

Polyhedral monocarbaborane chemistry. Carboxylic acid derivatives of the $[closo-2-CB_9H_{10}]^-$ anion

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Reaction of $B_{10}H_{14}$ with *para*-(OHC) C_6H_4 (COOH) in aqueous KOH gives the $[nido-6-CB_9H_{11}-6-(C_6H_4-para-COOH)]^-$ anion **1** which upon cluster closure with iodine in alkali solution gives the $[closo-2-CB_9H_9-2-(C_6H_4-para-COOH)]^-$ anion **2**; an analogous procedure with $B_{10}H_{14}$ and glyoxalic acid OHCCOOH gives the $[closo-2-CB_9H_9-2-(COOH)]^-$ anion **4** via the $[arachno-6-CB_9H_{13}-6-(COOH)]^-$ anion **3**.

There is interest in the functionalization of stable *closo* boranes and *closo* dicarbaboranes for use as synthons or building-blocks for potential life-science^{1,2} and nano-architectural applications.^{3,4,5} Our laboratory has become interested in extending this functionalisation chemistry to the intermediate monocarbaboranes. Monocarbaboranes offer complementary charge and polarity possibilities compared to the boranes on one hand and to the dicarbaboranes on the other hand. In this regard, monocarbaborane units with synthetically useful amine residues $\{NH_2\}$ are readily available. These $\{NH_2\}$ units may be directly bound to the monocarbaborane cluster, as in the $[1-(H_2N)-closo-1-CB_{11}H_{11}]^-$ anion that is isolatable from the classical route to the *closo* twelve-vertex monocarbaborane clusters,^{6,7} or less directly bound, as in the isomers of $[para-(H_2N)-C_6H_4-closo-CB_9H_9]^-$ pioneered by Sivaev and co-workers.^{8,9} Carboxylate units are complementary to $\{NH_2\}$ groupings in synthetic reactions,^{9,10} and in this context we here report preliminary results on the hitherto elusive carboxylic acid $\{COOH\}$ derivatives of the *closo* $\{CB_9\}$ residue. We have established examples that show that the acid unit can be bound either directly to the carbon atom of the constituents of the cluster, or indirectly, here by utilization of a $\{para-C_6H_4(COOH)\}$ unit bound to the cluster. Both procedures make initial use of the Brellochs Reaction¹¹ for the direct generation of functional ten-vertex $\{CB_9\}$ monocarbaboranes from the reaction of functional aldehydes with *nido*- $B_{10}H_{14}$, and further demonstrate the useful versatility of this reaction.

Thus, 4-carboxybenzaldehyde, *para*-(OHC) C_6H_4 (COOH), reacts in strong alkaline solution with *nido*- $B_{10}H_{14}$ to form the ten-vertex $[nido-6-CB_9H_{11}-6-(C_6H_4-para-COOH)]^-$ anion **1**, isolatable in 62% yield as its $[NEt_4]^+$ salt **1a**.^{12a} In strong alkaline solution anion **1** thence reacts with elemental iodine with cage closure to form the $[closo-2-CB_9H_9-2-(C_6H_4-para-COOH)]^-$ anion **2**, isolatable as its $[NEt_4]_3[CB_9H_9(C_6H_4COOH)]_2Br$ double salt **2a** in 73% yield.^{12b} In a similar manner, by the successive dissolution in strong alkaline solution of glyoxylic acid monohydrate, $[OHCCO_2H(OH_2)]$, and *nido*- $B_{10}H_{14}$, the $[arachno-6-CB_9H_{13}-6-(COOH)]^-$ anion **3** can be obtained in 53% yield as its $[NEt_4]^+$ salt **3a**.^{12c} In strong alkaline solution anion **3** undergoes cage closure with elemental iodine to give the $[closo-2-CB_9H_9-2-(COOH)]^-$ anion **4**, isolatable as its $[NEt_4]^+$ salt **4a** in 92% yield.^{12d} Both new *closo* anions **2** and **4** are characterised by single-crystal X-ray diffraction analysis,¹³ anion **4** in its $[NEt_4]^+$ salt **4a**, and anion **2** in the $[NEt_4]_3[CB_9H_9(C_6H_4COOH)]_2Br$ double salt **2a** (Fig. 1). Salient interatomic dimensions are given in the caption to Fig. 1.

The crystallographically determined cluster structure of anion **2** is relatively symmetrical across the B(1)C(2)B(10) plane. By contrast, the crystallographic analysis of intramolecular C–B distances in anion **4** gives an apparent significant asymmetry about C(2). There are two independent molecules of **4** in the crystal of **4a**. In molecule A, C(2)–B(3) is much shorter than C(2)–B(5), and, conversely, C(2)–B(6) is much longer than C(2)–B(9). At first sight, it is tempting to ascribe this to differential *trans* effects arising from C=O versus COH in the $\{COOH\}$ group, but molecule B shows the converse asymmetry, with C(2)–B(3) being much longer than C(2)–B(5), and C(2)–B(6) is much shorter than C(2)–B(9), suggesting a crystallographic artefact. A more definitive difference between anions **2** and **4** is that the C(2)–B(1) distance in the directly carboxylated cluster species **4** is shorter than C(2)–B(1) in **2**, and C(2)–C(3) in **4** is shorter than both C(2)C(21) and C(24)–

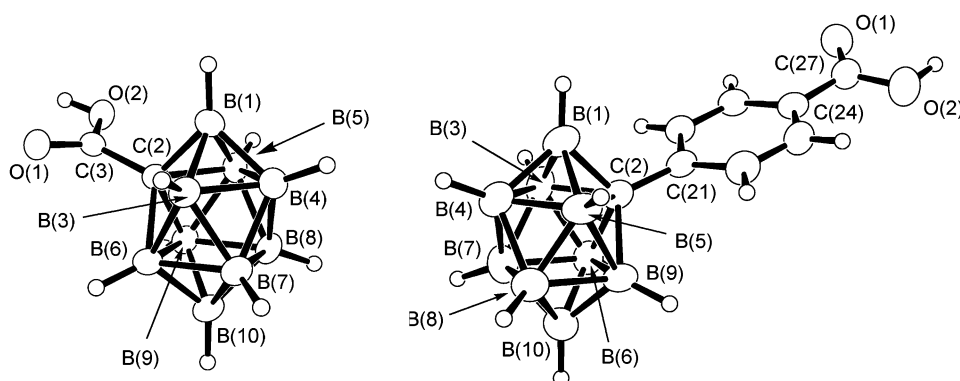


Fig. 1 Crystallographically determined molecular structures¹³ of (left) the $[closo-2-CB_9H_9-2-(C_6H_4-para-COOH)]^-$ anion **2** in its $[NEt_4]_3[CB_9H_9(C_6H_4COOH)]_2Br$ double salt **2a** and (right) the $[closo-2-CB_9H_9-2-(COOH)]^-$ anion **4** in its $[NEt_4]^+$ salt **4a**. In **2a** the C(2)–C(21) distance is 1.497(4), the C(24)C(27) distance is 1.492(4) Å, the O(1)C(27) distance is 1.207(4) Å, the O(2)C(27) distance is 1.320(4) Å and the O(1)C(27)O(2) angle is 123.5(3)°; within the cluster, C(2)B(1) is 1.637(4), C(2)B(3) is 1.753(5), C(2)B(5) is 1.769(4), C(2)B(6) is 1.752(4) and C(2)B(9) is 1.756(4) Å. There are two independent molecules, A and B, of **4** in the unit cell of **4a**; the molecular structure of only one of these (anion A) is shown. Dimensions for the anions A and B are closely related (see text). In anion A, the C(2)C(3) distance is 1.465(3) Å, the O(1)C(3) distance is 1.221(2) Å, the O(2)C(3) distance is 1.293(2) Å and the O(1)C(3)O(2) angle is 123.14(18)°; within the cluster, C(2)B(1) is 1.603(3), C(2)B(3) is 1.703(3), C(2)B(5) is 1.761(3), C(2)B(6) is 1.754(3) and C(2)B(9) is 1.730(3) Å. In anion B, the C(2)C(3) distance is 1.473(3) Å, the O(1)C(3) distance is 1.188(2) Å, the O(2)C(3) distance is 1.291(2) Å and the O(1)C(3)O(2) angle is 121.57(19)°; within the cluster, C(2)B(1) is 1.606(3), C(2)B(3) is 1.765(3), C(2)B(5) is 1.698(3), C(2)B(6) is 1.732(3) and C(2)B(9) is 1.732(3) Å.

C(27) in **2**, which suggest some multiple-bonding character in the cluster-to-carboxylate linkage C(2)–C(3) in **4**. There is also an interesting difference in intermolecular interaction behaviour when the anions in **2a** and **4a** are compared. Whereas hydrogen bonding between the carboxylic acid residues in **2a** results in an association of pairs of anions **2** to give conventional carboxylic acid dimeric units, for anion **4** the hydrogen bonding in **4a** gives a less common assembly of four {COOH} units, rather than the dimeric configuration. We hope to address these and related phenomena in more detail when this and related work is complete and presented in full description.

It is anticipated that these carboxylic acid species, and analogous derivatives of related cluster species, will constitute very useful intermediates for molecular architectural constructions and for the synthesis of molecules to be investigated for potential life-science applications. They offer opportunity for derivatisation for further useful functionalization, e.g. for acid chloride formation which could be useful for the generation of amide linkages, and for reduction to alcohols and subsequent reoxidation to aldehydes, both of which offer further synthetic potential. Also, in principle, they can be isomerised to their *closo*-1-monocarbadecaborane isomers,⁸ permitting more subtle permutations in molecular configuration that could be useful in the fine-tuning of any emerging effect chemistry. We currently devise experimentation to examine some of these possibilities.

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- 12 All reactions were carried out under dry N₂, followed by work-up in air. (a) **Anion 1**, *para*-(OHC)C₆H₄(COOH) (15 g, 100 mmol) was added to a stirred solution of KOH (11.2 g, 200 mmol) in H₂O (100 ml) at 0 °C, and after 5 min, B₁₀H₁₄ (2.0 g, 16.4 mmol) was added. The orange solution was stirred for 3 h at ca. 20 °C, cooled to 0 °C, aqueous HCl (5%, 100 ml) added dropwise, the solution filtered, and [NEt₄]⁺Br[−] (4.20 g, 20 mmol) added to the filtrate. The [NEt₄]⁺ salt **1a** of the [*nido*-6-CB₉H₁₁-6-(C₆H₄-*para*-COOH)][−] anion **1** precipitated as a white solid, which was filtered off and dried *in vacuo* (2.46 g, 10.2 mmol, 62 %). NMR, (CD₃)₂CO, 294–299 K, ordered as assignment δ(¹¹B)/ppm [δ(¹H)/ppm]: BH(10) +2.2 [+3.89], BH(1) −2.7 [+3.38], BH(4) −20.8 [+1.29], BH(6,7) −25.5 [+0.92], BH(3,5) −28.4 [+1.73], BH(7,8) −28.4 [+0.64]; additionally δ(¹H)(COOH) +10.79 (broad), δ(¹H)(Ph) at +7.72 (2H) and +6.99 (2H) (both apparent doublets) and δ(¹H)(Et) at +3.49 (8H, quartet) and +1.40 ppm (12H, triplet), also δ(¹³C)(COOH) +173.0, δ(¹³C)(Ph) +153.2 (1C), +135.7 (1C), +128.9 (2C) and +127.0 (2C), with δ(¹³C)(cluster) +62.7 and δ(¹³C)(Et) +7.2 and +52.4 ppm. (b) **Anion 2**. A solution of **1a** (2.46 g, 10.2 mmol) in aqueous HCl (10%, 100 ml) was extracted with Et₂O (3 × 50 ml), the organic layers separated, combined, aqueous KOH (ca. 1 M; 200 ml) added, and the Et₂O evaporated *in vacuo*. Elemental I₂ (2.0 g, 8.0 mmol) was added to the resulting alkaline aqueous solution, which was then stirred for 3 h at ca. 20 °C, then cooled to 0 °C, whereupon Na₂SO₃ (1.26 g, 10 mmol) and aqueous HCl (5%, 100 ml) were added, the solution filtered, and [NEt₄]⁺Br[−] (2.1 g, 10.0 mmol) added to the filtrate. After brief stirring, the [NEt₄]⁺[NEt₄]Br double salt **2a** of the [*closo*-2-CB₉H₉-2-(C₆H₄-*para*-COOH)][−] anion **2** precipitated as a white microcrystalline solid, which was filtered off and dried *in vacuo* (4.32 g, 7.45 mmol, 73%). NMR, (CD₃)₂CO, 294–299 K, ordered as assignment δ(¹¹B)/ppm [δ(¹H)/ppm]: BH(10) +2.2 [+3.89], BH(1) −2.7 [+3.38], BH(4) −20.8 [+1.29], BH(6,7) −25.5 [+0.92], BH(3,5) −28.4 [+1.73], BH(7,8) −28.4 [+0.64]; additionally δ(¹H)(COOH) +10.79 (broad), δ(¹H)(Ph) at +7.72 (2H) and +6.99 (2H) (both apparent doublets) and δ(¹H)(Et) at +3.48 (16H, quartet) and +1.39 ppm (24H, triplet); also δ(¹³C)(COOH) at +167.1, δ(¹³C)(Ph) at +150.9 (1C), +141.9 (1C), +128.5 (2C) and +126.7 (2C), δ(¹³C)(cluster) at +47.12 and δ(¹³C)(Et) at +7.1 and +52.5 ppm. (c) **Anion 3**. [OHCCO₂H(OH₂)] (9.2 g, 100 mmol) was added to a stirred solution of KOH (11.2 g, 200 mmol) in H₂O (100 ml) at 0 °C, and, after 5 minutes, B₁₀H₁₄ (2.0 g, 16.4 mmol) was added. The yellow solution was stirred for 2 h at ca. 20 °C. [NEt₄]⁺Br[−] (4.2 g, 20 mmol) added, the solution cooled to 0 °C and aqueous HCl (5%, 150 ml) added dropwise. The [NEt₄]⁺ salt **3a** of the [*arachno*-6-CB₉H₁₃-6-(COOH)][−] anion **3** precipitated as a white solid that was filtered off and dried *in vacuo* (2.68 g, 8.73 mmol, 53%). NMR, (CD₃)₂CO, 294–299 K, ordered as assignment δ(¹¹B)/ppm [δ(¹H)/ppm]: BH(4) −0.6 [+2.35], BH(2) −9.4 [+2.02], BH(5,7) −9.4 [+2.43], BH(9) −20.0 [+1.14], BH(8,10) −27.9 [+0.89] and BH(1,3) −39.1 [+0.46], with δ(¹H) for μH(7,8)/(5,10) at −3.61 and for CH(6) at −0.75 ppm; additionally δ(¹H)(COOH) +10.14 (broad), δ(¹H)(Et) at +3.45 (8H, quartet) and +1.38 (12H, triplet) ppm, with δ(¹³C)(COOH) at +172.4, δ(¹³C)(cluster) at +17.0 and δ(¹³C)(Et) at +7.0 and +51.9 ppm. (d) **Anion 4**. A solution of **3a** (2.68 g, 8.73 mmol) in aqueous HCl (10%, 100 ml) was extracted with Et₂O (3 × 50 ml), the organic layers separated and combined, then aqueous KOH (ca. 1.5 M; 300 ml) was added to these, and the Et₂O evaporated *in vacuo*. Elemental I₂ (6.0 g, 24 mmol) was added to the resulting alkaline aqueous solution, which was then stirred for 3 h at ca. 20 °C, cooled to 0 °C, and then Na₂SO₃ (2.92 g, 23 mmol), and [NEt₄]⁺Br[−] (2.10 g, 10 mmol) were added, followed by aqueous HCl (5%, 200 ml) dropwise. After brief stirring, the white microcrystalline precipitate of the [NEt₄]⁺ salt **4a** of the [*closo*-2-CB₉H₉-2-(COOH)][−] anion **4** was filtered off, washed with H₂O (50 ml) and dried *in vacuo* (1.31 g, 8.03 mmol, 92%). NMR, (CD₃)₂CO, 294–299 K, ordered as assignment δ(¹¹B)/ppm [δ(¹H)/ppm]: BH(10) +0.81 [+3.76], BH(1) −5.2 [+3.53], BH(4) −21.7 [+1.20], BH(6,7) −26.7 [+0.92], BH(3,5) −29.2 [+1.49], BH(7,8) −29.7 [+0.51]; additionally δ(¹H)(COOH) +10.52 (broad), δ(¹H)(Et) at +3.52 (8H, quartet) and +1.40 ppm (12H, triplet), with δ(¹³C)(COOH) at +173.6, δ(¹³C)(cluster) at +45.8 and δ(¹³C)(Et) at +7.1 and +52.4 ppm.
- 13 Crystallographic data. The [NEt₄]₃[CB₉H₉(C₆H₄COOH)]₂Br double salt **2a** of anion **2**: C₄₀H₈₈B₁₈BrN₃O₄: *M* = 949.62, monoclinic (colourless prism from Et₂O-acetone), Space Group C2/c, *a* = 23.2400(4), *b* = 20.6240(4), *c* = 11.8850(2) Å, β = 103.3860(10)°, *U* = 5541.74(17) Å³, *D*_{calc} = 1.138 Mg m^{−3}, *Z* = 4, Mo-Kα, λ = 0.71073 Å, μ = 0.781 mm^{−1}, *T* = 150(2) K, *R*₁ = 0.065 for 4834 reflections with *I* > 2σ(*I*), and *wR*₂ = 0.1722 for all 6354 unique reflections; CCDC 211907. The [NEt₄]⁺ salt **4a** of anion **4**: C₂₆H₆₀B₁₈N₂O₄: *M* = 587.28, monoclinic (colourless prism from Et₂O-acetone), Space Group C2/c, *a* = 30.0062(3), *b* = 15.1936(2), *c* = 16.7407(2) Å, β = 112.0290(10)°, *U* = 7074.93(14) Å³, *D*_{calc} = 1.106 Mg m^{−3}, *Z* = 8, Mo-Kα, λ = 0.71073 Å, μ = 0.063 mm^{−1}, *T* = 150(2) K, *R*₁ = 0.0726 for 5668 reflections with *I* > 2σ(*I*), and *wR*₂ = 0.2306 for all 6957 unique reflections; CCDC 211908. See <http://www.rsc.org/suppdata/cc/b3/b311853n/> for crystallographic data in .cif or other electronic format. Methods and programs were standard (Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307).