we ascribe the relatively high residuals to the crystallographic disorder in both anion and cation, and to the relatively poor quality of the crystal used.

In the case of the [$Me_3NCH_2C_6H_5$]$^+$ salt, the cation is ordered but the same disorder is apparent in the anion; all non-H atoms were refined with anisotropic thermal parameters, and all H atoms [except that *endo* to B(10), which was treated similarly as above] were located from $\Delta F$ maps and freely refined, albeit with an overall isotropic thermal parameter, 0.0510 (13) Å$^2$ at convergence; weights were assigned according to $w^{-1} = [\sigma^2(F) + 0.002546F^2]$; $R = 0.0637$, $wR = 0.0930$, $S = 1.084$; max. shift/e.s.d. in final cycle < 0.01; max. and min. residues in final $\Delta F$ synthesis 0.94 and −0.30 e Å$^{-3}$, respectively; the former 1.59–1.84 Å from the facial C or B atoms.

**Discussion.** Table 1* lists coordinates of refined non-H atoms and equivalent isotropic thermal

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55795 (56 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1027]

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å$^2$) *for non*-H *atoms in* [HN($C_2H_5$)$_3$][7,8-Ph$_2$-7,8-*nido*-$C_2B_9H_{10}$]

$$U_{\rm eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

| | *x* | *y* | *z* | $U_{\rm eq}$ |
|---|---|---|---|---|
| B(1) | 0.2764 (5) | 1.0369 (5) | 0.6872 (4) | 0.064 (4) |
| B(2) | 0.2111 (5) | 0.9131 (5) | 0.7057 (4) | 0.064 (4) |
| B(3) | 0.3716 (5) | 0.8841 (5) | 0.6418 (5) | 0.070 (4) |
| B(4) | 0.4574 (5) | 0.9292 (5) | 0.7136 (4) | 0.064 (4) |
| B(5) | 0.3532 (6) | 0.9879 (5) | 0.8239 (5) | 0.075 (5) |
| B(6) | 0.1933 (6) | 0.9790 (5) | 0.8204 (4) | 0.071 (4) |
| C(7) | 0.3530 (4) | 0.7386 (4) | 0.7539 (3) | 0.048 (3) |
| C(8) | 0.4916 (4) | 0.7489 (4) | 0.7557 (3) | 0.045 (3) |
| B(9) | 0.4926 (5) | 0.8022 (5) | 0.8627 (4) | 0.061 (4) |
| B(10) | 0.3227 (5) | 0.8435 (5) | 0.9324 (4) | 0.069 (4) |
| B(11) | 0.2444 (5) | 0.7905 (5) | 0.8539 (4) | 0.059 (4) |
| C(71) | 0.3635 (4) | 0.6146 (4) | 0.7246 (3) | 0.054 (3) |
| C(72) | 0.3595 (5) | 0.6205 (5) | 0.6114 (4) | 0.094 (5) |
| C(73) | 0.3601 (7) | 0.5063 (7) | 0.5881 (5) | 0.127 (6) |
| C(74) | 0.3662 (7) | 0.3832 (6) | 0.6783 (5) | 0.128 (6) |
| C(75) | 0.3751 (7) | 0.3738 (5) | 0.7913 (5) | 0.117 (6) |
| C(76) | 0.3744 (5) | 0.4878 (5) | 0.8137 (4) | 0.090 (4) |
| C(81) | 0.6275 (4) | 0.6341 (4) | 0.7262 (3) | 0.048 (3) |
| C(82) | 0.6866 (4) | 0.6612 (4) | 0.6178 (3) | 0.061 (3) |
| C(83) | 0.8148 (5) | 0.5542 (5) | 0.5969 (4) | 0.077 (4) |
| C(84) | 0.8847 (5) | 0.4181 (5) | 0.6819 (4) | 0.083 (4) |
| C(85) | 0.8260 (5) | 0.3894 (5) | 0.7909 (4) | 0.081 (4) |
| C(86) | 0.6997 (4) | 0.4954 (4) | 0.8126 (4) | 0.067 (4) |
| N | 0.1087 (6) | 1.1281 (6) | 1.2206 (5) | 0.1194 (17) |
| C(11*A*) | 0.1076 (13) | 1.2369 (13) | 1.2586 (12) | 0.109 (4) |
| C(11*B*) | 0.1150 (14) | 1.1252 (14) | 1.3724 (11) | 0.112 (4) |
| C(12) | 0.0109 (10) | 1.2626 (10) | 1.3697 (8) | 0.177 (3) |
| C(21*B*) | 0.136 (3) | 1.244 (3) | 1.129 (3) | 0.259 (11) |
| C(21*A*) | 0.1769 (13) | 1.1357 (14) | 1.0901 (12) | 0.101 (4) |
| C(22*B*) | 0.1199 (17) | 1.2309 (20) | 1.0170 (14) | 0.123 (5) |
| C(22*A*) | 0.0947 (14) | 1.3151 (15) | 1.0018 (11) | 0.104 (4) |
| C(31*A*) | 0.214 (3) | 0.966 (3) | 1.3061 (20) | 0.214 (9) |
| C(31*B*) | 0.1687 (18) | 0.9453 (20) | 1.2417 (14) | 0.140 (5) |
| C(32*A*) | 0.2042 (14) | 0.8458 (15) | 1.2973 (12) | 0.107 (4) |
| C(32*B*) | 0.3185 (18) | 0.8887 (17) | 1.2571 (14) | 0.142 (5) |

Table 2. *Interatomic distances* (Å) *and interbond angles* (°) *in* [HN($C_2H_5$)$_3$][7,8-Ph$_2$-7,8-*nido*-$C_2B_9H_{10}$]

| | | | |
|---|---|---|---|
| B(1)—B(2) | 1.766 (8) | B(10)—B(11) | 1.795 (8) |
| B(1)—B(3) | 1.738 (8) | C(71)—C(72) | 1.379 (7) |
| B(1)—B(4) | 1.747 (8) | C(71)—C(76) | 1.376 (7) |
| B(1)—B(5) | 1.779 (8) | C(72)—C(73) | 1.391 (9) |
| B(1)—B(6) | 1.802 (8) | C(73)—C(74) | 1.371 (10) |
| B(2)—B(3) | 1.741 (8) | C(74)—C(75) | 1.374 (10) |
| B(2)—B(6) | 1.764 (8) | C(75)—C(76) | 1.381 (8) |
| B(2)—C(7) | 1.716 (7) | C(81)—C(82) | 1.383 (6) |
| B(2)—B(11) | 1.778 (8) | C(81)—C(86) | 1.394 (6) |
| B(3)—B(4) | 1.729 (8) | C(82)—C(83) | 1.382 (7) |
| B(3)—C(7) | 1.758 (7) | C(83)—C(84) | 1.367 (8) |
| B(3)—C(8) | 1.731 (7) | C(84)—C(85) | 1.389 (8) |
| B(4)—B(5) | 1.735 (8) | C(85)—C(86) | 1.369 (7) |
| B(4)—C(8) | 1.704 (7) | N—C(11*A*) | 1.437 (16) |
| B(4)—B(9) | 1.799 (8) | N—C(11*B*) | 1.873 (16) |
| B(5)—B(6) | 1.820 (8) | N—C(21*B*) | 1.48 (3) |
| B(5)—B(9) | 1.775 (8) | N—C(21*A*) | 1.654 (16) |
| B(5)—B(10) | 1.794 (8) | N—C(31*A*) | 1.60 (3) |
| B(6)—B(10) | 1.769 (8) | N—C(31*B*) | 1.704 (21) |
| B(6)—B(11) | 1.753 (8) | C(11*A*)—C(12) | 1.618 (18) |
| C(7)—C(8) | 1.590 (5) | C(11*B*)—C(12) | 1.363 (19) |
| C(7)—B(11) | 1.631 (7) | C(21*B*)—C(22*B*) | 1.49 (4) |
| C(7)—C(71) | 1.489 (6) | C(21*A*)—C(22*A*) | 1.682 (22) |
| C(8)—B(9) | 1.638 (7) | C(31*A*)—C(32*A*) | 1.43 (3) |
| C(8)—C(81) | 1.505 (5) | C(31*B*)—C(32*B*) | 1.46 (3) |
| B(9)—B(10) | 1.839 (8) | | |
| B(2)—B(1)—B(3) | 59.6 (3) | B(4)—C(8)—C(81) | 120.6 (3) |
| B(2)—B(1)—B(6) | 59.2 (3) | C(7)—C(8)—C(81) | 118.6 (3) |
| B(3)—B(1)—B(4) | 59.5 (3) | B(9)—C(8)—C(81) | 118.4 (3) |
| B(4)—B(1)—B(5) | 58.9 (3) | B(4)—B(9)—B(5) | 58.1 (3) |
| B(5)—B(1)—B(6) | 61.1 (3) | B(4)—B(9)—C(8) | 59.2 (3) |
| B(1)—B(2)—B(3) | 59.4 (3) | B(5)—B(9)—B(10) | 59.5 (3) |
| B(1)—B(2)—B(6) | 61.4 (3) | B(5)—B(10)—B(6) | 61.4 (3) |
| B(3)—B(2)—C(7) | 61.1 (3) | B(5)—B(10)—B(9) | 58.5 (3) |
| B(6)—B(2)—B(11) | 59.3 (3) | B(6)—B(10)—B(11) | 58.9 (3) |
| C(7)—B(2)—B(11) | 55.6 (3) | B(2)—B(11)—B(6) | 60.0 (3) |
| B(1)—B(3)—B(2) | 61.0 (3) | B(2)—B(11)—C(7) | 60.3 (3) |
| B(1)—B(3)—B(4) | 60.5 (3) | B(6)—B(11)—B(10) | 59.8 (3) |
| B(2)—B(3)—C(7) | 58.8 (3) | C(7)—C(71)—C(72) | 123.4 (4) |
| B(4)—B(3)—C(8) | 59.0 (3) | C(7)—C(71)—C(76) | 119.3 (4) |
| C(7)—B(3)—C(8) | 54.2 (3) | C(72)—C(71)—C(76) | 117.2 (4) |
| B(1)—B(4)—B(3) | 60.0 (3) | C(71)—C(72)—C(73) | 121.6 (5) |
| B(1)—B(4)—B(5) | 61.4 (3) | C(72)—C(73)—C(74) | 120.2 (6) |
| B(3)—B(4)—C(8) | 60.6 (3) | C(73)—C(74)—C(75) | 118.7 (6) |
| B(5)—B(4)—B(9) | 60.3 (3) | C(74)—C(75)—C(76) | 120.7 (6) |
| C(8)—B(4)—B(9) | 55.7 (3) | C(71)—C(76)—C(75) | 121.6 (5) |
| B(1)—B(5)—B(4) | 59.6 (3) | C(8)—C(81)—C(82) | 123.0 (4) |
| B(1)—B(5)—B(6) | 60.1 (3) | C(8)—C(81)—C(86) | 118.8 (4) |
| B(4)—B(5)—B(9) | 61.7 (3) | C(82)—C(81)—C(86) | 118.1 (4) |
| B(6)—B(5)—B(10) | 58.6 (3) | C(81)—C(82)—C(83) | 120.7 (4) |
| B(9)—B(5)—B(10) | 62.0 (3) | C(82)—C(83)—C(84) | 120.8 (5) |
| B(1)—B(6)—B(2) | 59.4 (3) | C(83)—C(84)—C(85) | 118.9 (5) |
| B(1)—B(6)—B(5) | 58.8 (3) | C(84)—C(85)—C(86) | 120.6 (5) |
| B(2)—B(6)—B(11) | 60.7 (3) | C(81)—C(86)—C(85) | 120.8 (4) |
| B(5)—B(6)—B(10) | 60.0 (3) | C(11*A*)—N—C(21*A*) | 111.5 (9) |
| B(10)—B(6)—B(11) | 61.3 (3) | C(11*A*)—N—C(31*A*) | 108.2 (12) |
| B(2)—C(7)—B(3) | 60.1 (3) | C(11*B*)—N—C(21*B*) | 113.3 (14) |
| B(2)—C(7)—B(11) | 64.1 (3) | C(11*B*)—N—C(31*B*) | 102.8 (9) |
| B(2)—C(7)—C(71) | 120.6 (3) | C(21*B*)—N—C(31*B*) | 131.7 (15) |
| B(3)—C(7)—C(8) | 62.0 (3) | C(21*A*)—N—C(31*A*) | 104.1 (12) |
| B(3)—C(7)—C(71) | 118.8 (3) | N—C(11*A*)—C(12) | 114.0 (10) |
| C(8)—C(7)—C(71) | 118.6 (3) | N—C(11*B*)—C(12) | 103.7 (10) |
| B(11)—C(7)—C(71) | 118.1 (4) | N—C(21*B*)—C(22*B*) | 104.3 (21) |
| B(3)—C(8)—B(4) | 60.4 (3) | N—C(21*A*)—C(22*A*) | 106.8 (10) |
| B(3)—C(8)—C(7) | 63.7 (3) | N—C(31*A*)—C(32*A*) | 115.1 (20) |
| B(3)—C(8)—C(81) | 117.6 (3) | N—C(31*B*)—C(32*B*) | 99.8 (13) |
| B(4)—C(8)—B(9) | 65.1 (3) | | |

parameters, and Table 2 details internuclear distances not involving H atoms and selected interbond angles thereby derived for the [HNEt$_3$]$^+$ salt. Equivalent information for the [Me$_3$NCH$_2$C$_6$H$_5$]$^+$ salt is contained in Tables 3 and 4, respectively. Fig. 1 shows a perspective view of a single molecule of the anion (that actually plotted is the [HNEt$_3$]$^+$ salt, but the anion in both determinations appears practically identical) and gives the atomic numbering scheme. Note that H(*endo*) appears as H(12) in the determination of the [HNEt$_3$]$^+$ salt and H(10*B*) in the determination of the [Me$_3$NCH$_2$C$_6$H$_5$]$^+$ salt.

These structural studies confirm the identity of the anion as [7,8-Ph$_2$-7,8-*nido*-C$_2$B$_9$H$_{10}$]$^-$. As expected (Wade, 1971), the anion geometry is that of a *nido* fragment of an icosahedron. In both determinations the anion suffers partial disorder, manifested by the appearance of electron density (0.64 e Å$^{-3}$ in the case of the [HNEt$_3$]$^+$ salt; 0.94 e Å$^{-3}$ in the case of the [Me$_3$NCH$_2$C$_6$H$_5$]$^+$ salt) in the 12th icosahedral position. As each of the anion's phenyl substituents appear ordered it is likely that in both cases this residual electron density arises from incomplete occupation of the B(3) cage position, but the degree of disorder is clearly small and in neither case is the refined $U_{\rm eq}$ value of B(3) anomalously large when this atom is refined with full occupancy. Most of the triethylammonium cation is also disordered.

The anions have near $C_s$ symmetry about a plane passing through B(1), B(3) and B(10). The lower pentagonal rings [B(2), B(3), B(4), B(5), B(6)] are essentially planar {$\sigma = 0.003$ and 0.016 Å for [HNEt$_3$]$^+$ and [Me$_3$NCH$_2$C$_6$H$_5$]$^+$ salts, respectively [$\sigma = (\sum z_i^2)^{1/2}$, where $z_i$ is the displacement of the *i*th atom from the least-squares plane]}, but the upper C$_2$B$_3$ rings are not ($\sigma = 0.049$ and 0.050 Å, respectively), each being folded into an envelope conformation. In the case of the [HNEt$_3$]$^+$ salt, this fold (4.4°)

Table 3. *Fractional coordinates and equivalent isotropic thermal parameters* (Å$^2$) *for non*-H *atoms in* [$(CH_3)_3NCH_2Ph$][7,8-$Ph_2$-7,8-*nido*-$C_2B_9H_{10}$]

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| B(1) | 0.5435 (3) | −0.68272 (14) | −0.30457 (22) | 0.0367 (15) |
| B(2) | 0.54174 (25) | −0.60240 (13) | −0.27735 (22) | 0.0343 (14) |
| B(3) | 0.3969 (3) | −0.63991 (14) | −0.35050 (25) | 0.0424 (17) |
| B(4) | 0.39660 (25) | −0.71428 (12) | −0.28893 (23) | 0.0342 (14) |
| B(5) | 0.54012 (24) | −0.72280 (13) | −0.17422 (22) | 0.0343 (14) |
| B(6) | 0.63337 (25) | −0.65163 (13) | −0.16668 (23) | 0.0356 (15) |
| C(7) | 0.40440 (20) | −0.59031 (10) | −0.23629 (18) | 0.0277 (12) |
| C(8) | 0.32363 (20) | −0.65294 (10) | −0.24159 (18) | 0.0276 (12) |
| B(9) | 0.39669 (24) | −0.70195 (12) | −0.14091 (22) | 0.0324 (14) |
| B(10) | 0.54984 (24) | −0.66878 (13) | −0.06127 (22) | 0.0327 (14) |
| B(11) | 0.53948 (25) | −0.59203 (12) | −0.12985 (22) | 0.0334 (14) |
| C(71) | 0.32655 (21) | −0.53165 (10) | −0.26517 (19) | 0.0316 (12) |
| C(72) | 0.2476 (3) | −0.51717 (12) | −0.37649 (22) | 0.0436 (15) |
| C(73) | 0.1721 (3) | −0.46427 (14) | −0.3961 (3) | 0.0516 (17) |
| C(74) | 0.1727 (3) | −0.42440 (13) | −0.3068 (3) | 0.0526 (18) |
| C(75) | 0.25170 (25) | −0.43740 (13) | −0.1963 (3) | 0.0469 (16) |
| C(76) | 0.32641 (23) | −0.49036 (11) | −0.17596 (22) | 0.0367 (14) |
| C(81) | 0.17885 (20) | −0.64790 (10) | −0.27410 (18) | 0.0278 (11) |
| C(82) | 0.09892 (23) | −0.66809 (11) | −0.38085 (21) | 0.0363 (13) |
| C(83) | −0.03526 (23) | −0.66437 (12) | −0.40560 (23) | 0.0414 (15) |
| C(84) | −0.09154 (24) | −0.64015 (13) | −0.3252 (3) | 0.0474 (16) |
| C(85) | −0.01311 (23) | −0.61965 (12) | −0.21893 (24) | 0.0434 (15) |
| C(86) | 0.12052 (21) | −0.62343 (11) | −0.19342 (22) | 0.0350 (13) |
| N | −0.02785 (17) | −0.82683 (9) | −0.18356 (16) | 0.0327 (11) |
| C(1) | 0.0961 (3) | −0.79193 (14) | −0.1679 (3) | 0.0498 (17) |
| C(2) | −0.1174 (3) | −0.78885 (13) | −0.13586 (23) | 0.0422 (15) |
| C(3) | 0.0022 (3) | −0.88648 (12) | −0.11812 (25) | 0.0426 (15) |
| C(4) | −0.08716 (25) | −0.83870 (13) | −0.31385 (20) | 0.0411 (15) |
| C(41) | −0.21154 (24) | −0.87444 (12) | −0.34244 (21) | 0.0402 (14) |
| C(42) | −0.3309 (3) | −0.84562 (15) | −0.36198 (25) | 0.0512 (17) |
| C(43) | −0.4436 (3) | −0.87970 (18) | −0.3839 (3) | 0.0662 (22) |
| C(44) | −0.4363 (3) | −0.94263 (20) | −0.3873 (4) | 0.082 (3) |
| C(45) | −0.3207 (3) | −0.97157 (17) | −0.3727 (4) | 0.0785 (25) |
| C(46) | −0.2090 (3) | −0.93769 (14) | −0.3493 (3) | 0.0571 (19) |

Table 4. *Interatomic distances* (Å) *and interbond angles* (°) *in* [$(CH_3)_3NCH_2Ph$][7,8-$Ph_2$-7,8-*nido*-$C_2B_9H_{10}$]

| | | | |
|---|---|---|---|
| B(1)—B(2) | 1.771 (4) | B(9)—B(10) | 1.800 (4) |
| B(1)—B(3) | 1.775 (4) | B(10)—B(11) | 1.843 (4) |
| B(1)—B(4) | 1.779 (4) | C(71)—C(72) | 1.396 (4) |
| B(1)—B(5) | 1.795 (4) | C(71)—C(76) | 1.393 (3) |
| B(1)—B(6) | 1.789 (4) | C(72)—C(73) | 1.385 (4) |
| B(2)—B(3) | 1.753 (4) | C(73)—C(74) | 1.373 (4) |
| B(2)—B(6) | 1.765 (4) | C(74)—C(75) | 1.381 (4) |
| B(2)—C(7) | 1.704 (4) | C(75)—C(76) | 1.381 (4) |
| B(2)—B(11) | 1.787 (4) | C(81)—C(82) | 1.391 (3) |
| B(3)—B(4) | 1.772 (4) | C(81)—C(86) | 1.398 (3) |
| B(3)—C(7) | 1.722 (4) | C(82)—C(83) | 1.390 (4) |
| B(3)—C(8) | 1.728 (4) | C(83)—C(84) | 1.378 (4) |
| B(4)—B(5) | 1.758 (4) | C(84)—C(85) | 1.383 (4) |
| B(4)—C(8) | 1.719 (3) | C(85)—C(86) | 1.383 (4) |
| B(4)—B(9) | 1.792 (4) | N—C(1) | 1.497 (4) |
| B(5)—B(6) | 1.827 (4) | N—C(2) | 1.498 (3) |
| B(5)—B(9) | 1.758 (4) | N—C(3) | 1.497 (3) |
| B(5)—B(10) | 1.768 (4) | N—C(4) | 1.529 (3) |
| B(6)—B(10) | 1.784 (4) | C(4)—C(41) | 1.497 (4) |
| B(6)—B(11) | 1.770 (4) | C(41)—C(42) | 1.386 (4) |
| C(7)—C(8) | 1.602 (3) | C(41)—C(46) | 1.373 (4) |
| C(7)—B(11) | 1.636 (3) | C(42)—C(43) | 1.378 (5) |
| C(7)—C(71) | 1.506 (3) | C(43)—C(44) | 1.366 (5) |
| C(8)—B(9) | 1.630 (3) | C(44)—C(45) | 1.358 (6) |
| C(8)—C(81) | 1.497 (3) | C(45)—C(46) | 1.365 (5) |
| B(2)—B(1)—B(3) | 59.25 (16) | C(7)—C(8)—C(81) | 117.40 (18) |
| B(2)—B(1)—B(6) | 59.46 (15) | B(9)—C(8)—C(81) | 119.05 (18) |
| B(3)—B(1)—B(4) | 59.80 (16) | B(4)—B(9)—B(5) | 59.35 (15) |
| B(4)—B(1)—B(5) | 58.92 (15) | B(4)—B(9)—C(8) | 60.10 (14) |
| B(5)—B(1)—B(6) | 61.28 (15) | B(5)—B(9)—B(10) | 59.60 (15) |
| B(1)—B(2)—B(3) | 60.49 (16) | B(5)—B(10)—B(6) | 61.88 (15) |
| B(1)—B(2)—B(6) | 60.79 (16) | B(5)—B(10)—B(9) | 59.03 (15) |
| B(3)—B(2)—C(7) | 59.75 (15) | B(6)—B(10)—B(11) | 58.39 (15) |
| B(6)—B(2)—B(11) | 59.76 (15) | B(2)—B(11)—B(6) | 59.51 (15) |
| C(7)—B(2)—B(11) | 55.83 (14) | B(2)—B(11)—C(7) | 59.52 (14) |
| B(1)—B(3)—B(2) | 60.26 (16) | B(6)—B(11)—B(10) | 59.15 (15) |
| B(1)—B(3)—B(4) | 60.21 (16) | C(7)—C(71)—C(72) | 123.71 (21) |
| B(2)—B(3)—C(7) | 58.72 (15) | C(7)—C(71)—C(76) | 119.18 (20) |
| B(4)—B(3)—C(8) | 58.82 (15) | C(72)—C(71)—C(76) | 117.02 (22) |
| C(7)—B(3)—C(8) | 55.32 (14) | C(71)—C(72)—C(73) | 121.00 (25) |
| B(1)—B(4)—B(3) | 59.99 (16) | C(72)—C(73)—C(74) | 121.0 (3) |
| B(1)—B(4)—B(5) | 61.00 (15) | C(73)—C(74)—C(75) | 118.9 (3) |
| B(3)—B(4)—C(8) | 59.33 (15) | C(74)—C(75)—C(76) | 120.4 (3) |
| B(5)—B(4)—B(9) | 59.37 (15) | C(71)—C(76)—C(75) | 121.69 (23) |
| C(8)—B(4)—B(9) | 55.26 (14) | C(8)—C(81)—C(82) | 122.65 (20) |
| B(1)—B(5)—B(4) | 60.08 (15) | C(8)—C(81)—C(86) | 119.11 (20) |
| B(1)—B(5)—B(6) | 59.20 (15) | C(82)—C(81)—C(86) | 118.22 (21) |
| B(4)—B(5)—B(9) | 61.28 (15) | C(81)—C(82)—C(83) | 120.59 (22) |
| B(6)—B(5)—B(10) | 59.49 (15) | C(82)—C(83)—C(84) | 120.60 (24) |
| B(9)—B(5)—B(10) | 61.37 (15) | C(83)—C(84)—C(85) | 119.4 (3) |
| B(1)—B(6)—B(2) | 59.75 (15) | C(84)—C(85)—C(86) | 120.39 (25) |
| B(1)—B(6)—B(5) | 59.52 (15) | C(81)—C(86)—C(85) | 120.83 (22) |
| B(2)—B(6)—B(11) | 60.73 (15) | C(1)—N—C(2) | 108.75 (20) |
| B(5)—B(6)—B(10) | 58.63 (15) | C(1)—N—C(3) | 108.60 (20) |
| B(10)—B(6)—B(11) | 62.47 (15) | C(1)—N—C(4) | 108.02 (19) |
| B(2)—C(7)—B(3) | 61.53 (16) | C(2)—N—C(3) | 109.90 (19) |
| B(2)—C(7)—B(11) | 64.65 (15) | C(2)—N—C(4) | 110.80 (19) |
| B(2)—C(7)—C(71) | 122.25 (18) | C(3)—N—C(4) | 110.70 (19) |
| B(3)—C(7)—C(8) | 62.52 (15) | N—C(4)—C(41) | 113.89 (21) |
| B(3)—C(7)—C(71) | 116.54 (19) | C(4)—C(41)—C(42) | 121.96 (24) |
| C(8)—C(7)—C(71) | 116.47 (18) | C(4)—C(41)—C(46) | 119.86 (24) |
| B(11)—C(7)—C(71) | 120.62 (19) | C(42)—C(41)—C(46) | 118.2 (3) |
| B(3)—C(8)—B(4) | 61.85 (15) | C(41)—C(42)—C(43) | 120.8 (3) |
| B(3)—C(8)—C(7) | 62.16 (15) | C(42)—C(43)—C(44) | 119.0 (3) |
| B(3)—C(8)—C(81) | 117.13 (19) | C(43)—C(44)—C(45) | 121.0 (4) |
| B(4)—C(8)—B(9) | 64.64 (15) | C(44)—C(45)—C(46) | 119.8 (4) |
| B(4)—C(8)—C(81) | 120.61 (18) | C(41)—C(46)—C(45) | 121.2 (3) |

is convex about the C(8)···B(10) vector, whereas for the [$Me_3NCH_2C_6H_5$]$^+$ salt the fold (4.2°) is concave about the B(9)···B(11) vector. However, these structural differences are slight, as is demonstrated by the calculation of an overall root-mean-square misfit (Macgregor, Wynd, Gould, Moulden, Taylor, Yellowlees & Welch, 1991) of only 0.024 Å between the $C_2B_9$ portions of both anions.

The major deviation form $C_s$ symmetry of the anions in the solid state, indeed the major structural difference between the anions in the two crystallographic determinations, resides in the twists of the phenyl substituents about their C(cage)—C(aryl) bonds. As previously noted (Lewis & Welch, 1993*a*), it is convenient to describe these twists by the parameter $\theta$. In both salts of [7,8-$Ph_2$-7,8-*nido*-$C_2B_9H_{10}$]$^-$ studied herein, $\theta$ values are generally low, so that in a broad sense both phenyl groups can be described as lying essentially orthogonal to the open $C_2B_3$ carbaborane face. In detail, however, both phenyl rings in each salt are measurably twisted from this extreme position in a conrotatory manner, recording $\theta$ values of 5.6 [ring C(71)–C(76)] and 10.0° [ring C(81)–C(86)] in the [$HNEt_3$]$^+$ salt, and 17.9 [C(71)–C(76)] and 20.0° [C(81)–C(86)] in the [$Me_3NCH_2C_6H_5$]$^+$ salt. Molecular-orbital (MO) calculations at the extended Hückel level on 1,2-$Ph_2$-1,2-*closo*-$C_2B_{10}H_{10}$ (Lewis & Welch, 1993*a*) imply that the energies required for twists of these magnitudes are well within the range of crystal packing forces, and it may be significant in this respect that, in the crystal of the [$Me_3NCH_2C_6H_5$]$^+$ salt, ring C(81)–C(86) is proximal to the C(1)$H_3$ methyl group of the cation [shortest contacts H(14)···C(81) 2.75 (3), H(14)···C(82) 2.84 (3), H(14)···C(86) 2.82 (3) Å]. Were these contacts to be responsible for the twist of the C(81)–

C(86) ring it would be likely that the C(71)–C(76) ring would twist in the same sense by roughly the same amount as a consequence of interphenyl intramolecular crowding. In the following paper (Lewis & Welch, 1993*b*), a further example of this structural cooperation between the adjacent phenyl rings of carbaboranes is described.

Inclusion of one or both phenyl rings in the misfit calculations has the expected results; the $\{C_2B_{10}[C(81)–C(86)]\}$ fragments have an r.m.s. misfit of 0.086 Å and the $\{C_2B_{10}[C(71)–C(76)]\}$ fragments an r.m.s. misfit of 0.160 Å, the greatest individual misfits occurring for the *ortho* and *meta* C atoms. For $\{C_2B_{10}[C_6]_2\}$ fragments the r.m.s. misfit is 0.184 Å.

The C(7)—C(8) distance, 1.590 (5) Å in the $[HNEt_3]^+$ salt and 1.602 (3) Å in the $[Me_3NCH_2C_6H_5]^+$ salt, is substantially less than the C(cage)—C(cage) distance in 1,2-$Ph_2$-1,2-*closo*-$C_2B_{10}H_{10}$ (Lewis & Welch, 1993*a*). This is an important result since it shows that aryl-bearing cage C atoms can approach to within reasonably short distances [for comparison, C—C in [7,8-*nido*-$C_2B_9H_{12}]^-$ is 1.542 (4) Å (Buchanan, Hamilton, Reed & Welch, 1990)] and it supports the conclusion (Lewis & Welch, 1993*a*) that there is an electronic contribution to the long C(cage)—C(cage) connectivity in 1,2-$Ph_2$-1,2-*closo*-$C_2B_{10}H_{10}$ at low $\theta$ values. In fact, the change in the C(cage)—C(cage) length is only one of three measurable structural differences between 1,2-$Ph_2$-1,2-*closo*-$C_2B_{10}H_{10}$ and [7,8-$Ph_2$-7,8-*nido*-$C_2B_9H_{10}]^-$, the others being ⟨facial B—B⟩ and ⟨facial B—C⟩, where facial refers to the open $C_2B_3$ face of the *nido* polyhedron as a capping $\{BH\}^{2+}$ fragment is replaced by an *endo* [to B(10)] proton. Table 5 summarizes the relevant parameters and shows that from 1,2-$Ph_2$-1,2-*closo*-$C_2B_{10}H_{10}$ to [7,8-$Ph_2$-7,8-*nido*-$C_2B_9H_{10}]^-$, ⟨facial B—B⟩ lengthens, ⟨facial B—C⟩ shortens and, as previously noted, C—C shortens.

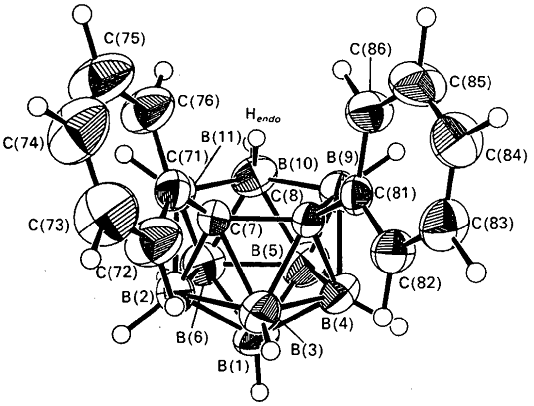

Fig. 1. Perspective view of [7,8-$Ph_2$-7,8-*nido*-$C_2B_9H_{10}]^-$ ($[HNEt_3]^+$ salt, 50% thermal ellipsoids, except for H atoms which have artificial radii of 0.1 Å for clarity).

Table 5. *Comparison of key molecular parameters* (Å) *in* 1,2-$Ph_2$-1,2-*closo*-$C_2B_{10}H_{10}$ *and* [7,8-$Ph_2$-7,8-*nido*-$C_2B_9H_{10}]^-$

| | 1,2-$Ph_2$-1,2-*closo*-$C_2B_{10}H_{10}$ | [7,8-$Ph_2$-7,8-*nido*-$C_2B_9H_{10}]^-$ |
|---|---|---|
| ⟨Facial B—B⟩ | 1.767 (8)[a,g] | 1.819 (25)[b,g] |
| ⟨Facial B—C⟩ | 1.710 (5)[c,g] | 1.634 (3)[d,g] |
| ⟨C—C⟩ | 1.727 (4)[e,h] | 1.596 (4)[f,h] |

Notes: (*a*) average of 8 measurements over 2 molecules, range 1.754 (6)–1.781 (6) Å; (*b*) average of 4 measurements over 2 molecules, range 1.795 (8)–1.843 (4) Å; (*c*) 8 measurements, 1.700 (5)–1.715 (5) Å; (*d*) 4 measurements, 1.630 (3)–1.638 (7) Å; (*e*) 2 measurements, 1.720 (4) and 1.733 (4) Å; (*f*) 2 measurements, 1.590 (5) and 1.602 (3) Å; (*g*) e.s.d. of mean from $(\text{e.s.d.})^2 = [\sum(\kappa_i - \kappa_{\text{bar}})^2]/(N-1)$ where $\kappa_i$ is the $i$th e.s.d. and $\kappa_{\text{bar}}$ the mean of $N$ similar types; (*h*) e.s.d. of mean is mean e.s.d.

These changes are fully analogous to those previously identified in the comparison of [3-$PPh_3$-3,1,2-*closo*-$CuC_2B_9H_{11}]^-$ (Do, Kang, Knobler & Hawthorne, 1987) and [7,8-*nido*-$C_2B_9H_{12}]^-$ (Buchanan, Hamilton, Reed & Welch, 1990), and have been traced (Hamilton & Welch, 1990) to differing degrees of depopulation of the filled $\pi$ MO's of [7,8-*nido*-$C_2B_9H_{11}]^{2-}$ by zero-electron three-orbital ($\{R_3PCu\}^+$ or $\{BH\}^{2+}$) and zero-electron one-orbital ($H^+$) units.

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