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Theoretical insights and quantitative prediction of the nature of boron–chalcogen (O, S, Se, Te) interactions using the electron density and the electron localisation function (ELF)

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Abstract

Local electronic structure of the boron-chalcogen bond B-Ch (Ch = O, S, Se, Te) has been investigated from the perspective of topological analysis of the electron localisation function (ELF) and the electron density. Calculations were carried out for H_3BO_3 and 27 experimentally known organoboron compounds with B-Ch bonds deposited in Cambridge Structural Database (CSD), and showed that the B-Ch bonds are covalent with similar values of basin populations (1.50 - 2.26e). They can be characterised as 2-center-2-electron bonds and the nature of the B-O bond differs from the B-Ch (Ch = S, Se, Te) bonds. The AIM analysis shows positive values of the Laplacian of $\rho(\mathbf{r})$ for BCP characterising the B-O bonding and negative values for the B-Ch (Ch = S, Se, Te) bonding. The covalency of the B-O bond may come from dative mechanism. The topological analysis of the ELF shows the B-O bond exhibits the highest median polarity of 0.82 among the studied B-Ch bonds, mainly formed by electrons from the O atom. Polarity is clearly smaller for B-Ch (Ch = S, Se, Te) bonds and its values are between 0.03 and 0.55. The covalency of the boron-chalcogen bond, predicted by calculating differences between electronegativity values is anticorrelated with the basin population for the $V(\text{B},\text{Ch})$ basin.

I. Introduction

Berzelius published the first work associated with boron chalcogenide in 1824, however the synthesis of organoboron with chalcogen atoms remained problematic for the next 150 years [1]. This is due to the fact that chalcogenoborates have a tendency to remain in an amorphous rather than a crystalline state. Moreover, pure elemental boron was very difficult to obtain. In addition, both reaction products and reagents are oxidised and may be also hydrolysed by air. High temperature syntheses began to be widely used to overcome these problems in over past 40 years [2].

Boron atoms in trigonal planar coordination with chalcogen atom can be found mainly in sulphur reaction mixtures with a low boron sulphide content. If the ratio of $M_2S:B_2S_3$ where M = (alkali metal, Ag, Tl) is smaller than 1:1, the boron centre is sp^3 hybridised. Perthioborates with Li^+ and Na^+ are known with a sp^2 hybridized boron centre and have structures containing planar $B_2S_5^{2-}$ groups with five-membered B_2S_3 rings and one additional exocyclic S atoms on each B atom [3]. The first perselenoborates with alkaline earth metal BaB_2Se_6 and BaB_4Se_{13} were synthesised at high temperatures from barium selenide, boron, and selenium [4]. The thioborate formed from $B_{10}S_{20}$ units was shown to be a highly polymeric macrotetrahedral 3d network [5]. In the $Li_{6-x}Cs_xB_{10}E_{18}$ ($x \sim 1$; $E = S, Se$) and $Na_6B_{10}Se_{18}$ new polymeric-layered anion networks connected by Li and Cs cations were observed [6]. The $Li_{6-2x}Ba_{1+x}B_{10}Se_{19}$ and $Li_{3+x}Na_{5-x}B_{10}Se_{19}$, similarly to $Li_{6-2x}Sr_{2+x}B_{10}Se_{20}$ ($x = 0.7$) were reported as excellent candidates for mechanistic analysis of ionic conductivity measurements [7,8,9]. Selenoborate $Cs_8[B_{12}(BSe_3)_6]$ (Cs_830) was obtained from the caesium selenide, boron, and selenium at high-temperature solid state synthesis [10]. Studies of icosahedral- B_{12} containing selenoborates have led to a new crystalline phase for $Na_6[B_{18}Se_{17}]$ containing neighbouring $\{B_{12}Se_{18}\}$ cluster moieties [11].

The work reported in the current paper focuses on the local nature of the boron-chalcogen (B-Ch) interactions investigated by topological analysis of the electron localisation function (ELF) [12], $\eta(r)$, as proposed by Silvi and Savin [13] and the electron density, $\rho(r)$, proposed by Bader [14]. Both are modern methods for investigating electronic structure of molecules. An electronic structure of a molecule in topological analysis of ELF is represented by local maxima (attractors) and localisation basins of $\eta(r)$ field, characterising covalent bonds, lone pairs, core regions, and valence shells in atoms [15]. The integration of $\rho(r)$ over localisation basins

corresponds to calculated electron population, \bar{N} , of chemical bonds, lone pairs, and core regions [16].

The paper is organised as follows: firstly, fundamentals of topological analysis of ELF are described using a simple and well known H_3BO_3 molecule; secondly one selected molecule from Cambridge Structural Database (CSD), namely the trimethylammonio-dicyano(methylmercapto)borate, has been analysed for all B-Ch (Ch = O, S, Se, Te) bonds; thirdly the statistical analysis of 27 organoboron compounds with B-Ch interactions are presented and discussed. Finally, the results are summarised.

When talking about the boron–chalcogen interaction in this paper, we use ‘B-Ch’ in general, but the notation: B-O, B-S, B-Se or B-Te found in the text describes an actual bond type obtained from topological analysis of $\eta(\mathbf{r})$ function.

II. Computational details

The Gaussian 16 (G16) programme [17] has been used to optimise all the investigated structures containing B-Ch bond. The exchange-correlation functional M06-2X [18] and the standard Pople basis set 6-311+G(d,p) [19,20] have been used as implemented in the G16. To describe the nature of B-O, B-Se, and B-Te bonding, the crystal structures with B-S bonding have been used and the S atoms have been replaced with O, Se, and Te atoms, respectively. The molecules containing the B-Te bond have been studied using the def2-TZVPD basis set [21], where 28 core electrons have been replaced by a small effective core potential (ECP) [22]. Other atoms have been described using the standard 6-311+G(d,p) basis set. The def2-TZVPD basis set and ECP have been obtained from Turbomole programme library [23].

All optimised structures have been verified by vibrational analysis, with no imaginary frequencies present. All the molecules have been investigated in a singlet electronic state, using the RHF formalism. The wavefunction stability have been tested for each of the optimised structure (keyword ‘stable’), and no instabilities have been observed.

A single-point energy calculations have been subsequently carried out using the optimised structures in order to generate sets of molecular orbitals (wfn files) for topological analysis of $\eta(\mathbf{r})$ and $\rho(\mathbf{r})$ fields. Topological analyses of the electron localisation function and the electron density have been carried out using Multiwfn [24] and TopMod 09 [25] packages. For the Te derivatives, wavefunction files have been obtained using all electron TZVPall basis set [26]

from the Turbomole programme. Topological analyses of $\eta(\mathbf{r})$ and $\rho(\mathbf{r})$ fields have been implemented using a grid of points with a step size of 0.05 bohr.

Graphical representations of optimised structures and isosurfaces have been prepared using the Chimera [27]. The Cambridge Structural Database (version 5.39, November 2017) [28] have been used to analyse B \cdots O, B \cdots S, B \cdots Se, and B \cdots Te contacts.

III. Results and discussion

1. The principles of the topological analysis of ELF

The details of topological analysis of electron localisation function (ELF) will be presented for the electronic structure of the H₃BO₃ molecule (see Figure S1a in the supplementary material). A motivation for this is to familiarise the reader with two methods of quantum chemical topology (QCT) [29]. Formally, the H₃BO₃ molecule contains six 2-center-2-electron (2c-2e) covalent-polarised bonds (see Figure S1b in the supplementary material): three O-H bonds, formally single with 2e and three B-O bonds, formally single with 2e. In the valence space of the O atoms, four unpaired electrons, grouped in two lone pairs in Lewis representation are expected. Since the B atom has empty p-orbitals, the lone pair contribution in the dative B \leftarrow O bonding is also probable.

The $\eta(\mathbf{r})$ field for the H₃BO₃ molecule is characterised by 13 core and valence attractors. Each attractor can be classified to the synaptic type and this concept has been introduced by Silvi et al. [30]. The synapticity is used for characterisation of a multicentre bonding [16].

Electron density of atomic cores is characterised by the C(B), C(O1), C(O2), and C(O3) core attractors. The 2c-2e bonds, O-H and B-O, are represented by the disynaptic V(O1,H1), V(O2,H2), V(O3,H3), and V(B,O1), V(B,O2), V(B,O3) attractors and basins. The formal lone pairs of oxygen atoms are represented by three monosynaptic V(O1), V(O2), and V(O3) attractors and basins. The disynaptic attractors V(B,O), localised approximately in the midpoints of the B-O bonds confirm that the bonds have partially covalent character. The protonated attractors, V(O1,H1), V(O2,H2), V(O3,H3) are found in the positions of the H atoms and their presence confirms partially covalent O-H bonds.

The integration of $\rho(\mathbf{r})$ for a basin localised for ELF yields the basin population values, \bar{N} , which are collected in Table S1 in the supplementary material. The values obtained for the bonds and lone pairs can be then compared with formal values predicted by the Lewis formula

or MO theory. Thus, the character of the chemical bonds can be described more precisely. For the B-O bonds, the basin population $V(\text{B},\text{O})$ of 2.01e matches nearly perfectly the formal values of 2e. Thus, a single type of the B-O bond is confirmed by the ELF-topological approach. Similarly, two lone pairs on each O atoms are confirmed, because the values of 4.10e are obtained for the non-bonding basins $V_{i=1,2,3}(\text{O}_i)$ which is very close to the formal 4e.

Analysis of the B and Ch atomic contributions to the $V(\text{B},\text{Ch})$ localisation basin, $\text{B}|V(\text{B},\text{Ch})$, $\text{Ch}|V(\text{B},\text{ch})$ has been subsequently performed as proposed by Raub and Jansen [31]. In addition, the polarity index, p_{BCh} (or p_{ChB}) is calculated, which ranges between 0 (homopolar bonds) and 1 (idealised ionic bonds).

For the $V(\text{B},\text{O})$ basins, the p_{OB} value is 0.80. The B-O bond is therefore highly polarised towards the O atom. The contribution of the B atom to the $V(\text{B},\text{O})$ basin is 0.20e (~10%) and is much smaller than that of the O atom, 1.81e (~90%). The results support the covalent-polarized type of the bonding.

Finally, topological analysis of the $\rho(\mathbf{r})$ field in the H_3BO_3 molecule has been carried out. The values of electron density, $\rho_{(3,-1)}(\mathbf{r})$, and Laplacian, $\nabla^2\rho_{(3,-1)}(\mathbf{r})$ for the bond critical points, are shown in Table S1 in the supplementary material. The analysis has been focused on the nature of the boron-oxygen bonds. The B-O bond exhibits high value of $\rho_{(3,-1)}(\mathbf{r})$, 1.370 $\text{e}/\text{\AA}^3$ and a significant positive value of $\nabla^2\rho_{(3,-1)}(\mathbf{r})$, 21.255 $\text{e}/\text{\AA}^5$. Thus, a typical topological signature for the covalent bonding of B-O is not observed, since the positive sign of $\nabla^2\rho_{(3,-1)}(\mathbf{r})$ suggests depletion rather than concentration of the electron density around the bond critical point (BCP). Such characteristic is typical for the dative bond and this result stays in agreement with about 90% contribution of electron density from the O atom to the B-O bond.

In summary, topological analysis of $\eta(\mathbf{r})$ field yields the picture corresponding very well with the classical representation of the electronic structure of H_3BO_3 with three single B-O bonds and two lone pairs for each oxygen atom. The shared-electron type of the B-O bond is supported by topological analysis of $\rho(\mathbf{r})$ field.

2. Comparison of the B-Ch (Ch = O, S, Se, Te) bond in single molecule using topological analysis of ELF

The nature of the boron-chalcogen bonds, B-Ch (Ch = O, S, Se, Te) depends on the chalcogens properties, Ch, which change going down the periodic table. According to the

Allred-Rochow scale [32] the electronegativity values are 3.50 (O), 2.44 (S), 2.48 (Se), 2.01 (Te), and the polarisability values are 5.3 (O), 19.4 (S), 28.9 (Se), 38 (Te), respectively [33]. The absolute values of the electronegativity difference, $|\chi_B - \chi_{Ch}|$, between the B and Ch atoms (in Allred-Rochow scale) are 1.49 (B-O), 0.43 (B-S), 0.47 (B-Se), and 0.00 (B-Te), respectively. Thus, the population of the B-Ch bond should increase going down the periodic table exhibiting increasingly covalent character. On the other hand, the B-Ch bond becomes longer with the heavier atoms and the valence electrons may be more effectively screened from nuclei. In summary, it is not evident whether the valence electrons - from perspective of topological analysis of $\eta(r)$ function - are accumulated in the bonding region increasing covalency or whether the electrons will prefer a localisation in the non-bonding regions (formal lone pairs) of the Ch atom. In addition, very similar electronegativities, but different polarisabilities for S and Se further complicate the picture.

In order to compare properties of the B-Ch bonds, a single molecule, namely the trimethylammonio-dicyano(methylmercapto)borate [34] (ref. code ABEMID) with the boron - sulphur bond, has been selected from the CSD. The sulphur atom has been substituted with the O, Se and Te atoms, then the structures were re-optimised and the electronic structures were investigated using topological analysis of ELF.

The ABEMID molecule possesses the boron-sulphur bond (B-S), formally 2c-2e covalent-polarised bond, assuming the fulfilment of the octet rule for all the atoms. From the topological analysis of ELF perspective at least one bonding attractor should be found between the B and S atoms.

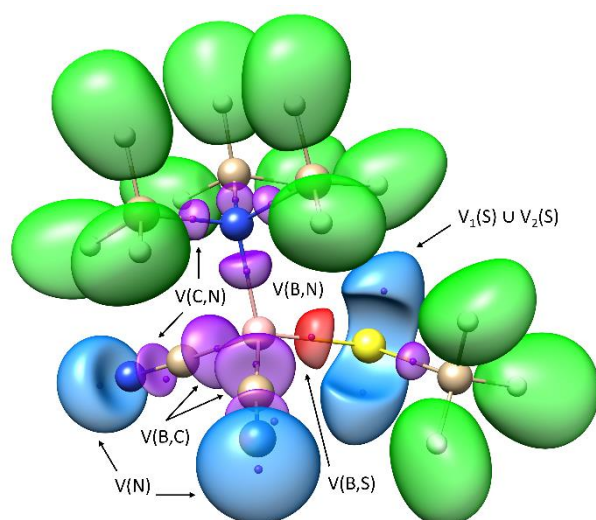


Figure 1. The localisation domains for the ABEMID (trimethylammonio-dicyano(methylmercapto)borate) molecule.

The electronic structure of ABEMID is characterised by 11 core and 28 valence attractors. The same number of attractors have been obtained when the S atom has been replaced by O, Se, and Te atoms. Figure 1 illustrates the localisation domains and the positions of the valence attractors in the field of $\eta(r)$. The values of topological parameters for $\eta(r)$ and $\rho(r)$ fields are presented in Table 1. The substitution of S by other chalcogen atoms does not change its topology of ELF, therefore their electronic structure will be discussed altogether.

Table 1. The topological parameters for the B-Ch (Ch = O, S, Se, Te) bonds calculated for the ABEMID molecule and its derivatives where the S atom has been replaced by the O, Se, and Te atoms. The calculations were carried out at the DFT(M06-2X)/6-311+G(d,p) and DFT(M06-2X)/6-311+G(d,p), def2-TZVPD(Te) computational levels.

Param./Bond	B–O	B–S	B–Se	B–Te
Geometric parameter				
$r_{\text{opt}}(\text{B,Ch})$ (Å)	1.415	1.898	2.043	2.254
Electron localisation function				
\bar{N} (e)	1.65	1.74	1.72	1.68
$\text{B} \text{V}(\text{B,Ch})$ (e)	0.15	0.45	0.61	0.81
$\text{Ch} \text{V}(\text{B,Ch})$ (e)	1.50	1.29	1.11	0.87
p_{ChB}	0.82	0.49	0.29	0.03
Electron density				
$\rho_{(3,-1)}(\mathbf{r})$ (e/Å ³)	1.236	0.897	0.790	0.667
$\nabla^2\rho_{(3,-1)}(\mathbf{r})$ (e/Å ⁵)	16.519	-5.953	-4.374	-2.571

$r_{\text{opt}}(\text{B,Ch})$ - the optimised bond length

\bar{N} - the basin population for $\text{V}(\text{X},\text{Y})$

$\text{B}|\text{V}(\text{B,Ch})$ - the contribution of the B quantum atom to the $\text{V}(\text{B,Ch})$ localisation basin

$\text{Ch}|\text{V}(\text{B,Ch})$ - the contribution of the Ch quantum atom to the $\text{V}(\text{B,Ch})$ localisation basin

p_{ChB} - the polarity index for the Ch-B bond

$\rho_{(3,-1)}(\mathbf{r})$ - the electron density value for the B-Ch bond critical point

$\nabla^2\rho_{(3,-1)}(\mathbf{r})$ - the Laplacian value for the B-Ch bond critical point

The B-Ch bond, formally single, is characterised by one valence bonding attractor and basin, i.e. $\text{V}(\text{B},\text{O})$, $\text{V}(\text{B},\text{S})$, $\text{V}(\text{B},\text{Se})$, and $\text{V}(\text{B},\text{Te})$. Thus, two-centre covalent character of the bonding is confirmed regardless of the chalcogen atom. The population of the bonding basin

ranges between 1.65e (B-O) and 1.74e (B-S). Those values are smaller than 2e therefore the nature of the bond should be described using two types of the Lewis formulas: B-Ch (dominant) and B^+Ch^- , B^-Ch^+ . The boron-chalcogen bond is dominated by a covalent character (single bond), but also exhibits some contribution of the ionic nature. Generally, there is no clear linear covalency change going down XIII group as measured by the value of \bar{N} for V(B,Ch).

The polarity of the B-Ch bond, p_{ChB} , decreases from 0.82 (B-O) to 0.03 (B-Te). This means electron density is polarised towards chalcogen atom, which donates more electron density to the bond than the B atom. The smallest atomic contribution of the B atom to V(B,Ch) basin is 0.15e (B-O) and the largest is 0.81e (B-Te). The chalcogen atom's contribution to the V(B,Ch) basin decreases from oxygen (1.50e) to tellurium (0.87e). Percentage contribution of electron density for B-O is smaller than 10% from boron onwards. Similar value for B-O has also been obtained for the H_3BO_3 molecule. Interestingly, the smallest p_{ChB} has been found for the Te derivative, which is caused by similar values of atomic contributions from both B and Te atoms to the B-Te bond. This result confirms classical covalent character of the B-Te interaction with the smallest $|\chi_B - \chi_{Ch}|$ value.

The electronic structure of ABEMID molecule studied by topological analysis of $\rho(r)$ field consists of 45 critical points: 23 NCPs and 22 BCPs. The same number of critical points has been obtained for the O, Se, and Te derivatives. The $\rho_{(3,-1)}(r)$ value for B-O is large (1.236 $e/\text{\AA}^3$) and decreases to 0.667 $e/\text{\AA}^3$ for B-Te. Assuming that the covalency of the B-Ch bond is larger when the value of $|\chi_B - \chi_{Ch}|$ is smaller, i.e. going down the group, such covalency should be reflected by increasing the value of $\rho_{(3,-1)}(r)$. However, such effect has not been observed. Similar result has been obtained for the $\nabla^2\rho_{(3,-1)}(r)$ values. The B-O bond here exhibits a high positive $\nabla^2\rho_{(3,-1)}(r)$ value of 16.519 $e/\text{\AA}^5$, similarly to the equivalent bond in H_3BO_3 . A positive value in conjunction with a relatively large value of $\rho_{(3,-1)}(r)$, suggests that the bond has a dative character. However, for the B-S, B-Se, and B-Te bonds, $\nabla^2\rho_{(3,-1)}(r)$ is negative (-5.953, -4.374, and -2.571 $e/\text{\AA}^5$, respectively), thus electron density is accumulated around BCP, and the bonds are of covalent-polarised type. In addition, it is worth noticing that for the B-Ch bonds, with more covalent character, the absolute values of $\nabla^2\rho_{(3,-1)}(r)$ are decreasing.

To sum up, obtained results show that the nature of the B-O bond is different than other B-Ch bonds (S, Se, Te).

3. The nature of the boron-chalcogen bonding based on topological analysis of ELF

In order to get a deeper insight into the nature of the B-Ch (Ch = O, S, Se, Te) bonds, comparative topological analysis of ELF have been carried out for 27 organoboron compounds with the B-Ch bond.

Firstly, the molecules with the B-S bond have been selected from the CSD and their structures have been optimised at the DFT level (see Computational details). The optimised structures are presented in Figure S2 in the supplementary material. Analysis of the B \cdots S contact distances in crystal structures shows that approximately 95% of the B \cdots S interactions occur at distances between 1.74 and 2.14 Å. The histogram of the B \cdots S distances is presented in Figure 2. The 40% of compounds contains the B-S bonds in the range from 1.90 to 1.98 Å. The DFT-optimised bond lengths $r_{\text{opt}}(\text{B,S})$, are between 1.794 Å and 1.987 Å and are in good agreement with the contacts distances found in the CSD data.

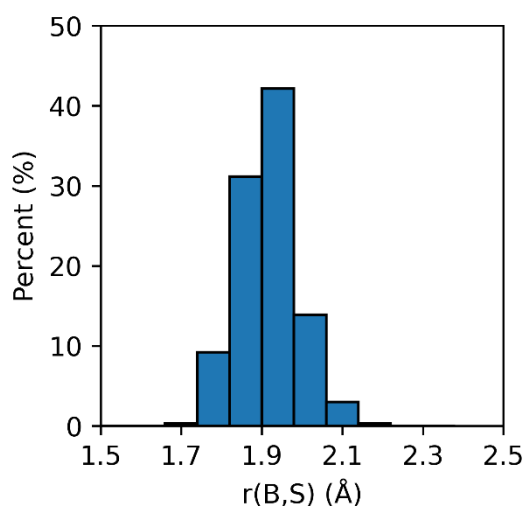


Figure 2. The histogram of the B \cdots S bond distances for the crystal structures deposited in Cambridge Structural Database.

Secondly, the S atom has been substituted by the O, Se, and Te atoms. Their structures were re-optimised and the topological analysis of $\eta(r)$ function were subsequently performed. The values of $r_{\text{opt}}(\text{B,Ch})$, basin populations for $V(\text{B,Ch})$, \bar{N} , atomic contributions to the $V(\text{B,Ch})$ basin, $\text{B}|V(\text{B,Ch})$, $\text{Ch}|V(\text{B,Ch})$, and polarity indices, p_{ChB} , are presented in Table 2.

The values of $r_{\text{opt}}(\text{B,Ch})$ for the oxygen, selenium and tellurium range from 1.359 to 1.536 Å, 1.924 to 2.123 Å, and 2.115 to 2.316 Å, respectively. A substantial elongation of $r_{\text{opt}}(\text{B,Ch})$

bonds is observed from O to S. In contrast, a relatively small change to the optimised distances is found when atom changes from S to Se and from Se to Te.

Table 2. The optimised distance of the B-Ch bond, $r_{\text{opt}}(\text{B,Ch})$, and numerical parameters of the boron - chalcogen bond obtained from topological analysis of ELF. The 27 molecules with the B-S bond have been selected from CSD and the calculations were performed for the derivatives where the S atom has been replaced by the O, Se, and Te atoms.

Param./Bond	B–O		B–S		B–Se		B–Te	
	Range	Median	Range	Median	Range	Median	Range	Median
$r_{\text{opt}}(\text{B,Ch})$ (Å)	1.359 – 1.536	1.384	1.794 – 1.987	1.827	1.924 – 2.123	1.967	2.115 – 2.316	2.175
\bar{N} (e)	1.56 – 2.26	2.04	1.60 – 2.22	2.01	1.54 – 2.21	2.00	1.50 – 2.12	1.90
$\text{B V}(\text{B,Ch})$ (e)	0.10 – 0.21	0.17	0.26 – 0.50	0.41	0.32 – 0.76	0.59	0.51 – 1.10	0.95
$\text{Ch V}(\text{B,Ch})$ (e)	1.42 – 2.11	1.84	1.21 – 1.73	1.55	1.04 – 1.53	1.32	0.82 – 1.14	0.99
p_{ChB}	0.79 – 0.88	0.82	0.46 – 0.69	0.55	0.27 – 0.60	0.34	0.00 – 0.35	0.03

\bar{N} - the basin population

$\text{B|V}(\text{B,Ch})$ - the contribution of the boron atom to the B-Ch bond

$\text{Ch|V}(\text{B,Ch})$ - the contribution of the chalcogen atom to the B-Ch bond

p_{ChB} - the polarity index

Topological analysis of ELF, carried out for 27 molecules, yields the bonding disynaptic attractors, $\text{V}(\text{B,Ch})$, for all the B-Ch bonds investigated. Thus, all boron - chalcogen bonds have covalent-polarised nature. Population values calculated for all the $\text{V}(\text{B,Ch})$ basins (Ch = O, S, Se, Te), characterising all the investigated molecules (see Table 2), are between 1.50e and 2.26e. The B-O, B-S, B-Se, and B-Te bonds do not form any sets of well separated ranges of populations. The result is very similar to the basin populations (1.65e - 1.74e) obtained for the ABEMID molecule and its O, Se, Te-derivatives. The analysis of median values shows smaller basin population for longer B-Ch bonds: 2.04e (O), 2.01e (S), 2.00e (Se), and 1.90e (Te). However, the observed effect is rather small. Because, the values of \bar{N} for $\text{V}(\text{B,Ch})$ are close to formal value of 2e, expected for the single bond, we may roughly state, that all B-Ch bonds have two-center-two-electron character (2c-2e).

Based on the Lewis representations, the boron-chalcogen bonds can be described using the following resonance structures: B-Ch, B⁺Ch⁻, and B⁻Ch⁺. Small contributions of the ionic structures B⁺Ch⁻ (B⁻Ch⁺) could explain a smaller than 2e value of basin populations. Populations larger than 2e result from a double B=Ch bond participation in a resonance equilibrium. However, the amount above 2e is very small and therefore that double character is deemed negligible. In general, the character of boron - chalcogen bonds is covalent-polarised character and well represented by the single B-Ch bond.

The largest (absolute) value of the electronegativity difference, $|\chi_{\text{B}} - \chi_{\text{Ch}}|$, between the B and O atoms is 1.49. Thus, assuming that the amount of electrons „concentrated” in the V(B,O) basin is a measure of the covalency, the B-O bonds should be the least covalent among all B-Ch bonds. This hypothesis has not been fully confirmed, due to the values of basin populations for B-O bonds (1.56e - 2.26e) very similar to the range of \bar{N} obtained for the B-S bonds (1.60e - 2.22e) and other bonds (see Table 2). The median value for \bar{N} does not show any clear difference either between B-O (2.04e) and B-S (2.01e), B-Se (2.00e), and B-Te (1.90e) bonds, although some trend is emerging. However, the correlation with decreasing values of $|\chi_{\text{B}} - \chi_{\text{Ch}}|$ is opposed to that expected. It appears that theoretically more covalent bonds are related to smaller values of the basin population for V(B,Ch).

In order to study a relationship between topological parameters for the B-Ch bonds and $r_{\text{opt}}(\text{B,Ch})$ bond length, the model of the linear regression has been applied. The values of \bar{N} for the V(B,Ch) basin, the atomic contributions to the V(B,Ch) basin and polarity indices p_{ChB} have been considered.

Analysis of the relationship between basin populations for V(B,Ch) and $r_{\text{opt}}(\text{B,Ch})$ presented in Figure 3 shows larger values of \bar{N} for shorter bonds. Thus, the shorter B-Ch bonds exhibit more covalent character. Such effect is evident when assuming that the slope of the regression line increases from -4.536 e/Å (B-O) to -2.204 e/Å (B-Te). The smallest value of slope has been obtained for B-O and the largest for B-Te. The boron-tellurium bonds become less covalent as measured by the basin population, in the fastest way on growing bond length. This effect can be explained by atomic orbital overlap (covalent contribution) and also the smallest ionic contribution. The covalent component depends strongly on the interatomic distance and is the main cause of the observed electron depletion. The B-S and B-Se bond values on the slope are similar and therefore will have a similar bonding character.

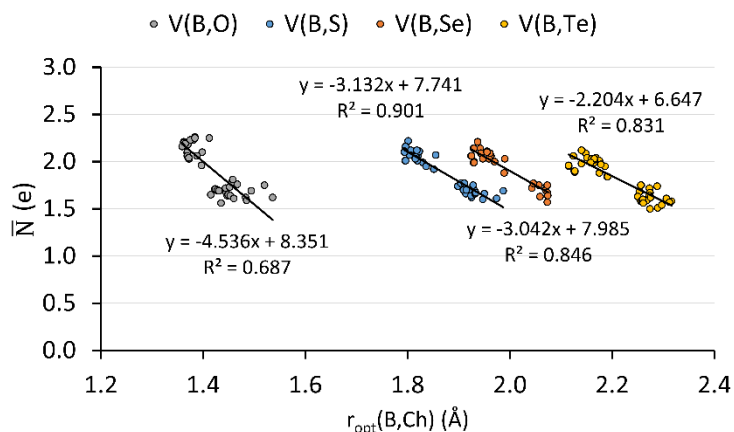


Figure 3. The relationship between the basin population \bar{N} of V(B,Ch) (Ch = O, S, Se, Te) and the optimised $r_{\text{opt}}(\text{B,Ch})$ bond length. The linear model is used in the regression analysis.

The polarity of the boron-chalcogen bond, measured by the polarity index, p_{ChB} , shows that the bonds are polarised towards the chalcogen atom, which delivers larger amount of electron density to the B-Ch bond. The p_{ChB} values are in the range from 0.88 to 0.79 (B-O), from 0.60 to 0.27 (B-S), from 0.69 to 0.46 (B-Se), and from 0.35 to 0.00 (B-Te). Thus, decreasing difference in electronegativity between the B and Ch atoms is reflected in decreasing difference in polarity of the B-Ch bond. Such effect is well illustrated using the median value for p_{ChB} 0.82 (B-O), 0.55 (B-S), 0.34 (B-Se), and 0.03 (B-Te). It is worth noting that the range of the p_{ChB} values for the B-O bonds is much smaller than the values for other B-Ch bonds. Electronic nature of the B-O bonds appear to be different than the nature of other B-Ch bonds. Similar conclusion can be drawn by analysing a graphical representation of the relationship between the p_{ChB} index and $r_{\text{opt}}(\text{B,Ch})$ bond length shown in Figure 4c. The boron-oxygen bonding character has been previously investigated by one of us in ref. [35] and current results are in good agreement with the published data. Some interesting results have been obtained for B-Te, where the smallest value of p_{ChB} is 0, which indicates an idealised covalent character. Such lack of polarity is in a good agreement with electronegativity difference between the B and Te atoms (Allen-Rochov scale) of 0.00.

Analysis of atomic contributions to the bonding basin can give information about the „morphology” of the B-Ch chemical bond. The respective values are shown in Table 2. Median values of the B atom contribution, represented by $\text{B|V}(\text{B,Ch})$, are between 0.17e (B-O) and 0.95e (B-Te). The chalcogen atoms’ contributions, $\text{Ch|V}(\text{B,Ch})$, are between 1.84e (B-O) and 0.99e (B-Te). Going down XIII group of the periodic table the contribution of the boron atom gradually increases and that of the chalcogen atom decreases. All the B-Ch bonds studied

are formed by electron density, deriving mainly from chalcogen atoms. Using the language of MO theory such results could be associated with dative bonding created by occupied orbitals of Ch atom interacting with empty p-orbitals of the B atom. Unfortunately, a distinction between the dative-covalent and covalent-(un)polarized bond in the framework of topological analysis of ELF is only possible using analysis of the decomposition reaction, which is beyond the scope of this study.

Analysis of relationships between the $B|V(B,Ch)$, $Ch|V(B,Ch)$, and $r_{opt}(B,Ch)$ values, modelled by linear regression, presented graphically in Figures 4a and 4b, reveals very small dependence between both parameters. Generally, an elongation of the B-O bond results in decreasing value of the atomic contribution. This result is understandable given that stretching of A-B bond diminishes the population of the bonding basin $V(A,B)$.

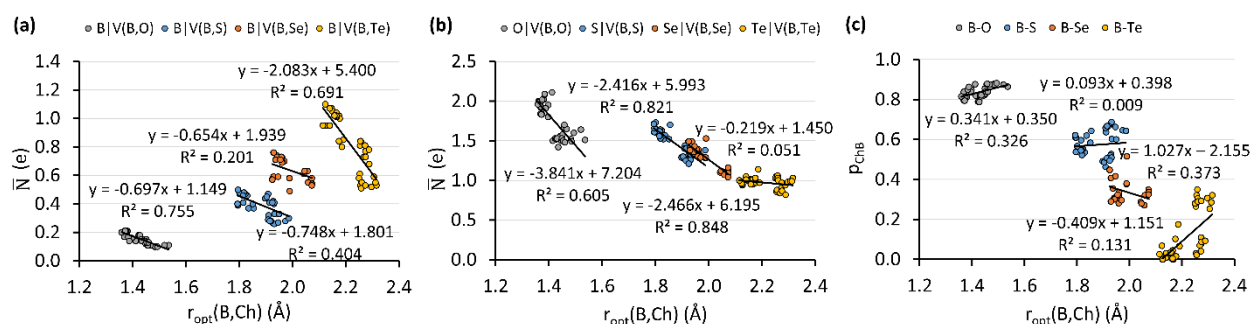


Figure 4. a) The relationship between the boron atomic contribution, $B|V(B,Ch)$, to the localisation basin $V(B,Ch)$ and the optimised $r_{opt}(B,Ch)$ bond length, b) The relationship between the chalcogen atomic contribution, $Ch|V(B,Ch)$, to the localisation basin $V(B,Ch)$ and the optimised $r_{opt}(B,Ch)$ bond length, c) The relationship between the polarity index value, p_{ChB} , and the optimised $r_{opt}(B,Ch)$ bond length. The linear model has been used in the regression analysis for all cases.

4. The nature of the B-Ch bonds based on topological analysis of $\rho(r)$ field

The nature of the boron-chalcogen bond in 27 molecules has been characterised using the values of the electron density for the (3,-1) bond critical point, $\rho_{(3,-1)}(r)$, the Laplacian of the electron density, $\nabla^2\rho_{(3,-1)}(r)$, ellipticity, $\varepsilon_{(3,-1)}(r)$, and the values of the delocalisation index, DI, a measure of electron density delocalised between quantum atoms B and Ch. The respective values are collected in Table 3. Furthermore, those parameters have been analysed in respect to the bond length, $r_{opt}(B,Ch)$. Graphical representations for the analysed data are presented in Figure 5.

Table 3. The numerical parameters of the boron - chalcogen bond obtained from topological analysis of $\rho(\mathbf{r})$ field. The 27 molecules with the B-S bond have been selected from CSD and the calculations were performed for the derivatives where the S atom has been replaced by the O, Se, and Te atoms.

Param./Bond	B-O		B-S		B-Se		B-Te	
	Range	Median	Range	Median	Range	Median	Range	Median
$\rho_{(3,-1)}(\mathbf{r})$ ($e/\text{\AA}^3$)	0.896 – 1.383	1.301	0.718 – 1.036	0.986	0.654 – 0.936	0.855	0.588 – 0.799	0.746
$\nabla^2\rho_{(3,-1)}(\mathbf{r})$ ($e/\text{\AA}^5$)	12.417 – 22.406	21.185	-6.071 – 1.325	-4.344	-6.504 – 3.503	-5.624	-3.617 – 2.172	-2.945
$\varepsilon_{(3,-1)}(\mathbf{r})$	0.001 – 0.219	0.045	0.000 – 0.293	0.073	0.009 – 0.197	0.103	0.016 – 0.250	0.136
DI	0.318 – 0.558	0.423	0.445 – 0.846	0.663	0.512 – 1.022	0.855	0.618 – 1.230	1.028

$\rho_{(3,-1)}(\mathbf{r})$ - the electron density value for the bond critical point

$\nabla^2\rho_{(3,-1)}(\mathbf{r})$ - the Laplacian value for the bond critical point

$\varepsilon_{(3,-1)}(\mathbf{r})$ - the ellipticity for bond critical point

DI - the delocalisation index for the B and Ch atoms

When analysing the B-Ch bonds taking into account a decreasing absolute value of electronegativity (Allred-Rochow) difference between the B and Ch atoms, $|\chi_B - \chi_{Ch}|$, i.e. in the order: B-O (1.49), B-S (0.43), B-Se (0.47), B-Te (0.00), the increasing covalency is expected, reflected by increasing value of $\rho_{(3,-1)}(\mathbf{r})$, because more electron density should be accumulated around BCP. When considering the associated value of the Laplacian of $\rho_{(3,-1)}(\mathbf{r})$ an interesting question appears as to whether the absolute value of $\nabla^2\rho_{(3,-1)}(\mathbf{r})$ will increase with the expected increase covalency of the B-Ch bonds.

For the $\rho_{(3,-1)}(\mathbf{r})$ parameter the largest values, between 0.896 and 1.383 $e/\text{\AA}^3$, have been found for the B-O bonds, which are the shortest among all B-Ch bonds investigated. This result suggests the B-O bond has covalent-polarised character. It is worth emphasising that the largest values of $\rho_{(3,-1)}(\mathbf{r})$ correspond to the largest difference of the atomic electronegativities among all B-Ch bonds.

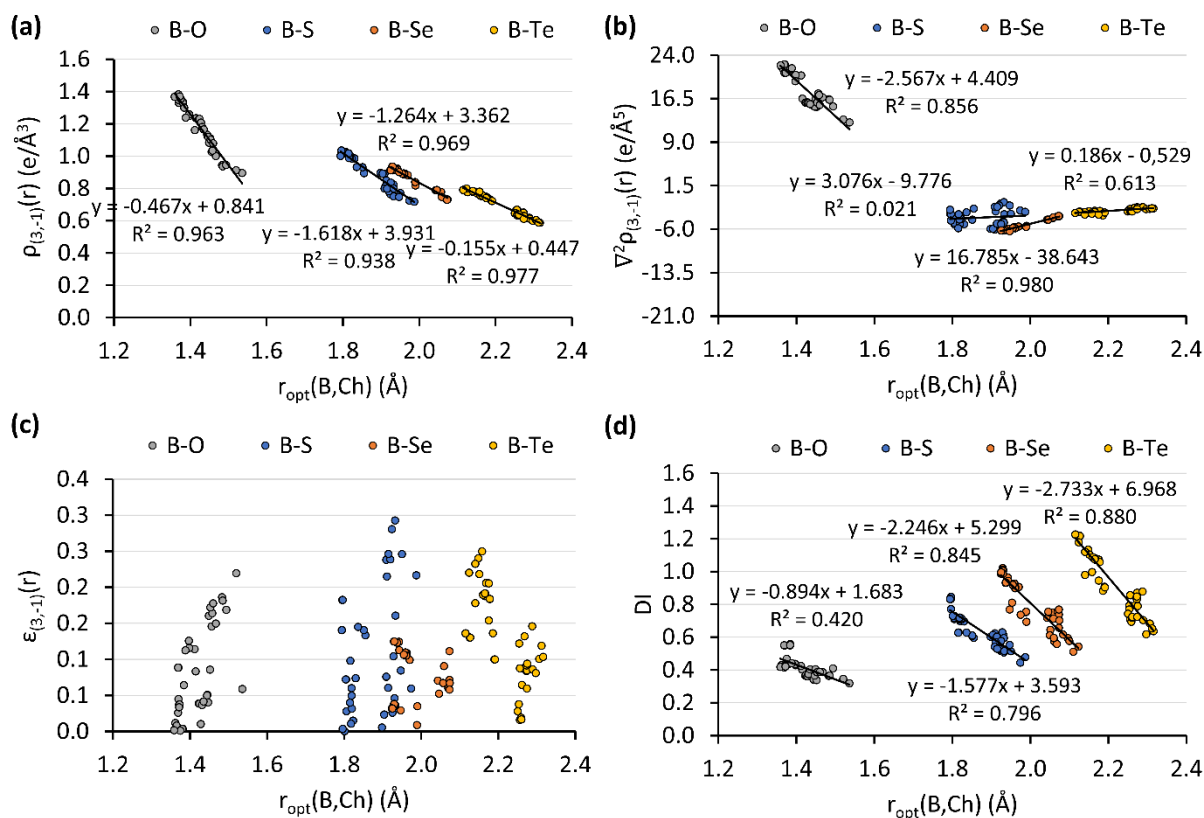


Figure 5. a) The relationship between the electron density value for BCP in the B-Ch (Ch = O, S, Se, Te) bond, $\rho_{(3,-1)}(r)$, and the optimised $r_{\text{opt}}(\text{B,Ch})$ bond length, b) The relationship between the Laplacian of the electron density, $\nabla^2\rho_{(3,-1)}(r)$, value for BCP and the optimised $r_{\text{opt}}(\text{B,Ch})$ bond length, c) The relationship between the ellipticity, $\epsilon_{(3,-1)}(r)$, value for BCP and the optimised $r_{\text{opt}}(\text{B,Ch})$ bond length, d) The relationship between the delocalisation index, DI, calculated for the B and Ch atoms and the optimised $r_{\text{opt}}(\text{B,Ch})$ bond length. The linear model has been used in the regression analysis for all cases.

Interestingly, the values for the B-S, B-Se, and B-Te bonds (0.718-1.036 e/Å³, 0.654-0.936 e/Å³, and 0.588-0.799 e/Å³, respectively) are not in an increasing order as it has been expected (see Figure 5a). The B-Ch bonds, going down the periodic table, do not exhibit increasing amount of electron density for the BCP. This is evident when analysing median values of $\rho_{(3,-1)}(r)$, (see Table 3), decreasing from 1.301 e/Å³ (O) through 0.986 (S), 0.855 (Se) to 0.746 e/Å³ (Te). The bond character is correlated with $r_{\text{opt}}(\text{B,Ch})$ bond length, the longer the bond the smaller is covalency. The electron density for BCP is depleted along with increasing bond length, and such effect is most evident for the B-O bonds and decrease in the order: B-S, B-Se, and B-Te.

The Laplacian values for electron density for BCP of the B-O bond are positive (12.417–22.406 e/Å⁵) and also present the largest absolute values among all B-Ch bonds investigated. The positive value of $\nabla^2\rho_{(3,-1)}(r)$ suggests depletion of electron density around BCP and together with the large values of $\rho_{(3,-1)}(r)$ confirms the dative character of the B-O bond. This conclusion

is in partial agreement with obtained ELF results. Going from the oxygen to the heavier chalcogens a change of the sign for $\nabla^2\rho_{(3,-1)}(r)$ is observed. The values for B-S, B-Se, and B-Te bonds are negative in all cases. Thus, the electron density is concentrated around BCP and the bonds have covalent-polarised character. The nature of these bonds is different than that of the B-O bond. Change of the bonding character is also well reflected by median values of $\nabla^2\rho_{(3,-1)}(r)$ for the B-Ch bonds: -4.344 (B-S), -5.624 (B-Se), and -2.945 (B-Te) $e/\text{\AA}^5$, respectively. Those values may support the conclusion from the previous section that the B-Ch bonds with decreasing value of $|\chi_B-\chi_{Ch}|$ actually do not exhibit features of increasing covalent character. However, one should be cautious when interpreting the value obtained for the B-Te bonds, because a different basis set has been used.

The ellipticity at the BCP can be a measure of anisotropy of the curvature of the electron density in the directions normal to the bond [36]. The obtained values of $\varepsilon_{(3,-1)}(r)$ are not correlated with $r_{opt}(B,Ch)$. The $\varepsilon_{(3,-1)}(r)$ values for B-O and B-S are small and range between 0.000 and 0.293. However, going down periodic table an insignificant increase of $\varepsilon_{(3,-1)}(r)$ from 0.009 to 0.197 (B-Se) and from 0.016 to 0.250 (B-Te) can be noted, but in all cases $\varepsilon_{(3,-1)}(r)$ is small indicating isotropy of the electron density at BCP. Similar results were obtained for the dative bond, B-N, in H_3B-NH_3 molecule [37].

The delocalisation index, DI, is a quantitative measure of the number of electron pairs delocalized between two atomic basins. It is very often considered to be equivalent to the topological bond order [38]. Ideally for 2c-2e covalent bond, a number of electron pairs exchanged between the B and Ch quantum atoms should be close to 1. Values of the DI for the B-O and B-S are between 0.318 and 0.558 (median 0.423) and between 0.445 and 0.846 (median 0.663), respectively. Those values are smaller than 1.000, which do not confirm B-O and B-S bonds to be typically single bonds from a perspective of topological analysis of $\rho(r)$. However, for the B-Se and B-Te bond delocalisation index yields 0.512-1.022 (median 0.855) and 0.618-1.230 (median 1.028), where the highest obtained DI value is above 1.000 and therefore suggests a single bond. This results is in a good agreement with the ELF analysis and with published data for B-N bond [37]. It is worth noting that values of DI gradually increase from 0.318 (O) to 1.230 (Te) when going down the periodic table (median). This confirms increasingly covalent character for the B-Ch interactions in agreement with classical description based on the difference between the electronegativity values, $|\chi_B-\chi_{Ch}|$ decreasing from O to Te. The analysis of the relationship between DI values and $r_{opt}(B,Ch)$ lengths, presented in Figure 5d, shows small negative slope of the regression line for the B-O bonds, which increases

going the group. It seems that the bonds with expected larger covalent character are more susceptible to loss of electron pairs, which are exchanged between quantum atoms, at bond dissociation.

Since both the DI index and the population of $V(B,Ch)$ can be an indicator of bond order, it is interesting to study a relationship between them. The regression analysis has been used with the linear model (see Figure 6). It is evident, however, that both parameters do not show the same characteristic of the boron - chalcogen interaction.

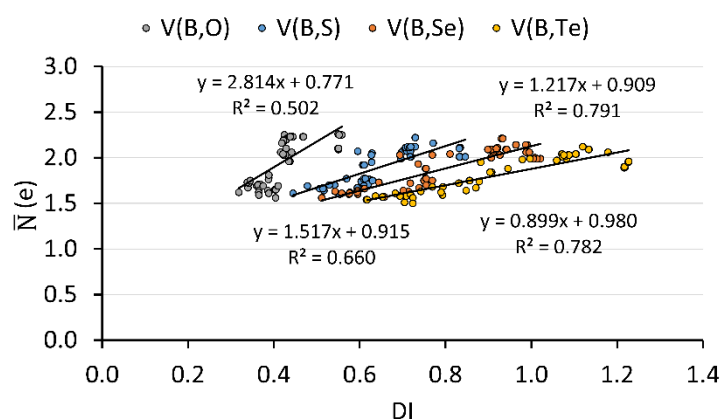


Figure 6. The relationship between the population, \bar{N} , for the localisation basin $V(B,Ch)$, which corresponds to the B-Ch two-center bond from ELF-topological perspective, and the delocalisation index, DI, calculated for the B and Ch atoms in topological analysis of the electron density field. The linear model has been used in the regression analysis.

The slope of the regression line decreases in the chemical group from 2.814 (B-O) to 0.899 (B-Te). Thus, the increase of DI is associated with the increase of basin population for the $V(B,Ch)$ basin. Such effect is expected, since a number of exchanged electron pairs between quantum atoms should be correlated with the basin (bond) population. However, this effect decreases when the B-Ch bond is formed by a less electronegative chalcogen atom, i.e. with a larger expected covalency. It is the strongest for the covalent-dative B-O bond, for which the number of electron pairs exchanged between the B and O atoms is the smallest among all investigated B-Ch bonds.

Interestingly, for the DI value of zero, indicating no exchange of electron pairs between the B and Ch quantum atoms (no covalent bonding), the value of the $V(B,Ch)$ is much larger than zero: 0.771 (O), 0.915 (S), 0.909 (Se), 0.980 (Te). In general, for the $A \cdots B$ interaction, which is not covalent type, the $V(A,B)$ bonding basin is absent and the basin population should be zero. The values larger than zero may be explained as the leftover of electron density in the

B-Ch bond, described by the $V(\text{B},\text{Ch})$ basin, after heterolytic dissociation of the B-Ch bond. The study by Krokidis et al. [39] shows that the dissociation of the A-B bond represented by the $V(\text{A},\text{B})$ basin yields initially two monosynaptic basins $V(\text{A})\cdots V(\text{B})$, subsequently annihilated step by step. In our case the $V(\text{B},\text{Ch})$ basin should be split into $V(\text{B})$ and $V(\text{Ch})$ basins, when covalent-polarised type is considered or into $V(\text{Ch})$ basin when the B-Ch bond is covalent-dative with Ch atom donating a bonding pair. The populations: 0.771e (O), 0.915e (S), 0.909e (Se), 0.980e (Te) can correspond to the $V(\text{O})$, $V(\text{S})$, $V(\text{Se})$ and $V(\text{Te})$ basins, resulting from the $V(\text{B},\text{Ch})$ annihilation.

IV. Conclusions

The electronic structure of the boron-chalcogen bond, B-Ch (Ch = O, S, Se, Te) has been explained using topological analysis of $\eta(\mathbf{r})$ and $\rho(\mathbf{r})$ fields. Both methods yield results independent from molecular orbitals chosen for the analysis.

Calculations carried out for 27 experimentally known molecules show that the B-Ch bonds are principally covalent with similar values of the basin populations (1.50-2.26e). They can be roughly characterised as 2-center-2-electron bonds. Covalency of the B-Ch bond, measured by population for the $V(\text{B},\text{Ch})$ basin, decreases with the increase of the $r_{\text{opt}}(\text{B},\text{Ch})$ length.

The nature of the B-O bond differs from the nature of the B-Ch (Ch = S, Se, Te) bonds. The B-O bond has the highest degree of the polarity of 0.82 (median) among all the studied B-Ch bonds. The oxygen quantum atom delivers about 90% (median) of electron density of $V(\text{B},\text{Ch})$. The B-O bond has a large positive value of $\nabla^2\rho_{(3,-1)}(\mathbf{r})$ as oppose to negative values obtained for the other B-Ch bonds. From perspective of AIM methodology, this result can indicate a partially dative character of the B-O bond. Correlation between $\bar{N}[V(\text{B},\text{Ch})]$ and $r_{\text{opt}}(\text{B},\text{Ch})$ shows much steeper curve for the B-O bonds than for the other B-Ch bonds. This means more rapid loss of covalency for the former.

The B-S and B-Se bonds are similar in the nature, due to similar values of the topological parameters obtained. The basin populations of $V(\text{B},\text{Ch})$ are close to 2e, corresponding to the idealised single bond. The negative values of $\nabla^2\rho_{(3,-1)}(\mathbf{r})$ indicate covalent-polarised character with electron density shared by both atoms. The polarity of the bonds (median) of 0.55 (S), and 0.34 (Se) is clearly smaller than that calculated for the B-O bonds.

The B-Te had also a covalent-polarised character ($\nabla^2\rho_{(3,-1)}(\mathbf{r}) < 0$), and the population of its $V(\text{B},\text{Ch})$ basin is similar to that obtained for the bonds formed by lighter chalcogens.

However, the bond is almost equally formed by electrons from both atoms with the low value of the polarity index, p_{ChB} of 0.03 (median).

We believe that our study based on topological analysis of $\rho(r)$ and $\eta(r)$ fields increases knowledge about the nature of the boron–chalcogen interactions.

V. Acknowledgments

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VI. Conflicts of interest

The authors declare no conflict of interest with regard to the publication of this article.

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