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Communication

Crystal Structure of 3-(Anthracen-2′-yl)-*ortho*-carborane

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Abstract

Crystal molecular structure of 3-(anthracen-2′-yl)-*ortho*-carborane was determined by single crystal X-ray diffraction study at 100 K. The asymmetric cell unit contains two enantiomeric pairs of molecules, in one of which the intramolecular dihydrogen bond CH...HB is formed with the participation of the C(1)H hydrogen of the anthracene substituent, and in the other with the participation of the C(3)H hydrogen. In all molecules, the polycyclic aromatic and carborane fragments are rotated relative to each other in such a way that the C-C bond of the *ortho*-carborane cage is approximately parallel to the plane of the aromatic substituent. According to quantum chemical calculations, the minimum energy corresponds to the formation of an intramolecular dihydrogen bond C(1)H...HB(4/7), whereas the C(3)H...HB(4/7) bond is formed rather as a result of intermolecular interactions in the crystal lattice.

Keywords: *ortho*-carborane; anthracene; crystal molecular structure; single crystal X-ray diffraction

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1. Introduction

ortho-Carborane derivatives with polycyclic aromatic substituents attached to carbon atoms have recently attracted increasing attention from researchers as a promising platform for stimuli-responsive luminescence smart materials due to their aggregation-induced emission [1–3]. At the same time, derivatives of *ortho*-carborane with polycyclic aromatic substituents at boron atoms have been studied to a much lesser extent. At present, there are only a few examples of *B*-substituted *ortho*-carborane derivatives with tricyclic (anthracene [4–7]) or tetracyclic (pyrene [7,8]) aromatic substituents. Moreover, information about the structure of these compounds is even more rare; in the literature, there are data on the crystal structures of three *B*-substituted derivatives of *ortho*-carborane with pyrene substituents [7] and only one derivative with an anthracene substituent [6]. In the latter case, this is the structure of 3-(anthracen-9′-yl)-*ortho*-carborane.

In this communication, we report the crystal structure of isomeric 3-(anthracen-2′-yl)-*ortho*-carborane, which we recently prepared by Pd-catalyzed cross-coupling reaction of anthracen-2-yl zinc bromide with 3-iodo-*ortho*-carborane [7].

2. Results and Discussion

It was found that the luminescent properties of *C*-substituted polycyclic aryl-*ortho*-carboranes are largely determined by the mutual orientation of the planar organic substituent and the carborane cage [9–11]. In most of the aryl-substituted *ortho*-carboranes, when the carborane C-C bond is coplanar with the aryl π-plane, there is virtually no electronic interaction between them. Therefore, the emission band in this conformation is

associated with the transition from the locally excited (LE) state of the aryl substituent. In contrast, when the C-C bond in *ortho*-carborane is perpendicular to the π-plane of the aryl group, the carborane cage can serve as an electron acceptor. As a result, in such conformers, photoexcitation will lead to intramolecular charge transfer (ICT) and subsequent generation of a significant emission band with an ICT character.

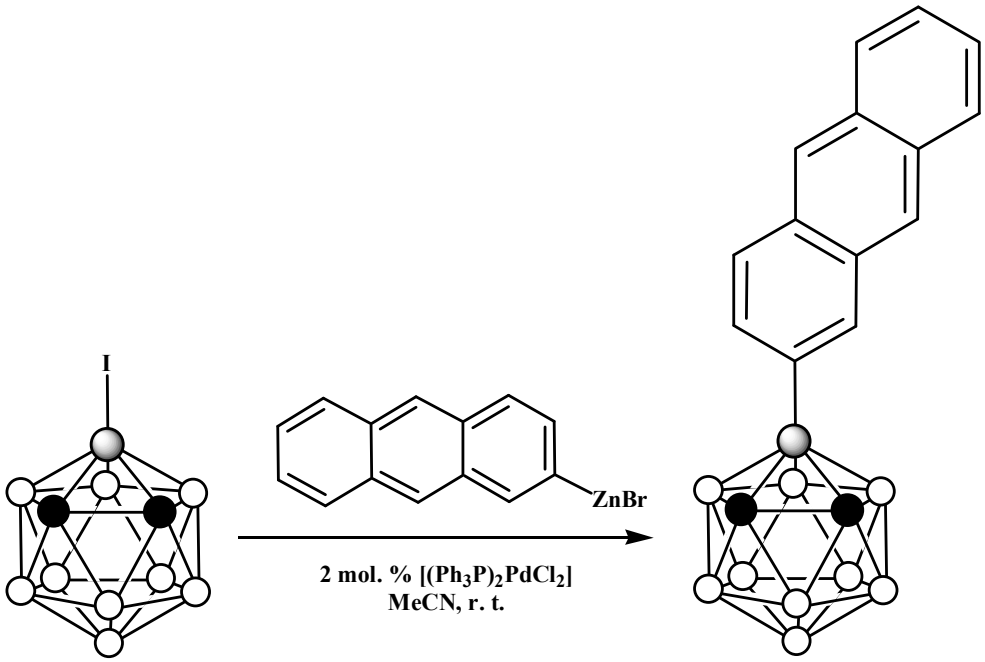
The simplest example of a *C*-aryl derivative of *ortho*-carborane is 1-phenyl-*ortho*-carborane. In an isolated molecule, the structure of which was determined by gas-phase electron diffraction, the torsion angle C_{carb}-C_{carb}-C_{ar}-C_{ar} θ is 25° [12]. This is close to the values characterized by the minimum energy, which were found using HF (θ = 25° [12]) and DFT (θ = 30.2° [13]) quantum chemical calculations [13]. In the crystalline state, 1-phenyl-ortho-carborane can exist in the form of two polymorphic modifications (α- and β-forms), the molecules of which differ in the orientation of the phenyl ring with θ values equal to 22.2° and 18.3° in the α- and β-forms, respectively [12,14,15]. A notable contribution to the stabilization of the most preferred conformation is made by the presence of intramolecular H...H interactions between the carborane cage and the phenyl ring [15]. At the same time, since the rotational barrier of the phenyl ring is very small, in solution there is an equilibrium between the different rotational conformers, which is confirmed by ^{1}H NMR spectroscopy data [16]. It is worth noting that in the structure of polymorph β, in contrast to polymorph α, in addition to the intramolecular H...H contacts, there are numerous intermolecular H...H contacts [15]. An increase in the size of the substituent leads to a predominance of the role of intermolecular contacts, as a result of which they can have a determining effect on the conformational structure of the molecule in the solid state. Moreover, different polymorphs of the same compound may demonstrate various luminescent behaviors [17].

As for B(3)-substituted aryl derivatives of *ortho*-carborane, in which the substituent is attached to the boron atom adjacent to carbon atoms rather than to one carbon atom, little is known about their geometry and its potential effect on luminescent properties. Although the synthesis of 3-aryl-*ortho*-carborane derivatives was first described more than 50 years ago [18], only limited information is available on their crystal structure. At the same time, it should be noted that in most structures of 3-phenyl-*ortho*-carboranes, intramolecular CH...HB contacts are observed, rather than CH...HC contacts characteristic of *C*-aryl derivatives of *ortho*-carborane [4,19,20]. However, in the crystal structure of 3-(pyren-1′-yl)-*ortho*-carborane, it is the CH...HC contact, together with the additional CH...HB contact involving the fused ring, that "directs" the pyrene moiety almost perpendicular to the C-C bond of the carborane [7]. On the other hand, in the structure of 3-(anthracen-9′-yl)-*ortho*-carborane, the substituent adopts an intermediate orientation between perpendicular and parallel to the C-C bond of the carborane cage in the presence of shorter CH...HC and longer CH...HB intramolecular contacts involving the fused rings of the substituent [6].

3-(Anthracen-2′-yl)-*ortho*-carborane was prepared by Pd-catalyzed cross-coupling reaction of anthracen-2-yl zinc bromide with 3-iodo-*ortho*-carborane, as earlier described (Scheme 1) [7].

3-(Anthracen-2′-yl)-*ortho*-carborane crystallizes in chiral space group $P2_1$, and its asymmetric unit cell contains four molecules, which is a relatively rare case. The molecule is chiral. It is seen that in each pair of molecules (***A***,***D*** (Figure 1 top) and ***B***,***C*** (Figure 1 bottom)), the molecules are almost related to each other by the mirror plane.

We tried to solve and refine the structure of 3-(anthracen-2′-yl)-*ortho*-carborane in the centrosymmetric space group $P2_1/n$. It led to significant disorder in one carborane cage and unstable refinement. Based on that, we believe that correct space group is $P2_1$ with four independent molecules.



Scheme 1. Synthesis of 3-anthracen-2′-yl-*ortho*-carborane.

Two slightly different conformations, with respect to the orientation of the anthracene substituent relative to the carborane cage, are observed (Figure 2, molecules ***A*** (left) and ***B*** (right)).

In molecule ***A***, a shortened C(4A)-H(4AA)...H(4A)-B(4A) contact is observed (2.37 Å in molecule ***A*** and 2.34 Å in molecule ***D***), while in molecule ***B***, the anthracene substituent is slightly rotated around the C(3)-B(3) bond to form a shortened C(16B)-H(16B)...H(7B)-B(7B) contact (2.39 Å in molecules ***B*** and ***C***).

To gain a deeper insight into the structure and intramolecular interactions in 3-(anthracen-2′-yl)-*ortho*-carborane, quantum chemical calculations were carried out. The PBE0 functional with the triplet-zeta basis set was used, the reliability of which for molecular geometry, non-covalent interactions and conformational analysis has been confirmed by our recent studies [21–23]. As initial geometries for optimization, both experimentally observed conformations (molecules ***A*** and ***B***) were used. However, only one of them (conformation ***B*** Figure 2 (right)) corresponds to the true minimum. The theoretically obtained electron density of the optimized geometry of 3-(anthracen-2′-yl)-*ortho*-carborane was processed using the topological theory by R. Bader [24,25] to search for bond critical points (BCP) between noncovalently bonded atoms. Indeed, BCP between H16B and H7B atoms was localized. To estimate the energy of the H...H contact, we used LMS correlation between the energy and the potential energy density at BCP [26] which is often used to estimate the energy of non-covalent interactions [27–30]. The energy of the H16...H7 contact is equal to −1.4 kcal/mol, which stabilizes conformation ***B***. However, such energy is comparable to energies of intermolecular interactions, and conformation ***A*** is the result of intermolecular interactions in the crystal.

The presence of the planar aromatic fragment in such a dipolar molecule (the calculated dipole moment of 3-(anthracen-2′-yl)-*ortho*-carborane is 2D) may imply the formation of π...π stacking interactions. However, no such interactions are observed. Instead, the crystal packing is stabilized by close H...π and B-H...H-C contacts.

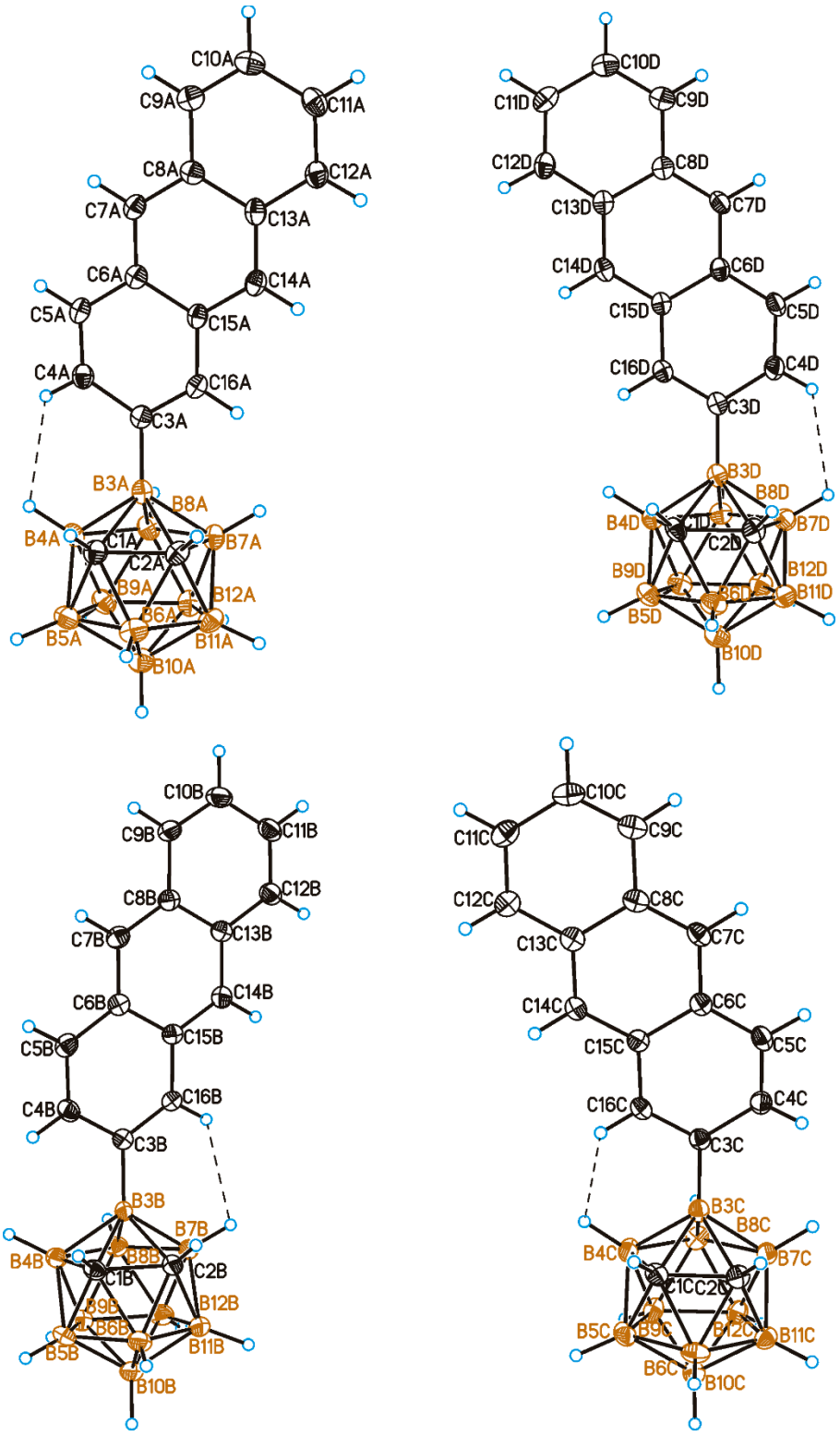


Figure 1. General view of four independent molecules of 3-(anthracen-2′-yl)-*ortho*-carborane showing atomic labeling scheme. Thermal ellipsoids are given at 50% probability level.

We have considered the immediate molecular environment of all four independent molecules and calculated the interaction energies of the central molecule with each of its nearest neighbors (pairwise interaction energies). Each molecule in the crystal has eleven neighbors. Of these, four interactions occur between molecules of the same symmetry (***A***. . .***A***, ***B***. . .***B***, ***C***. . .***C***, ***D***. . .***D***), and one interaction occurs between pseudo-centrosymmetric

molecules (***A***. . .***D*** and ***B***. . .***C***). The remaining six interactions are formed between symmetrically independent molecules. The results are presented in Table S1. As a result of all these interactions, the molecules form a complex three-dimensional structure. However, Table S1 shows that each molecule has its strongest interaction with two neighboring molecules. Based on the energies given in Table S1, the crystal packing of 3-(anthracen-2′-yl)-*ortho*-carborane can be viewed as built up of columns along the *b* axis, in which the molecules are linked by the strongest H. . .π interactions, while the intercolumn bonds are provided by weaker H. . .π and H. . .H interactions (Figure 3).

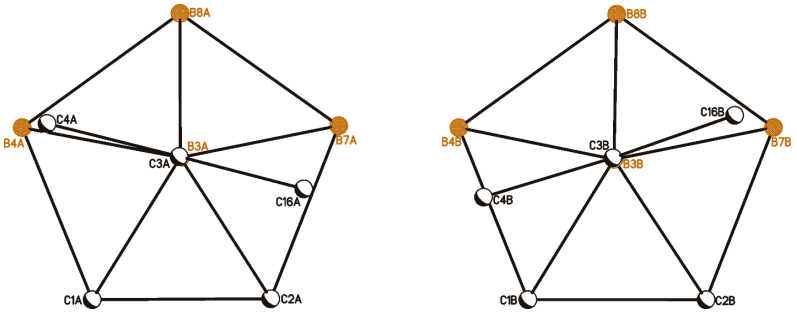


Figure 2. Projection of the anthracene substituent plane onto the C1-C2-B4-B8-B7 face of *ortho*-carborane.

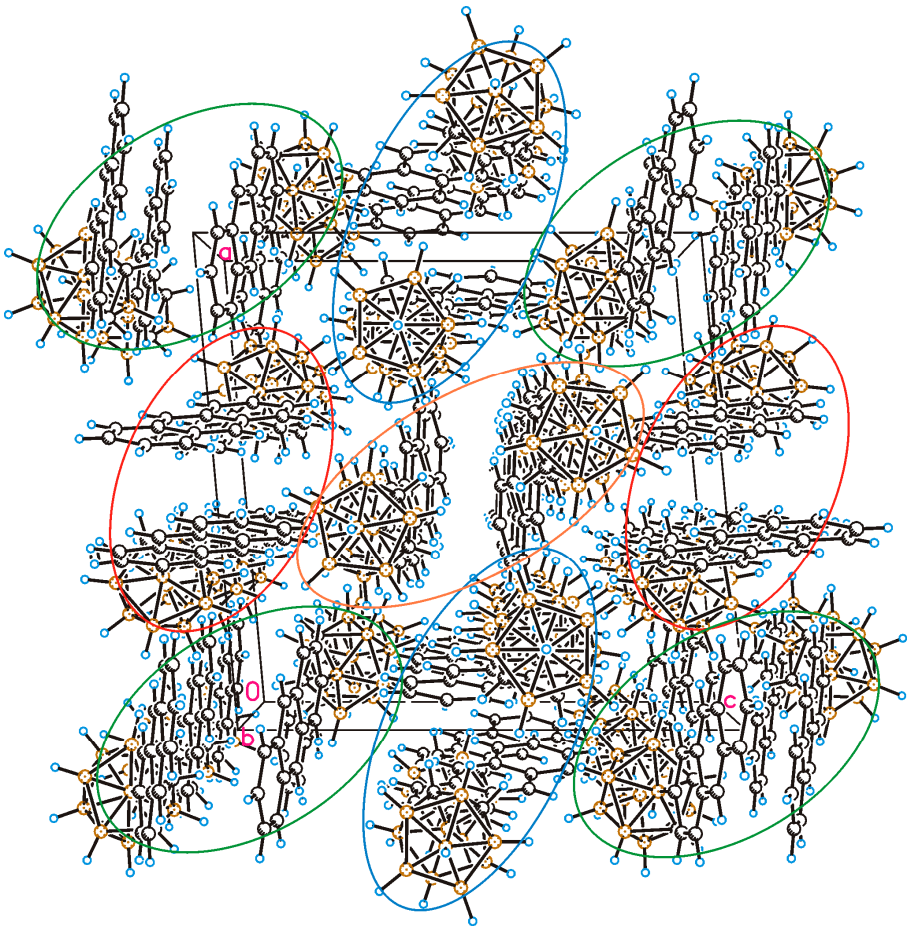


Figure 3. Crystal-packing fragment of 3-(anthracen-2′-yl)-*ortho*-carborane. Projection onto *ac* plane. Columns are perpendicular to the plane of figure and are shown by ovals. Blue-columns from molecules ***A***; green-columns from molecules ***B***; orange-columns from molecules ***C***; and red-columns from molecules ***D***.

3. Materials and Methods

3.1. General Methods

3-Iodo-*ortho*-carborane [31], and bis(triphenylphosphine)palladium dichloride [$(Ph_3P)_2PdCl_2$] [32] were prepared according to the literature procedures. Anhydrous cobalt dibromide was prepared from cobalt bromide hexahydrate by heating at 160 °C under vacuum for 3 h and stored under an argon atmosphere. Acetonitrile was dried using standard procedure [33]. The reaction progress was monitored by thin-layer chromatography (Merck F254 silica gel on aluminum plates (Merck KGaA, Darmstadt, Germany)) and visualized using 0.5% $PdCl_2$ 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 (^{1}H), 128.3 MHz (^{11}B), and 100.0 MHz (^{13}C) were recorded with a Varian Inova-400 spectrometer (see Figures S1–S15 in Supplementary Materials). The signals in the ^{1}H and ^{13}C NMR spectra were referenced to Me_4Si, whereas the signals in the ^{11}B NMR spectra were referenced to $BF_3{\cdot}Et_2O$. High resolution mass spectra were recorded on an LCMS-9030 device (Shimadzu, Japan) using electrospray ionization mass spectrometry (ESI-MS). Molecular ions in the spectra were analyzed and matched with the appropriately calculated m/z and isotopic profiles in the LabSolutions v.5.114 program.

3.2. Synthesis of 3-(Anthracen-2′-yl)-ortho-carborane

3-(Anthracen-2′-yl)-*ortho*-carborane was prepared as described in the literature [7]. Allyl chloride (82 µL, 77 mg, 1.00 mmol) and trifluoroacetic acid (25 µL) were added to a blue mixture of zinc powder (490 mg, 7.50 mmol) and anhydrous $CoBr_2$ (55 mg, 0.25 mmol) in 5 mL of freshly distilled acetonitrile and the resulting dark orange mixture was stirred at room temperature for 15 min. Then 2-anthracenyl bromide (643 mg, 2.50 mmol) was added and the reaction mixture was stirred at room temperature for another 45 min. Then 3-iodo-*ortho*-carborane (270 mg, 1.00 mmol) and [$(Ph_3P)_2PdCl_2$] (14 mg, 0.02 mmol) were added, and the reaction mixture was stirred at room temperature overnight. Then the mixture was filtered, and the residue was washed with hot acetone (until traces of carborane-containing products disappeared on TLC). The organic phases were combined, concentrated under reduced pressure with the addition of silica, and subjected to column chromatography on silica using a mixture of *n*-hexane: ethyl acetate (9:1.5, *v*/*v*) as eluent to obtain 3-(anthracen-2′-yl)-*ortho*-carborane as a pale green crystalline solid (265 mg, yield 83%). ^{1}H{^{11}B} NMR (400 MHz, acetone-d_6): δ 8.55 (1H, s, CH_{Ar}), 8.50 (2H, s, CH_{Ar}), 8.07 (3H, m, CH_{Ar}), 7.77 (1H, d, J = 8.6 Hz, CH_{Ar}), 7.51 (2H, m, CH_{Ar}), 4.87 (2H, br s, CH_{Carb}), 2.58 (2H, br s, BH_{Carb}), 2.51 (2H, br s, BH_{Carb}), 2.44 (2H, br s, BH_{Carb}), 2.29 (2H, br s, BH_{Carb}), 2.20 (1H, br s, BH_{Carb}) ppm. ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6): δ C_{Ar}-B not observed, 135.5 (CH$_{Ar}$), 133.2 (C_{Ar}), 132.9 (C_{Ar}), 132.5 (C_{Ar}), 132.0 (C_{Ar}), 129.7 (CH$_{Ar}$), 129.1 (CH$_{Ar}$), 129.0 (CH$_{Ar}$), 128.4 (CH$_{Ar}$), 127.5 (CH$_{Ar}$), 126.8 (CH$_{Ar}$), 126.7 (CH$_{Ar}$), 126.5 (CH$_{Ar}$), 58.9 (CH$_{Carb}$) ppm. ^{11}B NMR (128 MHz, acetone-d_6): δ −3.0 (2B, d, J = 148 Hz, *B(9,12)*), −4.5 (1B, s, *B(3)*-C), −8.8 (1B, d, J = 149 Hz, *B(8)*), −12.5 (3B, d, J = 154 Hz, *B(4,7,6/10)*), −13.3 (3B, d, J = 164 Hz, *B(5,6/10,11)*) ppm. ^{1}H{^{11}B} NMR (400 MHz, $CDCl_3$): δ 8.44 (1H, s, CH_{Ar}), 8.43 (1H, s, CH_{Ar}), 8.28 (1H, s, CH_{Ar}), 8.02 (3H, m, CH_{Ar}), 7.61 (1H, d, J = 8.6 Hz, CH_{Ar}), 7.51 (2H, m, CH_{Ar}), 3.85 (2H, br s, CH_{Carb}), 2.54 (4H, br s, BH_{Carb}), 2.46 (2H, br s, BH_{Carb}), 2.27 (2H, br s, BH_{Carb}), 2.22 (1H, br s, BH_{Carb}) ppm. ^{11}B NMR (128 MHz, $CDCl_3$): δ −2.3 (2B, d, J = 149 Hz, *B(9,12)*), −4.9 (1B, s, *B(3)*-C), −8.4 (1B, d, J = 152 Hz, *B(8)*), −12.8 (3B, d, J = 156 Hz, *B(4,7,6/10)*), −13.5 (3B, d, J = 161 Hz, *B(5,6/10,11)*) ppm. HRMS-ESI (m/z): obsd. 320.2569 [M]$^+$, calcd. for $C_{16}H_{20}B_{10}$: 320.2571 [M]$^+$.

3.3. Single Crystal X-Ray Diffraction Study

Single crystals suitable for X-ray diffraction study were prepared by slow evaporation of a solution of 3-(anthracen-2′-yl)-*ortho*-carborane in acetone. Single crystal X-ray diffraction experiment was carried out using SMART APEX2 CCD diffractometer (Bruker Scientific LLC, Billerica, MA, USA) (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, ω-scans) at 100 K. Collected data were processed by the SAINT and SADABS programs incorporated into the APEX2 program package [34]. The structure was solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. The positions of hydrogen atoms of the anthracene substituents were calculated and included in the refinement within isotropic approximation using the riding model. H atoms of the carborane cages were found in the difference Fourier maps and refined isotropically. The refinement was carried out with the SHELXTL program [35]. The CCDC number 2489838 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic data for 3-(anthracen-2′-yl)-*ortho*-carborane: $C_{16}H_{20}B_{10}$ are monoclinic, space group $P2_1$: a = 16.1771(11) Å, b = 13.6919(9) Å, c = 16.4224(11) Å, β = 95.155(2)°, V = 3622.8(4) Å^3, Z = 8, M = 320.42, d_{cryst} = 1.175 g·cm^{-3}. $wR2$ = 0.1084 calculated on F^2_{hkl} for all 15853 independent reflections with $2\theta < 54.1°$, (*GOOF* = 1.030, R = 0.0475 calculated on F_{hkl} for 13099 reflections with $I > 2\sigma(I)$).

Supplementary Materials: Figures S1–S13: NMR spectra of 3-(anthracen-2′-yl)-*ortho*-carborane; Figures S14 and S15: HRMS spectra of 3-(anthracen-2′-yl)-*ortho*-carborane; Table S1: Types of intermolecular interactions and pair interaction energies (kcal/mol) of the molecules with their closest environment in the crystal of 3-(anthracen-2′-yl)-*ortho*-carborane.

Author Contributions: Synthesis and purification, A.V.S.; synthesis and NMR study, S.A.A.; single crystal X-ray diffraction, quantum chemical calculations, and manuscript preparation, K.Y.S.; supervision, manuscript concept, and preparation, I.B.S. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: Crystallographic data for the structure of 3-(anthracen-2′-yl-*ortho*-carborane) was deposited in the Cambridge Crystallographic Data Centre as supplementary publication CCDC 2489838.

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