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Journal of Molecular Structure 785 (2006) 167-169

Journal of MOLECULAR STRUCTURE

www.elsevier.com/locate/molstruc

Example of an intramolecular, non-classical C–H $\cdots \pi$ hydrogen bonding interaction in an Arylcarborane derivative

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Received 19 July 2005; received in revised form 5 October 2005; accepted 6 October 2005 Available online 11 November 2005

Abstract

The synthesis and X-ray diffraction study of 3-(2-biphenyl)-1,2- $C_2B_{10}H_{11}$, **1**, provides an example of an *intramolecular* non-classical C–H··· π hydrogen bonding interaction in which the same aromatic π -electron-donating group which interacts with the carborane C–H is also connected to the carborane cage.

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Keywords: Carborane; C-H-X interaction; Intramolecular; Crystal structure

1. Introduction

The rigid geometry and three-dimensional nature of the isomeric icosahedral carborane ($C_2B_{10}H_{12}$) cages makes them excellent candidates as building blocks for macromolecules and supramolecular assemblies [1-5]. Because of the diverse chemistry of their carborane C-H and B-H vertices, carborane derivatives are an attractive choice for crystal engineering [6]. Also, the acidity of the carborane C-H vertices enables the formation of hydrogen bonds [7], generating supramolecular structures. The well-established intermolecular hydrogen bonding interactions involving carboranes are: classical C-H···O hydrogen bonds [2], bifurcated C-H···(O)₂ hydrogen bonds [8], non-classical C-H $\cdots\pi$ hydrogen bonds [9], and B-H···H-N interactions [10]. The known carborane cage C-H interactions are C–H···X (X=O, N, P, S, H, π , halogens) [7]. Reported instances of *intramolecular* C-H···X hydrogen bonding interactions in 1,2-carboranes are limited [7]. Herein is reported the synthesis and crystal structure of 3-(2-biphenyl)- $1,2-C_2B_{10}H_{11}$, 1, which was prepared as part of our ongoing efforts to increase the scope of derivatization of the 3-vertex of the $1,2-C_2B_{10}H_{12}$ carborane cage.

2. Experimental section

2.1. General considerations

Standard Schlenk line and glove-box techniques were employed for the manipulation of water- and air-sensitive reagents and products. Solvents used were reagent-grade, dried over an appropriate drying agent and distilled under nitrogen flow. Tetrahydrofuran was distilled from a sodium-benzophenone still prior to use. 2-biphenylmagnesium bromide was obtained from Aldrich Chemical Co. and used as received. *trans*-Dichlorobis(triphenylphosphine)palladium (II) was obtained from Strem Chemical Co. and used as received.

2.2. Physical measurements

The ¹H, ¹³C and ¹¹B NMR spectra were recorded on a Brucker ARX 500 spectrometer. Chemical shifts for ¹H and ¹³C NMR spectra were referenced to signals of residual ¹H and ¹³C present in deuteriated solvents. Chemical shifts values for ¹¹B NMR spectra were referenced relative to external BF₃·OEt₂ (δ =0.0 ppm with negative values indicating an upfield shift). Mass spectra was obtained using a VG Autospec (EI) mass spectrometer.

3. Synthesis of 1, 3-(2-biphenyl)-1,2- $C_2B_{10}H_{11}$

To a stirred mixture of 10 mmol (2.7 g) of 3-I-1,2- $C_2B_{10}H_{11}$ and 0.2 mmol (140 mg) of *trans*-Dichlorobis(triphenylphosphine)palladium (II) in 25 mL of anhydrous THF at 0 °C was

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added 40 mmol (80 mL of 0.5 M solution) of 2-biphenylmagnesium bromide in diethyl ether. After the addition was completed, the reaction mixture was set to reflux for 36 h. The reaction was checked by ¹¹B NMR and was stopped when the starting material was gone. The reaction mixture was then cooled to room temperature. An additional 100 mL of ether was added, and the excess Grignard reagent was quenched by the dropwise addition of water. The water layer was washed with ether $(3 \times 15 \text{ mL})$. The combined organic layers were washed with 3×15 mL of 3% HCl solution and then water and dried over MgSO₄. The solvent was removed under vacuum leaving a solid white residue. The crude product was purified by recrystallization from hexane giving white crystals of pure 3-(2-phenylphenyl)-1,2- $C_2B_{10}H_{11}$ 1. Yield=97% (2.9 g, 9.7 mmol). Mp: 91 °C ¹H NMR (δ, ppm, C₆D₆) 7.90–6.89 (m, 9H), 2.38 (br, s, 2H). ¹¹B NMR (δ , ppm, C₆D₆) -1.87 (d, 2B, J_{B-H} 144), -4.3 (s, 1B), -7.3 (d, 1B, J_{B-H} 144), -11.2 $(d, 3B, J_{B-H} 161), -12.8 (d, 2B, J_{B-H} 176), -14.0 (d, 1B, J_{B-H} 176)$ 140). ¹³C NMR (δ, ppm, C₆D₆) 146.4–127.3 (s, aromatic CH), 56.0 (s, carborane CH). HR-EIMS: *m/z*: calc. 298.2496; found 298.2505. v (KBr)/cm⁻¹ 3091, 3059 (carborane C–H).

CCDC 271931 contains the supplementary crystallographic data for this communication.

4. Results and discussion

The crystal structure of **1** provides a new example of an *intramolecular* non-classical C–H··· π hydrogen bonding interaction in which the same aromatic π -electron-donating group which interacts with the carborane C–H is also connected to the carborane cage. To our knowledge, only two previous [11,12] examples of carborane compounds exhibiting cage C–H···phenyl ring π *intramolecular* hydrogen bonding interaction have been reported.

Functionalization of the 1,2-carborane cage at the 3-vertex was achieved by the palladium-catalyzed reaction of 3-I-1,2- $C_2B_{10}H_{11}$ with 2-biphenylmagnesium bromide [13–15]. Colorless crystals of 1 were grown from a 1:1 hexane:ethyl acetate solution by slow evaporation of the solvent. The structure of 1 was confirmed by X-ray crystal analysis, which revealed a novel structural phenomenon (Fig. 1). In the biphenyl substituent, the maximum deviation of C1L to C6L from the plane through these 6 atoms is 0.003(1) Å and the maximum deviation of C7L to C12L from the plane through these 6 atoms is 0.0138(9) Å. An interesting feature of the structure is the angle between the normals to these two phenyl planes, 88.99(4)°. The twisting of these rings can also be described in accord with the following torsional angles: C5L-C6L-C7L- $C12L = 89.84(16)^{\circ}, C1L - C6L - C7L - C12L = -89.29(15)^{\circ}.$ The twist of the 2-biphenyl substituent along the C6L–C7L bond (Fig. 1) allows the least squares plane through C7L-C8L-C9L-C10L-C11L-C12L to come in close proximity to the hydrogen on the C1 cage carbon (C1-H…aromatic centroid separation of 2.43 Å). This arrangement is suitable for an intramolecular non-classical C-H··· π hydrogen bonding interaction. The C-H··· π centroid angle in **1** is 155.6°.



Fig. 1. ORTEP of compound 1.

In previously [1] reported compounds where intermolecular non-classical C–H··· π hydrogen bonding interactions were observed, the carborane C–H··· π aromatic centroid separations were 2.48 and 2.46 Å. C–H stretching frequencies have been reported [9] for the carborane C–H··· π bond between 3066 and 3059 cm⁻¹. The solid state IR of compound **1** exhibits two distinct stretching frequencies at 3091 and 3059 cm⁻¹ which suggests that the lower energy stretching mode (3059 cm⁻¹) corresponds to the C–H··· π interaction. In the ¹H NMR, the two cage C–H protons appear as a singlet at 2.38 ppm. This unusual up-field shift of the C–H protons of the carborane cage can be attributed to their close proximity to the phenyl ring of the biphenyl moiety there-by resulting in an increased shielding effect.

Compound 1 is similar to 3-phenyl-1,2- $C_2B_{10}H_{11}$ whose crystal structure has been previously reported [16,17]. A comparison of the bond angles at the ipso-carbon atoms of the phenyl substituent for this compound and for compound **1** $[117.71(3), 117.12(17) \text{ and } 117.38(12)^{\circ}, \text{ respectively}]$ indicates that there is very little difference in the electron donation by the carborane cage. Examination of the molecular geometry of 1 reveals that the carborane cage has a near icosahedral structure, with the C-B distances in the range 1.681(2)-1.7373(18) Å, B-B distances in the range 1.752(2)-1.791(2) Å and a C-C bond length of 1.6173(17) Å. The presence of a biphenyl substituent in 1has a significant influence on the geometry of the carborane cage resulting in the lengthening of the B3-B4, B3-B8 and B3-B7 distances by approximately 0.01 Å with respect to the B5-B6, B6-B10 and B10-B11 bonds, similar to the effect of a phenyl [16] group in 3-phenyl-1,2- $C_2B_{10}H_{11}$. Atoms C1 and C2 are 3.097(2) and 3.385(2) Å from the plane through C7L to C12L, respectively.

This study demonstrates an additional structural presentation for 1,2-carborane C–H $\cdots\pi$ interactions.

Acknowledgements

We are grateful to the National Science Foundation (Grant No. CHE-0111718) and equipment grants (CHE-9871332) and (CHE-9974928) for their support of this research. We also thank US Borax, Inc. for a generous grant-in aid.

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