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[*closo*-B$_{10}$H$_8$-1,10-(COOH)$_2$]$^{2-}$: a building block for functional materials?†

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[*closo*-B$_{10}$H$_8$-1,10-(COOH)$_2$]$^{2-}$ was obtained in five steps and 40% overall yield from [*closo*-B$_{10}$H$_{10}$]$^{2-}$. It can be converted to [*closo*-B$_{10}$H$_8$-1,10-(CO)$_2$] and subsequently to carbonium ylides [*closo*-B$_{10}$H$_8$-1-COOH-10-(C(NRCH$_2$)$_2$)]. The diacid, its derivatives and also di-ylide [*closo*-B$_{10}$H$_8$-1,10-(C(NHMe)$_2$)$_2$] are characterized by spectroscopic and single crystal XRD methods augmented with DFT methods.

The carboxylic group, COOH, is one of the most ubiquitous and versatile functionalities in chemistry, materials and biology.[1] Its properties are defined by the electronic and steric nature of the substituent to which it is connected. Among the most unusual carboxylic acids with low acidity are **1A**$^{2-}$ and **1B**$^{2-}$ derived from the Sigma-aromatic dianions [*closo*-B$_{12}$H$_{12}$]$^{2-}$ (**A**$^{2-}$)[2] and [*closo*-B$_{10}$H$_{10}$]$^{2-}$ (**B**$^{2-}$),[3] respectively (Fig. 1). Boron clusters, including anions **A**$^{2-}$ and **B**$^{2-}$, are of importance in the development of functional materials for photonic,[4] sensory,[5] medicinal,[6] energy storage and other applications.[7] The dicarboxylic acids **1A**$^{2-}$ and **1B**$^{2-}$ are potential ditopic building blocks for materials, such as coordination polymers[8] and functional metal–organic frameworks.[9] They also serve as useful starting compounds for other derivatives of anions **A**$^{2-}$ and **B**$^{2-}$, including highly basic ketones,[10] through standard functional group transformations.[10,11]

The previously described preparation of diacids **1**$^{2-}$ is cumbersome, involving either high-pressure Co-catalyzed carbonylation of the dianion **A**$^{2-}$ to form **2A** or diazotization of the dianion [*closo*-B$_{10}$H$_{10}$]$^{2-}$ (**B**$^{2-}$) followed by high pressure

thermolysis of the resulting [*closo*-B$_{10}$H$_8$-1,10-(N$_2$)$_2$] in the presence of CO (100 MPa and 140 °C) and hydrolysis.[11,12] The latter three-step process is low yield (12–17%) and inconvenient, discouraging further investigation of [*closo*-B$_{10}$H$_8$-1,10-(COOH)$_2$]$^{2-}$ (**1B**$^{2-}$) and its derivatives since the original reports by the DuPont group in the mid 60s.[10–12] The access to 1,10-disubstituted derivatives of dianion **B**$^{2-}$, such as diacid **1B**$^{2-}$, is complicated by the preferential substitution at the equatorial positions (B2–B9) rather than at the two apical sites of the parent [*closo*-B$_{10}$H$_{10}$]$^{2-}$ cluster.[3]

Herein we report convenient and efficient access to the diacid [*closo*-B$_{10}$H$_8$-1,10-(COOH)$_2$]$^{2-}$ (**1B**$^{2-}$) and its formal anhydride [*closo*-B$_{10}$H$_8$-1,10-(CO)$_2$] (**2B**). The latter can serve as a valuable precursor to esters and a novel class of diaminocarbonium ylides. We also provide complete NMR characterization, present four molecular structures, and augment experimental data with DFT results.

Preparation of diacid **1B**$^{2-}$ was initially attempted through hydrolysis of the readily available dinitrile [*closo*-B$_{10}$H$_8$-1,10-(CN)$_2$]$^{2-}$ (**3B**$^{2-}$).[13] The high electron density at the CN group made **3B**$^{2-}$ unreactive towards nucleophiles, while it surprisingly smoothly underwent *N*-methylation with CF$_3$SO$_3$Me (Scheme 1). The resulting bis zwitterion **4B** readily reacted under basic conditions and hydrolysed to the desired acid **1B**$^{2-}$. To complete the hydrolysis process, the reaction mixture
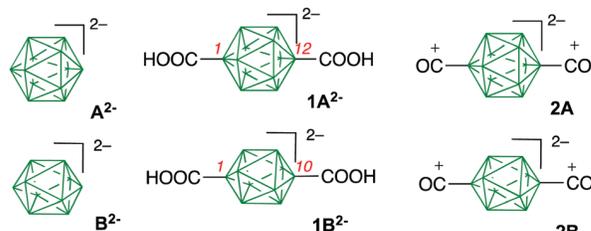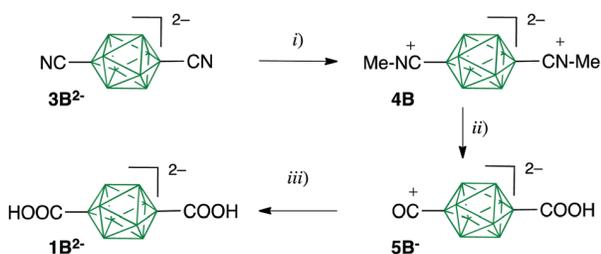
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Fig. 1 Structures of the parent dianions **A**$^{2-}$ and **B**$^{2-}$ and their dicarbonyl derivatives **1**$^{2-}$ and **2**. Substitution positions are indicated by the red numbers.

Scheme 1 Synthesis of dicarboxylic acid **1B²⁻**. Reagents and conditions: (i) CF₃SO₃Me, CH₂Cl₂, 0 °C to rt, 16 h, 67%; (ii) 1. aq NaOH, MeCN, 50 °C, 10 min; 2. Conc. HCl, 15 min; 3. aq NaOH, 50 °C, vacuum, 20 min; 4. Conc. HCl, CH₂Cl₂, [Bu₄N]⁺Cl⁻, stirring 5 min, 94%; (iii) [Bu₄N]⁺[OH]⁻, MeCN, rt, quant. yield.

Fig. 3 Left: The ¹¹B{¹H} NMR spectrum and the downfield portion of the ¹³C{¹H} NMR spectrum of **5B[Bu₄N]**. Right: Mid-range IR of **5B[Bu₄N]**.

was treated with aqueous HCl and subsequently with NaOH to remove MeNH₂. Addition of HCl and [Bu₄N]⁺Cl⁻, followed by extraction with CH₂Cl₂ gave carbonyl acid [*closo*-B₁₀H₈-10-CO-1-COOH]⁻ (**5B[Bu₄N]**) in 94% yield based on the zwitterion **4B** (Scheme 1) or 81% overall yield after recrystallization (acetone/water). The diacid **1B[Bu₄N]** was obtained by treatment of **5B[Bu₄N]** with [Bu₄N]⁺OH⁻. Overall, the diacid was obtained in five steps in about 40% yield from anion **B²⁻**, which is over twice the yield of the previously reported method.[11b,12]

The structure of **5B⁻** was confirmed with single crystal XRD (Fig. 2) and a strong IR stretching band at 2130 cm⁻¹ (Fig. 3). The experimental C≡O distance of 1.119(2) Å (calcd. at 1.222 Å) is the same as that in **2A**[14] but shorter than in the B(2) derivative [*closo*-B₁₀H₉-2-CO]⁻ (1.131(6) Å).[15]

The ¹³C{¹H} NMR spectrum for **5B⁻** contained two downfield quartets ascribed to the two carbonyl groups coupled to the apical ¹¹B nuclei (Fig. 3). DFT calculations indicate that the signal at 173.8 ppm (calcd at 178.1 ppm) is associated with the C≡O group, while the COOH group appears at 192.0 (calcd at 195.2 ppm). This result is consistent with the presence of only one quartet at 194.4 ppm in the ¹³C NMR spectrum of diacid **1B²⁻**. The ¹¹B{¹H} NMR revealed that the two apical substituents in **5B⁻** have vastly different electronic effects. In agreement with DFT calculations, the strongly electron-accepting carbonyl group at the B(10) position redistributes electron density in the {*closo*-B₁₀} cluster causing significant deshielding of the B(1)

position (33.0 ppm, calcd 36.4 ppm) and consequently shielding the B(10) position (−27.8 ppm, calcd −25.8 ppm).

The facile isolation of monoacid **5B[Bu₄N]** was surprising, although consistent with the previously noted relatively high stability of the C≡O group in aqueous solutions of dicarbonyl derivative **2B**.[11b] In contrast, the 12-vertex analogue **2A** easily undergoes hydration in water, as evident from the solid state structure of the bis-zwitterion [*closo*-B₁₂H₁₀-1,12-(C(OH)₂)₂].[14] The differential reactivity of the two carbonyl derivatives **2A** and **2B** towards water and the observation of protonated monoacid **6** (Fig. 4) are well reproduced by DFT calculations. The results show that the equilibrium reaction in water is shifted more to the hydrate **6A** for the 12-vertex dicarbonyl **2A** (ΔH = −2.77 kcal mol⁻¹, Fig. 4), while the 10-vertex analogue prefers the carbonyl form **2B** (ΔH = 0.52 kcal mol⁻¹). The pronounced preference for the C≡O vs. dihydroxycarbonium group in **B** is related to the stabilizing electronic interaction between the C≡O group and the cluster {*closo*-B₁₀} at the apical positions (Fig. 4), which are absent in **2A**.[16] These apical substituent interactions in derivatives of **B²⁻** are also responsible for the thermal stability of the isoelectronic [*closo*-B₁₀H₈-1,10-(N₂)₂],[12] very low reactivity of the [*closo*-B₁₀H₈-1,10-(CN)₂] (**3B²⁻**)[13] and its high effectiveness as a ligand,[17] and moderate hydrolytic stability of **4B**.

Functional group transformations of diacid **1B²⁻** and preparation of synthetically useful derivatives were previously demonstrated using dicarbonyl compound **2B**,[11a] which is formally an acid anhydride of **1B²⁻**. In this work, **2B** was

Fig. 2 Displacement ellipsoid diagrams for acid **5B[Bu₄N]**, ester **7B[Et₄N]**, carbonium zwitterion **9B**, and ester **13B-a[Bu₄N]**. For geometrical parameters see the text and ESI.† Thermal ellipsoids are at the 50% probability level. The cations are omitted for clarity. Color codes: C-gray, B-green, O-red, N-blue.
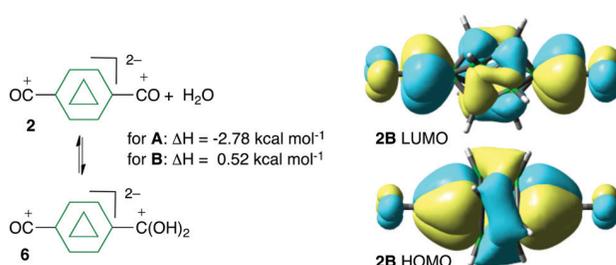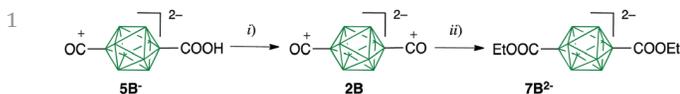

Fig. 4 Left: Equilibrium hydration of **2** to form **6** and DFT enthalpy change ΔH calculated in PhCl dielectric medium. Right: The HOMO and the LUMO contours of **2B**. MO isovalue = ±0.03 (e Bohr⁻³)¹/².
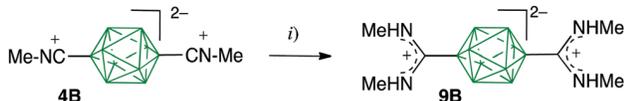
Scheme 2 Synthesis of **2B** and ester **7B^{2-}**. Reagents and conditions: (i) Ion exchange resin, H$_2$O/MeCN 6 : 4, qunat. yield; (ii) 1. NaOEt, EtOH; 2. [Et$_4$N]$^+$Cl$^-$, 62% yield.

Scheme 4 Synthesis of carbonium ylides **11B**, **12B$^-$** and [**13B-a**]$^-$. Reagents and conditions: (i) RNHCH$_2$CH$_2$NHR, CH$_2$Cl$_2$ quant. yield. (ii) PPSE, MeCN, 115 °C, 12 h, **a** 63% and **b** 57% yield. (iii) [Bu$_4$N]$^+$OH$^-$ (40% in H$_2$O), MeCN, **a** 75% and **b** 69% yield. (iv) Recrystallization from aqueous EtOH, 89% yield.
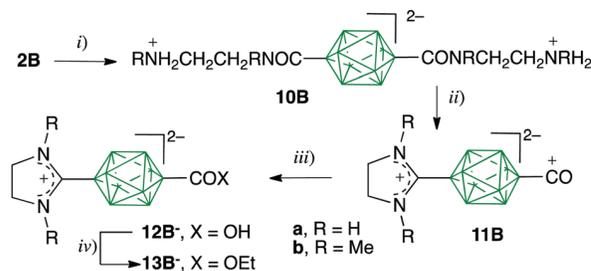
obtained by passing a solution of monoacid **5B[Bu$_4$N]** through Dowex ion-exchange resin to remove the [Bu$_4$N]$^+$ cation followed by evaporation of the solution to dryness. The resulting solid was essentially pure **2B**, as evident from the presence of a strong IR band at 2140 cm^{-1} (calcd at 2193 cm^{-1}), the absence of the C=O band at around 1650 cm^{-1}, and a single downfield quartet at 170.1 ppm (calcd at 175.3 ppm) in the ^{13}C{^{1}H} NMR spectrum. Reaction of dicarbonyl derivative **2B** with NaOEt in EtOH followed by treatment with [Et$_4$N]$^+$Cl$^-$ gave the known[11b] diethyl ester **7B[Et$_4$N]**. The ester was purified on silica gel passivated with [Et$_4$N]$^+$[HCO$_3$]$^-$ and isolated in 62% overall yield. Attempts at purification using untreated SiO$_2$ gave only hydrolysis products. Another piece of evidence for hydrolytic instability of **7B[Et$_4$N]** is provided by the appearance of free EtOH during acquisition of the ^{13}C NMR spectrum Scheme 2.

Single crystal XRD analysis of **7B[Et$_4$N]** demonstrated that the C=O distance is 1.236$_{avrg}$ Å (Fig. 2; calcd. 1.222 Å) similar to that in the monoacid (1.252(1) Å) and longer than in typical esters (*e.g.* 1.202(2) Å in methyl adamantane-1-carboxylate, **8**).[18] The elongation results from the transfer of a significant electron density from the {*closo*-B$_{10}$} to the C=O group ($q_O = -0.674$ and WBO$_{C=O} = 1.682$ for **7B^{2-}**; *c.f.* $q_O = -0.618$ and WBO$_{C=O} = 1.728$ for **8**) and is consistent with the low frequency absorption in the IR region (exp. 1646 and calcd 1674 cm^{-1} for **7B^{2-}**; *c.f.* exp. 1724[19] and calcd 1748 cm^{-1} for **8**). The significant negative charge on the C=O group is consistent with the observed high aptitude for protonation and facile acid-catalyzed hydrolysis of the ester.

Finally, addition of methylamine to bis-zwitterion **4B** cleanly gave the bis-ylide **9B** in a high yield (Scheme 3). Analysis of a single crystal of **9B** grown from EtOH showed a nearly planar Me−N−C−N−Me fragment connected to the {*closo*-B$_{10}$} cluster by a 1.581$_{avrg}$ Å bond (calcd. 1.572 Å) and exhibiting two orientations of the Me groups (Fig. 2). The C−N distances range from 1.323(2) to 1.327(2) Å (calcd 1.329 Å and 1.333 Å) and are similar to those reported for several rare examples of similar boron cluster carbonium ylides obtained *via* different routes.[20] The NBO analysis demonstrated that each nitrogen atom contributes 0.37 e$^-$ of the lone pair to the carbonium center resulting in the C−N bond order of about WBO$_{C-N} = 1.36$ and the overall carbon atom charge $q_c = 0.411$.

Such carbonium ylides are potential bidentate ligands for metal ions[21] and could also be obtained from the dicarbonyl compound **2B**. Thus, reaction of **2B** with NH$_2$CH$_2$CH$_2$NH$_2$ or MeNHCH$_2$CH$_2$NHMe gave the zwitterionic diamides **10B-a** and **10B-b**, respectively. Upon treatment with TMS polyphosphate (PPSE) the diamides **10B** underwent dehydration-cyclization of one amide group and a loss of one amino group from the second amide giving the monocarbonyl derivatives **11B-a** and **11B-b** in about 60% yield (Scheme 4). Treatment of **11B** with [Bu$_4$N]$^+$OH$^-$ smoothly leads to carboxylic acids **12B[Bu$_4$N]** isolated by chromatography in about 70% yield. Interestingly, reaction of the diamide **10B-a** with POCl$_3$ gave mainly **2B**. Attempts at recrystallization of acid **12B-a[Bu$_4$N]** from aqueous EtOH gave crystalline ethyl ester **13B-a[Bu$_4$N]** as the sole product.

Single crystal XRD analysis of **13B-a[Bu$_4$N]** revealed a slightly twisted 2-imidazolinium ring at the B(10) position in a nearly eclipsed conformation, as shown in Fig. 2. The B(10)−C (1.558(2) Å) and the average C(2)−N (1.324$_{avrg}$ Å) distances compare well to the DFT calculated values 1.549 and 1.332 Å, respectively. The twist of the five membered ring measured by the N−C−C−N atoms is 16.8(1)°, which compares to the DFT derived value 15.2°. The bonding and the charge distribution in the N−C−N fragment of the imidazolinium ring in [**13B-a**]$^-$ determined by NBO calculations is similar to that in the bis ylide **9B** (*vide supra*): WBO$_{C-N} = 1.34$ and $q_c = 0.424$. Experimental and DFT calculated IR absorption bands indicate that the 2-imidazolinium ring has two characteristic, symmetric and asymmetric, N−C stretching vibrational modes in the range of 1530–1580 cm^{-1}.

In summary, we report a convenient, high-yield synthesis of dicarboxylic acid **1B^{2-}**, making it available for further studies. Dehydration of the protonated diacid gives its formal acid anhydride **2B**, a useful intermediate for the preparation of functional derivatives, such as ester **7B^{2-}** and hydrolytically stable carbonium ylides **11B** and **12B$^-$**. The imidazolinium derivatives and also bis-ylide **9B** represent a new, potentially broad class of zwitterionic derivatives of anion [*closo*-B$_{10}$H$_{10}$]$^{2-}$ (**B^{2-}**), with a possible application as building blocks for metal complexes and functional MOF's.

Scheme 3 Synthesis of bis-carbonium ylide **9B**. Reagents and conditions: (i) MeNH$_2$ (40% in EtOH), MeCN, 76% yield.

Conflicts of interest

There are no conflicts to declare.

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