1,12-Diiodo-Ortho-Carborane: A Classic Textbook Example of the Dihalogen Bond †

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Abstract: The crystal structure of 1,12-diiodo-ortho-carborane 1,12-I2-1,2-C2B10H10 was determined by single crystal X-ray diffraction. In contrary to earlier studied 1,12-dibromo analogue 1,12-Br2-1,2-C2B10H10, its crystal packing is governed by the presence of the intermolecular I···I dihalogen bonds between the iodine atom attached to the carbon atom (acceptor) and the iodine atom attached to the antipodal boron atom (donor) of the carborane cage. The observed dihalogen bonds belong to the II type and are characterized by classical parameters: shortened I···I distance of 3.5687(9) Å, C−I···I angle of 172.61(11)° and B−I···I angle of 92.98(12)°.

Keywords: carborane; iodo derivatives; dihalogen bond; X-ray structure; quantum chemical calculations

1. Introduction

Carboranes [CB11H12]− and C2B10H12, in which one or two vertices in boron icosahedron are replaced by a carbon unit, are a fascinating family of compounds with exceptional chemical and thermal robustness, unique geometry, rigidity, and synthetic versatility [1]. Selective chemical substitution of hydrogen atoms at carbon or boron atoms in these clusters allows for their use as rigid, three dimensional scaffolds upon which to construct new materials, such as liquid crystals [2–5], nonlinear optical materials [6–9], carborane-based anticrowns [10], and even in drug design [11,12]. As rigid molecules of fixed length, carboranes can be used as building blocks (“molecular tinkertoys”) [13–18] for supramolecular assemblies, such as porous coordination polymers or metal–organic frameworks (MOFs) [19–22]. Another type of supramolecular structures with the participation of carboranes is based on the acidity of their CH groups, which demonstrate a high potential for hydrogen bonding. Indeed, intermolecular C−H···O and C−H···N hydrogen bonding, including bifurcated interactions, features in much of the supramolecular chemistry of carboranes [23,24]. Functionalization of carboranes with different substituents including halogen atoms opens an opportunity to the formation diverse noncovalent interactions [25,26]. Thus, the intermolecular C−H···X−B hydrogen bonds were found to stabilize crystal structures of fluoro- [27], bromo- [28] and iodo- [29–34] derivatives of ortho-carborane. Alternatively, hydrogen atoms bonded to the carbon atoms can also be replaced by halogen atoms. It should be noted that when substituted at a carbon atom, carborane acts as an electron-attracting group with respect to a substituent, while when substituted at boron atoms it plays the role of an electron-releasing group. The further the location of a substituent is from carbon atoms, the higher the electron-releasing ability is the carborane cage [35].
Halogen bonds are one of the strongest noncovalent intermolecular interactions, and are formed between the σ-hole of a halogen atom and nucleophile [36–39]. In the case of halogen bonds in which both atoms are halogens, the σ-hole is activated by electron acceptor substitution of a halogen while donor substituents are necessary to increase ability of lone pair donation of the second halogen atom. Therefore, in the case when halogen atoms are simultaneously introduced to the carborane carbon atom and the boron atom is antipodal to it, this makes the formation of intermolecular halogen bonds possible, where the halogen atom attached to the carbon atom plays the role of an acceptor, and the halogen atom bonded to boron acts as a donor. Thus, the B,C-dihalogen-substituted carboranes represent a unique class of small molecules, in the crystals of which the formation of intermolecular dihalogen bonds could be possible without the participation of the second component. In particular, one might expect a formation of the intermolecular dihalogen bonds for 1,12-dihalo-ortho-carboranes 1,12-X2-1,2-C2B10H10. However, the recent study of the crystal structure of 1,12-Br2-1,2-C2B10H10 showed that in this case, instead of the formation of the intermolecular C-Br···Br-B dihalogen bonds, the formation of the C-H···Br-B hydrogen and C-Br···H-B halogen bonds occurs [28]. On the other hand, the σ-hole size, which is the determining factor in the formation of a halogen bond, depends on both the electronic effect of the substituent and the electronegativity of the halogen atom [40–42]. This prompted us to study intermolecular interactions in an analogous diiodine derivative 1,12-I2-1,2-C2B10H10 using single crystal X-ray diffraction and quantum chemical calculations.

2. Results and Discussion

Despite the fact that the syntheses of the C-iodo derivatives of ortho-carborane were first reported more than 50 years ago [43,44], they were on the periphery of mainstream carborane chemistry developments, and were not even well characterized [34,45]. In this way, they radically differ from the B-iodo derivatives of ortho-carborane, which have found active use in the synthesis of B-alkyl and aryl derivatives by means of Pd-catalyzed cross-coupling reactions [46–52]. Therefore, the synthesis of the C-iodo derivatives of ortho-carborane is not an easy task.

In this respect, the synthesis and characterization of the C-halogen derivatives of the carba-closo-dodecaborate anion [1-X-1-CB11H11]− (X = F, Cl, Br, I) are described much better [53]. Moreover, the preparation of its 1,12-diiodo derivative [1,12-I2-1-CB11H11]−, containing iodine atoms in opposite positions of the boron backbone, has recently been described [54]. However, in the case of anionic carboranes, it is rather difficult to find a cation, on the one hand, will not form additional non-covalent bonds with the anion and, on the other hand, will be small enough not to hinder the formation of intermolecular dihalogen bonds between the anions. In addition, unlike the C-substituted ortho-carborane, the C-substituted carba-closo-dodecaborate anion has no or negligible electron-withdrawing effects [55].

An attempt to prepare 1,12-I2-1,2-C2B10H10 by the reaction of the lithium derivative of 9-iodo-ortho-carborane with iodine in 1,2-dimethoxyethane resulted in the expected formation of a mixture of 1,9-I2-1,2-C2B10H10 and 1,12-I2-1,2-C2B10H10 derivatives (1:1). However, in contrast to the similar dibromo derivatives 1,9-Br2-1,2-C2B10H10 and 1,12-Br2-1,2-C2B10H10 [56], we failed to separate this mixture. Nevertheless, we managed to obtain the desired 1,12-diiodo derivative as a by-product of the cross-coupling reaction of 9-iodo-ortho-carborane with phenylmagnesium bromide. Another by-product of this reaction was 1-iodo-ortho-carborane, which we also obtained by direct reaction of the lithium derivative of ortho-carborane with iodine. Notably, formation of similar products of iodine migration in the process of cross-coupling of B-iodo carboranes with Grignard reagents was noted earlier [57].

As mentioned in the Introduction, no Br···Br halogen bond was observed in the crystal structure of 1,12-dibromo-ortho-carborane 1,12-Br2-1,2-C2B10H10 [28]. It should be noted that similarities and differences between bonding preferences of the bromine
atom in comparison to iodine atom, on the one hand, and chlorine atom, on the other hand, was the subject of extensive studies [58–61]. Based on comparison of the crystal packing of 1-Ph-2-X-ortho-carboranes (X = F, Cl, Br, I), it was shown that both Br and I form Hal···π interactions, while neither Cl or F participate in such interactions [58]. Study of N-(2-halo-2,2-dinitroethyl)pyrrolidine-2,5-diones (Hal = F, Cl, Br) [59] has revealed that both Cl and Br participate in halogen bonding, but bromine interacts with the carbonyl oxygen atom (the strongest donor site), while chlorine prefers to connect to much weaker donors, namely, oxygen atoms of the nitro group. Based on the above, it becomes unclear a priori which packing motif should be expected in the crystal of 1,12-diiodo-ortho-carborane.

Single crystals of 1,12-I₂-1,2-C₂B₁₀H₁₀ suitable for X-ray study were obtained in the form of thin plates by slow evaporation of chloroform solution. An asymmetric unit cell of 1,12-I₂-1,2-C₂B₁₀H₁₀ contains one molecule (Figure 1). The I1–C1 bond length (2.121(2) Å) is slightly longer than average X-ray value for I–C (aromatic) bonds (2.095 Å [62]) and is significantly shorter than the B₁₂–I₁₂ bond (2.179(2) Å).

Figure 1. General view of 1,12-I₂-1,2-C₂B₁₀H₁₀. Thermal ellipsoids are given at 50% probability level.

The main packing motif of the crystal structure of 1,12-I₂-1,2-C₂B₁₀H₁₀ is represented by infinite chains along the b direction formed by the C–I···I–B dihalogen bonds of II type [37,63] (the I(12)···I(1′) distance is 3.5687(9) Å, the B(12)-I(12)···I(1′) and I(12)···I(1′)-C(1′) angles are 92.98(12) and 172.61(11)°, respectively) (Figure 2), which is very different from 1,12-Br₂-1,2-C₂B₁₀H₁₀ studied earlier.

In order to find out the reason of observed differences as well as peculiarities of the crystal packing of 1,12-I₂-1,2-C₂B₁₀H₁₀, we used energetic analysis of intermolecular contacts, that is frequently invoked for crystal packing study [64–66]. We calculated halogen bonded dimer for both compound 1,12-I₂-1,2-C₂B₁₀H₁₀ and similar dimer in which iodine atoms are replaced with bromines. The results are presented in Figure 3 and Table 1. The calculated dimer of 1,12-I₂-1,2-C₂B₁₀H₁₀ is characterized by the structure similar to that found experimentally. The I···I distance is somewhat shorter, while C–I···I and B–I···I angles and B–H···I distances are close to experimentally observed values. Topological analysis of calculated electron density for 1,12-I₂-1,2-C₂B₁₀H₁₀ dimer has revealed additional stabilization of the dimeric structure with the B–H···I hydride–halogen bonds that was not evident from the consideration of bare X-ray data. From Table 1, it can be seen that energy of the I···I contact is sizably higher than that of the B–H···I contacts; therefore, the I···I dihalogen bond can be considered as the structure-forming interaction in the crystal of 1,12-I₂-1,2-C₂B₁₀H₁₀. In contrary, optimized geometry of dimeric 1,12-dibromo-ortho-carborane appeared to be quite different. The C–Br···Br angle significantly deviates from 180°. As a consequence, energy of the Br···Br interactions is relatively small and becomes comparable to the B–H···Br interactions which are also formed between two molecules in the dimer. It means that the Br···Br interactions are no more structure-forming ones. These results are in qualitative agreement with a previous experiment [26], according to which, no Br···Br halogen bond is observed in the crystal of 1,12-Br₂-1,2-C₂B₁₀H₁₀.
Figure 2. Crystal packing fragment of 1,12-I$_2$-1,2-C$_2$B$_{10}$H$_{10}$. Halogen bonded chains are formed along axis $b$.

Figure 3. Noncovalent bonding in dimers of 1,12-I$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (left) and 1,12-Br$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (right).

Table 1. Characteristics of intermolecular noncovalent interactions for dimers of 1,12-I$_2$-1,2-C$_2$B$_{10}$H$_{10}$ and 1,12-Br$_2$-1,2-C$_2$B$_{10}$H$_{10}$.

| Distance in Å or Angle in Deg. | Energy in kcal/mol |
|-------------------------------|--------------------|
| 1,12-I$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (X-ray) | 1,12-I$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (calc) | 1,12-Br$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (calc) | 1,12-I$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (calc) |
| X12X1' | 3.5687(9) | 3.455 | 3.704 | -2.9 | -1.0 |
| B12-X12···X1' | 92.98(12) | 94.3 | 91.1 |
| X12···X1'-C1'H7···X1' | 172.61(11) | 175.9 | 147.6 |
| H11···X1' | 3.58(2) | 3.51 | 3.25 | -0.5 | -0.7 |
| H7···H5' | 3.58(2) | 3.52 | 3.37 | -0.5 | -0.5 |
| H11···H4' | - | - | 2.67 | - | -0.5 |
| X12X1' | - | - | 2.61 | - | -0.6 |

The above results have demonstrated computational ability for, at least, qualitative explanation and prediction of the main crystal packing motif for dihalogen derivatives of ortho-carborane. Based on that, we made an attempt to predict the possibility of halogen bond formation in 1,3-I$_2$-1,2-C$_2$B$_{10}$H$_{10}$ and 1,9-I$_2$-1,2-C$_2$B$_{10}$H$_{10}$. Those isomers were chosen because they can be experimentally obtained from the available 3- and 9-iodo-ortho-carboranes, while synthesis of other possible isomers is troublesome. In Figure 4 and Table 2, the results of calculation of dimers of the 1,3- and 1,9-isomers are presented.
Figure 4. Noncovalent bonding in dimers of 1,9-I₂-1,2-C₂B₁₀H₁₀ (left) and 1,3-I₂-1,2-C₂B₁₀H₁₀ (right).

Table 2. Characteristics of intermolecular noncovalent interactions for halogen-bonded dimers of 1,3-I₂-1,2-C₂B₁₀H₁₀ and 1,9-I₂-1,2-C₂B₁₀H₁₀.

|                  | 1,9-I₂-1,2-C₂B₁₀H₁₀ | 1,3-I₂-1,2-C₂B₁₀H₁₀ |
|------------------|---------------------|---------------------|
|                  | Distance or Angle   | Energy              | Distance or Angle   | Energy              |
| I₉···I₁'         | 3.461               | -2.7                | I₃···I₁'            | 3.54                |
| B₉-I₉···I₁'      | 92.7                |                      | B₃-I₃···I₁'         | 90.1                |
| I₉···I₁'-C₁'     | 174.1               |                      | I₃···I₁'-C₁'        | 170.7               |
| H₁₂···I₁'        | 3.47                | -0.6                | H₈···I₁'            | 3.44                |
| H₈···I₁'         | 3.49                | -0.6                | H₁₀···I₁'           | 3.42                |

One can see that 1,9-I₂-1,2-C₂B₁₀H₁₀ demonstrates the same system of close contacts and nearly the same energetic properties of halogen-bonded dimer of 1,12-I₂-1,2-C₂B₁₀H₁₀. The energy of a halogen bond is only 0.2 kcal/mol less; B₉-I₉···I₁' and I₉···I₁'-C₁' only slightly deviate from 90 and 180°, respectively, while energies of B–H···I interactions are only 0.1 kcal/mol higher. It allows consideration of the I···I halogen bond as a predominant interaction in the potential crystal structure of 1,9-I₂-1,2-C₂B₁₀H₁₀.

When looking at halogen-bonded dimers built up of 1,3-I₂-1,2-C₂B₁₀H₁₀, one can observe a clear trend of weakening of the I···I halogen bonds and simultaneous strengthening of the B–H···I interactions and increases in their roles in stabilizing dimeric structures upon approaching the iodine substituent from its position at B₁₂ to B₃. During movement of the iodine atom from B₁₂ to B₃, quantitative changes due to the weakening of the I···I halogen bonds can be transformed to qualitative changes, which can result in the disappearance of the I···I halogen bonds from the crystal structure of 1,3-I₂-1,2-C₂B₁₀H₁₀.

In conclusion, 1,12-diiodo-ortho-carborane was obtained and its crystal structure was determined by X-ray diffraction, which revealed the existence of the I···I halogen bond in its crystal structure, in contrast to 1,12-dibromo-ortho-carborane. Based on quantum chemical calculation, we have determined preferences of the type of noncovalent interactions in 1,12-diiodo- and 1,12-dibromo-ortho-carboranes which appeared to be in agreement with experimental findings. Based on our results, we can predict the formation of the I···I halogen bonds in 1,9-diiodo-ortho-carborane, while our results cannot provide solid support for the formation of such bonds in the 1,3-isomer. This question is still open and can be answered experimentally. Synthesis and crystal growth of 1,9- and 1,3-diiodo-ortho-carboranes is in progress in our group.

3. Materials and Methods

3.1. General

Compounds 9-ido-ortho-carborane and bis(triphenylphosphine)palladium(II) dichloride were prepared according to the literature procedures [67,68]. Solvents 1,2-dimethoxyethane and diethyl ether were dried using standard procedures [69]. Phenyl iodide was distilled at boiling point. All other chemical reagents were purchased from Sigma Aldrich, Acros
Organics and ABCR and used without purification. All reactions were carried out in an argon atmosphere. The reaction progress was monitored by thin-layer chromatography (Merck F254 silica gel on aluminum plates) and visualized using 0.5% PdCl₂ in 1% HCl in aq. MeOH (1:10). Acros Organics silica gel (0.060–0.200 mm) was used for column chromatography. The NMR spectra at 400.1 MHz (¹H), 128.4 MHz (¹³B) and 100.0 MHz (¹³C) were recorded with a Varian Inova 400 spectrometer. The residual signal of the NMR solvent relative to Me₄Si was taken as an internal reference for ¹H and ¹³C NMR spectra; ¹³B NMR spectra were referenced using BF₃·Et₂O as an external standard.

3.2. Cross-Coupling of 9-Iodo-Ortho-Carborane with PhMgBr

Phenyl iodide (0.70 mL, 1275 mg, 6.25 mmol) was added to a mixture of magnesium turnings (228 mg, 9.38 mmol) in fresh distilled diethyl ether (25 mL). The resulting mixture was heated under reflux for 1 h. Then, 9-iodo-ortho-carborane (675 mg, 2.50 mmol) was added, and the reaction was stirred at room temperature for another 1 h. Then, copper(I) iodide (25 mg, 0.13 mmol, catalytic amount) was added. The reaction was heated under reflux for 16 h and 6% HCl in water (50 mL) was added. The organic layer was separated; the water layer was washed with diethyl ether (3 × 50 mL). The organic phases were combined, dried over Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using a mixture of chloroform and petroleum ether (1:3, v/v) to give, along with the expected 9-phenyl-ortho-carborane, pale-yellow solids of 1-iodo-ortho-carborane (15 mg, yield 2%) and 1,12-diiodo-ortho-carborane (20 mg, yield 2%) as side products.

Compound 1-I-1,2-C\textsubscript{10}H\textsubscript{10}: ¹H NMR (CDCl₃, ppm): δ 3.78 (1H, br s, CH\textsubscript{carb}), 3.7–0.7 (10H, br m, BH). ¹³B NMR (CDCl₃, ppm): δ 0.7 (1B, d, J = 151 Hz), −4.0 (1B, d, J = 154 Hz), −7.8 (4B, d, J = 125 Hz), −9.0 (2B, d, J = 111 Hz), −11.7 (1B, d, J = 167 Hz).

Compound 1,2-I₂-1,2-C\textsubscript{10}H\textsubscript{10}: ¹H NMR (CDCl₃, ppm): δ 3.86 (1H, br s, CH\textsubscript{carb}), 4.1–0.6 (9H, br m, BH). ¹³B NMR (CDCl₃, ppm): δ 0.9 (1B, d, J = 156 Hz), −5.8 (2B, d, J = 160 Hz), −7.8 (2B, d, J = 173 Hz), −8.7 (2B, d, J = 183 Hz), −10.7 (2B, d, J = 168 Hz), −16.7 (1B, s).

3.3. General Synthetic Procedure of C-Iodination of Ortho-Carborane and Its B-I Derivatives

The 2.25 M BuLi in hexanes was added to a mixture of carborane in fresh distilled 1,2-dimethoxyethane (10 mL). The mixture was stirred for 1 h at room temperature and was heated under reflux for 16 h and 6% HCl in water (50 mL) was added. The organic phase was combined, dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by column chromatography on silica using a mixture of chloroform and petroleum ether (1:3, v/v) to give, along with the expected 9-phenyl-ortho-carborane, pale-yellow solids of 1-iodo-ortho-carborane (15 mg, yield 2%) and 1,12-diiodo-ortho-carborane (20 mg, yield 2%) as side products.

Compound 1,12-I₂-1,2-C\textsubscript{10}H\textsubscript{10}: ¹H NMR (CDCl₃, ppm): δ 3.40 (1H, br s, CH\textsubscript{carb}), 4.5 (2B, d, J = 183 Hz), 6.8 (6B, d, J = 168 Hz), 10.7 (2B, d, J = 168 Hz), −16.7 (1B, s).

3.4. Synthesis of 1-Iodo-Ortho-Carborane

The 2.25 M BuLi in hexanes (0.40 mL, 0.90 mmol) was added to a mixture of ortho-carborane (144 mg, 1.00 mmol) in fresh distilled 1,2-dimethoxyethane (10 mL). The mixture
was stirred for 1 h at room temperature, and I$_2$ (381 mg, 1.50 mmol) was added by one portion. The reaction was stirred at room temperature overnight and Na$_2$S$_2$O$_3$·5H$_2$O (1000 g, 4.03 mmol) in water (10 mL) and diethyl ether (15 mL) were added. The organic layer was separated; the water layer was washed with diethyl ether (25 mL). The organic phases were combined, dried over Na$_2$SO$_4$, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica using petroleum ether as an eluent to give a pale-grey crystalline solid of 1-I-1,2-C$_2$B$_{10}$H$_{11}$ (160 mg, yield 59%).

3.5. X-ray Diffraction Study

Single crystal X-ray diffraction experiments were carried out using a SMART APEX2 CCD diffractometer (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, ω-scans) at 120 K. Collected data were processed by the SAINT and SADABS programs incorporated into the APEX2 program package [70]. The structures were solved by the direct methods and refined by the full-matrix least-squares procedure against $F^2$ in anisotropic approximation. The refinement was carried out with the SHELXTL program [71]. The CCDC numbers (2070233 for 1,12-I$_2$-C$_2$B$_{10}$H$_{10}$ and 2074102 for 1-I-C$_2$B$_{10}$H$_{11}$) contain the supplementary crystallographic data for this paper. These data can be found in the Supplementary Materials or obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, accessed on 15 March 2021.

Crystallographic data for 1,12-I$_2$-1,2-C$_2$B$_{10}$H$_{10}$: C$_2$H$_{10}$B$_{10}$I$_2$ are monoclinic, space group $P2_1/c$: $a = 7.1919(8)$ Å, $b = 15.8202(17)$ Å, $c = 11.1509(12)$ Å, $β = 108.809(2)^\circ$, $V = 1201.0(2)$ Å$^3$, $Z = 4$, $M =$ 396.00, $d_{\text{cryst}} = 2.190$ g cm$^{-3}$. $wR2 = 0.0365$ calculated on $F^2_{\text{bd}}$ for all 3557 independent reflections with 2$θ < 60.4^\circ$, (GOF = 1.067, $R = 0.0161$ calculated on $F_{\text{bd}}^2$ for 3314 reflections with $I > 2\sigma(I)$).

Crystallographic data for 1-I-1,2-C$_2$B$_{10}$H$_{11}$: C$_2$H$_{10}$B$_{10}$I are orthorhombic, space group $Pnma$: $a = 13.8323(9)$ Å, $b = 8.9644(6)$ Å, $c = 8.4539(5)$ Å, $V = 1048.27(12)$ Å$^3$, $Z = 4$, $M =$ 270.11, $d_{\text{cryst}} = 1.711$ g cm$^{-3}$. $wR2 = 0.0747$ calculated on $F^2_{\text{bd}}$ for all 1344 independent reflections with 2$θ < 56.1^\circ$, (GOF = 1.143, $R = 0.0327$ calculated on $F_{\text{bd}}^2$ for 1203 reflections with $I > 2\sigma(I)$).

3.6. Quantum Chemical Calculations

All quantum chemical calculations were carried out with the Gaussian09 program [72]. The PBE0 functional with the triple zeta basis set was found to be reliable for the calculation of noncovalent intra- and intermolecular interactions [73–75] and was adopted throughout this study. Initial geometries for the optimization of all dimers considered in this study were based on the X-ray structure of a dihalogen-bonded dimer of 1,12-I$_2$-C$_2$B$_{10}$H$_{10}$ (symmetry code is 1 − $x$, −0.5 + $y$, 0.5 − $z$). All dimeric associates were fully optimized and converged to the energy minima. Theoretical electron density was treated within the AIM approach [76] using the AIMAll program package [77]. For energy ($E$) estimation, we used the $E = 1/2V(r)$ formula [78,79], in which $V(r)$ is the potential energy density at the bond critical point between interacting atoms. It has frequently been shown that this approach to describe noncovalent interactions demonstrates realistic energetic characteristics [80–82].

**Supplementary Materials:** The following are available online at https://www.mdpi.com/article/10.3390/cryst11040396/s1, Figure S1: Asymmetric part of 1-I-1,2-C$_2$B$_{10}$H$_{11}$ molecule showing numbering scheme and the disorder of the C2/B4 atoms; Figure S2: General view of 1-I-1,2-C$_2$B$_{10}$H$_{11}$; Figure S3: Halogen bonded dimer of 1-I-1,2-C$_2$B$_{10}$H$_{11}$, and complete crystallographic data (cif-files) for compounds 1-I-1,2-C$_2$B$_{10}$H$_{11}$ and 1,12-I$_2$-1,2-C$_2$B$_{10}$H$_{10}$.

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