

# The gas-phase structure of 1-selena-*closo*-dodecaborane(11), 1-SeB<sub>11</sub>H<sub>11</sub>, determined by the concerted use of electron diffraction and computational methods†‡

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The molecular structure of 1-selena-*closo*-dodecaborane(11), 1-SeB<sub>11</sub>H<sub>11</sub>, has been determined by the concerted use of quantum chemical calculations and gas-phase electron diffraction. The structure has C<sub>5v</sub> symmetry and is distorted from a regular icosahedron mainly through the expansion of the pentagon of boron atoms adjacent to selenium, with r<sub>a3,1</sub>(B–B) = 192.2(2) pm. The Se–B bond length is extremely well determined [r<sub>a3,1</sub>(Se–B) = 212.9(2) pm] and this is reflected by a pronounced peak in the radial-distribution curve. The accuracy of the experimental structure, as well as that calculated at the MP2/962(d) level, has been gauged by comparison of the <sup>11</sup>B chemical shifts (calculated at two different gauge-including atomic orbitals (GIAO) levels) with experimental NMR values. The inclusion of electron correlation in the magnetic property calculations (GIAO-MP2) gave superior results to those carried out using GIAO-Hartree–Fock.

## Introduction

The systematic replacement of {BH}<sup>2-</sup> vertices in the highly symmetrical borane [*closo*-B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> can lead to a variety of 12-vertex *closo* heteroboranes (see Fig. 1 for an example). For example, isoelectrolobal<sup>1</sup> species such as {S}, {Se} and {CH}<sup>-</sup> give rise to the heteroboranes *closo*-1-SB<sub>11</sub>H<sub>11</sub>, *closo*-1-SeB<sub>11</sub>H<sub>11</sub> and [*closo*-1-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> respectively. [*closo*-1-CB<sub>11</sub>H<sub>12</sub>]<sup>-</sup> is an archetypical weakly-coordinating anion;<sup>2</sup> the structure of the free ion has been described.<sup>3</sup> Continuing along the first row of the periodic table, NH is isoelectronic with {BH}<sup>2-</sup> and its substitution into [*closo*-B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> gives *closo*-1-NB<sub>11</sub>H<sub>12</sub>, the structure of which has been determined by a combination of gas-phase electron diffraction (GED) and computational methods.<sup>4</sup> The B–N and B–B separations in *closo*-1-NB<sub>11</sub>H<sub>12</sub> are calculated to lie within a relatively small range (approximately 10 pm), which makes the structure determination from GED data much more difficult. In fact, four models with C<sub>5v</sub> symmetry fit the data almost equally well.

Previous gas-phase studies of boron clusters with *closo* structures have suggested that amplitudes of vibration both for adjacent atom pairs and for those more widely separated have similar values. For example, in the case of *closo*-1-SB<sub>11</sub>H<sub>11</sub>,<sup>5</sup> a C<sub>5v</sub>-symmetric structure has been determined by GED, in which there is a distortion from regular icosahedral geometry, consisting mainly of a substantial expansion of the pentagonal belt adjacent to the

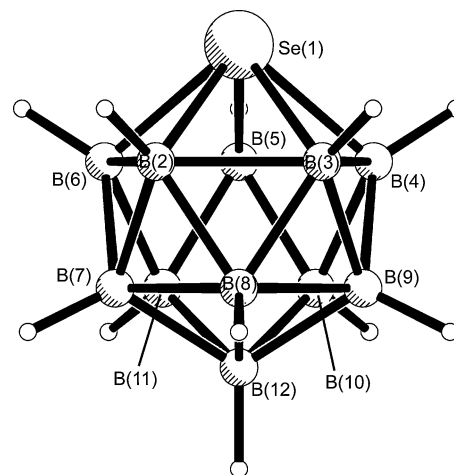


Fig. 1 Molecular structure, including numbering scheme, for 1-SeB<sub>11</sub>H<sub>11</sub>. Hydrogen atoms are given the same number as the boron to which they are attached [e.g. H(2) is bonded to B(2)].

sulfur atom. The B–B distances around this pentagon refined to 190.5(4) pm, significantly greater than the other B–B distances which lie in a narrow range from 177.7 to 178.3 pm. The S–B bond length is the longest in the molecule at 201.0(5) pm. The amplitudes of vibrational parameters are consistent with those found for similar structures, e.g. 5.1(4) and 6.8(3) pm for B(2)–B(3) and B(2)⋯B(9), respectively. It is noteworthy that the latter value is smaller than that for S–B(2) [7.1(4) pm] even though the two atoms are on opposite sides of the molecule, rather than adjacent. This strongly supports the idea that a *closo* structure is quite rigid.

Structure determinations on the basis of the *ab initio* (or DFT)/GIAO/NMR method<sup>6</sup> have long since reached the confidence levels of X-ray structure determinations.<sup>7</sup> Theoretical assessments of structures are made not only on the basis of

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† Dedicated to Professor Kenneth Wade on the occasion of his 75th birthday.

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computed geometries but also on chemical shift calculations, because  $\delta(^{11}\text{B})$  values are very sensitive to small geometric changes. The level of agreement between calculated and experimental  $^{11}\text{B}$  chemical shifts serves as a criterion for assessing the accuracy of a particular geometry.

Here we describe the structure determination of 1-selena-closododecaborane(11), 1-SeB<sub>11</sub>H<sub>11</sub>, by the combined use of quantum chemical calculations and gas-phase electron diffraction.

## Experimental

### Synthesis

1-SeB<sub>11</sub>H<sub>11</sub> was prepared<sup>8</sup> by the reaction of Et<sub>3</sub>NH<sup>+</sup>B<sub>11</sub>H<sub>14</sub><sup>-</sup> with SeO<sub>2</sub> in a mixture of aqueous NaOH and hexane. 1.0 g (4.2 mmol) of Et<sub>3</sub>NH<sup>+</sup>B<sub>11</sub>H<sub>14</sub><sup>-</sup> was dissolved in an excess of 10% NaOH in water (50 ml) before Et<sub>3</sub>N was evaporated *in vacuo*. 50 ml of hexane and 1.1 g (10.0 mmol) of SeO<sub>2</sub> were added into the reaction mixture under nitrogen. The mixture was stirred at 60 °C for 24 h. The organic layer was separated and the hexane evaporated *in vacuo*. The crude product was purified by sublimation at 70 °C at a pressure of 1.3 Pa. A yield of 0.24 g of 1-SeB<sub>11</sub>H<sub>11</sub> was obtained (30%, based on Et<sub>3</sub>NH<sup>+</sup>B<sub>11</sub>H<sub>14</sub><sup>-</sup>).

### Gas-phase electron diffraction (GED)

Data were collected for 1-SeB<sub>11</sub>H<sub>11</sub> using the Edinburgh gas-phase electron diffraction (GED) apparatus.<sup>9</sup> An accelerating voltage of 40 kV was used, resulting in an electron wavelength of approximately 6.0 pm. Scattering intensities were recorded on Kodak Electron Image films at two nozzle-to-film distances, namely 87.8 and 249.9 mm, to maximise the scattering angle over which data were collected. In order to obtain suitable vapour pressures and to prevent condensation in the nozzle, the sample and nozzle were heated to 155 and 170 °C respectively for the longer nozzle-to-film distance, and 175 and 185 °C for the shorter distance.

The weighting points for the off-diagonal weight matrices, correlation parameters and scale factors for both camera distances for all molecules are given in Table S1.† Also included are the electron wavelengths determined using the scattering patterns for benzene, which were recorded immediately after the sample patterns. The photographic films were scanned using an Epson Expression 1680 Pro flatbed scanner as part of a method that is now used routinely in Edinburgh and described elsewhere.<sup>10</sup> The data-reduction and least-squares refinement processes were carried out using the ed@ed program<sup>11</sup> employing the scattering factors of Ross *et al.*<sup>12</sup>

### Theoretical methods

Some calculations were performed using the resources of the National Service for Computational Chemistry Software (NSCCS)<sup>13</sup> running the Gaussian 03 suite of programs.<sup>14a</sup> Others were carried out using Gaussian 98<sup>14b</sup> on a cluster of Intel Xeon and Opteron workstations and PCs at the MPI Mülheim. A single minimum on the potential-energy surface of 1-SeB<sub>11</sub>H<sub>11</sub> was identified as representing a C<sub>5v</sub>-symmetric structure. With this symmetry constraint, geometries were optimised first at the restricted Hartree–Fock (RHF) level of theory with the 3–21G(d) basis set<sup>15</sup> on all atoms followed by the 6–31G(d) basis set<sup>16</sup> and then using MP2<sup>17</sup> to include the energy due to electron correlation. All MP2 calculations were spin-restricted and frozen-core, using one of the following all-electron (AE) basis-set combinations: 641(d) on Se and 6–31G(d) on B and H (denoted AE1), 641(d) on Se and 6–311+G(d)<sup>18</sup> on B and H (denoted AE2), and 962(d) on Se and 6–31G(d) on B and H (denoted AE3). The 641(d) and 962(d) basis sets for Se are Binning and Curtiss' [6s4p1d] contraction<sup>19</sup> of Dunning's (14s11p5d) primitive set.<sup>20</sup> These basis-set combinations have performed very well for similar types of molecules.<sup>21</sup>

Additional calculations were performed using the quasi-relativistic Stuttgart–Dresden effective core potential (ECP)<sup>22</sup> for Se with the polarised double-zeta valence basis set augmented with a diffuse sp set<sup>23</sup> and a d polarisation function,<sup>24</sup> together with 6–31G(d) basis on B and H (denoted ECP1). Values for salient bond lengths and angles calculated at the MP2 level are given in Table 1.

Force constants were calculated at the RHF/AE1 level and subsequently used, along with the program SHRINK,<sup>25</sup> to obtain initial amplitudes of vibration, and third derivatives of energy (giving cubic anharmonicity terms) were used to give curvilinear, perpendicular distance-correction terms for use in the GED refinement. Thus, the structure obtained from the refinement is of the type r<sub>a3,1</sub>. For a full discussion of the a3,1 nomenclature see ref. 26. Although the force field was calculated at a low level and was not scaled, the amplitudes of vibration given by SHRINK are suitably accurate as starting values.

Magnetic shieldings were calculated using the GIAO-HF and GIAO-MP2 methods<sup>27</sup> that are incorporated into the Gaussian 98 suite of programs.<sup>14b</sup> The individual gauge for localised orbitals (IGLO-II and IGLO-DZ) basis sets<sup>28</sup> were used throughout for B and H respectively, together with one of the following basis sets for Se: 962+(d)<sup>29</sup> (denoted AE4), the above-mentioned ECP with its augmented valence basis (denoted ECP2), and IGLO-II without f functions<sup>30</sup> (denoted II').

Additional NMR calculations were performed using the MP2/AE3 optimised geometry with the Amsterdam density functional (ADF) code<sup>31</sup> employing the BP86 functional.<sup>32</sup> The two-component relativistic zeroth-order regular approximation

**Table 1** Selected bond lengths and angles for 1-SeB<sub>11</sub>H<sub>11</sub> calculated at the MP2 level using a variety of basis sets<sup>a</sup>

	Se–B(2)	B(2)–B(3)	B(2)–B(7)	B(7)–B(8)	B(7)–B(12)	Se–B–H	B(12)–B(7)–H
MP2/AE1	210.5	190.6	175.9	178.7	178.0	110.2	123.5
MP2/AE2	213.3	191.3	176.5	179.5	178.8	109.0	124.0
MP2/ECP1	213.2	190.7	175.7	178.8	178.8	109.2	123.6
MP2/AE3	213.2	190.9	175.8	178.8	178.0	109.2	123.6

<sup>a</sup> All distances in pm and angles in degrees. See text for further details of the basis sets used. See Fig. 1 for atom numbering.

**Table 2** Calculated and experimental  $^{11}\text{B}$  NMR chemical shifts<sup>a</sup> for *closo*-1- $\text{SeB}_{11}\text{H}_{11}$ 

	$\delta(^{11}\text{B})/\text{ppm}$		
	B(2–6)	B(7–11)	B(12)
GIAO-HF/II//MP2/AE3	-1.4	-4.8	26.3
GIAO-HF/ECP2//MP2/AE3	-0.8	-4.6	26.7
GIAO-HF/AE4//MP2/AE3	-1.4	-4.6	26.6
GIAO-HF/ECP2//GED	-1.2	-4.6	26.4
GIAO-BP86/TZP//MP2/AE3	-6.5	-7.1	22.7
ZORA-BP86(SO) <sup>b</sup> /TZP//MP2/AE3	-6.9	-7.2	22.7
sc <sup>c</sup> -ZORA-BP86/TZP//MP2/AE3	-5.9	-7.3	22.7
GIAO-MP2/AE4//MP2/AE3	-3.3	-3.5	25.0
GIAO-MP2/ECP2//MP2/AE3	-3.2	-3.4	24.6
GIAO-MP2/AE4//GED	-3.6	-3.6	24.6
GIAO-MP2/ECP2//GED	-3.5	-3.6	24.2
Experimental	-4.4	-5.3	22.2

<sup>a</sup> Relative to  $\text{BF}_3\cdot\text{OEt}_2$ , in ppm; see text for description. <sup>b</sup> Relativistic computation including SO coupling; see text for further details. <sup>c</sup> Estimated scalar ZORA values from the ZORA-DFT(SO) results by subtracting the SO contribution from the sigma values.

(ZORA) method<sup>33</sup> including scalar and spin-orbit (SO)<sup>34</sup> corrections was employed for these computations. We have used the triple-zeta basis set plus one polarisation function (denoted TZP; from the ADF library) for all atoms.  $^{11}\text{B}$  chemical shifts were calculated relative to  $\text{B}_2\text{H}_6$  and converted to the usual  $\text{BF}_3\cdot\text{OEt}_2$  scale using the experimental  $\delta(^{11}\text{B})$  value for  $\text{B}_2\text{H}_6$  of 16.6 ppm.<sup>7</sup> Absolute shieldings obtained at each level are given in ref. 21. NMR chemical shifts are given in Table 2.

## Results and discussion

### GED study

On the basis of the calculations described above, a  $C_{5v}$ -symmetric model was written describing 1- $\text{SeB}_{11}\text{H}_{11}$ . The geometry was described in terms of eight refinable parameters, comprising six bond lengths and differences and two angles (Table 3). The atom numbering used in the descriptions of the parameters is shown in Fig. 1. The Se–B bond lengths were identical and described

**Table 3** Refined ( $r_{\text{a3,1}}$ ) and calculated ( $r_{\text{c}}$ ) geometric parameters for 1- $\text{SeB}_{11}\text{H}_{11}$  from the GED study<sup>a,b</sup>

	Parameter	$r_{\text{a3,1}}$	$r_{\text{c}}$	Restraint
<i>Independent</i>				
$p_1$	$r_{\text{Se-B}}$	212.9(2)	213.2	—
$p_2$	$r_{\text{B-B}}$ average	180.19(7)	179.9	—
$p_3$	$r_{\text{B-B}}$ difference 1	15.1(2)	13.8	0.5
$p_4$	$r_{\text{B-B}}$ difference 2	2.4(4)	2.3	0.5
$p_5$	$r_{\text{B-B}}$ difference 3	2.2(4)	2.2	0.5
$p_6$	$r_{\text{B-H}}$ mean	118.0(2)	118.9	—
$p_7$	$\angle\text{B}(12)\text{-B}(7)\text{-H}$	122.9(8)	123.6	1.0
$p_8$	$\angle\text{Se-B}(2)\text{-H}$	109.6(9)	109.2	1.0
<i>Dependent</i>				
$p_9$	B(2)–B(3)	192.2(2)	190.9	—
$p_{10}$	B(2)–B(7)	175.9(9)	175.8	—
$p_{11}$	B(7)–B(8)	179.0(3)	178.8	—
$p_{12}$	B(7)–B(12)	178.0(2)	178.0	—

<sup>a</sup> Refers to an MP2/AE3 calculation. <sup>b</sup> Distances ( $r$ ) are in pm, and angles ( $\angle$ ) are in degrees. See text for parameter definitions and Fig. 1 for atom numbering. The figures in parentheses are the estimated standard deviations of the last digits.

using  $p_1$ . Four different B–B bonds were identified in the structure [B(2)–B(3), B(2)–B(7), B(7)–B(8) and B(7)–B(12)] and these were described using the weighted average of the distances [to account for the fact that symmetry equivalents of B(2)–B(7) occur twice as often as the others] and differences between them. The formal definitions of  $p_2$ – $p_5$  were as follows:

$$p_2 = \{[\text{B}(2)\text{-B}(3)] + 2[\text{B}(2)\text{-B}(7)] + [\text{B}(7)\text{-B}(8)] + [\text{B}(7)\text{-B}(12)]\}/5$$

$$p_3 = [\text{B}(2)\text{-B}(3)] - \{2[\text{B}(2)\text{-B}(7)] + [\text{B}(7)\text{-B}(8)] + [\text{B}(7)\text{-B}(12)]\}/4$$

$$p_4 = [\text{B}(7)\text{-B}(8)] - \{2[\text{B}(2)\text{-B}(7)] + [\text{B}(7)\text{-B}(12)]\}/3$$

$$p_5 = [\text{B}(7)\text{-B}(12)] - [\text{B}(2)\text{-B}(7)]$$

The four different B–B bond lengths were then described using  $p_2$ – $p_5$  as follows:

$$\text{B}(2)\text{-B}(3) = p_2 + 4p_3/5$$

$$\text{B}(2)\text{-B}(7) = p_2 - p_3/5 - p_4/4 - p_5/3$$

$$\text{B}(7)\text{-B}(8) = p_2 - p_3/5 + 3p_4/4$$

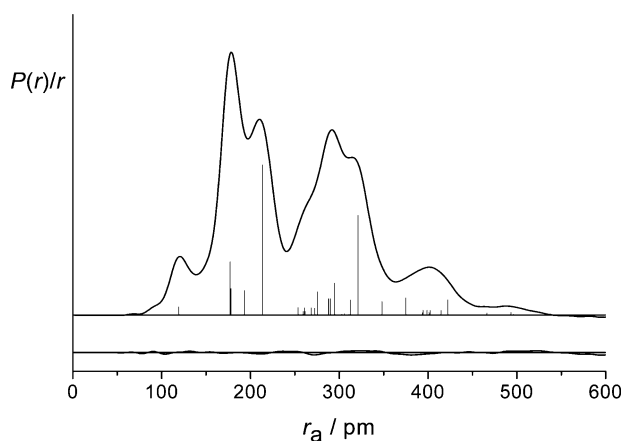
$$\text{B}(7)\text{-B}(12) = p_2 - p_3/5 - p_4/4 + 2p_5/3$$

A single B–H bond length was used ( $p_6$ ), reflecting the fact that the MP2/6-311+G\* calculations showed that the symmetrically unique distances differed by only 0.1 pm. The angles defining the positions of the different hydrogens were more varied and were described by B(12)–B(7)–H ( $p_7$ ) and Se–B(2)–H ( $p_8$ ).

All eight independent geometric parameters were refined using a least-squares method and restraints were applied, using the SARACEN method,<sup>35</sup> to parameters that could otherwise not be refined (Table 3). The restraints were based on values calculated at the MP2/AE3 level and the uncertainties were derived from the change in value of that parameter during the series of calculations that were performed. Additionally, nine groups of amplitudes of vibration were refined. See Table S2 for a list of amplitudes of vibration.‡ Some of the amplitudes of vibration refined with small uncertainties, resulting in the differences between the refined and calculated values appearing quite stark. For example,  $u_{24}$  which is an  $\text{Se}\cdots\text{B}$  non-bonded distance was calculated to be 7.0 pm but refined to 8.6(1) pm. This is not surprising as the level of calculation used was low and the force field was not scaled. The success of the refinement can be assessed numerically using the final  $R$  factor, which was  $R_{\text{G}} = 0.079$  ( $R_{\text{D}} = 0.054$ ), and visually using the goodness-of-fit of the radial-distribution and difference curves as seen in Fig. 2, and the molecular-scattering intensity curves (Fig. S1‡). The least-squares correlation matrix is given in Table S3 and coordinates for the final GED structure and for the calculated structure [MP2/AE3] are given in Tables S4 and S5 respectively.‡

### GIAO calculations

The good agreement between the experimental and calculated  $^{11}\text{B}$  NMR chemical shifts, in particular at the GIAO-MP2 level (see Table 2), strongly suggests that the set of MP2/AE3 internal coordinates is a good representation of the molecular geometry of *closo*-1- $\text{SeB}_{11}\text{H}_{11}$ . This is corroborated by a single-point energy calculation for the experimental geometry of *closo*-1- $\text{SeB}_{11}\text{H}_{11}$  at



**Fig. 2** Experimental radial-distribution curve and theoretical-minus-experimental difference curve for the refinement of 1-SeB<sub>11</sub>H<sub>11</sub>. Before Fourier inversion the data were multiplied by  $s \exp(-0.00002s^2) / [(Z_{\text{Se}} - f_{\text{Se}})(Z_{\text{B}} - f_{\text{B}})]$ .

the MP2/AE3 level, which finds this structure only 2.2 kJ mol<sup>-1</sup> higher in energy than the fully optimised one. We can therefore be confident that the corresponding GED parameters describe the gas-phase molecular geometry well.

The NMR shifts for the boron atoms not adjacent to Se [*i.e.* those for B(2–6) and B(12)] show little dependence on the level of theory, although the latter is antipodally coupled with Se,<sup>36</sup> and is more sensitive to the inclusion of electron correlation (compare SCF and MP2 values in Table 2). According to natural bond orbital analysis, the bonding between Se and B atoms in *closo*-1-SeB<sub>11</sub>H<sub>11</sub> has predominantly p character, *e.g.* sp<sup>6.46</sup> for Se–B(2), equating to 86.4% p character [MP2/AE1]. No large spin–orbit corrections are therefore to be expected for calculations of the <sup>11</sup>B magnetic shieldings, since such effects are usually transmitted *via* a Fermi-contact-type relay mechanism, which is very effective when bonds with high s character are involved,<sup>37</sup> as also found in *arachno*-Se<sub>2</sub>B<sub>8</sub>H<sub>10</sub>.<sup>21</sup> The explicit ZORA approach unambiguously confirmed this expectation (compare the nonrelativistic and relativistic (ZORA) BP86 values in Table 2). As with *arachno*-Se<sub>2</sub>B<sub>8</sub>H<sub>10</sub>, scalar relativistic effects have additionally been assessed by comparing GIAO-HF/AE4 and GIAO-HF/ECP2 results, which differ at most by 0.6 ppm for any of the <sup>11</sup>B nuclei. Therefore relativistic effects can be considered as negligible.

### Effect of including Se in the cage

The inclusion of a selenium atom leads to a substantial lengthening of the B–B linkages in the pentagonal belt adjacent to Se. This is also obvious in the MP2/AE3 structure, although to a lesser extent (see Tables 2 and 3). The same trend is observed for 1-SB<sub>11</sub>H<sub>11</sub>:  $r_{\text{a}} = 190.4(1)$  pm,<sup>5</sup>  $r_{\text{c}} = 187.6$  pm at MP2/6–31G\*.<sup>38</sup> All other B–B bonds are similar in length, and these distances were determined experimentally by introducing differences between them as flexible restraints. It is noteworthy that the experimental amplitudes of vibration (Table S2<sup>†</sup>) are similar to those for *closo*-1-SB<sub>11</sub>H<sub>11</sub>,<sup>5</sup> with the values for bonded and non-bonded cage distances almost identical.

There is also a considerable influence of the Se atom on the electron distribution within the selenaborane. According to natural population analysis (NPA) at the HF/II//MP2/AE3

level Se is positively charged (0.68). A similar value (0.61) is computed for the sulfur atom in 1-SB<sub>11</sub>H<sub>11</sub> (HF/II, using the RMP2(fc)/6–31G\* geometry taken from ref. 38), where a positive charge on sulfur was found to be consistent with experimentally determined dipole moments of 12-X-1-SB<sub>11</sub>H<sub>10</sub> derivatives.<sup>38</sup> The slightly different NPA charges in 1-SB<sub>11</sub>H<sub>11</sub> and 1-SeB<sub>11</sub>H<sub>11</sub> are also in line with the dipole moments (calculated at the same level) of 3.5 and 4.0 D respectively. As a consequence of the change in charge distribution on going from the parent [B<sub>12</sub>H<sub>12</sub>]<sup>2-</sup> to XB<sub>11</sub>H<sub>11</sub> (X = S, Se), the corresponding nucleus-independent chemical shifts (NICS)<sup>39</sup> at the cage centres change from –34.5 ppm for the parent (GIAO-HF/II//RMP2(fc)/6–31G\*)<sup>40</sup> to –29.2 ppm for both SB<sub>11</sub>H<sub>11</sub> and 1-SeB<sub>11</sub>H<sub>11</sub> (the same model chemistries were used as for the NPA analyses). These results suggest that XB<sub>11</sub>H<sub>11</sub> should be somewhat less aromatic than the parent dianion, with its regularly dispersed negative charge and zero dipole moment. Note that the NICS values for these two XB<sub>11</sub>H<sub>11</sub> derivatives are very close to those computed for other experimentally available *closo*-heteroboranes, *e.g.* 2,1- and 6,1-PCB<sub>8</sub>H<sub>9</sub> (–28.9 and –30.0 ppm respectively at GIAO-HF/II//RMP2(fc)/6–31G\*).<sup>41</sup> For the presently unsynthesised congener 1-OB<sub>11</sub>H<sub>11</sub>, the predicted NPA charge on O is –0.68, and the NICS value is –30.2 ppm (employing the same computational protocol as for 1-SB<sub>11</sub>H<sub>11</sub>). The high electronegativity of O (reflected in its negative charge) is likely to increase the electron deficiency in the rest of the cluster, which may make preparation of such a *closo*-oxaborane even more problematic, although the presence of oxygen in a single-cluster borane framework has been achieved in *nido*-[OB<sub>11</sub>H<sub>12</sub>]<sup>-</sup>.<sup>42</sup>

In summary, we have determined the molecular structure of 1-SeB<sub>11</sub>H<sub>11</sub> experimentally using gas-phase electron diffraction, and computationally using appropriate levels of theory and basis sets. The accuracy of the GED structure has been gauged by the excellent agreement with experiment of the <sup>11</sup>B chemical shifts calculated at the GIAO-MP2 level from the GED coordinates. Computed energies support this conclusion.

The tellurium homologue adds to the family of 12-vertex *closo* systems, and in particular to those containing a group 16 element.<sup>43</sup> 1-TeB<sub>11</sub>H<sub>11</sub> has been synthesised and characterised by <sup>11</sup>B NMR spectroscopy and mass spectrometry,<sup>8</sup> but not structurally. Efforts to prepare it once again in order to determine its precise molecular structure are in progress.

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