

Short Note

Crystal Structure of 9-Dibenzylsulfide-7,8-dicarba-*nido*-undecaborane 9-Bn₂S-7,8-C₂B₉H₁₁

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Abstract: The crystal structure of 9-dibenzylsulfide-7,8-dicarba-*nido*-undecaborane 9-Bn₂S-7,8-C₂B₉H₁₁ was determined by a single-crystal X-ray diffraction. One of the benzyl groups is located above the open face of the carborane cage with a short H···H distance (2.29 and 2.71 Å for two symmetrically independent molecules) between the BHB-bridging hydrogen atom of the carborane fragment and the *ortho*-CH group of the aromatic ring. Topological analysis has revealed the existence of a critical bond point with a calculated energy of −0.8 kcal/mol in accordance with an X-ray diffraction molecular geometry. The crystal packing analysis revealed that this benzyl group is also involved in π-stacking interactions, while another benzyl group participates in numerous weak H···π, H···H and van der Waals interactions.



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1. Introduction

nido-Carborane derivatives bearing sulfonium and ammonium substituents are widely used for the synthesis of π-complexes of transition metals or metallocarboranes [1–6], as well as various neutral functional derivatives of *nido*-carboranes [7–13]. A single-crystal X-ray diffraction study of asymmetrically substituted dialkylsulfonium derivatives of *nido*-carborane 9-R₂S-7,8-C₂B₉H₁₁ [8,9,14] as well as their C- and B-substituted analogues [15–20], revealed that the SR₂ group in all cases is turned in such way, that the lone pair of the sulfur atom is antiperiplanar to the B(9)–B(10) bond, while their ¹H and ¹³C-NMR spectra indicate the absence of free rotation around the B(9)–S bond.

Analysis of the ¹H-NMR spectrum of the previously synthesized 9-dibenzylsulfonium derivative of *nido*-carborane 9-Bn₂S-7,8-C₂B₉H₁₁ [21] revealed the nonequivalence of the benzyl groups: the signal of the CH₂ protons of one benzyl group appears as a singlet, while the signal of the CH₂ protons of the other group appears as two doublets. Taking into account the achirality of the sulfur atom in this compound, it can be assumed that there is an interaction between the carborane cage and one of the benzyl groups, which hinders its rotation resulting in non-equivalence of the benzyl protons. To shed light on this issue, we carried out a detailed study of the structure of 9-Bn₂S-7,8-C₂B₉H₁₁ using a single-crystal X-ray diffraction and quantum-chemical calculations.

2. Results and Discussion

The molecular crystal structure of 9-Bn₂S-7,8-C₂B₉H₁₁ was determined by a single-crystal X-ray diffraction study. An asymmetric unit cell contains two molecules (A and A') which differ slightly in the orientation of the SBn₂ substituent. As mentioned in the

introduction, in the *nido*-carboranes substituted with the $S(CH_2R')CH_2R''$ groups at position B(9), the orientation of the substituent is such that one C(8)-B(9)-S-C angle is in the range of $85\text{--}115^\circ$ and the other in the range of $170\text{--}140^\circ$. In 9-Bn₂S-7,8-C₂B₉H₁₁, the corresponding torsion angles for both symmetrically independent molecules are characterized by expected values (Table 1).

Table 1. Selected torsion angles which define molecular conformation of the titled compound.

Torsion Angle	Molecule A	Molecule A'	Calculation
C(8)-B(9)-S(1)-C(1)	91.2(2)	113.4(2)	112.9
C(8)-B(9)-S(1)-C(10)	−163.5(2)	−140.7(2)	−141.0
B(9)-S(1)-C(1)-C(2)	−65.8(2)	−84.2(2)	−77.8
B(9)-S(1)-C(10)-C(11)	−165.0(2)	179.7(2)	−177.2

At the same time, according to the literature data, no regularities in the orientation of the R' and R'' groups were observed. For example, in recently studied 9-ClCH₂(Me)S-7,8-C₂B₉H₁₁ [9], three conformers with respect to rotation around the S-C bond were found by quantum-chemical calculations and intramolecular noncovalent attractive H...Cl contacts were observed in two of them. Due to the relatively low rotation barrier, all three conformers can exist in solution; however, no conformer with intramolecular noncovalent contacts was observed in the crystal structure.

In the case of 9-Bn₂S-7,8-C₂B₉H₁₁, the benzyl group directed downwards relatively to the open pentagonal face of the *nido*-carborane ligand does not form any intramolecular contacts, while the aromatic ring of the other benzyl group is located above the open face, which might imply intramolecular interactions. We found that the H(9A)...H(12) distance (shown by a dashed line in Figure 1) is 2.29 and 2.71 Å in two symmetrically independent molecules. It is interesting to note here that, in the recently studied 9-Bn(Me)S-7,8-C₂B₉H₁₁ [8], no intramolecular shortened contacts were observed between the benzyl group and the carborane cage; as a consequence, the aryl ring is involved in extensive intermolecular bonding.

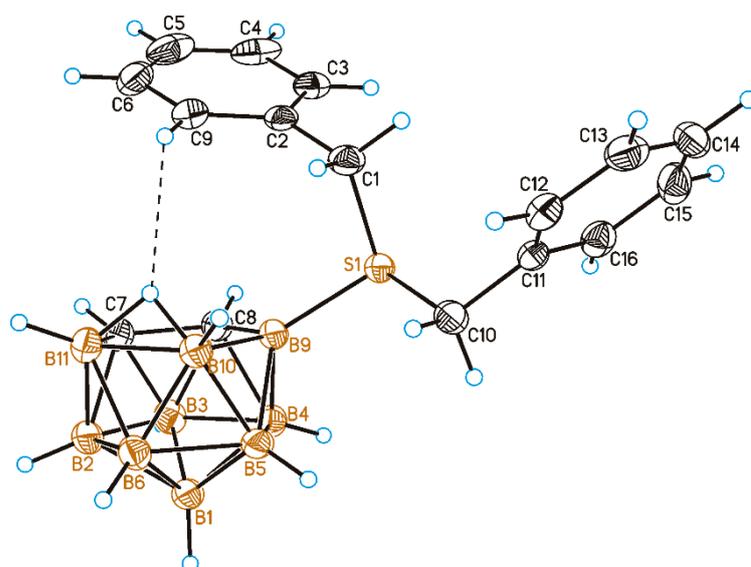


Figure 1. A general view of 9-Bn₂S-7,8-C₂B₉H₁₁ showing atomic numbering. Only the first independent molecule (A) is presented. Thermal ellipsoids are drawn at a 50% probability level. Noncovalent C-H...H-B interaction is shown by a dashed line.

To find the preferred conformation of the isolated molecule of 9-Bn₂S-7,8-C₂B₉H₁₁ for a better understanding of both intra- and intermolecular contacts, we carried out quantum-chemical calculation using the Gaussian program [22] and PBE0 functional with a

triple-zeta basis set, which proved to be reliable for studying of molecular geometry [23–26]. To search for noncovalent intramolecular interactions, the AIM topological theory [27] was utilized. The search for bond critical points was carried out using the AIMAll program [28]. The estimation of the interacting atoms' energy was based on its correlation with the potential energy density at the bond critical point $E = 1/2V(r)$ [29,30]. Such correlation is often utilized for energetic analysis of a variety of organic compounds [24,31–33].

The calculated geometry (Table 1) is close to the geometry of the A' molecule. Topological analysis revealed the presence of the bond critical point between the H(9A) and H(12) atoms in accordance with our suggestion based on the X-ray geometry of the molecule (Figure 1). The calculated energy of this contact is -0.8 kcal/mol. The crystal packing analysis demonstrates that the upwards-directed benzyl group is involved in the π -stacking interactions (Figure 2), while the other benzyl group participates in numerical weak $H\cdots\pi$, $H\cdots H$ and van-der-Waals interactions.

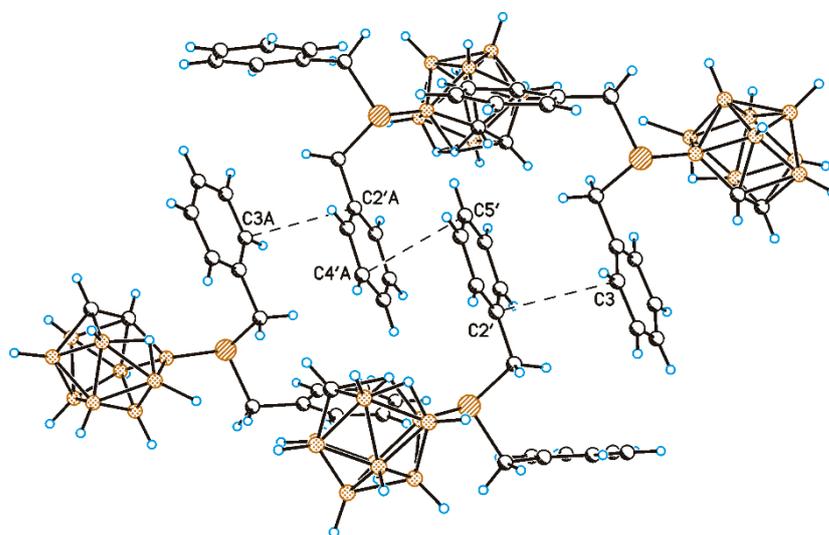


Figure 2. Crystal packing fragment of the titled compound showing stacking aggregates. The shortest intermolecular contacts are denoted by dashed lines. Distances $C(3)\cdots C(2')$ and $C(5')\cdots C(4')$ are equal to 3.383(3) and 3.364(3) Å, respectively.

In conclusion, the molecular crystal structure of compound 9-Bn₂S-7,8-C₂B₉H₁₁ was determined. The observed relative orientation of the benzyl groups allowed the formation of both intramolecular noncovalent interactions, intermolecular π - π stacking and $H\cdots\pi$ interactions in addition to the ordinary van der Waals contacts.

3. Materials and Methods

Synthesis of the 9-dibenzylsulfonium derivative of *nido*-carborane 9-Bn₂S-7,8-C₂B₉H₁₁ was described in the literature [21]. Its NMR spectral data are as follows: ¹H-NMR (400 MHz, CDCl₃), δ : 7.38 (10H, m, Ph), 4.43 (1H, d, CHHPH, $J = 13.3$ Hz), 4.17 (2H, s, CH₂Ph), 4.13 (1 H, d, CHHPH, $J = 13.3$ Hz), 1.93 (2H, br.s, CH_{carb}), -3.31 (1H, br.s, BHB bridge), ¹³C{¹H}-NMR (100 MHz, CDCl₃), δ : 130.34 (Ph), 130.05 (Ph), 129.97 (Ph), 129.76 (Ph), 129.61 (Ph), 129.57 (Ph), 129.52 (Ph), 129.43 (Ph), 52.01 (C_{carb}), 47.98 (CH₂), 46.10 (CH₂), 38.52 (C_{carb}), ¹¹B-NMR (128 MHz, CDCl₃), δ : -4.0 (1B, d, $J = 130$ Hz), -8.1 (1B, s), -11.5 (1B, d, $J = 130$ Hz), -16.7 (1B, d, $J = 116$ Hz), -17.8 (1B, d, $J = 165$ Hz), -23.3 (1B, d, $J = 149$ Hz), -26.0 (1B, d, $J = 144$ Hz), -29.5 (1B, d, $J = 109$ Hz), -36.5 (1B, d, $J = 144$ Hz). MS (EI): found; m/z : 347 (M)⁺; calculated for C₁₆H₂₅B₉S (M)⁺ = 347.

A single-crystal X-ray diffraction experiment was carried out using the SMART APEX2 CCD diffractometer ($\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, graphite monochromator, ω -scans) at 120 K. Collected data were processed by the SAINT and SADABS programs incorporated into the APEX2 program package [34]. The structure was solved by 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 [35]. The CCDC number 2083954 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 9-Bn₂S-7,8-C₂B₉H₁₁: C₁₆H₂₅B₉S are monoclinic, the space group $P2_1/n$: $a = 11.4570(6)$ Å, $b = 25.5132(14)$ Å, $c = 13.5873(7)$ Å, $\beta = 102.813(3)^\circ$, $V = 3872.7(4)$ Å³, $Z = 8$, $M = 346.71$, $d_{\text{cryst}} = 1.189$ g·cm⁻³, $wR2 = 0.0911$ calculated on F^2_{hkl} for all 7507 independent reflections with $2\theta < 52.0^\circ$, ($GOF = 0.990$, $R = 0.0416$ calculated on F_{hkl} for 6230 reflections with $I > 2\sigma(I)$).

Supplementary Materials: The following are available online, the NMR spectra X-ray diffraction data for 9-Bn₂S-7,8-C₂B₉H₁₁.

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Conflicts of Interest: The authors declare no conflict of interest.

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