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Synthesis of the first 11-vertex *arachno*-dicarbathiaborane anion, $[1,6,7\text{-}C_2SB_8H_{11}]^-$. Theoretical refinement of its structure

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Abstract

The addition of elemental sulphur to the 10-vertex *nido* dicarborane $[6,9\text{-}C_2B_8H_{10}]^{2-}$(**2**) engenders the new 11-vertex species $[1,6,7\text{-}C_2SB_8H_{11}]^-$ (**2**), which has been structurally characterised using the ab initio/GIAO/NMR method and by deductions made from observations on its reaction chemistry. These combined studies revealed **2** to adopt a structure that is formally derived from the hypothetical parent $[closo\text{-}B_{13}H_{13}]^{2-}$ anion by removal of two adjacent six-coordinate and five-coordinate vertices. Since the GIAO calculations of ^{11}B and ^{13}C chemical shifts, employing the RMP2/6-31G* geometry, showed an excellent agreement with the experimental findings, in particular those for $\delta(^{11}B)$ and $\delta(^{13}C)$ that were computed at the GIAO-RMP2/II′ level, the RMP2/6-31G* parameters can be deemed a good representation of the molecular structure of **2** in solution. The other possible structural alternatives of **2** could be ruled out on the basis of geometrical, energetic, and NMR criteria.

Keywords: Boranes; Heteroboranes; NMR spectroscopy; Geometry optimisation; GIAO

1. Introduction

Polyhedral boron chemistry is greatly enriched by heteroatom insertion reactions that engender expanded cage systems or hybrid clusters [1]. In this context, it is important to establish new and efficient atom-insertion synthetic methods. Traditional sulphur-insertion reactions, leading to the formation of thia- or dithiaborane clusters, include the reaction of boranes or carboranes with sulphur reagents such as ammonium polysulfide [2,3], thionitrosodimethylamine [2,3] or $KHSO_3$ [4]. It was also found, several years ago, that the reaction of [*arachno*-4-CB_8H_{14}] with elemental sulphur in the presence of triethylamine leads to sulphur atom insertion [5]. A similar reaction of sulphur with $[nido\text{-}SB_9H_{10}]^-$ results in sulphur insertion into the *nido*-SB_9 cage framework to produce the new *arachno*-dithiaborane cluster anion, $[arachno\text{-}2,3\text{-}S_2B_9H_{10}]^-$ [6]. Here we describe a simple sulphur-atom insertion into the dianion $[nido\text{-}6,9\text{-}C_2B_8H_{10}]^{2-}$ (**1**) [7] and the structural characterisation of **2**.

2. Experimental

All reactions were carried out with the use of standard vacuum and inert-atmosphere techniques. THF was dried over Na and distilled before use.

2.1. NMR spectroscopy

NMR spectra were recorded at 9.4 T on a Varian MERCURY 400 High Resolution System. The

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proton-detected, double and triple-resonance NMR experiments were performed using a Varian Inova-500 NMR spectrometer operating at using a Nalorac(r) triple-resonance probe optimised for proton observation (indirect detection), with the other two channels tuned for ^{13}C and ^{11}B observation. ^{13}C NMR was observed using a Varian Inova-400 NMR spectrometer, operating at 400.16 MHz for ^{1}H observation and 100.629 MHz for ^{13}C observation. Data were recorded at 294–297 K for CD_3CN solutions unless otherwise indicated. Complete assignments of **2** were made using indirect-detection of ^{13}C via proton observation, specifically, gHSQC [8], gHMQC [9], and gHMBC [10] experiments (gradient-heteronuclear single quantum coherence spectroscopy, gradient-heteronuclear multiple quantum coherence spectroscopy, and gradient-heteronuclear multiple bond coherence spectroscopy). 500 MHz ^{1}H–^{1}H COSY experiments were performed with and without broadband ^{11}B decoupling. Broadband ^{11}B decoupling was achieved using the GARP phase-modulation sequence [11]. Unambiguous ^{11}B assignments were achieved using the gradient-selected 2-D ^{11}B–^{11}B COSY experiment [12].

The proton-detected NMR experiments were performed using a Varian Inova-500 NMR spectrometer operating at using a Nalorac(r) triple-resonance probe optimised for proton observation (indirect detection), with the other two channels tuned for ^{13}C and ^{11}B observation. Carbon-13 NMR was observed using a Varian Inova-400 NMR spectrometer, operating at 400.16 MHz for ^{1}H observation and 100.629 MHz for ^{13}C observation.

2.2. Mass spectroscopy

Low resolution spectra were obtained using a Magnum GC/MS ion trap (Finnigan MAT, USA), Mass spectroscopy measurements of ionic compounds were performed on a Bruker Esquire-LC Ion trap instrument using electrospray ionisation.

2.3. TLC chromatography

The purity of the products were also checked on Silufol (Kavalier, silica gel on aluminium foil; detection by iodine vapour, followed by spraying with 2% aqueous $AgNO_3$).

2.4. IR spectroscopy

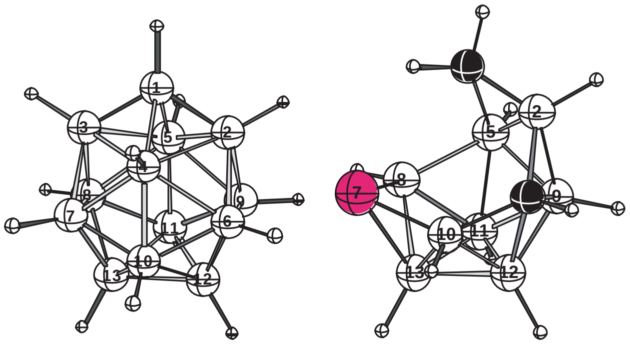
IR spectra were measured on PYE UNICAM PU 9512 spectrometer with data station.

2.5. Computational details

Most of the calculations used the GAUSSIAN 94 program package [13] and were performed on the Power Challenge XL computer of the Supercomputing Center of the Charles University in Prague. The geometry optimisations of **2B** and **2C** began at SCF levels (3-21G*, 6-31G*) without symmetry restriction (C_1). Frequency calculations for the final structure **2C**, carried out at the SCF/6-31G* level, determined the nature of the stationary point. The minimum on the respective potential energy hypersurface was characterised with zero imaginary frequency (NIMAG = 0). Further optimisations at RMP2(fc)/6-31G* included also the effect of electron correlation (fc stands for the frozen core approximation but it is omitted for reasons of simplicity throughout the text). For selected geometry parameters, see Fig. 1. The chemical shieldings were calculated first at an SCF level using the GIAO (gauge-invariant atomic orbital) method incorporated in the GAUSSIAN 94 and utilised a II Huzinaga basis set (TZP) [14] well-established for the computations of magnetic properties [15]. The final level of the calculations of chemical shieldings was GIAO-MP2 with a II′ Huzinaga basis set (same as II but a DZ Huzinaga basis is used on hydrogen atoms).

2.6. Synthesis of [1,6,7-$C_2SB_8H_{11}$]$^-$

To 0.7 g (4.2 mmol) of the disodium salt of anion **1** dissolved in 15 ml of dry THF was added 0.32 g (10 mmol) of sulphur. The reaction mixture was stirred overnight at room temperature, during which time its colour turned red. This red mixture was cooled down to 0 °C after 20 h and hexane (40 ml) and 20 ml of distilled water were added whilst stirring. Separation of the hexane layer lead to the identification of small amounts of carborane species [1,6-$C_2B_8H_{10}$], [4,6-$C_2B_7H_{13}$] and



[*closo*-$B_{13}H_{13}$]$^{2-}$ **2C**

Fig. 1. Relation of [*closo*-$B_{13}H_{13}$]$^{2-}$ and the true structural alternative of [1,6,7-$C_2SB_8H_{11}$]$^-$, **2C**, both optimised at the RMP2/6-31G* level. Selected interatomic distances (Å, the B–B interatomic distances are shown as an average value, apart from those that are anomalously large, which are stated individually): $(B–B)_{av}$ 1.772, B(8)–B(13) 1.895, B(10)–B(13) 1.893, B(2)–B(5) 1.893, S(7)–B(8) 1.897, S(7)–B(10) 1.909, S(7)–B(13) 1.929, C(6)–B(2) 1.667, C(6)–B(9) 1.687, C(6)–B(10) 1.606, C(6)–B(12) 1.686, C(1)–B(2) 1.548, C(1)–B(5) 1.685, $(B–H)_{av}$ 1.199.

large amounts of polysulphanes. The water layer was then precipitated by a saturated solution of Ph_4PCl (alternatively, the following counter-ions can be used: Cs^+, Me_4N^+, and Bu_4N^+). The resultant yellow precipitation gave 1.2 g (60.6%) of white crystals after crystallisation from a mixture of CH_2Cl_2 and hexane. NMR data for **2C** are as follows: $\delta(^{11}B)$ (experimental, GIAO-SCF/II//RMP2/6-31G*, GIAO-RMP2/II′//RMP2/6-31G*, multiplicity, intensity, $^1J_{BH}$ and assignment: −7.2, −8.2, −7.4 [d, 1B, 150, B(2)]; −39.9, −40.7, −42.1 [d, 1B, 137, B (5)]; 22.5, 27.2, 22.6 [d, 1B, 154, B (8)]; 8.5, 11.4, 10.0 [d, 1B, 146, B(9)]; −6.2, −4.7, −6.8 [d, 1B, 143, B(10)]; −24.3, −21.2, −26.7 [d, 1B, 139, B(11)]; −9.9, −8.2, −10.9 [d, 1B, 154, B(12)]; −23.3, −21.5, −23.7 [d, 1B, 169, B(13)], all theoretical [^{11}B–^{11}B] COSY crosspeaks were observed, except for B(8)–B(13), both of which are adjacent to sulphur atom; $\delta(^{13}C)$ (experimental, GIAO-SCF/II//RMP2/6-31G*, GIAO-RMP2/II′//RMP2/6-31G*): 52.8, 42.5, 60.5 [C(1)]; 13.9, 7.3, 19.0 [C(6)], 131.35 [$C_{phenyl}(4')$] 135.70 [$C_{phenyl}C(2',3',5',6')$] 136.10 [$C_{phenyl}(1')$] $\delta(^1H)$ (assignments for individual cluster [BH] protons by ^1H–{^{11}B(selective)} measurements) +4.37(H8) +3.75(H9), +2.42(H2), +2.23(H10), +2.77(H12), +1.35(H13), +1.22(H11), −0.68(H5), $\delta(^1H)$ +7.79[m, CH_{phenyl}]+ 1.52 [q, $CH(1)_{exo}$], +1.01[s, $CH(6)_{carb}$], +0.29[s, $CH(1)_{endo}$] from theoretical [^1H–^1H] COSY crosspeaks were observed: H(B8)–H(B11); H(B9)–H(B12), H(B9)–H(B2), H(B9)–H(B5), H(B9)–H(C6), H(B2)–H($C1_{exo}$), H(B2)–H(C6), H(B2)–H($C1_{endo}$), H(B12)–H(B10), H(B11)–H(B13), H(B10)–H($C1_{endo}$), H(B5)–H($C1_{endo}$), H(B5)–H($C1_{exo}$), H($C1_{exo}$)–H($C1_{endo}$), IR spectrum contained bands at 3064ms, 2536vs, 2401sh, 1582s, 1478ms, 1432vs, 1182w, 1180w, 1106vs, 1054s, 993ms, 956w, 904w, 756ms, 722vs, 684vs, 522vs MS ESI: $m/z = 153.8$ (counted 153.66). *Anal.* Calc. for $C_{26}B_8H_{31}SP$ C, 63.34; H, 31.34; S, 6.50%; Found: 63.18, H, 31.21; S, 6.82%.

2.7. Hydrolysis of anion 2 by dilute hydrochloride acid

To 0.7 g (4.2 mmol) of the disodium salt of anion **1** dissolved in 15 ml of dry THF was added 0.32 g (10 mmol) of sulphur. Reaction mixture was stirred over night at room temperature and the colour of the solution turned red. THF was distilled off from the resultant mixture and to the residue was added pentane, which gave a suspension that was cooled down to 0 °C and to which 10 ml of diluted HCl was slowly added under vigorous stirring. The organic layer was then separated, and after evaporation of hexane, 0.55 g of white solid was isolated. After separation on a column of SiO_2 was isolated 0.1 g of [5-HS-4,6-$C_2B_7H_{12}$] (**3**) [16], $\delta(^{11}B)$ (multiplicity, intensity, $^1J_{BH}$ and assignment) 0.45[d, 2B,155, B(7,9)], 7.5[s, 1B, B(5)], −15.1[d, 2B, 162, B91,2)], −29.3[d, 1B, 151/44, B(8)], 49.8[d, 1B, 149, B(3)]; $m/z = 146$, m.p. 103–6 °C (106–8 °C in literature) and 0.2 g of [4,6-$C_2B_7H_{13}$] (**4**) [17].

3. Results and discussion

The addition of elemental sulphur to a stirred solution of anion **1** in THF produced the new dicarbathiaborane anion $[1,6,7\text{-}C_2SB_8H_{11}]^-$ (**2**) [18], which is the first example of an 11-vertex *arachno*-thiacarborane.

$$\underset{\mathbf{1}}{[6,9\text{-}C_2B_8H_{10}]^{2-}} + S \rightarrow \{SC_2B_8H_{10}\}^{2-}$$
$$\rightarrow \underset{\mathbf{2}}{[1,6,7\text{-}C_2SB_8H_{11}]^-}$$

Despite the successful growing of crystals of various salts (Cs^+, Me_4N^+, Bu_4N^+, and Ph_4P^+) of compound **2**, disordered single-crystal X-ray diffraction data precluded determination of its solid-state structure. ^1H and ^{13}C NMR spectroscopy confirmed the existence of CH_2 and CH groups in the thiacarborane **2**, and observed [^{11}B–^{11}B] COSY crosspeaks provided information on the cage positions of the boron atoms, but since many cross peaks in the 2D COSY ^1H NMR spectrum were not observed, the cluster positions of heteroatoms could not be assigned unambiguously. The structure of the new anion **2** is thus suggested herein from the results of the so-called ab initio/GIAO/NMR method, which is a structural tool that has been extensively applied to the elucidation of the molecular structures of many boranes and heteroboranes [19]. It is particularly useful in cases where conventional experimental structural elucidation approaches have failed [20]. In this context, the ab initio/GIAO/NMR method was applied to compound **2** and conclusively evoked a cluster-structure of 11-vertex *arachno* geometry, derived by the removal of two vertices from a hypothetical 13-vertex *closo*-deltahedron as shown in Fig. 1 [21]. (In a theoretical context, the basic geometric arrangement for 13-vertex *closo*-borane cages is a docosahedron structure, and is, thus, the basis of our discussion. However, we do pay note to the recent reporting of the first 13-vertex dicarbaborane compound ($C_2B_{11}H_{13}$), which is of henicosahedral symmetry [22].)

Thus, when starting from a 13-vertex docosahedral structural motif, there are in principle only three possible cage geometries for an 11-vertex *arachno* system [6] that vary as to which two vertices are removed from this hypothetical, superaromatic [23], [*closo*-$B_{13}H_{13}$]$^{2-}$ type structure, i.e. the removal of B(2) and B(3), B(1) and B(4), or B(3) and B(4) give rise to the structures A, B, and C, respectively (see the parent compound in Fig. 1).

Initially, it was expected that **2** would adopt the molecular shape B [18], in analogy with [*arachno*-2,3-$S_2B_9H_{10}$]$^-$ (see above) [6]. Hence, the geometry optimisations of **2** started with this anticipated geometry (**2B**). Interestingly, quite different geometries were obtained at SCF and RMP2 levels, the latter of which takes the electron correlation into account. A boron atom in **2B** is "bonded" to S and "nonbonded" to C(H_2) at RMP2/

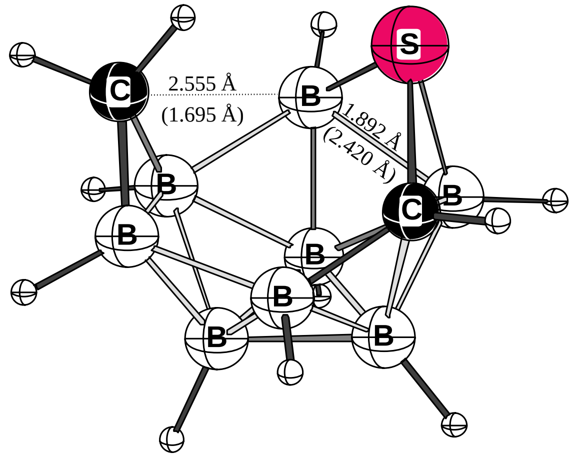


Fig. 2. Theory-employed dependent structure **2B** as optimised at RMP2/6-31G* (SCF/6-31G*).

6-31G*, whereas the opposite feature was observed at SCF/6-31G*, see Fig. 2.

Usually interatomic separations differ only by 5–10% when comparing SCF and RMP2 values for this class of compounds (SCF B–B and C–B lengths are overestimated with respect to the RMP2 ones) [24]. This sensitivity towards the computational level is indicative of a very flat potential energy surface for the motion of this critical boron atom. Such a phenomenon, which is occasionally observed in the structural chemistry of carbocations [25], is quite sparse in the family of boron clusters [26].

The calculated ^{11}B and ^{13}C NMR chemical shifts for **2B** correlated very poorly with those found experimentally: The corresponding deviations were more than 25 and 10 ppm when employing the 6-31G* and RMP2/6-31G* geometries respectively. Further possible regioisomers, differing only in the positions of the boron and carbon atoms around the open hexagonal face (i.e. that have CH_2 and CH vertices interchanged) but still adopting shape B, were computed. For these isomers, an unusual dependence on which theoretical level used recurred for some inter-atomic separations, as well as a strong disagreement between the calculated and measured chemical shifts. It appears that upon introducing a third heteroatom (as in the title compound), structures of type B that are observed for compounds with two heteroatoms (e.g. [*arachno*-2,3-$S_2B_9H_{10}$]$^-$ [6]) are no longer preferred. Indeed, Plešek reported the synthesis and structural characterisation of another three-heteroatom-derivative, [*arachno*-$C_2NB_8H_{13}$], which adopts the cage geometry **C** [27]. Consequently, we carried out the geometry optimisation starting from the latter arrangement (**2C**). No problems were encountered when optimising **2C,** and the resulting SCF/6-31G* and RMP2/6-31G* geometries showed only minor quantitative but no qualitative differences, in line with the results obtained for many boranes and heteroboranes so far investigated [28]. For the RMP2/6-31G* geometry of **2C** depicted in Fig. 1, the fit between the calculated and experimental ^{11}B chemical shifts turned out to be consistently good. However, the best correlation between calculated and experimental data is found at the GIAO-MP2/II′//RMP2/6-31G* level, with a maximum deviation of ≈2 ppm for $\delta(^{11}B)$ values. It is worth noting that the ^{13}C chemical shifts, in particular their large separation, are also reproduced quite well [29] (for the individual values see Section 2). We also investigated the next likely structural alternative, still adopting the molecular shape C, which has the C(6) and B(10) vertices interchanged, but this structure is higher in energy than **2C** by 36.8 kcal/mol and shows poor correlation between theoretical and experimental chemical shifts. On this basis, this structural alternative can be ruled out. Additionally, if compound **2** were to adopt the geometry **2A**, we would expect to find a higher degree of symmetry to be reproduced in the ^{11}B NMR spectrum. As no such high degree of symmetry is found in the ^{11}B NMR spectrum of **2** the structural alternative **2A** can be assumed to be incorrect and, thus, discarded as a feasible structure.

The RMP2/6-31G* parameters of **2C** reveal some interesting features. The presence of sulphur is obviously a principal source of the distortion with respect to the B_{11} framework derived from [*closo*-$B_{13}H_{13}$]$^{2-}$. The B(8)S(7)B(10) angle is larger than the B(8)B(7)B(10) angle in [*closo*-$B_{13}H_{13}$]$^{2-}$ by ≈36° (cf. 96.2° and 59.9°, respectively). Such a difference in the values of BSB angles does not occur in those calculated for other *arachno* systems [30]. Conversely, the BCB angles in **2C** only marginally deviate from the corresponding BBB angles in the parent compound (cf. B(2)C(1)B(5) of 71.5° versus 69.3° and B(9)C(6)B(12) of 62.3° versus 59.9°), see Fig. 1 also for selected interatomic distances.

In brief conclusion, **2C** can be deemed a good representation of the molecular structure of **2** in solution.

The positions of the two carbon atoms and sulphur atom were also confirmed by the hydrolysis of anion **2** under acid conditions, which produced a 5-HS-4,6-$C_2B_7H_{10}$ (**3**) [16] and [*arachno*-4,6-$C_2B_7H_{13}$] as shown below.

$$\underset{\mathbf{2}}{[1,6,7\text{-}C_2SB_8H_{11}]^-} \rightarrow \underset{\mathbf{3}}{5\text{-}HS\text{-}4,6\text{-}C_2B_7H_{10}}$$
$$+\ \underset{\mathbf{4}}{4,6\text{-}C_2B_7H_{13}}$$

The formation of **3** can be explained as the degradation of **2** by dilute HCl that removes the sulphur atom and boron atom (2) to yield [*arachno*-4,6-$C_2B_7H_{13}$] (**4**) [17], which is subsequently attacked by sulphur in the 5 position to form the mercapto derivative **3**. The same compound was obtained after direct $AlCl_3$-catalysed sulphydrylation of **4** by sulphur [15], which adds weight to the above hypothesis of sulphur atom removal followed by reinsertion. However, there is also the possibility that such cluster changes could be the result of complex rearrangement mechanism.

4. Supplementary material

Calculated coordinates for **2C** at the RMP2(fc)/6-31G* level are available from the authors on request.

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(b) B(6)S(8)B(7) of 97.6° (RMP2/6-31G*) in arachno-4,6,8-$C_2SB_6H_8$, D. Hnyk, M. Hofmann, P.v.R. Schleyer, Collect. Czech. Chem. Commun. 64 (1999) 993.