



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

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- + Dedicated to Professor Alan J. Welch in occasion of his retirement at Herriot-Watt University and in recognition of his outstanding contribution in the carborane chemistry.

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 calculationsy

1. Introduction

Carboranes $[CB_{11}H_{12}]^-$ and $C_2B_{10}H_{12}$, 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], carboranebased 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 $C-H\cdots O$ and $C-H\cdots N$ 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-withdrawing 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].



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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 \cdots Br-B dihalogen bonds, the formation of the $C-H \cdots Br-B$ hydrogen and $C-Br \cdots H-B$ 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 $[1-X-1-CB_{11}H_{11}]^-$ (X = F, Cl, Br, I) are described much better [53]. Moreover, the preparation of its 1,12-diiodo derivative $[1,12-I_2-1-CB_{11}H_{10}]^-$, 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 that, 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- I_2 -1,2- $C_2B_{10}H_{10}$ 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- I_2 -1,2- $C_2B_{10}H_{10}$ and 1,12- I_2 -1,2- $C_2B_{10}H_{10}$ derivatives (1:1). However, in contrast to the similar dibromo derivatives 1,9- Br_2 -1,2- $C_2B_{10}H_{10}$ and 1,12- Br_2 -1,2- $C_2B_{10}H_{10}$ [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 $Br \cdots Br$ halogen bond was observed in the crystal structure of 1,12-dibromo-*ortho*-carborane 1,12- Br_2 -1,2- $C_2B_{10}H_{10}$ [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- I_2 -1,2- $C_2B_{10}H_{10}$ 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- I_2 -1,2- $C_2B_{10}H_{10}$ 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- I_2 - I_2 - $C_2B_{10}H_{10}$ 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- I_2 - $I_$ tacts, 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- I_2 - I_2 - $C_2B_{10}H_{10}$ is characterized by the structure similar to that found experimentally. The I \cdots I distance is somewhat shorter, while C–I \cdots I and B–I \cdots I angles and B-H···I distances are close to experimentally observed values. Topological analysis of calculated electron density for 1,12- I_2 - I_2 - $C_2B_{10}H_{10}$ 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 $I \cdots I$ contact is sizably higher than that of the B-H $\cdots I$ 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-orthocarborane appeared to be quite different. The $C-Br \cdots Br$ angle significantly deviates from 180° . As a consequence, energy of the Br \cdots Br interactions is relatively small and becomes comparable to the B–H \cdots Br interactions which are also formed between two molecules in the dimer. It means that the $Br \cdots Br$ 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- $C_2B_{10}H_{10}$. Halogen bonded chains are formed along axis *b*.



Figure 3. Noncovalent bonding in dimers of 1,12-I₂-1,2-C₂B₁₀H₁₀ (left) and 1,12-Br₂-1,2-C₂B₁₀H₁₀ (right).

Table 1. Ch	naracteristics of intermo	ecular noncovalent inte	ractions for dimers	s of 1,12-I ₂ -1,2-C ₂ I	3 ₁₀ H ₁₀ and 1	$1,12-Br_2-1,2-C_2B_{10}H_{10}$.
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	Distar	nce in Å or Angle in	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)	1,12-Br 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		
$X12 \cdots X1'$ - $C1'H7 \cdots X1'$	172.61(11)	175.9	147.6		
$H11 \cdots X1'$	3.58(2)	3.51	3.25	-0.5	-0.7
$H7 \cdots H5'$	3.58(2)	3.52	3.37	-0.5	-0.5
$H11 \cdots H4'$	-	-	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-I₂-1,2-C₂B₁₀H₁₀ and 1,9-I₂-1,2-C₂B₁₀H₁₀. 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 $1,3-I_2-1,2-C_2B_{10}H_{10}$ and $1,9-I_2-1,2-C_2B_{10}H_{10}$.

1	l,9-I ₂ -1,2-C ₂ B ₁₀ H ₁₀		1,3-I ₂ -1,2-C ₂ B ₁₀ H ₁₀			
	Distance or Angle	Energy		Distance or Angle	Energy	
$I9 \cdots I1'$	3.461	-2.7	$I3 \cdot \cdot \cdot I1'$	3.54	-2.3	
B9-I9 \cdots I1'	92.7		B3-I3 \cdots I1'	90.1		
I9· · · I1′-C1′	174.1		$I3 \cdot \cdot \cdot I1' - C1'$	170.7		
$H12 \cdots I1'$	3.47	-0.6	$H8 \cdots I1'$	3.44	-0.7	
$H8 \cdots I1'$	3.49	-0.6	$H10 \cdots I1'$	3.42	-0.7	

One can see that 1,9- I_2 -1,2- $C_2B_{10}H_{10}$ demonstrates the same system of close contacts and nearly the same energetic properties of halogen-bonded dimer of 1,12- I_2 -1,2- $C_2B_{10}H_{10}$. 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- I_2 -1,2- $C_2B_{10}H_{10}$.

When looking at halogen-bonded dimers built up of 1,3- I_2 -1,2- $C_2B_{10}H_{10}$, 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- I_2 -1,2- $C_2B_{10}H_{10}$.

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 \cdots 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 \cdots 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-iodo-*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 (¹¹B) 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; ¹¹B 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) in fresh distilled diethyl ether (25 mL) 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) with $[(Ph_3P)_2PdCl_2]$ (83 mg, 0.13 mmol, catalytic amount) were 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 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-C₂B₁₀H₁₁: ¹H NMR (CDCl₃, ppm): δ 3.78 (1H, br s, CH_{carb}), 3.7–0.7 (10H, br m, BH). ¹¹B 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 1,12-I₂-1,2-C₂B₁₀H₁₀: ¹H NMR (CDCl₃, ppm): δ 3.86 (1H, br s, CH_{carb}), 4.1–0.6 (9H, br m, BH). ¹¹B 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 I₂ was added by one portion. The reaction was stirred at room temperature overnight and Na₂S₂O₃·5H₂O (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 Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography on silica using diethyl ether as the eluent to give the corresponding C–I derivative.

Compound 1,2-I₂-1,2-C₂B₁₀H₁₀: 2.25 M BuLi in hexanes (1.00 mL, 2.25 mmol), *ortho*carborane (144 mg, 1.00 mmol) and I₂ (635 mg, 2.50 mmol) were used; a yellow crystalline solid was obtained (381 mg, yield 96%). ¹H NMR (CDCl₃, ppm): δ 3.9–0.8 (10H, br m, BH). ¹¹B NMR (CDCl₃, ppm): δ –2.5 (2B, d, J = 154 Hz), –4.5 (2B, d, J = 183 Hz), –6.8 (6B, d, J = 183 Hz).

Compounds 1,9- and 1,12-I₂-1,2-C₂B₁₀H₁₀: 2.25 M BuLi in hexanes (0.49 mL, 1.10 mmol), 9-iodo-*ortho*-carborane (135 mg, 0.50 mmol) and I₂ (305 mg, 1.20 mmol) were used; a pale-grey crystalline solid was obtained (80 mg, yield 20%). ¹H NMR (CDCl₃, ppm): δ 4.07 (1H, br s, CH_{carb}, 1,9-isomer), 3.87 (1H, br s, CH_{carb}, 1,12-isomer), 3.9–0.6 (20H, br m, BH, 1,9 + 1,12-isomers).

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 I₂ (381 mg, 1.50 mmol) was added by one portion. The reaction was stirred at room temperature overnight and $Na_2S_2O_3 \cdot 5H_2O$ (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_2SO_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_2B_{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-K α) = 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-I₂-C₂B₁₀H₁₀ and 2074102 for 1-I-C₂B₁₀H₁₁) 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-I₂-1,2-C₂B₁₀H₁₀: C₂H₁₀B₁₀I₂ are monoclinic, space group $P2_1/c$: a = 7.1919(8)Å, b = 15.8202(17)Å, c = 11.1509(12)Å, $\beta = 108.809(2)^\circ$, V = 1201.0(2)Å³, Z = 4, M = 396.00, $d_{cryst} = 2.190$ g·cm⁻³. wR2 = 0.0365 calculated on F^2_{hkl} for all 3557 independent reflections with $2\theta < 60.4^\circ$, (*GOF* = 1.067, R = 0.0161 calculated on F_{hkl} for 3314 reflections with $I > 2\sigma(I)$).

Crystallographic data for 1-I-1,2-C₂B₁₀H₁₁: C₂H₁₁B₁₀I are orthorhombic, space group *Pnma*: a = 13.8323(9)Å, b = 8.9644(6)Å, c = 8.4539(5)Å, V = 1048.27(12)Å³, Z = 4, M = 270.11, $d_{cryst} = 1.711$ g·cm⁻³. wR2 = 0.0747 calculated on F^2_{hkl} for all 1344 independent reflections with $2\theta < 56.1^\circ$, (*GOF* = 1.143, R = 0.0327 calculated on F_{hkl} 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 $1,12-I_2-C_2B_{10}H_{10}$ (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-C₂B₁₀H₁₁ molecule showing numbering scheme and the disorder of the C2/B4 atoms; Figure S2: General view of 1-I-1,2-C₂B₁₀H₁₁; Figure S3: Halogen bonded dimer of 1-I-1,2-C₂B₁₀H₁₁, and complete crystallographic data (cif-files) for compounds 1-I-1,2-C₂B₁₀H₁₁ and 1,12-I₂-1,2-C₂B₁₀H₁₀.

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References

- 1. Grimes, R.N. Carboranes, 3rd ed.; Academic Press: London, UK, 2016; 1042p. [CrossRef]
- Kaszynski, P.; Douglass, A.G. Organic derivatives of closo-boranes: A new class of liquid crystal materials. J. Organomet. Chem. 1999, 581, 28–38. [CrossRef]
- 3. Pecyna, J.; Pociecha, D.; Kaszynski, P. Zwitterionic pyridinium derivatives of [closo-1- CB₉H₁₀]- and [closo-1-CB₁₁H₁₂]- as high Δε additives to a nematic host. *J. Mater. Chem. C* 2014, *2*, 1585–1591. [CrossRef]
- Pecyna, J.; Kaszyński, P.; Ringstrand, B.; Pociecha, D.; Pakhomov, S.; Douglass, A.G.; Young, V.G. Synthesis and characterization of quinuclidinium derivatives of the [closo-1-CB₁₁H₁₂]-anion as potential polar components of liquid crystal materials. *Inorg. Chem.* 2016, 55, 40167–44025. [CrossRef]
- 5. Pecyna, J.; Jankowiak, A.; Pociecha, D.; Kaszyński, P. o-Carborane derivatives for probing molecular polarity effects on liquid crystal phase stability and dielectric behavior. *J. Mater. Chem. C* **2015**, *3*, 11412–11422. [CrossRef]
- Allis, D.G.; Spencer, J.T. Polyhedral-based nonlinear optical materials. 2. Theoretical investigation of some new high non-linear optical response compounds involving polyhedral bridges with charged aromatic donors and acceptors. *Inorg. Chem.* 2001, 40, 3373–3380. [CrossRef]
- Wang, H.-Q.; Wang, L.; Li, R.-R.; Ye, J.-T.; Chen, Z.-Z.; Chen, H.; Qiu, Y.-Q.; Xie, H.-M. Second-order nonlinear optical properties of carboranylated square-planar Pt(II) zwitterionic complexes: One-/two-dimensional difference and substituent effect. *J. Phys. Chem. A* 2016, 120, 9330–9340. [CrossRef] [PubMed]
- Jiang, P.; Wang, Z.; Moxey, G.J.; Morshedi, M.; Barlow, A.; Wang, G.; Quintana, C.; Zhang, C.; Cifuentes, M.P.; Humphrey, M.G. Syntheses and quadratic nonlinear optical properties of 2,7-fluorenylene- and 1,4-phenylene-functionalized o-carboranes. *Dalton Trans.* 2019, 48, 12549–12559. [CrossRef] [PubMed]
- Wang, H.-Q.; Ye, J.-T.; Zhang, Y.; Zhao, Y.-Y.; Qiu, Y.-Q. A thorough understanding of the nonlinear optical properties of BOD-IPY/carborane/diketopyrrolopyrrole hybrid chromophores: Module contribution, linear combination, one-/two-dimensional difference and carborane's arrangement. J. Mater. Chem. C 2019, 7, 7531–7547. [CrossRef]
- 10. Wedge, T.J.; Hawthorne, M. Multidentate carborane-containing Lewis acids and their chemistry: Mercuracarborands. *Coord. Chem. Rev.* 2003, 240, 111–128. [CrossRef]
- 11. Scholz, M.; Hey-Hawkins, E. Carbaboranes as Pharmacophores: Properties, Synthesis, and Application Strategies. *Chem. Rev.* **2011**, *111*, 7035–7062. [CrossRef] [PubMed]
- 12. Endo, Y. Carboranes as hydrophobic pharmacophores: Applications for design of nuclear receptor ligands. In *Boron-Based Compounds: Potential and Emerging Applications in Medicine;* Hey-Hawkins, E., Viñas Teixidor, C., Eds.; John Wiley & Sons Ltd.: Oxford, UK, 2018; pp. 3–19. [CrossRef]
- 13. Yang, X.; Jiang, W.; Knobler, C.B.; Hawthorne, M.F. Rigid-rod molecules: Carborods. Synthesis of tetrameric p-carboranes and the crystal structure of bis(tri-n-butylsilyl)tetra-p-carborane. *J. Am. Chem. Soc.* **1992**, *114*, 9719–9721. [CrossRef]
- Schöberl, U.; Magnera, T.F.; Harrison, R.M.; Fleischer, F.; Pflug, J.L.; Schwab, P.F.H.; Meng, X.; Lipiak, D.; Noll, B.C.; Allured, V.S.; et al. Toward a Hexagonal Grid Polymer: Synthesis, Coupling, and Chemically Reversible Surface-Pinning of the Star Connectors, 1,3,5-C₆H₃(CB₁₀H₁₀CX)₃. *J. Am. Chem. Soc.* **1997**, *119*, 3907–3917. [CrossRef]
- 15. Fox, M.A.; Cameron, A.M.; Low, P.J.; Paterson, M.A.J.; Batsanov, A.S.; Goeta, A.E.; Rankin, D.W.H.; Robertson, H.E.; Schirlin, J.T. Synthetic and structural studies on C-ethynyl- and C-bromo-carboranes. *Dalton Trans.* **2006**, 3544–3560. [CrossRef] [PubMed]
- 16. Safronov, A.V.; Sevryugina, Y.V.; Pichaandi, K.R.; Jalisatgi, S.S.; Hawthorne, M.F. Synthesis of closo- and nido-biscarboranes with rigid unsaturated linkers as precursors to linear metallacarborane-based molecular rods. *Dalton Trans.* **2014**, *43*, 4969–4977. [CrossRef]
- Himmelspach, A.; Warneke, J.; Schäfer, M.; Hailmann, M.; Finze, M. Salts of the dianions [Hg(12-X-closo-1-CB₁₁H₁₀)₂]₂-(X = I, C≡CH, C≡CFc, C≡CSiiPr₃): Synthesis and spectroscopic and structural characterization. *Organometallics* 2015, 34, 462–469. [CrossRef]
- 18. Zhang, K.; Shen, Y.; Liu, J.; Spingler, B.; Duttwyler, S. Crystal structure of a carborane endo/exo-dianion and its use in the synthesis of ditopic ligands for supramolecular frameworks. *Chem. Commun.* **2017**, *54*, 1698–1701. [CrossRef] [PubMed]

- 19. Farha, O.K.; Spokoyny, A.M.; Mulfort, K.L.; Hawthorne, M.F.; Mirkin, C.A.; Hupp, J.T. Synthesis and Hydrogen Sorption Properties of Carborane Based Metal–Organic Framework Materials. J. Am. Chem. Soc. 2007, 129, 12680–12681. [CrossRef]
- 20. Bae, Y.-S.; Farha, O.K.; Spokoyny, A.M.; Mirkin, C.A.; Hupp, J.T.; Snurr, R.Q. Carborane-based metal–organic frameworks as highly selective sorbents for CO₂ over methane. *Chem. Commun.* **2008**, 4135–4137. [CrossRef]
- Bae, Y.-S.; Spokoyny, A.M.; Farha, O.K.; Snurr, R.Q.; Hupp, J.T.; Mirkin, C.A. Separation of gas mixtures using Co(II) car-boranebased porous coordination polymers. *Chem. Commun.* 2010, 46, 3478–3480. [CrossRef]
- Kennedy, R.D.; Krungleviciute, V.; Clingerman, D.J.; Mondloch, J.E.; Peng, Y.; Wilmer, C.E.; Sarjeant, A.A.; Snurr, R.Q.; Hupp, J.T.; Yildirim, T.; et al. Carborane-based metal-organic framework with high methane and hydrogen storage capacities. *Chem. Mater.* 2013, 25, 3539–3543. [CrossRef]
- 23. Andrews, P.; Hardie, M.J.; Raston, C.L. Supramolecular assemblies of globular main group cage species. *Coord. Chem. Rev.* **1999**, 189, 169–198. [CrossRef]
- 24. Hardie, M.J.; Raston, C.L. Crystalline hydrogen bonded complexes of o-carborane. CrystEngComm 2001, 3, 162–164. [CrossRef]
- 25. Lo, R.; Fanfrlík, J.; Lepšík, M.; Hobza, P. The properties of substituted 3D-aromatic neutral carboranes: The potential for σ-hole bonding. *Phys. Chem. Chem. Phys.* **2015**, *17*, 20814–20821. [CrossRef]
- 26. Alkorta, I.; Elguero, J.; Oliva-Enrich, J.M. Hydrogen vs. Halogen Bonds in 1-Halo-Closo-Carboranes. *Materials* **2020**, *13*, 2163. [CrossRef] [PubMed]
- Glukhov, I.V.; Lyssenko, K.A.; Antipin, M.Y. Crystal packing of 8,9,10,12-tetrafluoro-o-carborane: H. F versus H. H contacts. Struct. Chem. 2007, 18, 465–469. [CrossRef]
- Fanfrlík, J.; Holub, J.; Růžičková, Z.; Řezáč, J.; Lane, P.D.; Wann, D.A.; Hnyk, D.; Růžička, A.; Hobza, P. Competition between Halogen, Hydrogen and Dihydrogen Bonding in Brominated Carboranes. *ChemPhysChem* 2016, 17, 3373–3376. [CrossRef]
- 29. Batsanov, A.S.; Fox, M.A.; Howard, J.A.K.; Hughes, A.K.; Johnson, A.L.; Martindale, S.J. 9,12-diiodo-1,2-dicarba-closododecaborane(12). *Acta Crystallogr. Sect. C Cryst. Struct. Commun.* 2003, 59, o74–o76. [CrossRef] [PubMed]
- 30. Barberà, G.; Viñas, C.; Teixidor, F.; Rosair, G.M.; Welch, A.J. Self-assembly of carborane molecules via C-H ... I hydrogen bonding: The molecular and crystal structures of 3-I-1,2-closo-C2B10H11. *J. Chem. Soc. Dalton Trans.* **2002**, *19*, 3647–3648. [CrossRef]
- 31. Vaca, A.; Teixidor, F.; Kivekäs, R.; Sillanpää, R.; Viñas, C. A solvent-free regioselective iodination route of ortho-carboranes. *Dalton Trans.* **2006**, *41*, 4884–4885. [CrossRef]
- 32. Ramachandran, B.M.; Knobler, C.B.; Hawthorne, M.F. Synthesis and structural characterization of symmetrical clo-so-4,7-I2-1,2-C₂B₁₀H₁₀ and [(CH₃)₃NH][nido-2,4-I2-7,8-C₂B₉H₁₀]. *Inorg. Chem.* **2006**, 45, 336–340. [CrossRef]
- 33. Barberà, G.; Vaca, A.; Teixidor, F.; Sillanpää, R.; Kivekäs, R.; Viñas, C. Designed synthesis of new ortho-carborane derivatives: From mono- to polysubstituted frameworks. *Inorg. Chem.* **2008**, *47*, 7309–7316. [CrossRef]
- Puga, A.V.; Teixidor, F.; Sillanpää, R.; Kivekäs, R.; Viñas, C. Iodinated ortho-carboranes as versatile building blocks to design intermolecular interactions in crystal lattices. *Chem. Eur. J.* 2009, 15, 9764–9772. [CrossRef]
- 35. Bregadze, V.I. Dicarba-closo-dodecaboranes C₂B₁₀H₁₂ and their derivatives. *Chem. Rev.* **1992**, *92*, 209–223. [CrossRef]
- 36. Clark, T.; Hennemann, M.; Murray, J.S.; Politzer, P. Halogen bonding: The σ-hole. J. Mol. Model. 2007, 13, 291–296. [CrossRef]
- 37. Cavallo, G.; Metrangolo, P.; Milani, R.; Pilati, T.; Priimagi, A.; Resnati, G.; Terraneo, G. The Halogen Bond. *Chem. Rev.* 2016, 116, 2478–2601. [CrossRef] [PubMed]
- Kolář, M.H.; Hobza, P. Computer Modeling of Halogen Bonds and Other σ-Hole Interactions. *Chem. Rev.* 2016, 116, 5155–5187. [CrossRef] [PubMed]
- Gilday, L.C.; Robinson, S.W.; Barendt, T.A.; Langton, M.J.; Mullaney, B.R.; Beer, P.D. Halogen Bonding in Supramolecular Chemistry. Chem. Rev. 2015, 115, 7118–7195. [CrossRef]
- 40. Kolář, M.; Hostaš, J.; Hobza, P. The strength and directionality of a halogen bond are co-determined by the magnitude and size of the σ-hole. *Phys. Chem. Chem. Phys.* **2014**, *16*, 9987–9996. [CrossRef] [PubMed]
- 41. Ivanov, D.M.; Kinzhalov, M.A.; Novikov, A.S.; Ananyev, I.V.; Romanova, A.A.; Boyarskiy, V.P.; Haukka, M.; Kukushkin, V.Y. H2C(X)–X…X– (X = Cl, Br) Halogen Bonding of Dihalomethanes. *Cryst. Growth Des.* **2017**, *17*, 1353–1362. [CrossRef]
- 42. Suponitsky, K.Y.; Burakov, N.; Kanibolotsky, A.L.; Mikhailov, V.A. Multiple Noncovalent Bonding in Halogen Complexes with Oxygen Organics. I. Tertiary Amides. *J. Phys. Chem. A* 2016, *120*, 4179–4190. [CrossRef]
- 43. Zakharkin, L.I.; Zhigareva, G.G.; Kazantsev, A.V. Some reactions of barene Gringard reagents. Zh. Obshch. Khim. 1968, 38, 89–92.
- 44. Zakharkin, L.I.; Podvisotskaya, L.S. Cleavage of 1,2-dihalobarenes by alcohols to C,C?-dihalodicarbaundecaboranes (13). *Russ. Chem. Bull.* **1966**, *15*, 742. [CrossRef]
- 45. Tupchauskas, A.P.; Stanko, V.I.; Ustynyuk, Y.A.; Khrapov, V.V. 1H-{11B} heteronuclear double resonance spectra of ortho-, meta-, and para-carboranes and some of their organotin derivatives. *J. Struct. Chem.* **1973**, *13*, 772–776. [CrossRef]
- 46. Zakharkin, L.; Kovredov, A.; Ol'Shevskaya, V.; Shaugumbekova, Z. Synthesis of B-organo-substituted 1,2-, 1,7-, and 1,12dicarbaclosododecarboranes(12). *J. Organomet. Chem.* **1982**, 226, 217–222. [CrossRef]
- Zakharkin, L.I.; Ol'Shevskaya, V.A.; Nesmeyanov'S, A.N. Synthesis of 9-Organyl-1,2 and 1,7-Dicarba-closo-dodecaboranes(12) via the Cross-Coupling Reactions between Organozinc Compounds and 9-Iodo-1,2- or 1,7-Dicarba-closo-dodecaboranes. *Synth. React. Inorg. Met. Chem.* 1991, 21, 1041–1046. [CrossRef]
- Zheng, Z.; Jiang, W.; Zinn, A.A.; Knobler, C.B.; Hawthorne, M.F. Facile Electrophilic Iodination of Icosahedral Carboranes. Synthesis of Carborane Derivatives with Boron-Carbon Bonds via the Palladium-Catalyzed Reaction of Diiodocarboranes with Grignard Reagents. *Inorg. Chem.* 1995, 34, 2095–2100. [CrossRef]

- Viñas, C.; Barbera, G.; Oliva, J.M.; Teixidor, F.; Welch, A.J.; Rosair, G.M. Are halocarboranes suitable for substitution reactions? The case for 3-I-1,2-closo-C₂B₁₀H₁₁: Molecular orbital calculations, aryldehalogenation reactions, ¹¹B NMR interpretation of closo-carboranes, and molecular structures of 1-Ph-3-Br-1,2-closo-C₂B₁₀H₁₀ and 3-Ph-1,2-closo-C₂B₁₀H₁₁. *Inorg. Chem.* 2001, 40, 6555–6562. [CrossRef] [PubMed]
- 50. Endo, Y.; Aizawa, K.; Ohta, K. Synthesis of 3-Aryl-1,2-dicarba-closo-dodecaboranes by Suzuki-Miyaura Coupling Reaction. *Heterocycles* **2010**, *80*, 369–377. [CrossRef]
- 51. Anderson, K.P.; Mills, H.A.; Mao, C.; Kirlikovali, K.O.; Axtell, J.C.; Rheingold, A.L.; Spokoyny, A.M. Improved synthesis of icosahedral carboranes containing exopolyhedral B C and C C bonds. *Tetrahedron* **2019**, *75*, 187–191. [CrossRef]
- 52. Anufriev, S.A.; Shmal'ko, A.V.; Suponitsky, K.Y.; Sivaev, I.B. One-pot synthesis of B-aryl carboranes with sensitive functional groups using sequential cobalt- and palladium-catalyzed reactions. *Catalysts* **2020**, *10*, 1348. [CrossRef]
- 53. Janoušek, Z.; Hilton, C.L.; Schreiber, P.J.; Michl, J. C-Halogenation of the closo-[CB₁₁H₁₂]- Anion. *Collect. Czechoslov. Chem. Commun.* **2002**, *67*, 1025–1034. [CrossRef]
- 54. Šembera, F.; Plutnar, J.; Higelin, A.; Janoušek, Z.; Císařova, I.; Michl, J. Metal complexes with very large dipole moments: The anionic carborane nitriles 12-NC-CB₁₁X₁₁- (X = H, F, CH₃) as ligands on Pt(II) and Pd(II). *Inorg. Chem.* **2016**, *55*, 3797–3806. [CrossRef]
- 55. Estrada, J.; Lugo, C.A.; McArthur, S.G.; Lavallo, V. Inductive effects of 10 and 12-vertex closo-carborane anions: Cluster size and charge make a difference. *Chem. Commun.* **2016**, *52*, 1824–1826. [CrossRef] [PubMed]
- 56. Plešek, J.; Hanslík, T. Chemistry of boranes. XXIX. The synthesis of isomeric 1,9- and 1,12-dibromo- l,2-dicarba-closododecaboranes. *Collect. Czechoslov. Chem. Commun.* **1973**, *38*, 335–337. [CrossRef]
- 57. Anufriev, S.A.; Sivaev, I.B.; Bregadze, V.I. Synthesis of 9,9[°],12,12[°]-substituted cobalt bis(dicarbollide) derivatives. *Russ. Chem. Bull.* **2015**, *64*, 712–717. [CrossRef]
- 58. Havránek, M.; Samsonov, M.A.; Holub, J.; Ružickova, Z.; Drož, L.; Ružicka, A.; Fanfrlík, J.; Hnyk, D. The influence of halogenated hypercarbon on crystal packing in the series of 1-Ph-2-X-1,2-dicarba-closo-dodecaboranes (X = F, Cl, Br, I). *Molecules* 2020, 25, 1200. [CrossRef]
- Dmitrienko, A.O.; Karnoukhova, V.A.; Potemkin, A.A.; Struchkova, M.I.; Kryazhevskikh, I.A.; Suponitsky, K.Y. The influence of halogen type on structural features of compounds containing α-halo-α,α-dinitroethyl moieties. *Chem. Heterocycl. Comp.* 2017, 53, 532–539. [CrossRef]
- 60. Wolff, M.; Okrut, A.; Feldmann, C. [(Ph)₃PBr][Br₃], [(Bz)(Ph)₃P]₂[Br₈], [(n-Bu)₃MeN]₂[Br₂₀], [C₄MPyr]₂[Br₂₀], and [(Ph)₃PCl]₂[Cl₂I₁₄]: Extending the Horizon of Polyhalides via Synthesis in Ionic Liquids. *Inorg. Chem.* **2011**, *50*, 11683–11694. [CrossRef]
- 61. Sonnenberg, K.; Mann, L.; Redeker, F.A.; Schmidt, B.; Riedel, S. Polyhalogen and Polyinterhalogen Anions from Fluorine to Iodine. *Angew. Chem. Int. Ed.* **2020**, *59*, 5464–5493. [CrossRef]
- 62. Allen, F.H.; Kennard, O.; Watson, D.G.; Brammer, L.; Orpen, A.G.; Taylor, R. Tables of bond lengths determined by X-ray and neutron diffraction. Part 1. Bond lengths in organic compounds. *J. Chem. Soc. Perkin Trans.* **1987**, *2*, S1–S19. [CrossRef]
- 63. Varadwaj, P.R.; Varadwaj, A.; Marques, H.M. Halogen bonding: A halogen-centered noncovalent interaction yet to be understood. *Inorganics* **2019**, *7*, 40. [CrossRef]
- 64. Suponitsky, K.Y.; Tsirelson, V.G.; Feil, D. Electron-density-based calculations of intermolecular energy: Case of urea. *Acta Crystallogr. Sect. A Found. Crystallogr.* 1999, 55, 821–827. [CrossRef] [PubMed]
- Suponitsky, K.Y.; Smol'Yakov, A.F.; Ananyev, I.V.; Khakhalev, A.V.; Gidaspov, A.A.; Sheremetev, A.B. 3,4-Dinitrofurazan: Structural Nonequivalence of ortho -Nitro Groups as a Key Feature of the Crystal Structure and Density. *ChemistrySelect* 2020, 5, 14543–14548. [CrossRef]
- 66. Dalinger, I.L.; Suponitsky, K.Y.; Pivkina, A.N.; Sheremetev, A.B. Novel melt-castable energetic pyrazole: A pyrazol-yl-furazan framework bearing five nitro groups. *Prop. Explos. Pyrotech.* **2016**, *41*, 789–792. [CrossRef]
- 67. Andrews, J.S.; Zayas, J.; Jones, M. 9-Iodo-o-carborane. Inorg. Chem. 1985, 24, 3715–3716. [CrossRef]
- 68. Itatani, H.; Bailar, J.C. Homogenous catalysis in the reactions of olefinic substances. V. Hydrogenation of soybean oil methyl ester with triphenylphosphine and triphenylarsine palladium catalysts. *J. Am. Oil Chem. Soc.* **1967**, *44*, 147–151. [CrossRef]
- 69. Armarego, W.L.F.; Chai, C.L.L. *Purification of Laboratory Chemicals*, 6th ed.; Butterworth-Heinemann: Burlington, NJ, USA, 2009. [CrossRef]
- 70. Bruker AXS. APEX2 and SAINT; Bruker AXS Inc.: Madison, WI, USA, 2014.
- 71. Sheldrick, G.M. Crystal structure refinement with SHELXL. Acta Cryst. 2015, 71, 3–8. [CrossRef]
- 72. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Montgomery, J.A.; Kudin, K.N., Jr.; Burant, J.C.; Millam, J.M.; et al. *Gaussian 03, Revision E.01*; Gaussian, Inc.: Wallingford, UK, 2004.
- 73. Anufriev, S.A.; Sivaev, I.B.; Suponitsky, K.Y.; Godovikov, I.A.; Bregadze, V.I. Synthesis of 10-methylsulfide and 10alkylmethylsulfonium nido-carborane derivatives: B–H···π Interactions between the B–H–B hydrogen atom and alkyne group in 10-RC≡CCH₂S(Me)-7,8-C₂B₉H₁₁. *Eur. J. Inorg. Chem.* 2017, *38*, 4436–4443. [CrossRef]
- 74. Anufriev, S.A.; Sivaev, I.B.; Suponitsky, K.Y.; Bregadze, V.I. Practical synthesis of 9-methylthio-7,8-nido-carborane [9-MeS-7,8-C₂B₉H₁₁]-. Some evidences of BH···X hydride-halogen bonds in 9- XCH₂(Me)S-7,8-C₂B₉H₁₁ (X = Cl, Br, I). *J. Organomet. Chem.* 2017, 849–850, 315–323. [CrossRef]
- 75. Suponitsky, K.Y.; Masunov, A.E. Supramolecular step in design of nonlinear optical materials: Effect of π ... π stacking aggregation on hyperpolarizability. *J. Chem. Phys.* **2013**, *139*, 094310. [CrossRef]

- 76. Bader, R.F.W. Atoms in Molecules: A Quantum Theory; Clarendon Press: Oxford, UK, 1990.
- 77. Keith, T.A. AIMAll; Version 15.05.18; TK Gristmill Software: Overland Park, KS, USA, 2015.
- 78. Espinosa, E.; Molins, E.; Lecomte, C. Hydrogen bond strengths revealed by topological analyses of experimentally observed electron densities. *Chem. Phys. Lett.* **1998**, *285*, 170–173. [CrossRef]
- 79. Espinosa, E.; Alkorta, I.; Rozas, I.; Elguero, J.; Molins, E. About the evaluation of the local kinetic, potential and total energy densities in closed-shell interactions. *Chem. Phys. Lett.* **2001**, *336*, 457–461. [CrossRef]
- 80. Suponitsky, K.Y.; Lyssenko, K.A.; Antipin, M.Y.; Aleksandrova, N.S.; Sheremetev, A.B.; Novikova, T.S. 4,4'-Bis(nitramino)azofurazan and its salts. Study of molecular and crystal structure based on X-ray and quantum chemical data. *Russ. Chem. Bull.* 2009, *58*, 2129–2136. [CrossRef]
- 81. Lyssenko, K.A. Analysis of supramolecular architectures: Beyond molecular packing diagrams. *Mendeleev Commun.* 2012, 22, 1–7. [CrossRef]
- 82. Suponitsky, K.Y.; Lyssenko, K.A.; Ananyev, I.V.; Kozeev, A.M.; Sheremetev, A.B. Role of weak intermolecular interactions in the crystal structure of tetrakis-furazano[3,4-c:3',4'-g:3",4"-o][1,2,5,6,9,10,13,14]octaazacyclohexadecine and its solvates. *Cryst. Growth Des.* **2014**, *14*, 4439–4449. [CrossRef]